Operando VIII

8th International Congress on Operando Spectroscopy

Book of Abstracts

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SLAC NATIONAL ACCELERATOR LABORATORY

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Preface

Welcome to Operando VIII, the 8th International Congress on Operando Spectroscopy. After 14 years the Operando Congress Series returns to the United States of America, and it is being held here at the beautiful setting of the historic Asilomar Conference Grounds in California, right at the coast of the Pacific Ocean. Operando VIII follows the congress series that started in 2003 in Lunteren, The Netherlands, and held every three years, in Toledo, Spain in 2006, Rostock, Germany in 2009, Brookhaven, USA in 2013, Deauville, France in 2015, Estepona, Spain in 2018, and after a five-year hiatus due to the COVID pandemic, in Grindelwald, Switzerland in 2023.

The Operando Congress is the most prominent international scientific meeting dedicated to advancing *in situ/operando* spectroscopy studies. These studies are aimed at providing spectroscopy data collected under operating conditions to understand the mechanisms of chemical reactions occurring at catalytic and other energy-related materials interfaces. *In-situ* and *operando* spectroscopy have become the cutting edge of catalysis research. Probing the physico-chemical properties of catalysts while simultaneously measuring catalytic activity and selectivity provides unprecedented insights into catalytic structure-activity relationships. The development of such fundamental relationships allows for the design of next generation catalysts.

Keeping the tradition of prior meetings, all participants of Operando VIII are housed at the Asilomar Congress Grounds, and the meeting presentations are held in a single conference room. The Operando meetings historically have been unique platforms for graduate students, postdoctoral fellows and other scientists at all stages of their careers to present and exchange new, innovative ideas. It also provides a space to discuss other issues in science that are crucial for professional development. The secluded space at the Asilomar Conference Grounds provides an ideal environment for intimate scientific discussions and for the development of friendships that can lead to long-term collaborations. Scientific exchange will be maximized by the diverse meeting program including invited plenary and keynote lectures, contributed lectures and posters presentations, and opportunities for networking and informal discussions during meals.

The over 120 high scientific quality abstracts we received were reviewed by the Program Committee which made the recommendation for the ~40 oral presentations selected. The invited plenary and keynote speakers were selected to cover a very broad range of topics in the field of *operando* studies, e.g., transient spectroscopy, microscopy, heterogeneous, homogeneous and electro catalysis, fundamental single atom catalysis.

Operando VIII could not have happened without the generous support of our sponsors from industry, academia and government. We are especially grateful for the primary sponsors of this meeting, the US Department of Energy, Office of Science, Basic Energy Sciences, the Stanford Synchrotron Radiation Light Source and the Pacific Northwest National Laboratory.

We wish all the participants a very successful meeting with lively scientific discussions, the development of new collaborations and friendships and a pleasant stay in Asilomar.

Simon R. Bare and János Szanyi

Oral Abstracts

Transient Pseudo-Random Binary Sequence (PRBS) Operando Reactor with Real-Time Adsorbate Monitoring for Mechanistic Identification

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Introduction

Transient experiments yield richer kinetic information than traditional steady-state methods but remain underutilized in the heterogeneous catalysis community due to biased perturbations and the complexity of transient data analysis. Current transient techniques, such as steady-state isotopic transient kinetic analysis (SSITKA) and temporal analysis of products (TAP), are improved using pseudo-random binary sequence (PRBS) perturbations [1-3]. Unlike single-pulse or step-change experiments utilized in SSITKA or TAP that probe limited frequencies, PRBS excites multiple frequencies simultaneously, providing richer, unbiased kinetic responses. Integration of PRBS with operando FTIR spectroscopy enables simultaneous tracking of gas-phase and surface species, providing unique and unbiased time-resolved transient data under realistic reaction conditions that enhance the predictive power of microkinetic models [4]. In this work, we apply PRBS-integrated operando FTIR spectroscopy and transient packed bed reactor experiments to investigate the oxidation of CO over Rh/TiO_2 catalysts containing both single-atom (SA) and nanoparticle (NP) Rh species. We demonstrate the capability of the PRBS approach to distinguish between distinct reaction pathways, with the relative active site concentrations quantified to correlate structure with reactivity.

Results & Discussion

Transient PRBS experiments have been performed in a packed-bed reactor with a modified commercial fast-pulsing valve and a mass spectrometer to study CO oxidation over Rh/TiO_2 catalysts (Figure 1a). Data collected at different temperatures is modeled to extract temperature-dependent elementary rate constants, activation energies and reaction orders. PRBS operando FTIR experiments simultaneously monitor gas-phase and surface species to determine whether CO_2 formation originates predominantly from CO di-carbonyl adsorbed on SA Rh sites (Figure 1b) or from linear/bridge CO adsorbed on NP Rh sites.

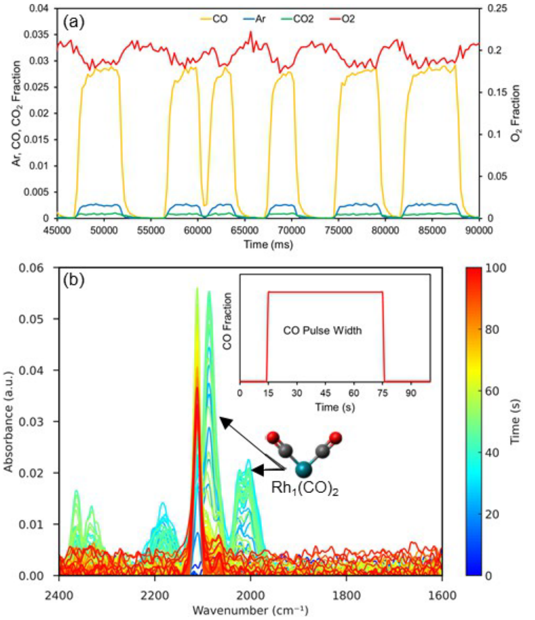

Figure1. (a) Snapshot of a CO PRBS sequence showing the temporal profiles of effluent gas species (CO, Ar, O_2, and CO_2). (b) Time-resolved profiles of gas-phase and adsorbed species acquired every 70 ms during a single CO pulse in the CO oxidation reaction over SA Rh/TiO_2.

Significance

This work demonstrates that transient PRBS Operando FTIR can accelerate kinetic studies while providing richer information to constrain microkinetic models. The approach enables faster identification of catalytic mechanisms.

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Revealing methanation-induced sintering in Rh/TiO$_2$ catalysts via operando X-ray thermometry

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Introduction

Rhodium (Rh) catalysts supported on rutile titanium dioxide (r-TiO$_2$) exhibit high activity for CO$_2$ hydrogenation, a key reaction in carbon utilization. The product distribution is strongly influenced by the structure of the Rh active sites, which in turn are susceptible to changes induced by the gas environment and local temperature. In this study, we employ a multimodal operando characterization approach, combining X-ray scattering and spectroscopy, to monitor the structural and chemical evolution of Rh species and r-TiO$_2$ support during catalyst activation, the dynamic stage bridging ambient conditions and the steady state. Our results identify CO$_2$ methanation as the dominant source of localized hot spots, which influence both the temperature profile within the catalyst bed and the trajectory of Rh particle growth, ultimately impacting reaction selectivity.

Results & Discussion

Using *operando* synchrotron-based characterization techniques, we monitored the structural evolution of Rh supported on r-TiO$_2$ during activation under various conditions in capillary reactor. When activated at fast (14 °C min^{-1}) and slow (3 °C min^{-1}) ramping rates in a CO$_2$/H$_2$ atmosphere, SAXS and XAS signatures appeared largely similar; however, the resulting product selectivity differed markedly. By tracking the lattice expansion of the r-TiO$_2$ support as an internal thermometer via *operando* XRD, we precisely captured the local thermal environment experienced by the catalyst during CO$_2$ hydrogenation and identified methanation as an important additional source of localized heat. Under fast temperature ramping, metallic Rh nuclei underwent rapid aggregation with limited time for uniform growth, leading to a broader particle size distribution and lower CH$_4$ activity. In contrast, slower temperature ramping allowed for more uniform particle growth over time, yielding smaller and more narrowly distributed Rh nanoparticles that exhibited higher CH$_4$ activity (Figure 1).

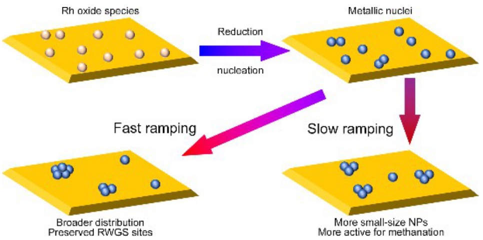

Figure 1. Proposed mechanisms of Rh particle evolution during fast and slow ramping activations.

Significance

These results highlights the importance of *operando* characterization in capturing catalyst dynamics across multiple length and time scales. The findings provide key insights into the thermal effects governing catalyst activation and demonstrate the utility of structural probes for quantitative temperature measurements under *operando* conditions.

Reaction–Driven Redispersion: A Low-Temperature Route to Catalyst Stability

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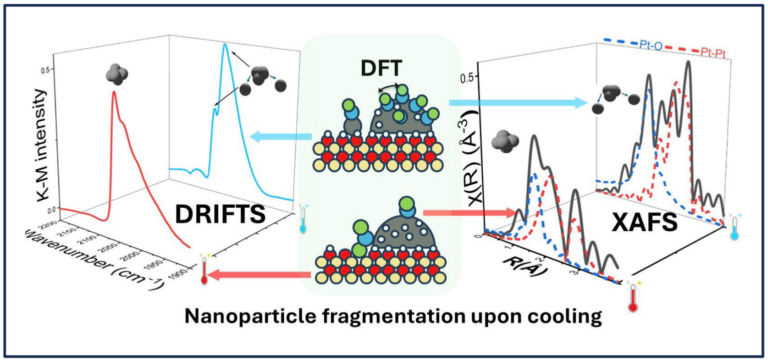
Introduction

Sintering of supported metal nanoparticles (NPs) remains one of the most persistent challenges in heterogeneous catalysis. Conventional redispersion strategies, such as oxidative–reductive cycling or oxychlorination, often require harsh treatments and/or hazardous reagents. Here, we demonstrate a new, reaction-driven, low-temperature redispersion pathway in which Pt nanoparticles partially fragment into atomically dispersed species during cooling under reactive environments.

Results & Discussion



Combination of XAFS, DRIFTS, XPS and TEM results elucidated the new NP fragmentation pathway, in which the driving force for fragmentation originated from the CO-CO repulsion and weakened Pt support interaction.

To separately assess the roles of metal–metal, metal–support, and metal–adsorbate interactions, we performed correlative studies by operando XAS, DRIFTS, AP-XPS, ex situ HAADF-STEM, and DFT modeling. The fragmentation is explained by the combined effects of strong Pt–CO interaction at undercoordinated sites, strong CO–CO repulsion, and relatively weak metal–support interaction. On CeO_2, where Pt can diffuse and restructure more easily, CO alone was sufficient to drive fragmentation. On CeO_2–TiO_2, interfacial confinement and vacancy pinning suppressed restructuring, and fragmentation occurred only when H_2 and CO were present together. In this case, hydrogen infiltration weakened Pt–Pt and Pt–support bonds, while CO_2 healed oxygen vacancies at CeO_2–TiO_2 interfaces, reducing anchoring strength and enabling CO-induced detachment of Pt–CO units. We further observed that this effect persists across particles with deliberately varied particle–support interactions.

Significance

Reaction-driven redispersion was observed for different nanoparticle types, supports and atmospheres. It has strong potential for reversing catalyst sintering under mild conditions.

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Access to study the electrode-electrolyte interface with modulation excitation X-ray spectroscopy

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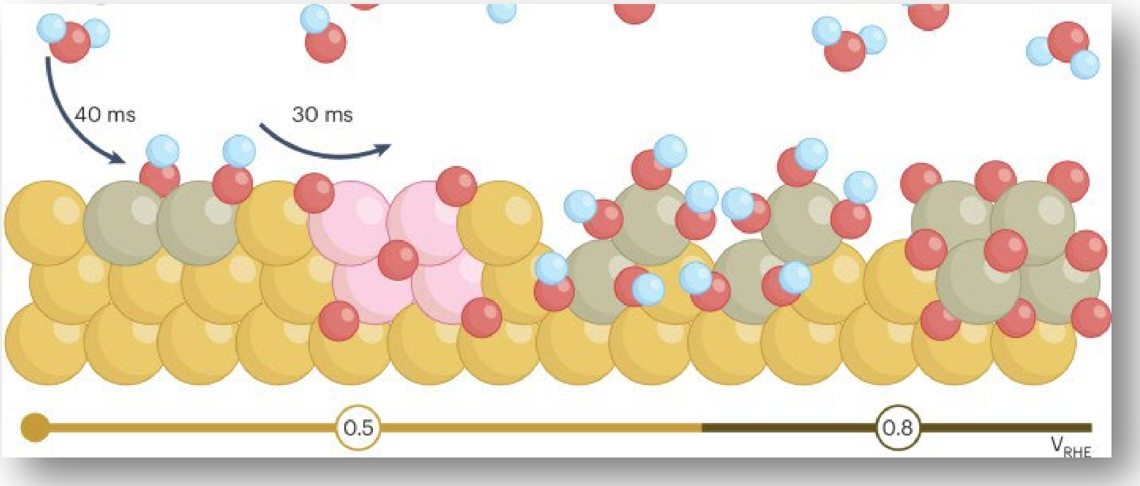

Scheme showing the evolution of the Cu-electrolyte interface in alkaline media after an anodic polarization step to 0.5 and 0.8 V vs. RHE. Adapted from reference 1 and the research highlight of Capdevila-Cortada, M., "Modulation to probe the interface", Nat. Catal. 2025, 8, 411.

Introduction

The central challenge in operando studies of electrochemical interfaces is isolating the spectral signature of active surface species from the overwhelming signal of spectator species (e.g., bulk electrode). Cu is the only catalyst promoting C–C coupling in CO_2 reduction, and this limitation has critically hindered progress in understanding its dynamic redox chemistry. Here, modulation excitation X-ray absorption spectroscopy (ME-XAS) provides unprecedented interfacial sensitivity, enabling us to deconvolve the kinetic evolution of the Cu interface with sub-second resolution.

Results & Discussion

We studied a polycrystalline 100 nm Cu electrode in an oxygen-free bicarbonate electrolyte; such conditions are relevant to diurnal start/stop operations by modulating the potential between 0 to 0.5 V_{RHE} and –0.4 to 0.8 V_{RHE}. In this ME-XAS approach, the X-ray absorbance is measured while the potential is modulated, and phase-sensitive detection (PSD) is used to demodulate the signal effectively isolating spectral features of only the species that respond to the applied potential; thus, filtering out static contributions (e.g., bulk atoms, spectator species, sources of noise, etc.) and providing access to the kinetics of interfacial dynamics with sub-second resolution. The phase-resolved Cu K-edge ME-XAS data revealed that stepping to 0.5 V_{RHE}, we observed the formation of Cu(I) through a distinct hydroxide intermediate. Our analysis shows that the hydroxide develops 30 ± 10 ms earlier than Cu_2O. Then, at 0.8 V_{RHE}, $Cu(OH)_2$ and CuO evolve and grow, with the hydroxide phase dominating the overall formation kinetics.[1] The ability to resolve interfacial dynamics provides a molecular-level picture of the earliest stages of Cu oxidation that was previously inaccessible. Furthermore, increasing the anodic potential to the oxygen evolution reaction (OER) region in mild alkaline media (>1.6 V_{RHE}) results in the formation of Cu(III) species on the surface.[2] Hitherto, no direct evidence of such OER-active species existed, which were primarily proposed by theory. First principles calculations and a Cu-H_2O revised Pourbaix diagram show that a square planar CuOOH with a bridge O* motif is the active site for water oxidation.

Significance

This work demonstrates that ME-XAS is a powerful tool for deconvoluting complex interfacial phenomena, providing time-resolved insights into dynamic processes at electrified electrode-electrolyte interfaces. Moreover, the methodology offers a new avenue for assessing durability and designing advanced accelerated stress testing (AST) protocols for a wide range of electrochemical systems.

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Modulation Excitation Spectroscopy beyond Phase-Sensitive Detection

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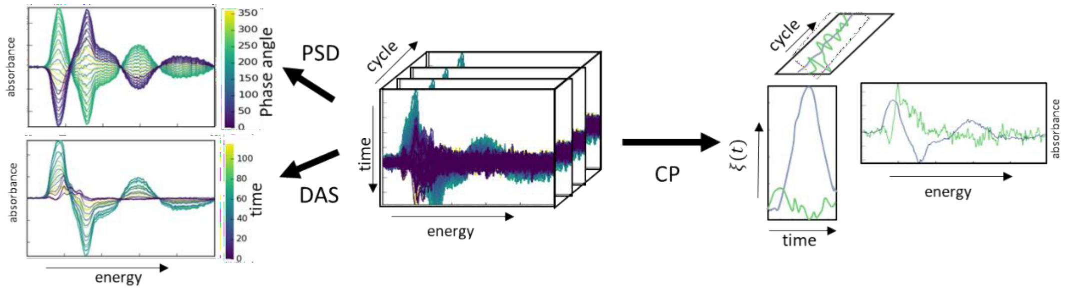
Introduction

Modulation Excitation Spectroscopy associated to Phase Sensitive Detection (MES-PSD) allows selectively detecting and identifying intermediates involved in chemical reactions.[1] Here we revisit the basis of Phase-Sensitive Detection (PSD) to assess its limitations and we provide alternative workflows for the analysis of ME spectra in the time-domain.

Results & Discussion

We show that PSD effectively performs a linear transformation of averaged difference spectra, efficiently suppressing noise but at the cost of reducing information on reaction profiles, which exhibit much stronger correlations in the phase domain than in the time domain. This (i) hinders the detection of transient surface intermediates and (ii) reduces the ability to discriminate between concurrent reactions. These effects are demonstrated through both simulations and analyses of recent open-source[2,3] and in-house experimental datasets.



PSD vs. DAS vs. CP decomposition of the 3-way tensor of ME spectra

We introduce two complementary multivariate workflows that allow analysis of ME spectra in the time-domain: MES-DAS (Denoise–Average–Subtract), which includes a multivariate denoising step *before* averaging and subtraction step, yielding difference time-domain difference spectra; and MES-CP (Candecomp/Parafac decomposition), which factorizes the 3-ways tensor of non-averaged spectra. Both approaches allow noise reductions competitive with PSD while maintaining the resolution of kinetic profiles. MES-CP further relaxes the reversibility constraints imposed by PSD, making it particularly promising for extending MES to a broader range of catalytic systems, in particular when surface accumulation/deactivation occurs.

Significance

If MES brings undisputed advantages, PSD should be used with caution, as noise reduction is also accompanied by a loss of information on active reactions and species. New workflows for the processing and analysis of time-domain modulation excitation spectra with better kinetic resolution and competitive noise reduction have been developed.

Acknowledgements. We acknowledge Agence Nationale de la Recherche under France 2030 (contract ANR-22-PEBB-0009) for support in the context of the MAMABIO project (B-BEST PEPR).

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Operando XAS Characterization of Aerobic Oxidation Catalysts for Plastic Deconstruction

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Introduction

The Mid-Century (MC) catalytic aerobic oxidation process is experiencing growing interest due to its potential to harness plastic waste as a feedstock to produce valuable oxygenated chemicals.[1] The oxidation chemistry is driven by Co, Mn, and Br-based organometallic catalysts, which undergo oxidation-reduction cycles to facilitate transformations of reaction intermediates.[2] However, the relationship between reaction conditions, Co/Mn/Br speciation, and oxidation rates are not well understood and as a result, process development efforts lack clear design targets. We present *operando* XAS experiments that elucidate relationships between catalyst coordination chemistry and oxidation activity.

Results & Discussion

Measurements were performed in a custom, continuous flow membrane reactor, which enabled control over catalyst composition, gas environment, temperature, and reaction time. Catalytic species were probed by Co, Mn, and Br K-edge XAS. The results reveal a complex interplay between catalytic species and oxidation rate. Co and Mn coordination with Br correlates with high conversion. However, in the absence of Br, Mn forms Mn^{3+} species that have a parasitic effect on the catalytic ability of Co. Br readily forms inactive organic bromides, which hinder catalysis (Figure 1). Co and Mn play a vital role in liberating Br from the organic species and allowing the active metal bromide catalysts to form.

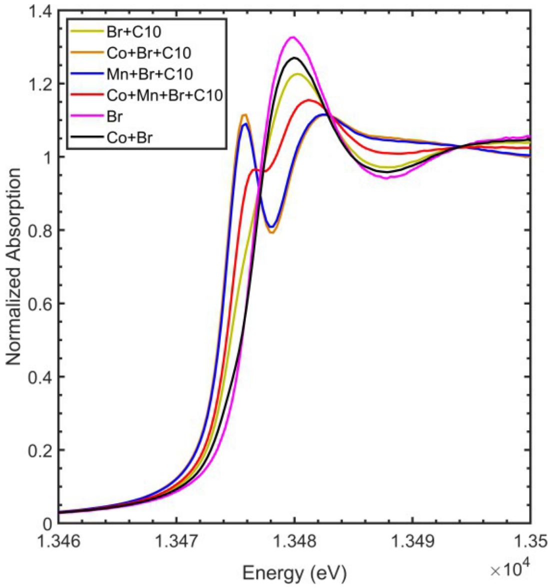

Figure 1. *Br K-edge XAS during aerobic oxidation of decane (C10). Measurements were conducted to assess the effect of inclusion and exclusion of different catalytic metals on Br speciation.*

Significance

The insights into catalyst speciation have clear process design implications. High Br concentrations are expected to yield optimal performance. On the other hand, Mn concentration must be carefully controlled to balance its promotional and inhibitory behaviors. Formation of organic bromide impacts product purity and highlights the need for methods to react organic bromide during catalyst recovery. These studies advance our understanding of the structure, chemical properties, and mechanisms of polymer deconstruction by MC aerobic oxidation and inform design directions for process optimization.

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Operando Analysis of Mechanocatalytic Reaction Environments

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Introduction

Mechanocatalysis utilizes the energy from collisions in ball mills to drive chemical reactions. The reaction environments are often intense and short-lived. Mechanocatalysis uniquely promotes reactions with tradeoffs between activation of stable reactants and thermodynamic limitations, such as ammonia synthesis,[1] and processing of solid feedstocks, such as plastics.[2] However, there is limited understanding of the extent to which the impact energy is converted into heat, strain, charge separation etc. and how specific reactants are converted in these reaction environments.

Results & Discussion

Heat formation from impacts of a 20 mm stainless steel milling within a 25 ml vessel in a Retsch MM400 vibratory mill was quantified by high-speed infrared thermography (Figure 1a). A milling frequency of 12 Hz was necessary for a measurable increase of the steady state surface temperature of the vessel. Above 17 Hz, an exponential increase was observed. The heat released generated from each collision was determined based on an energy balance model of the moving milling vessel. Depending on the feedstock in the vessel, about 40-60% of the kinetic energy of each impact were converted into heat with strain, fracturing, and ball motion in the opposite direction as other terms of the energy balance. The sound spectrum of the ball mill allowed for differentiating different types of mechanochemical events (Figure 1b). Below 11 Hz, the ball was predominantly in a rolling motion. At higher frequency, the sound spectrum was dominated by signals at the milling frequency and its harmonics indicating that a strong normal impact occurred with every direction change during the shaking motion. The impact of these reaction conditions on the rates of propane cracking and dehydrogenation will be discussed.

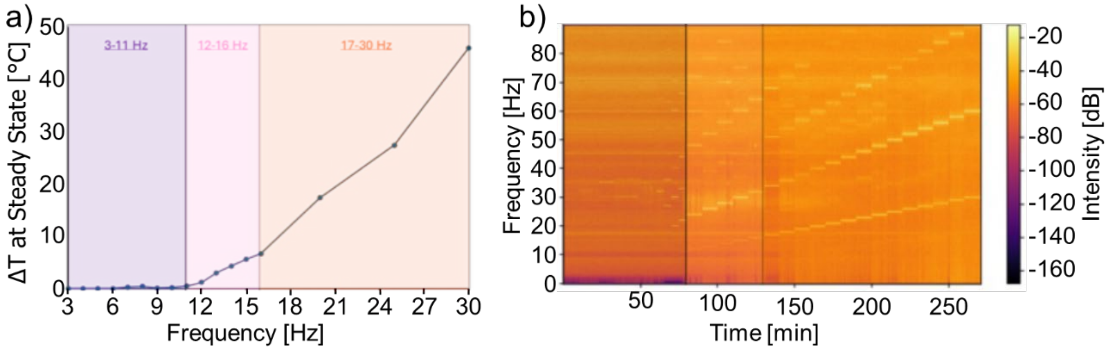

Figure 1. Effect of milling frequency on a) steady state temperature increase; b) the sound spectrum.

Significance

This contribution uses the infrared thermography and sounds spectra of ball mills to provide novel insight into the reaction conditions generated during milling of different feedstocks.

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PLENARY TALK

Understanding Cu-Catalyzed CO_2 Electrochemical Reduction via Operando Spectroscopies: Mechanism, Cation Effect and Devices

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Introduction

Electrochemical reduction of CO_2 to multicarbon products has been recognized as a promising pathway to upgrade the greenhouse gas and an excellent model reaction for mechanistic studies and device design.

Results & Discussion

This talk will cover how employment and development of operando spectroscopic techniques have helped advance the understanding key aspects in electrochemical CO_2 reduction reaction (CO_2RR) on Cu surfaces. Development of surface enhanced infrared absorption spectroscopy (SEIRAS) capable of operating at high pressures enabled the determination that CO coverage on Cu at electrochemical interfaces is at or below 0.05 ML, revealing the inconsistency between measured reaction order and the mainstream C-C coupling mechanism. Quantitative SEIRAS measurements at different temperatures led to experimentally measured CO adsorption enthalpies at electrochemical conditions, which enabled the proposed two-site model for Cu-catalyzed CO_2RR and quantitative analysis of the cation effect. Further, the development of confocal Raman spectroscopy capable of spatially resolving the cross-section of catalyst layer shows that speciations, and in turn activity, vary significantly across the catalyst layer, highlighting the importance of optimizing the mass transport in CO_2RR cells.

Significance

Development of spectroscopic techniques capable of probing electrochemical interfaces at high pressures and in devices is indispensable in achieving mechanistic understanding of Cu-catalyzed CO_2 electroreduction.

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PLENARY TALK

Single-Atom Alloy Catalysts: Born in a Vacuum, Tested in Reactors, and Understood In Silico

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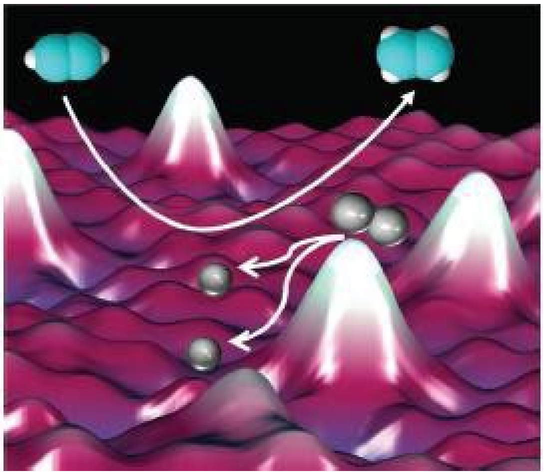

Scanning tunneling microscope (STM) image showing atomically-dispersed palladium atoms in a copper surface. The palladium atoms activate hydrogen enabling the industrially important acetylene-ethylene conversion with 100% selectivity

In this talk I will discuss a new class of heterogeneous catalysts called *Single-Atom Alloys* in which precious, re-active metals are utilized at the ultimate limit of efficiency[1-7]. These catalysts were discovered by combining atomic-scale scanning probes with more traditional approaches to study surface-catalyzed chemical reactions. This research provided links between atomic-scale sur-face structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. In collaboration with Maria Flytzani-Stephanop-oulos these concepts derived from our surface science and theoretical calculations have been used to design *Single-Atom Alloy* nanoparticle catalysts that are shown to perform industrially relevant reactions at realistic reaction conditions. For example, alloying elements like platinum and palladium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective hydrogenation and dehydrogenation reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis (Oxford University) and Michaelides (Cambridge University) that predicts reactivity trends for a wide range of *Single-Atom Alloy* combinations for important reaction steps like H-H, C-H, N-H, O-H, and CO_2 activation. Overall, I hope to highlight that this combined surface science, theoretical, and catalyst synthesis and testing approach provides a new and somewhat general method for the a priori design of new heterogeneous catalysts.

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From Modulation to Emergence: Dynamic Response Spectroscopy and the Nonlinear Dynamics of Catalytic Interfaces

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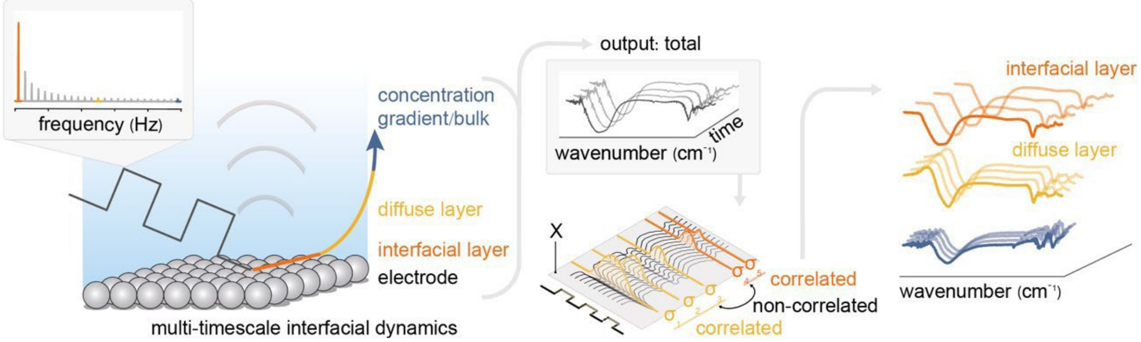
Introduction

Operando spectroscopy has transformed our view of catalytic interfaces, yet most experimental and analytical frameworks still rely on linear time-invariant (LTI) assumptions that presume steady, reversible dynamics. However, real electrocatalytic interfaces are neither stationary nor linear, they evolve across multiple timescales, where charge redistribution, solvent ordering, and surface restructuring are dynamically coupled. Capturing this emergent behavior demands a new approach.



Schematic representation of Dynamic Response Spectroscopy (DRS), resolving multi-timescale interfacial dynamics without assuming linear time invariance (LTI).

Results & Discussion

We introduce Dynamic Response Spectroscopy (DRS) as an operando approach and conceptual framework for disentangling multi-timescale, nonlinear interfacial dynamics without assuming LTI behavior[1]. By combining temporally structured perturbations with broadband, time-resolved spectroscopy and dimensionality-reduction techniques, DRS isolates distinct kinetic modes corresponding to interfacial and diffuse double-layer phenomena. Applied to CO_2 electroreduction over copper, DRS reveals that double-layer equilibration proceeds via discrete, avalanche-like reorganizations rather than continuous relaxation[2]. Extending this framework, we show how cation identity modulates the degree of interfacial coupling, as weakly hydrated cations (Cs^+, K^+) promote rigid, self-stabilizing water structures that suppress reversibility, whereas smaller cations (Na^+, Li^+) preserve dynamically reorienting solvation shells. Through coupling of DRS with machine-learning sequence (i.e., long short-term memory, LSTM) modeling we uncover causal relationships linking interfacial water dynamics, adsorbate stabilization, and catalytic selectivity, providing quantitative evidence for emergent behavior in electrochemical systems[3].

Significance

This work reframes operando spectroscopy within an emergentist paradigm, where system behaviors like catalytic function arise from nonlinear feedback between structure, field, and reactivity. By explicitly abandoning the LTI constraint, DRS exposes hidden dynamic order that conventional frequency-domain methods overlook. These insights redefine how we observe, interpret, and ultimately design catalytic interfaces under working conditions.

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Identifying active sites in selective oxidation catalysts using combined operando and transient analysis: from supported to bulk systems

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Introduction

Selective oxidation reactions are among the most important chemical processes but a scientific understanding of their mode of operation is still missing.[1] Recent progress in operando and transient analysis[2] has provided direct spectroscopic access to the active sites both of supported metal oxide[3] and bulk metal oxide[4] catalysts. We illustrate these findings for the (CO_2-assisted) oxidative dehydrogenation (ODH) of propane and discuss their implication for a rational catalyst design.

Results & Discussion

Focusing first on propane ODH over ceria-supported vanadia (VO_x/CeO_2)[3], using steady-state operando (IR, Raman, UV-Vis) and transient (isotope) modulation excitation spectroscopy (MES) IR spectroscopy, hydrogen transfer from propane to V=O is identified spectroscopically as the first (rate-determining) step, which is followed by hydrogen spill-over to ceria OH acting as lattice oxygen site. The nature of this V/O-heteroactive site is shown to be crucial for the mechanistic behavior, as shown by a comparison of CeO_2 and TiO_2[5] supports. Based on these new findings, rational catalyst design was successfully applied to $VO_x/TiO_2/CeO_2$ catalysts, by moderating the ceria oxygen reactivity with titania. VO_x/TiO_2 is shown to be also an excellent catalyst for CO_2-assisted ODH of propane, enabling TiO_2-supported CO_2 activation as revealed by multiple operando analysis.[6]

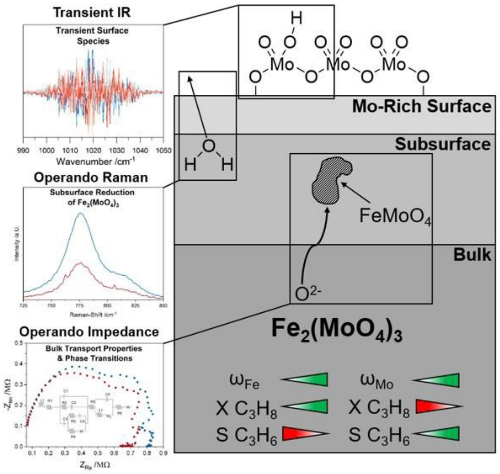

Fig. 1: Mechanism of bulk $Fe_2(MoO_4)_3$ *during ODH.*[4]

Moving from supported catalysts to commercial bulk metal oxides with their increased complexity, we applied operando (IR, multi-λ Raman, UV-Vis, impedance) and transient MES-IR analysis to identify terminating Mo=O sites and subsurface/ bulk oxygen ion transport within $Fe_2(MoO_4)_3$ as essential characteristics of catalyst functioning (see Fig. 1).[4] The interaction of surface and bulk is further elucidated by recently developed coupled operando Raman-XRD[7] and Raman-Mössbauer spectroscopy.

Significance

We demonstrate the potential of combining multiple steady-state operando analysis with transient spectroscopic methods for identification of active species and sites, as a scientific basis, for describing the characteristics of selective oxidation catalysts and for rational catalyst design.

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In-situ / operando spectroscopic investigations on kinetic and mechanistic aspects of homogeneously catalyzed hydroformylation

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Introduction

Homogeneous gas-liquid hydroformylation of alkenes to aldehydes belongs to the most important processes in chemical industry.[1] The reaction is catalyzed by cobalt or rhodium complexes at elevated partial pressures of carbon monoxide and hydrogen. Especially rhodium catalyst systems contain organo-phosphorus ligands by which the catalyst structure is altered and impacts highly the activity, selectivity and stability of the catalyst. High pressure infrared and NMR spectroscopy are used to identify the catalyst complexes and intermediates and characterize their molecular structures at real reaction conditions. Chemometric data analysis in combination with experimental design strategies are helpful to extract pure component spectra within a comprehensive component analysis in spectroscopic experiments.[2] Vibrational mode analysis based on DFT computations highly facilitates the assignment spectra to molecular structures.

Results & Discussion

In-situ/operando high pressure IR and NMR spectroscopy was used to perform studies on two prominent rhodium catalyst systems [$HRh(CO)_3$(TDTBPP)] and [$HRh(CO)_2$(BiPhePhos)].[3-5] Comprehensive characterizations on the network of involved complexes during the catalyst formation, catalysis and deactivation pathways were conducted. Spectrokinetic investigations were done to derive a kinetic model under the consideration of concentration-time data of organic educts and products and organometallic species. The role of alkene substrates and co-substrates CO and hydrogen on the rate control was also studied. Comparative investigations were undertaken for the P-ligand free rhodium catalyst system.[6] The reactivation of [$Rh_6(CO)_{16}$] towards active hydrido carbonyl rhodium(I) complexes by dosage of TDTBPP and BiPhePhos was investigated in detail.[7]

Significance

The results obtained from in-situ and operando spectroscopic investigations in the framework of several published studies lead to a comprehensive understanding of prominent catalyst systems for alkene hydroformylation.

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KEYNOTE TALK

Reversible Changes to Active Sites during Co-Reactions of Ethane, Carbon Dioxide, and Hydrogen Measured through *Operando* X-ray Absorption Spectroscopy

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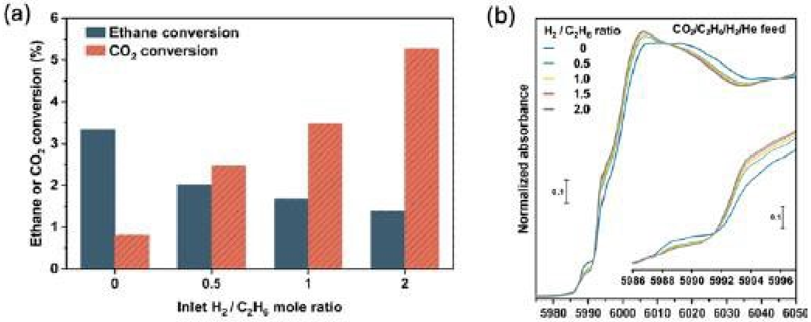
Introduction

Catalytic dehydrogenations of light alkanes present potential pathways for efficient chemical syntheses from natural gas feeds. It has been observed that co-reactions involving CO_2 and H_2 increase catalyst activities, facilitate high alkene selectivities at high alkane conversions, and extend catalyst lifetimes,[1] but the nature and magnitudes of these effects are highly catalyst dependent. This presentation describes recent work that brings new insights into changes to the state of catalyst active sites during these reactions.

Results & Discussion



Results from CO_2R-EDH reactor studies with Cr/Si-MFI. (a) Effects of co-feeding H_2 on steady-state ethane or CO_2 conversion. (d) Operando Cr K-edge XANES with Cr/Si-MFI during CO_2R-EDH (with/without co-fed H_2). Reactor study details to be provided in presentation.

Our work focuses on atomically dispersed cationic Cr stabilized by silanol nests of zeolites.[2] These catalysts contain well-defined active sites environments, do not facilitate competing dry reforming reactions, and are shown to be active and stable for both ethane dehydrogenation and CO_2 reduction reactions. An important outcome of that work[2] was that the activity enhancements correlate with a subtle shift in the population of coordination numbers among two distinct Cr-O scattering paths (defined by path length/bond length). We now study the role of co-fed H_2, commonly implemented to stabilize dehydrogenation systems. Our new results show that increasing the partial pressure of co-fed H_2 tends to increase rates of CO_2 conversion and decrease rates of ethane conversion (Fig 1a); the data make evident that metal centers preferentially activate H_2 over C_2H_6. We performed operando X-ray absorption spectroscopy measurements to examine the impact of H_2, which can exist in high concentrations in alkane DH systems, by measuring the Cr K-edge while varying H_2 partial pressure. Results (Fig. 1b) show increased red shift of the edge with increasing hydrogen partial pressure, which we show elsewhere is related to an alteration of the metal coordination environment. Many other results will be presented, including new operando EXAFS analysis.

Significance

Use of this material platform and methodology results in a greater understanding of an exciting method to co-upgrade ethane, CO_2, and H_2 into dry-basis streams of ethylene and syngas.

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Far-IR spectroscopy as a direct coordination environment probe in catalysis

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Introduction

Understanding the relationship between structure and activity in heterogeneous catalysts remains a persistent challenge. The use of *operando* spectroscopy techniques has enabled unprecedented insights, but techniques where both structure (i.e. catalyst material) and activity (i.e. adsorbates) are probed remain scarce. In this work, we put forward the use of *operando* far-IR (FIR) spectroscopy as a tool to enable single-technique insights into all aspects of catalysis.

Results & Discussion

Extension of mid-infrared spectroscopy, which typically mainly probes molecular vibrations of adsorbates, into the low energy region enables the identification of important vibrations present within catalytic materials: metal-adsorbate bonds, metal-metal bonds[1], and lattice phonon modes. By exploring the so-called 'fingerprint region', we show how FIR spectroscopy can be used to assess metal-adsorbate bonds (Fig.1a,c), metal-metal bonds in sub-nanometric metal clusters (Fig.1b,c), and probe the site-specific alkali-exchanged zeolite acidity (Fig.1d).

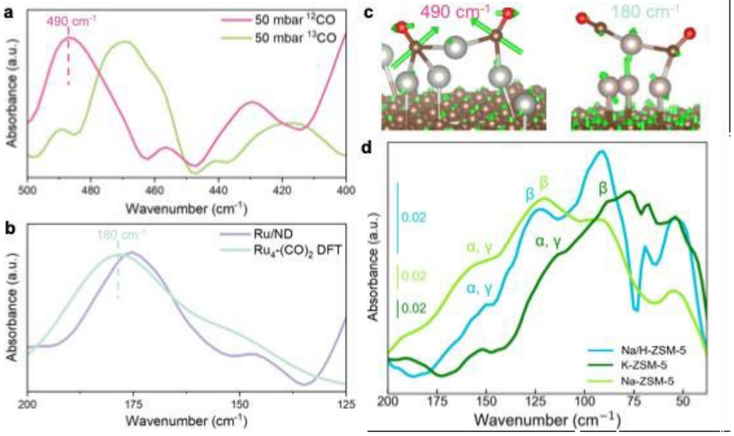

Figure 1. Capabilities of *operando* FIR spectroscopy. a) Ruthenium carbonyl species upon ^{12}CO and ^{13}CO (50 mbar) adsorption on a Ru/Nanodiamond sample. b) Density-functional theory-calculated carbonyl rocking and cluster skeletal modes. c) Ruthenium nanocluster skeletal modes. d) FIR spectra on alkali-exchanged ZSM-5 and site-specific band assignments.

Significance

Our findings demonstrate that FIR spectroscopy, albeit in its infancy, can evolve to be a powerful *operando* spectroscopy tool. Our suite of different case studies will pave the way for its implementation and usage in catalysis laboratories.

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Fe Monomers at Work: *Operando* Multi-spectroscopy Approach Identifies the Fe^{2+}/Fe^{3+} Pair Enabling N_2O-Assisted CH_4 Oxidation in Fe-Zeolites

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Introduction

Fe-zeolites hold significant promise in thermal catalysis, yet the nature of the active sites responsible for most redox reactions they catalyze remains debated due to contradictory *ex-situ* assignments, dynamic behavior, and spectator species. We addressed these challenges with an *operando* **multi-spectroscopic** (**EPR, RIXS, DRIFTS, DRUV, XAS, XES**) approach combined with **modulated excitation** and **phase-sensitive detection** (ME-PSD). This approach enabled extraction of spectroscopically derived kinetic data and descriptors, unambiguous identification of active sites, and disentanglement of key mechanistic steps in these complex materials at work.

Results & Discussion

High-time-resolution EPR allowed identifying and tracking monomeric Fe ions within six-membered rings (Fe_{6MR}) of Fe-SSZ-13, revealing a direct correlation of the kinetics of this Fe ions with N_2O decomposition and enabling their assignment as active sites.[1] Complementary multi-spectroscopic analysis (**EPR**, **RIXS**) provided crucial experimental evidence for a reaction mechanism in which N_2O activation and subsequent CH_4 oxidation to CH_3OH also occur at this axial monomeric Fe_{6MR} site (**EPR**), where Fe adopts a C_{4v}/D_{3h} symmetry (**kα-RIXS**). Ruling out the presence of $Fe^{4+}{=}O$ species from **kβ'-RIXS**, the active site was identified as a Fe_{6MR}^{3+}-O oxo. This highly reactive site readily interacts with CH_4 *via* H-abstraction, forming $CH_3^{\cdot}$ and Fe^{3+}-OH moieties (**ME-DRIFTS**). **ME-PSD** demonstrates a reversible Fe^{2+}/Fe^{3+} redox cycle that sustains continuous production of CH_3OH (confirmed by online μ-GC) through a $CH_3^{\cdot}$ radical rebound mechanism,[2] effectively coupling N_2O utilization with partial CH_4 oxidation over Fe-zeolites.

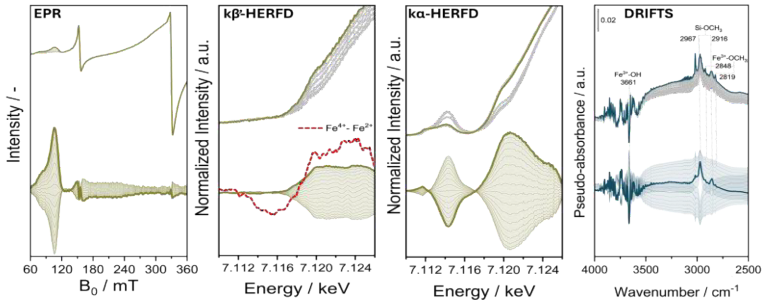

Figure 1. Time- and phase-resolved EPR, Kα and Kβ'-HERFD-XAS, DRIFTS spectra during ME experiment

Significance

This study showcases the advantage of combining various spectroscopic techniques coupled with ME-PSD to interrogate complex catalysts at work. Our findings are expected to guide the design of Fe-zeolites for industrially relevant reactions, enabling effective N_2O and CH_4 utilization.

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PLENARY TALK

Seizing materials structure in the act by multi-modal spectroscopy

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The understanding of the function of heterogeneous catalysts is key for their design but is often complicated by the potentially complex speciation of the active element and by the limited information on the nature of the active species that spectroscopy delivers at equilibrium reaction conditions. Spectroscopy, diffraction and microscopy techniques are available to the operando researcher to address the former issue, each one delivering specific structural information. Experiments under transient conditions such as in SSITKA, modulated excitation and stop-flow approaches are key tools to discriminate between active and spectator species in terms of both phases and adsorbates.

Examples will be presented for the characterization of solid catalysts in both gas and liquid environments using combinations of techniques (e.g. IR, UV, Raman, XAS, XRD, PDF, EPR), to exploit the perspective of material structure that each one provides, with the systematic use of modulated excitation protocols, to emphasize the contribution of key structural features. The experiments are conducted with different techniques but using the same setup and at different points in time. Ideally and on the same line, the same type of reactor cell is also used irrespective of technique, which is sometimes complicated by specific technical requirements. The quantitative correlation between catalytic experiments and spectroscopic signatures of species identified in this type of experiments is a central point of this approach and of operando spectroscopy.

The examples will cover material structure from SCR catalysts to zeolites for MTO and to synthesis of MOFs.

Significance

The examples of multi-modal spectroscopy, combining complementary spectroscopic techniques with the modulated excitation methodology, could stimulate research on other catalyst systems and promote the use of modulation protocols for advanced catalyst analysis. This approach delivers structural information going beyond what is possible with conventional methods, thus further strengthening the impact of operando spectroscopy.

Linking Cu Ion Speciation to SCR Reactivity in Cu-CHA Catalysts via Operando EPR Spectroscopy

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Introduction

Selective catalytic reduction (SCR) over Cu-CHA catalysts remains essential for controlling NO_x emissions from lean-burn engines. While detailed understanding of the reaction mechanism and Cu site dynamics has been obtained under on-road diesel exhaust conditions, issues arising from off-road applications and low-carbon fuel (H_2, NH_3 etc.) exhausts have not received enough attention. Because SCR performance depends strongly on the dynamic oxidation state and coordination of Cu ions, operando tools are required to resolve how Cu speciation evolves under realistic exhaust conditions typical of such conditions. In this work, operando electron paramagnetic resonance (EPR) spectroscopy is used to directly monitor Cu^{2+} populations, ligand environments, and redox dynamics during SCR, enabling clear links between Cu speciation and catalytic behavior.

Results & Discussion

Two case studies highlight the utility of operando EPR. First, for low-load and low-temperature SCR, we show how NH_3-to-NO ratio (ANR) governs the coordination environment of Cu^{2+}, transitioning from fully NH_3-solvated $Cu^{2+}(NH_3)_n$ complexes at low temperature to mixed Cu–N/Cu–O_L coordination at higher temperature. By resolving hyperfine and superhyperfine features (Fig. 1 shows an example spectra), operando EPR reveals that the number of NH_3 ligands on Cu^{2+} increases with ANR up to a critical value, beyond which excess NH_3 suppresses Cu mobility, slows SCR oxidation half cycle (OHC) kinetics, and leads to NH_3-inhibition of SCR. Quantification of Cu^{2+}/Cu_{Total} demonstrates a decreasing Cu^{2+} fraction with increasing ANR on low-Cu samples, consistent with slower reoxidation kinetics at high NH_3 coverage, whereas high-Cu samples remain resistant to this inhibition.

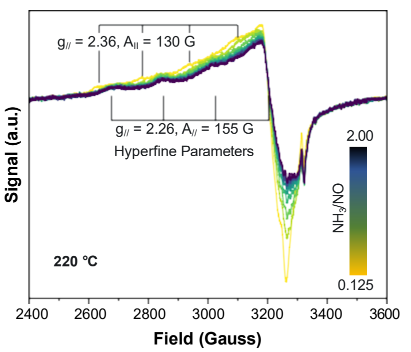

Fig.1: EPR spectra of Cu-CHA under SCR reaction conditions (500 ppm NO, 70-500 ppm NH_3, 10% O_2, 3% H_2O). Cu speciation changes with varying NH_3/NO, indicated by altered hyperfine $g_{//}$, $A_{//}$ & superhyperfine features within 3200-3400 G region.

Second, we investigate the impact of high H_2O- and H_2- conditions relevant to H_2 internal combustion engines (H_2-ICEs). Operando EPR shows that although the temperature-dependent $g_{//}$ and $A_{//}$ evolution of Cu^{2+} coordination is unaffected by H_2, the Cu^{2+} population remains markedly suppressed in the presence of H_2 due to persistent Cu^+ that fails to reoxidize during the SCR OHC. This pool of redox-inactive Cu^{2+} correlates directly with the loss of high-temperature SCR activity. Hydrothermal aging experiments further reveal that high H_2O weakens Cu-framework binding while H_2 accelerates redox-driven Cu de-anchoring, resulting in substantial depletion of isolated Cu^{2+} sites essential for SCR turnover.

Significance

Overall, operando EPR provides molecular-level insight into how NH_3, H_2O, and H_2 perturb Cu redox cycles, offering guidance for designing Cu-CHA catalysts optimized for next-generation lean-burn and hydrogen-fueled engines.

Understanding Localized heat transfer in Autothermal Reactions

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Introduction

Understanding heat-transfer events in heterogenous catalysis is important for controlling crucial performance markers, such as efficiency and selectivity. This is particularly true for autothermal reactions, where the localized heat at the catalyst level is necessary to drive otherwise thermodynamically unfavorable chemistry. As a model reaction we studied autothermal ammonia decomposition. This reaction usually requires high temperatures to achieve a suitable level of conversion[1], but by co-feeding a small amount of oxygen, it is possible to enable a sacrificial ammonia oxidation side reaction to provide the high temperatures required *in situ*[2]. In this study we measured the temperature profile at the catalyst nanoparticles across the bed, derived from the mean squared disorder parameter, to determine if the temperature at the nanoparticle level corresponds to the macroscopic reactor's temperature.

Results & Discussion

RuO_2/Al_2O_3 and Ru/Al_2O_3 were measured under He at various temperatures to produce a temperature calibration plot, based on the Debye-Waller factor obtained by fitting the data in Artemis. Subsequently a reaction mixture of 4:1 NH_3:O_2 was flown through RuO_2/Al_2O_3 and XAFS was measured at various points across the catalyst bed. Upon reaching a reactor temperature of 523 K it was possible to observe the reduction of RuO_2 to Ru starting from the front of the bed, while the end of the bed stayed predominantly oxidic. More interestingly, when observing the temperature profile, it is possible to observe two distinct areas of activity: the Ru metal inlet experiences high levels of exothermic ammonia oxidation, reaching temperatures >100 K above macroscopic temperatures, while the oxidic Ru outlet presents the endothermic ammonia decomposition, as evidenced by temperatures lower than the reactor temperature. However, it has to be noted that at outlet, while XANES linear combination fit has shown the presence of ~20% metallic Ru, EXAFS does only present RuO_2, suggesting the possibility that metal nanoclusters have formed and might have an active role in the ammonia decomposition.

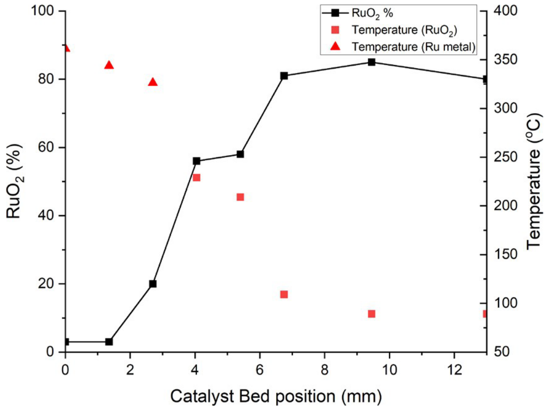

Figure 1: Temperature (from Debye-Waller fit) and composition (from XANES linear combination fit) map of catalyst nanoparticles across the catalyst bed

Significance

This study evidences how *operando* XAFS allows to differentiate between the macroscopic and local properties during the autothermal ammonia decomposition. Furthermore, the spatial resolution allows the identification of the distinct zones of operation and highlights a significant scope for better linking these coupled reactions.

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KEYNOTE TALK

High Spatial Resolution Operando IR Nanospectroscopy Reveals Structure-Reactivity Correlation in Pd Nanoparticles

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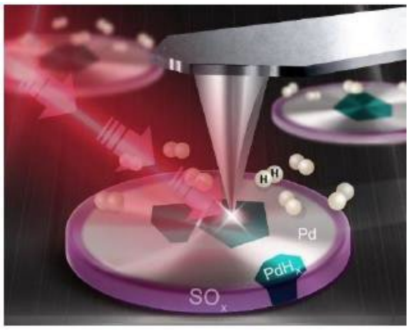
Introduction

Heterogeneities in the size, structure, and composition of catalytic nanoparticles make it essential to obtain chemical information at the nanoscale in order to understand how local variations in surface properties influence local and global reactivity patterns. We have recently demonstrated that infrared (IR) nanospectroscopy can reveal reactivity variations within single nanoparticles [1], uncover the influence of different atomic facets on the reactivity of catalytic nanocrystals [2], and map the distribution and strength of basic sites on mixed-oxide nanoparticles [3].

Results & Discussion

Herein, we employ *operando* IR nanospectroscopy, *operando* Kelvin probe force microscopy, and topographical imaging under reaction conditions to establish a correlation between structure, oxidation state, and reactivity of Pd nanoparticles, as well as the impact of SO_x poisoning on hydrogen sorption dynamics. It was identified that SO_x species preferentially adsorb at particle rims, strongly suppressing hydrogen (de)sorption kinetics. Continued H_2 exposure induces partial SO_x desorption and reduction. Individual nanoparticles exhibit highly variable reactivity due to selective poisoning of rim sites, identified as the most active sites for hydride formation [4].



Operando IR nanospectroscopy measurements mapped the distribution of SO_x *poisoners on single Pd nanoparticles and their impact on hydrogen (de)sorption and the transitioning between metallic Pd and Pd hydride.*

Significance

These findings highlight how trace-level poisoning can spatially reshape reactivity patterns, emphasizing the value of single-particle *operando* measurements for understanding catalyst (de)activation.

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KEYNOTE TALK

Dynamic Catalytic Sites for Selective CO/CO_2 Conversion

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Introduction

We report our efforts in understanding the catalytic activation and selective conversion of CO/CO_2 molecules in energy catalysis. Our focus is on resolving the dynamic structure of active sites and their adsorption-activation mechanisms during interfacial catalytic processes, quantitatively describing dynamic structure-activity relationships in heterogeneous catalysis at the atomic and molecular scale, and bridging the gap between surface science research and practical catalytic applications. Over the years, we have built a set of tools (Figure 1) that enable in-situ, real-time observation across temperature and pressure ranges from UHV to atmospheric pressure, and established precise construction and characterization methods for low-coordination oxide structures. By combining in-situ characterization techniques with computational modeling, we successfully constructed a comprehensive framework for analyzing dynamic structure-activity relationships in oxide catalysis [1-5].

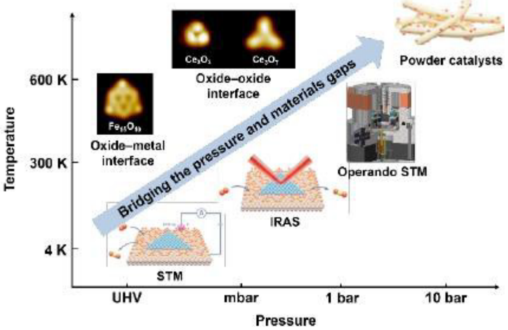

Figure 1. In-situ characterization platforms bridging the pressure and materials gaps

Results & Discussion

In our study of CO oxidation at FeO-Pt interfaces, we observed and elucidated at the atomic scale the reaction mechanisms and kinetics of CO oxidation catalyzed by interfacial sites, connecting catalytic studies from model systems to practical catalysts. The consistency in activation energies from model surfaces to powder catalysts and from UHV to 1 bar conditions [6] validates that surface science mechanisms can effectively aid practical catalyst design. Furthermore, we revealed the formation mechanism of dynamic active sites and their evolution during methanol synthesis reactions on CuZn systems. We proposed a strategy for synergistic thermodynamic and kinetic control of dynamic uniform $Zn_3(OH)_3$, achieving selective CO_2 hydrogenation to methanol. By stabilizing highly active sites through reaction environment control, we provide new pathways for efficient and selective COx conversion.

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Operando spectroscopic investigation to explain reactivity in LPMO-mimic Cu complexes in solution

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Introduction

Lytic polysaccharide monooxygenases (LPMO) are a class of monocopper enzymes that selectively oxidize recalcitrant crystalline carbohydrates, with crucial implications in the energy and biomass processing sectors.[1] Many synthetic attempts have focused on mimicking the structure of the active site of these enzymes,[2] with the objective of understanding their reaction mechanism and reaching similar catalytic efficiencies. Our study focuses on an imine-bis-imidazole Cu complex (C1) that mimics typical geometric and electronic parameters of the His-brace Cu site in LPMO (***Figure 1a***).

Results & Discussion

UV-Vis spectroscopy can be used to test the catalytic performance of LPMO mimic complexes in the oxidation of a modified sugar (paranitroglucopyranoside, PNPG) by H_2O_2.[2] A complex with the same N,N,N tridentate coordination but different bond lengths, Cu(terpy) (C2), performs significantly worse in catalysis (***Figure 1b and c***). The sigmoidal profile of product formation when the reaction is catalyzed by C1 suggests a two-step process, in which a reactive species is formed and subsequently consumed in a slower kinetic step. We present a multi-technique spectroscopic study of C1, in which we characterize the structural and electronic evolution of the complex and the reaction intermediate during catalysis using *operando* resonance Raman and X-ray absorption spectroscopy. The use of a microfluidics flow cell allows catalytic data (UV-Vis) to be simultaneously collected and drastically reduces the radiation dose on the sample by laser (Raman) and X-ray (XAS), preventing sample degradation. Preliminary XAS data confirm that C1 shares a very similar coordination environment with the typical LPMO active site (***Figure 1d***).

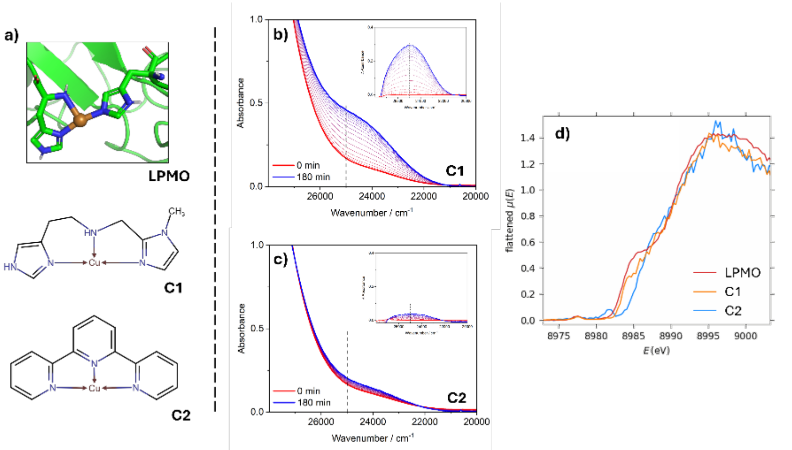

Figure 1. (a) Molecular structure of the active site of an LPMO compared to C1 and C2. (b, c) Catalytic performance of C1 and C2 in PNPG oxidation. (d) Comparison of XAS data collected for a LPMO, C1 and C2.

Significance

Our study showcases two important results: i) a full spectroscopic characterization of the complex while it performs catalysis will allow to study in detail its evolution during reaction, including the formation of a possible reaction intermediate, and ii) the possibility to easily connect a simple UV-Vis-based catalytic test (that is already used in the community) with resonance Raman and XAS will exemplify an accessible tool for *operando* spectroscopy that can be generalized to different catalysts and substrates in solution.

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Exploring Carbon Growth Dynamics during Catalytic Methane Pyrolysis with Operando Raman Spectroscopy

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Introduction: Catalytic methane (CH_4) pyrolysis is an interesting alternative to steam methane reforming (SMR) for the production of H_2, since instead of CO_2, solid carbon is produced and deposited on the catalyst. [1,2] This solid carbon could be a valuable co-product, however, optimizing its properties requires a more detailed understanding of the reaction and deactivation mechanisms, as well as the related kinetics. Raman spectroscopy can be used to study carbon formation, but has not yet been explored during catalytic CH_4 pyrolysis. In this work, operando Raman spectroscopy is used to investigate the carbon growth in catalytic CH_4 pyrolysis.

Results & Discussion: 15 wt.% $NiCu/Al_2O_3$ catalysts were tested for methane pyrolysis in a Harrick cell at different temperatures, and Raman spectra were acquired every minute. We observed the characteristic carbon bands, namely the D and G bands, develop over time-on-stream. An important parameter in Raman spectroscopy for carbon materials is the D/G ratio, which is an indicator for the number of defects in the carbon material. Surprisingly, when performing this reaction at a low temperature (400 °C, Fig. 1a), we observed a more prominent G band, and thus a more graphitized carbon. Fig. 1a shows not only much faster growth at 600 °C, but also a more defective carbon species. This also becomes clear from the D/G ratios, as shown in Fig. 1b, where the D/G ratio dipped first at 400 °C and only increased later, whereas it reached a stable level fast at 600 °C. Mass spectrometry shows that almost no H_2 is produced at 400 °C, but only at 600 °C. This indicates a much faster growth at higher temperatures, resulting in more defective carbon.

Significance: This research shows that operando Raman spectroscopy can determine differences in the growth dynamics of the carbon formation during CH_4 pyrolysis. These insights can be used to show the structural properties of the carbon product made and its dependency on relevant reaction conditions. Applying operando Raman spectroscopy with a related in-depth analysis on CH_4 pyrolysis opens the possibilities to investigate the growth mechanisms on many more catalysts.

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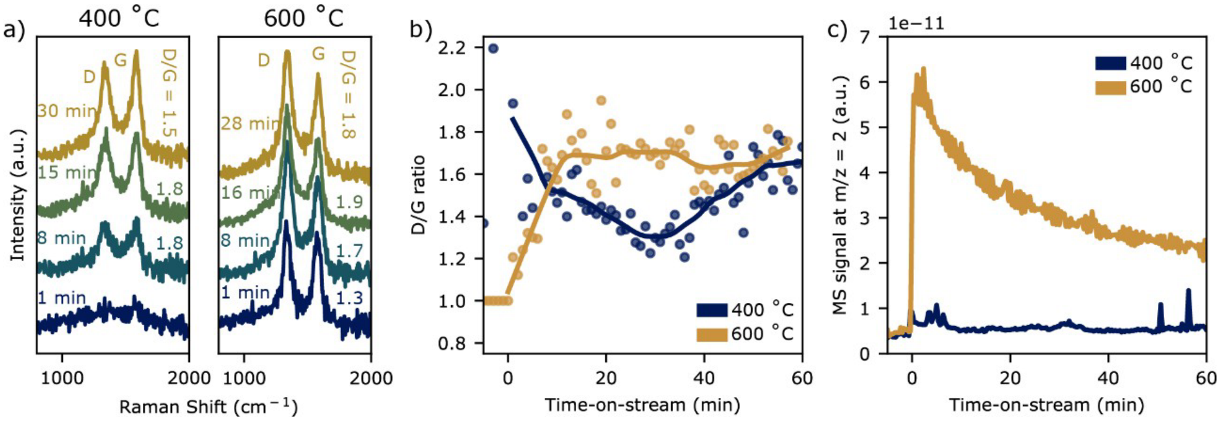

Figure 1a-c) Operando Raman spectra of a $NiCu/Al_2O_3$ catalyst during methane pyrolysis at different reaction temperatures over time. 20% CH_4/Ar, total flow = 50 ml/min, laser wavelength 532 nm, laser power 1.3 mW. d) D/G ratio, as derived from the Raman spectra, e) H_2 yield as measured with online mass spectrometry (MS), f) Measured D/G ratios and H_2 yields during the reaction temperature increase from 400 ℃ to 600 ℃ as a function of time-on-stream.

Redox Dynamics of Supported VO_x/CeO_2 during Methanol Oxidation Monitored with *Operando* UV-Vis-MS Spectroscopy

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Introduction: Supported VO_x/CeO_2 catalysts attracted much interest because of their high redox activity and behavior. During ethane ODH, surface VO_x sites were proposed to not undergo redox (stay as V^{5+}) and redox cycle is being performed by CeO_x sites ($Ce^{4+} \leftrightarrow Ce^{3+}$).[1] DFT calculations concluded that isolated surface VO_4 sites on model $CeO_2(111)$ thin films do not undergo redox during methanol ODH and redox is being performed by exposed surface CeO_x sites.[2] In contrast, transient studies during ethanol ODH observed that both surface VO_x and CeO_x undergo redox.[3,4] To address this conundrum, the roles of CeO_2 support and surface VO_x sites during methanol ODH by supported VO_x/CeO_2 catalysts were investigated with *operando* UV-Vis-MS spectroscopy.

Results & Discussion: *In situ* Raman spectroscopy confirmed that only surface VO_x sites were present on the CeO_2 support. *Operando* DR UV-Vis-MS spectroscopy during CH_3OH-temperature programmed surface reaction (TPSR) revealed that rates of HCHO formation and reduction of surface V^{5+} to $V^{4+/3+}$ are kinetically coupled, depicted in Fig.1. Interestingly, the redox CeO_2 support was found to provide lattice oxygen to re-oxidize surface $V^{4+/3+}$ before methanol was completely consumed. *Operando* concentration modulation excitation (c-ME) DR UV-Vis-MS spectroscopy during methanol ODH (switching O_2 on/off) for VO_x/CeO_2 revealed the apparent reduction kinetics of V^{5+} to $V^{4+/3+}$ to be slower than $V^{4+/3+}$ to V^{5+} re-oxidation kinetics.

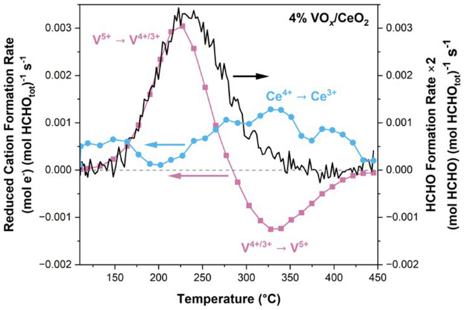

Figure 1. Formation rates of HCHO and $V^{4+/3+}$ & Ce^{3+} species *vs*. temperature for supported 4% VO_x/CeO_2 catalyst during CH_3OH-TPSR assessed via *operando* UV-Vis-MS spectroscopy. The positive and negative curves on the pink trace reflect reduction of V^{5+} and re-oxidation of $V^{4+/3+}$, respectively.

Significance: *Operando* DR UV-Vis-MS during CH_3OH ODH provided key insights about the redox of supported VO_x/CeO_2 catalysts at different temperatures that explain the apparent conundrum in the literature. At low temperatures of alcohol ODH (100-300 ^{0}C), both the surface VO_x sites and oxygen atoms from CeO_x are involved in redox. At high temperatures of ethane ODH (500-600 ^{0}C), lattice oxygen from the CeO_2 support rapidly re-oxidizes the reduced surface VO_x sites in a fast step that is not captured during non-transient measurements.

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In situ MAS NMR Reveals Insights into Hierarchical Zeolite Formation during Post-Synthetic Base Leaching

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Introduction

Zeolites rank among the most widely used materials in the chemical industry[1], with the global market expected to grow to USD 27.53 billion by 2033[2]. However, the use of zeolites is limited by diffusion constraints originating from their intrinsic microporous structure. Post-synthetic base leaching offers a cost-effective solution by creating hierarchical zeolites[3]. Yet the mechanisms linking aluminum role to pore formation in this process remain subject to debate.

Results & Discussion

In the in situ ^{29}Si MAS NMR spectra (Fig. 1a), ZSM-5 framework signals at −112, −105, and −103 ppm correspond to $Q^4_{(4Si)}$, $Q^4_{(3Si,1Al)}$, and $Q^3_{(3Si,1OH)}$. When base leaching begins, a −70 ppm Q^0 peak indicates dissolution of framework silicon. As leaching continues, Q^1, $Q^{2\Delta}$, and Q^2 species appear at −79, −82, and −87 ppm, followed by $Q^{3\Delta}$ and Q^3 resonances (−88 and −97 ppm) showing polymerization in solution.

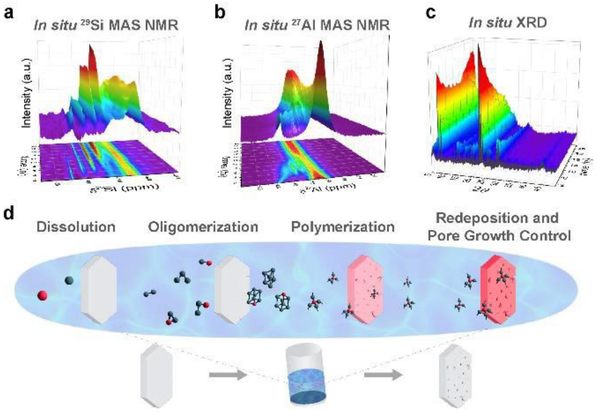

Fig. 1. In situ (a) ^{29}Si and (b) ^{27}Al MAS NMR spectra, and (c) in situ XRD during base leaching of ZSM-5. (d) The overall reaction scheme observed by in situ techniques.

At the start of the in situ ^{27}Al MAS NMR (Fig. 1b), no extra-framework aluminum (EFAL) signal is detected, while a resonance at 79 ppm ($Al(OH)_4^-$, q^0) appears, indicating rapid EFAL dissolution. Framework Al (FAL) signal gradually decreases over the first 3 h, reflecting its progressive dissolution. From 3–10 h, aluminum incorporates into silicate species in solution, evidenced by Si–Al oligomers at 75, 72, 66, and 61 ppm (q^1, $q^{2\Delta}$, q^3, q^4), with minor peaks at 70 (q^2) and 68 ppm ($q^{3\Delta}$). After ~8 h, liquid-phase Al adopts q^4 coordination (60 ppm), indicating polymerization of aluminum silicate species. In situ XRD shows decreasing diffraction intensities consistent with zeolite dissolution (Fig. 1c), slowing after 8 h with plane-dependent intensity decrease, indicating preferential leaching orientation. This aligns with q^4 Al formation, suggesting their participation in pore growth control. A schematic overview of the dissolution, oligomer formation, and subsequent polymerization with pore growth control captured by in situ techniques is provided in Fig. 1d.

Significance

This work demonstrates the insights of mesopore generation in zeolites during base leaching and enables more rational design of hierarchical zeolites for improved catalytic performance.

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Operando Microscopic and Spectroscopic Investigation of Metal–Oxide Interfaces in Mixed and Bimetallic Nanocatalysts

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Introduction

A bimetallic Pt alloy or mixed catalyst provides an ideal platform to probe the active metal–metal oxide interface, and operando techniques reveal that structural modulation and the coexistence of metallic Pt with oxidized transition-metal species significantly enhance catalytic pathways for CO oxidation.

Using PtNi, PtCo, and Pt/mesoporous Co oxide systems—as well as extending the concept to non-Pt alloys such as AuCu and AuPd—the studies demonstrate that reactive metal-oxide interfaces formed by surface oxidation or oxide encapsulation consistently boost catalytic activity.

Results & Discussion

A bimetallic Pt alloy or mixed catalyst is an excellent platform to uncover the contentious role of the metal–metal oxide interface because the alloyed transition metal can coexist with the Pt surface layer in the form of an oxidized species on the bimetal surface during catalytic reactions. The real-time imaging of catalytically reactive atomic sites using operando surface techniques including ambient pressure scanning tunneling microscopy can reveal the nature of reactive sites on the catalytic surfaces.

In this talk, I present in-situ observation results of structural modulation on Pt-based bimetal catalysts and mixed catalysts and its impact on the catalytic activity. We utilized PtNi, and PtCo that includes both of single crystal and nanoparticle surfaces as model catalysts, and showed the coexistence of Pt and metal oxide leads to the enhancement of catalytic activity, indicating these metal-oxide interfaces provide more efficient reaction path for CO oxidation [1,2]. The mixed catalysts composed of Pt nanoparticles and the mesoporous cobalt oxide exhibit the enhancement of catalytic activity while Pt is encapsulated by the oxide thin layers forming the reactive metal-oxide interfaces.

Our investigation employs various operando surface techniques, including ambient pressure scanning tunneling microscopy, ambient pressure X-ray photoelectron spectroscopy, and environmental transmission electron microscopy. Notably, mixed catalysts comprising Pt nanoparticles and mesoporous cobalt oxide demonstrate increased catalytic activity when Pt is encapsulated by oxide thin layers, forming reactive metal-oxide interfaces [3]. This principle can be applied to non-Pt bimetallic catalysts including AuCu [4], and AuPd [5].

Significance

Our findings reveal that the presence of metal and metal oxide coexisting at the interface enhances catalytic activity, suggesting that these metal-oxide interfaces offer more efficient reaction pathways for CO oxidation.

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Understanding the Phase Transition of Nickel Hydroxide using In-Situ X-ray Absorption Spectroscopy

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Introduction

Water electrolysis offers a promising approach for hydrogen production, but its efficiency is hindered by the kinetic barrier of the oxygen evolution reaction (OER). To overcome this limitation, Ni-based materials have emerged as a promising class of materials for enhanced OER in alkaline conditions. Notably, these materials undergo a phase transition to nickel hydroxide ($Ni(OH)_2$) during OER conditioning, sparking interest in understanding their structural transformations into $Ni(OH)_2$ and nickel oxyhydroxide (NiOOH). The two known phases of $Ni(OH)_2$, α-$Ni(OH)_2$ and β-$Ni(OH)_2$, can be charged to form β-NiOOH and γ-NiOOH, respectively. However, the instability and inconsistency of α-$Ni(OH)_2$ and γ-NiOOH have limited their study, whereas β-$Ni(OH)_2$ has been thoroughly characterized structurally. This study investigates the structural and chemical transformations of α-$Ni(OH)_2$ and β-$Ni(OH)_2$ at applied potentials using in situ X-ray absorption spectroscopy (XAS). By elucidating the transformation pathways of these $Ni(OH)_2$ phases, we provide new insights into the kinetic processes governing their conversion to NiOOH and their roles in the OER activities.

Results & Discussion

We synthesized α-$Ni(OH)_2$ and β-$Ni(OH)_2$ using precipitation of Ni ions in KOH solution. Their corresponding phases were confirmed by their powder X-ray diffraction (XRD) patterns, which exhibited distinct reflections characteristic of each phase, thereby verifying the successful synthesis of these nickel hydroxide materials. The OER activity of these materials was evaluated using cyclic voltammetry (CV) in 1 M KOH, which showed that both materials exhibit low OER activity, with α-$Ni(OH)_2$ displaying higher activity than β-$Ni(OH)_2$. The distinct differences of $Ni(OH)_2$ and NiOOH transition for these two different initial $Ni(OH)_2$ were observed under both the oxidative and reductive regions, indicating that the phase of the starting material plays a crucial role in determining the OER mechanism and activity. Furthermore, the CV results revealed that α-$Ni(OH)_2$ undergoes a more reversible phase transition between Ni^{2+} and Ni^{3+} states compared to β-$Ni(OH)_2$, which may contribute to its relatively higher OER activity and stability during electrochemical cycling.

In situ XAS measurements were performed to investigate the phase transitions occurring during OER using a step chronoamperometry (SCA) technique in our home-built in-situ electrochemical cell.[1] The SCA allows for precise control over the potential and current density during spectral acquisition. Figure 1 displays the plot of the SCA electrochemical data and their corresponding XANES spectra for α-$Ni(OH)_2$ and β-$Ni(OH)_2$, respectively. The results show that α-$Ni(OH)_2$ undergoes a reversible phase change from α-$Ni(OH)_2$ to γ-NiOOH and back to α-$Ni(OH)_2$, without apparent electrochemical aging due to overcharging at high voltage, indicating its stability and potential for long-term OER applications. In contrast, β-$Ni(OH)_2$ exhibits structural changes at the onset of OER at a higher potential. High-voltage overcharging converts β-$Ni(OH)_2$ to γ-NiOOH, and upon stepping back down to lower potentials, γ-NiOOH relaxes into a combination of α/β $Ni(OH)_2$. indicating a complex and irreversible phase transformation process. The XAS results reveal that the phase transition in α- $Ni(OH)_2$ occurs at a potential of around 1.425V vs RHE, where the material transforms into γ-NiOOH, accompanied by a significant increase in current density. In contrast, β-$Ni(OH)_2$ undergoes a more gradual phase transition, with the transformation to γ-NiOOH occurring over a wider range of potentials, indicating a less reversible and more complex process. Further kinetic analysis of the phase transition was performed and compared with our previous studies on the NiFe$(OH)_x$ structures.[2,3]

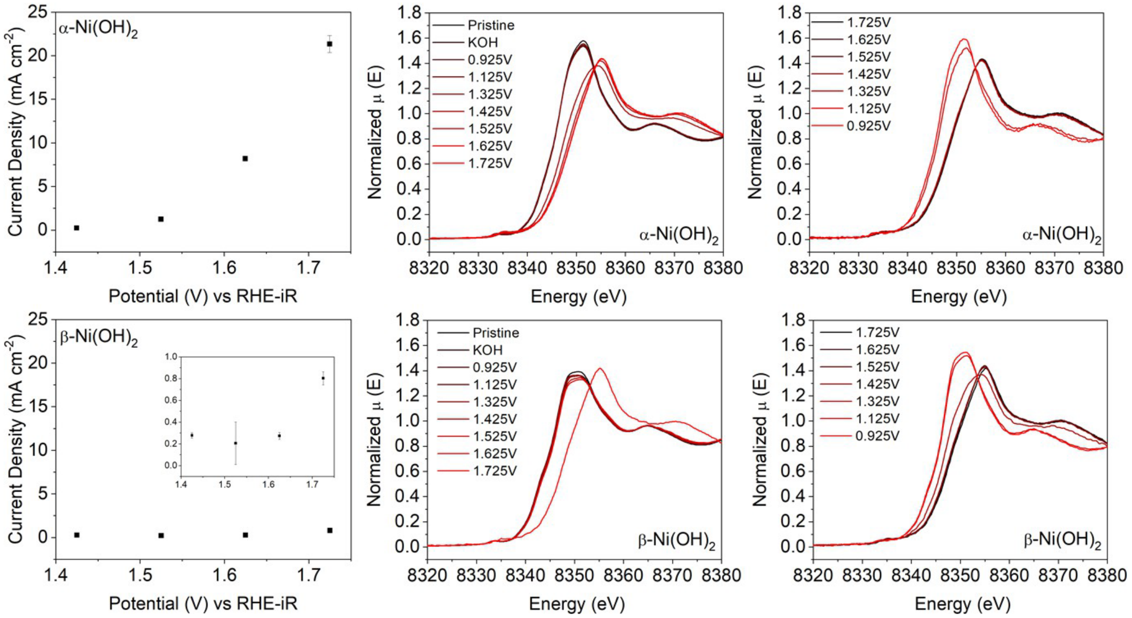

Figure 1. The plots of SCA electrochemical data and their corresponding XANES spectra for α-$Ni(OH)_2$ (Top Row) and β-$Ni(OH)_2$ (Bottom Row), respectively.

Significance

The Bode diagram provides a comprehensive illustration of the complex phase transformations that occur in $Ni(OH)_2$, including the conversion of α-$Ni(OH)_2$ to β-$Ni(OH)_2$ through ageing, α-$Ni(OH)_2$ to γ-NiOOH through charging, β-$Ni(OH)_2$ to β-NiOOH through charging, and finally β-NiOOH to γ-NiOOH through overcharging. This study delves into the critical aspect of investigating the effects of overcharging on α-$Ni(OH)_2$ and β-$Ni(OH)_2$, shedding light on their structural and electronic transformations. Our results show that α-$Ni(OH)_2$ remains relatively unchanged before and after overcharging. In contrast, overcharging of β- $Ni(OH)_2$ induces a significant expansion of the c-axis layer, facilitating the intercalation of anions into the layers, resulting in a unique combination of α/β-$Ni(OH)_2$. Furthermore, our findings demonstrate that β-$Ni(OH)_2$ can undergo a potential-driven conversion to α-$Ni(OH)_2$, accompanied by partial conversion of α-$Ni(OH)_2$ to γ-NiOOH. These findings provide valuable insights into the structural and electronic properties of $Ni(OH)_2$ during OER, which can inform the design of more efficient electrocatalysts for energy applications.

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KEYNOTE TALK

Operando Atomic-Scale Characterization of Catalysts in Liquid

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Introduction

Understanding catalytic function requires direct knowledge of how atomic structures evolve under realistic reaction environments. Recent developments in liquid phase TEM (LPTEM) and electrochemical liquid-cell TEM (e-LCTEM) now enable operando visualization of nanocatalysts in liquid with unprecedented spatiotemporal resolution. This work presents a unified operando framework linking 3D atomic arrangements, dynamic structural transitions, and electrocatalytic durability and activity.

Results & Discussion

Our operando liquid-phase TEM platform enables 3D atomic structure determination of individual nanocrystals freely rotating in liquid. We resolved full 3D atomic configurations of Pt nanocrystals and revealed significant intrinsic heterogeneity, variations in lattice strain, coordination, and defects, even among catalyst particles synthesized under identical conditions. These findings establish the necessity of single-particle–level structural analysis for catalytic systems. We further advanced this approach with time-resolved Brownian tomography, allowing sequential 3D reconstruction of catalysts undergoing chemical reactions. In oxidative etching experiments, we directly captured atom-by-atom dissolution from low-coordination sites and identified a transition from ordered FCC structures to disordered non-bulk configurations as particle size approached the sub-nanometer regime. This represents the first operando visualization of atomic-level degradation pathways in liquid and highlights the strongly dynamic nature of catalytic nanostructures. We also incorporated electrical biasing into a microfabricated liquid-cell TEM. This enabled reliable imaging of electrocatalysts under applied potentials. Using this e-LCTEM, we revealed a migration-gated degradation mechanism in Pt/C catalysts, where smaller nanoparticles exhibit enhanced mobility leading to coalescence and structural reconstruction, while larger particles degrade through localized dissolution. Such size-dependent electrochemical durability behavior cannot be accessed through ex-situ methods. Our recent studies of Cu-based electrocatalysts show that potential-driven dissolution, redeposition, and reconstruction strongly influence CO2 reduction pathways, altering intermediate spillover and product selectivity. Together, these results demonstrate that catalytic performance emerges from dynamic structural evolution, not static descriptors. Overall, our integrated operando LPTEM and e-LCTEM framework reveals how 3D atomic structures, reaction-driven transformations, and applied electrochemical bias collectively govern catalytic stability and activity, offering mechanistic insights essential for designing dynamic, next-generation electrocatalysts.

Significance

This work establishes an operando framework that directly visualizes and quantifies 3D atomic-scale catalyst evolution in liquid under electrical bias, enabling mechanistic correlations between structural transitions and catalytic performance. The methodology provides a path toward rational, dynamics-aware design of next-generation electrocatalysts.

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In-Situ Support-Wetting of Metal Cluster Regulates Catalytic Activity

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Introduction

The shape of supported metal particles regulates their catalytic reactivity. When the size of metal particles shrinks to the sub-nm range, their flattening, or the "wetting" of catalyst supports tend to occur,[1] inducing distinct performances. Related reports remain mostly serendipitous, without a systematic method to reveal the shape of sub-nm clusters, or a framework to rationalize/predict such support-wetting behaviors. We present a multi-model method combining *in-situ/operando* X-ray absorption spectroscopy (XAS), low-energy ion scattering (LEIS), and density functional theory (DFT) calculations to reveal metal-support wetting, and its implications in catalysis.[2]

Results & Discussion

Two series of Ru catalysts were synthesized on anatase TiO_2 (TiO_2-A) and CeO_2 supports, with Ru coverage between 0.05 and 1.5 Ru nm^{-2}. Under H_2 and at 533 K, Ru K-edge extended X-ray absorption fine structure (EXAFS) shows that, when Ru size enters sub-nanometer regime on CeO_2, the scattering from second-nearest Ru neighbors disappears, indicating the transformation of 3D-particles to 2D-rafts (**Fig. 1a**, red).[3] The dimensionality crossover is accompanied by the abrupt decrease in Debye Temperature (i.e., increase in disorder) and change in Ru−Ru bond length. *In-situ* LEIS analysis shows that sub-nm Ru clusters are of ~1-layer height, but grow three-dimensionally at larger size (**Fig. 1b**, red). Neither indicator of the Ru-support wetting was observed on TiO_2-A in the size range (blue). DFT validated the stronger wetting tendency by < Ru_{13} clusters on CeO_2 than TiO_2-A (**Fig. 1c**), while further revealing that surface oxygen vacancies formed on CeO_2 drive such structural behaviors. The transformation of Ru into 2D-rafts on CeO_2 induces drastic improvements in both activity and selectivity in polyolefin hydrogenolysis,[4] which is absent on TiO2-A, despite similar particle size.[2]

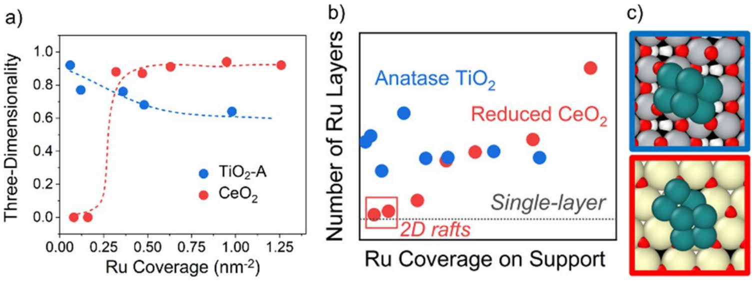

Fig. 1. a) The "three-dimensionality" of Ru particles calculated using the coordination numbers of the second- and first-nearest neighbors in the EXAFS; **b)** The average number of atomic layers in each Ru particle estimated from LEIS; **c)** DFT-predicted geometry of Ru_7 on TiO_2-A (top, a 3D structure) and CeO_2 (bottom, a 2D structure)

Significance

These results provide a novel systematic method to study metal-support wetting *in-situ/operando*. They reveal fundamental principles governing the shape, and thus reactivity of metal clusters.

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Seeing Nitrogen Differently: A New *Operando* Picture of Fe and FeCo Catalysts in Ammonia Decomposition

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Introduction

Ammonia decomposition is a promising route for carbon-free hydrogen, yet Fe-based catalysts suffer from strong Fe-N interactions that trap nitrogen, form stable nitrides, and suppress N_2 desorption. Although alloying Fe with a different metal such as Co enhances activity and stability,[1] the mechanistic origin of this promotion has remained unresolved due to the great challenge in resolving complicated surface nitrogen states (adsorbates, intermediates, and nitrides) under real reaction conditions. To overcome this limitation, we implement a unified *operando* soft X-ray approach that combines AP-XPS with 2D AEY-NEXAFS, enabling unprecedented chemical-state resolution of nitrogen on Fe and FeCo benchmark catalysts.

Results & Discussion

The integrated *operando* method directly reveals the dynamic evolution of surface nitrogen species exposing fundamental differences between Fe and FeCo catalysts. Our quantitative XPS analysis separates gas-, adsorbate-, and nitride-origin signals with high fidelity, while the 2D AEY-NEXAFS workflow offers enhanced surface specificity and separates coexisting nitride phases that remain challenging to be distinguished in standard fixed-kinetic-energy AEY-NEXAFS measurements due to spectral overlap (**Figure 1**).

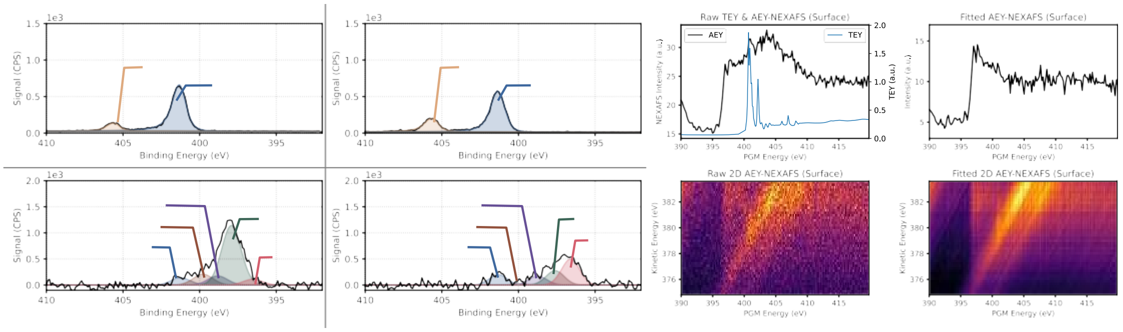

Figure 1. (a) *Operando* AP-XPS revealing gas-phase signals and surface nitrogen speciation (b) Example of 2D AEY-NEXAFS enabling deconvolution of spectral features for enhanced surface nitride probing sensitivity.

Using this dual-modality framework, we identify a clear mechanistic contrast: Fe rapidly accumulates nitrogen and locks into strongly bound surface nitride states, whereas FeCo avoids this deep nitridation and instead stabilizes a weakly-bound, dynamically recyclable surface environment. These *operando* observations provide direct evidence that the promotional effect of Co arises from reshaping Fe-N interactions and preventing kinetic nitrogen saturation.

Significance

This work introduces a novel *operando* X-ray approach for quantifying nitrogen speciation under realistic reaction conditions. The ability to resolve surface nitrides, adsorbates, and gas-phase species simultaneously offers new insight into how catalyst surfaces evolve and deactivate. By demonstrating how Co maintains Fe in a metastable, catalytically accessible state, our findings establish a generalizable design concept for developing earth-abundant Fe-based catalysts that resist nitrogen lock-up in ammonia decomposition.

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Mapping reactive zones in magnetic induction reactors by XRDCT

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Introduction

The incorporation of spatially resolved measurements into classic synchrotron techniques is enabling major advances in the field of catalysis. The advantage comes from probing catalytic materials not only under operational conditions, but also in their relevant physical form, i.e. applied as a coating to a large monolith, or inside a non-conventional reactor. The electrification of reactors has yielded a series of alternative heating approaches, with magnetic induction heating (MIH) offering significantly attractive routes. To this effect, an *operando* X-ray diffraction computed tomography experiment was performed during magnetically induced catalysis, with the aim of resolving heat gradients, heat transfer and exploring magnetic field effects. This system has shown superior performance for CO_2 reduction compared to the thermocatalytic route.[1]

Results & Discussion

The cobalt NPs are both the catalyst and the heating element in these experiments. The lattice parameter maps show the expansion of the Co under an alternating magnetic field, with significant differences in the lattice expansion as a function of location within the reactor (Figure 1). Accurate temperatures were obtained from calibration of the lattice parameter. Strong thermal gradients are present, with the centre and outside of the bed differing by 400°C. On changing from argon to a reaction gas mixture, the overall temperature decreased. Manipulation of the reactor within the electromagnetic coils confirmed that the gradients were not due to field gradients.

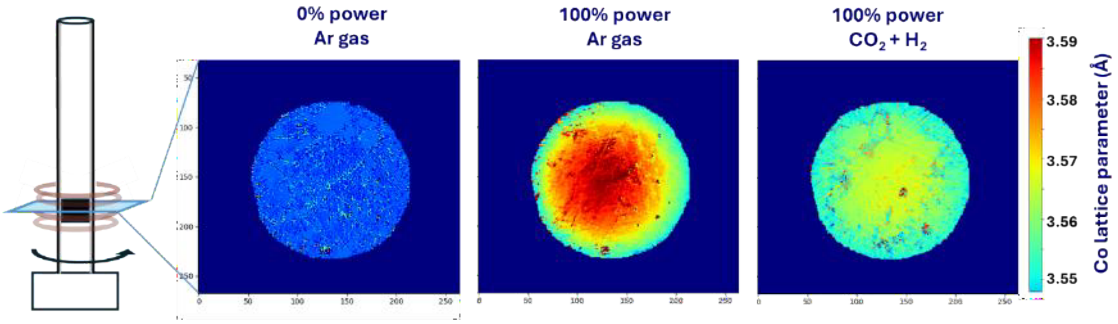

Figure 1 Schematic representation of the catalyst bed cross section imaged, with the Co lattice parameter mapped in the reconstructed bed under three different conditions, including either 0 or 100% magnetic power, and either argon gas or a CO2 + H2 reaction mixture.

Significance

Stark thermal gradients show opportunity for improved reactor design; in fact, the addition of appropriate insulation improved CO2 conversion by 14%. The lower temperature of the catalyst bed under reaction conditions is a result of the endothermic chemical reaction being catalysed. Accurate measurement of the catalyst temperature confirmed magnetic field effects are enhancing catalytic performance.

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Operando XAS in flow: identification of active sites for the conversion of methane to oxygenates in water

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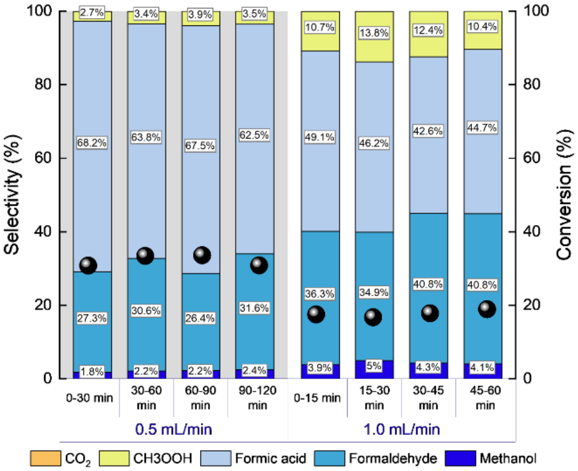
Introduction

Transition metal loaded zeolites have been explored in recent decades for the low temperature direct step-wise conversion of methane to methanol in the gas phase and to a lesser extent in the liquid phase, where Hutchings et al [1] have shown a viable catalytic pathway of methane conversion using H_2O_2 as an oxidant. We have explored the catalytic conversion of methane to oxygenates in water over Fe-ZSM-5 in flow as a function of residence time, H_2O_2 and methane concentration, temperature and initial Fe speciation (single atoms [2] vs clusters). This will be combined with an operando XAS study (beamtime scheduled at the SuperXAS [3] beamline (a beamline for true operando studies) of the Swiss Light Source in December 2025), where structure-activity/selectivity relationships will be established.



Methane to oxygenates conversion over Fe-ZSM-5 as a function of residence time. Conditions: CH_4 at 12 bar, 90 °C, ***x mL/min*** *flow, 25 mg catalyst, 50 mM H_2O_2*

Results & Discussion

Liquid phase (NMR and GC) and gas phase analytics (GC) showed higher conversion of methane to oxygenates with higher temperature and longer residence times (see Figure for the effect of residence time). Catalytic conversion could be sustained for at least four hours. Selectivity to the different oxygenates (methanol, formaldehyde, formic acid or CO_2) strongly depends on initial Fe speciation in Fe-ZSM-5, where we synthesized catalysts with Fe clusters or isolated Fe atoms [3]. We have developed a unique flow through reactor for operando XAS studies at the Fe K-edge (at pressures up to 30 bars), allowing to study for the first time the structure-selectivity/activity relationships of this catalytic system. Results will be presented based on the upcoming XAS beamtime in December.

Significance

The quest for low-temperature catalytic conversion of methane to valuable liquid oxygenates comes a step closer by understanding structure-selectivity relationships of Fe-ZSM-5 in a unique flow reactor for the catalytic conversion of methane to oxygenates.

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Operando Studies of Energy Conversion Devices by HAXPES

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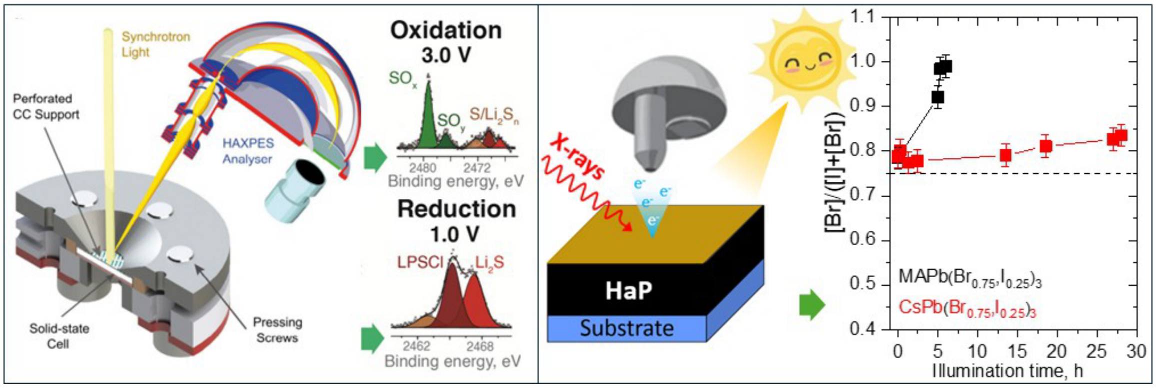
Introduction

Photoelectron spectroscopy is well known for its chemical sensitivity but is often limited in application because of its surface sensitivity. Using hard X-rays mitigates this issue and often enables in-situ and operando studies. This contribution presents latest results on HAXPES of battery and solar cell structures showcasing the in-situ/operando analytical abilities of BESSY II.



***Left**: Schematic of the developed operando cell that allows measurements of solid-state batteries. The spectra show the S 1s core level line monitoring how the sulfide-based solid electrolyte changes upon applying different voltages. **Right**: Schematic of the experimental setup to study the surface composition (here in particular the halide ratio) of different halide perovskites (HaP: MAPb(Br,I)$_3$ and CsPb(Br,I)$_3$) and how it changes upon illumination.*

Results & Discussion

Operando HAXPES experiments[1] were performed on a sulfide-based Li_6PS_5Cl solid electrolyte (SE) to monitor and understand its reduction/oxidation reactions upon lithiation/delithiation and resulting SE interphase (SEI) growth. The HAXPES data recorded at reducing conditions suggest that the SEI has a heterogeneous/layered microstructure with Li_2O preferentially located near the current collector, followed by Li_2S. Upon increasing the potential, Li_2O and Li_2S are gradually oxidized to form sulfite and sulfate species, along with oxidized sulfur species (polysulfides). These species convert back to the same major SEI components upon subsequent lithiation.

The impact of sample illumination on the chemical and electronic properties of mixed halide perovskite solar absorbers, based on the organic MA^+ and the inorganic Cs^+ cation was investigated. The hybrid perovskite absorber is revealed to undergo a pronounced phase transformation at the surface, driven by the photoinduced removal and degradation of its MA^+ cation and the complete depletion of surface I, due to the photo-activated redox decomposition of PbI_2. By comparison, the fully inorganic absorber shows only slight changes,[2] primarily to its halide content (i.e., loss of I). Based on these findings, the further advancement of fully inorganic perovskite materials stands as a promising strategy to improve the long-term stability of perovskite-based PV.

Significance

This demonstrates that the combination of HAXPES with a smart sample environment and experiment design enables the study of battery and solar cell structures at relevant conditions.

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Spatio-Temporal Insights into Supported Pd Nanoparticles Dynamics using Full-Field Hyperspectral XAS imaging

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Introduction

Supported palladium nanoparticles (PdNPs) are a key platform for investigating nanoparticle–support interactions, which can profoundly influence catalytic performance[1]. PdNPs exhibit exceptional activity in reactions such as hydrogenation[2] and CO oxidation[3], due to their unique structural and electronic properties. During these reactions, spatial heterogeneities may develop across the catalytic bed, driven by variations in local temperature and gas concentration gradients leading to structure and phase modifications. This study explores the spatial dynamics of hydride formation during H_2 pretreatment and its subsequent effect on CO oxidation over supported PdNPs catalysts. To achieve this, we applied spatio-temporally resolved full-field (FF) hyperspectral X-ray absorption spectroscopy (XAS) imaging implemented at ROCK (SOLEIL)[4].

Results & Discussion

Hyperspectral XAS imaging analysis enabled the extraction and identification of transient species, along with their corresponding spatial concentration profiles. First, speciation maps revealed distinct dynamics of PdH_x hydride transformation, in particular wavefront propagation across the catalytic bed, depending on the support composition (Al_2O_3- and TiO_2-supported PdNPs) and the pretreatment type (LC: low H_2 concentration or HC: high H_2 concentration). For the TiO_2-supported sample, metallic palladium formed after pretreatment was transformed into oxidic species during the CO oxidation reaction, showing a wavefront with directionality dependent on the heating versus cooling reaction stage. At room temperature after the reaction, the catalyst exhibited a steady-state distribution of Pd^0 and PdO species (Fig. A). Variations in the concentration profile of the oxidic species were identified depending on the presence or absence of PdH_x, as determined by the pretreatment conditions, which directly influence the hysteresis behavior observed for the TiO_2-supported sample (Fig. B).

Significance

FF hyperspectral XAS imaging unveiled spatially resolved structural and phase transformations within supported PdNPs catalysts at the micrometer scale, highlighting the dynamic interplay between support material, hydride formation, and oxidation behavior with second time resolution. By directly linking spatially resolved structural dynamics to catalytic performance, this study provides critical insights that can inform the rational design of more efficient and robust heterogeneous catalysts.

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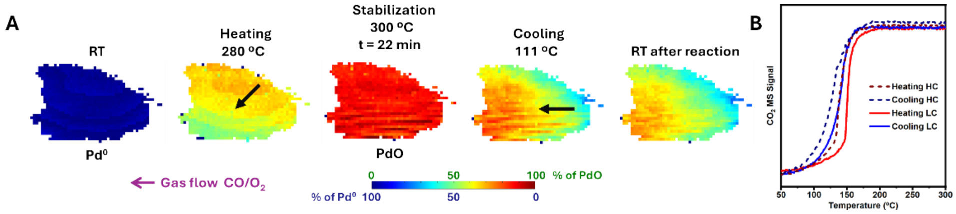

Fig. A) Speciation maps derived from the MCR-ALS minimization of the hyperspectral imaging data set during different stages of the CO oxidation reaction for TiO_2-supported PdNP. The black arrow indicates the preferential direction of the phase transitions, and the purple arrow indicate the gas flow direction (a mixture of 0.4% CO and 4.2% O_2 in He). The color gradient corresponds to the phases present at each stage, as indicated by the scale bar. **B)** Hysteresis loops of both Pd/Ti samples, derived from the mass spectrometry data collected during the measurement. LC and HC correspond to low and high hydrogen concentrations during the pretreatment, respectively.

KEYNOTE TALK

Introducing *Stimulando* Time-Resolved Infrared Spectroscopy to Study Intermittent Light-Stimulated CO_2 Hydrogenation

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Introduction

Resonant catalysis predicts that applying an intermittent stimulus, such as light, at high frequencies comparable to turnover frequencies (TOFs) can enhance activity by orders of magnitude and improve selectivity.[1] However, experimental evidence is so far rather limited due to a poor understanding of how such stimulation affects catalysts and reaction intermediates. Here, time-resolved "*stimulando*" infrared (IR) spectroscopy was used to observe catalyst materials under operating conditions and during light stimulation in the CO_2 hydrogenation over Ni-Ga-based catalysts as a model probe reaction (Fig. 1a, 1b).

Results & Discussion

Light-induced changes in surface species were tracked using steady-state and rapid-scan IR spectroscopy (Fig. 1c). Both analytical methods revealed a reversible decrease in CO and formate coverage under UV illumination. Furthermore, rapid-scan IR with millisecond time resolution demonstrated that the surface coverage of CO under light irradiation decreased with faster kinetics compared to the increase in CO surface coverage in the dark (Fig. 1d). Despite the observed changes in surface coverage of both CO and formates, the CO_2 hydrogenation performance was not significantly affected under the conditions studied herein.

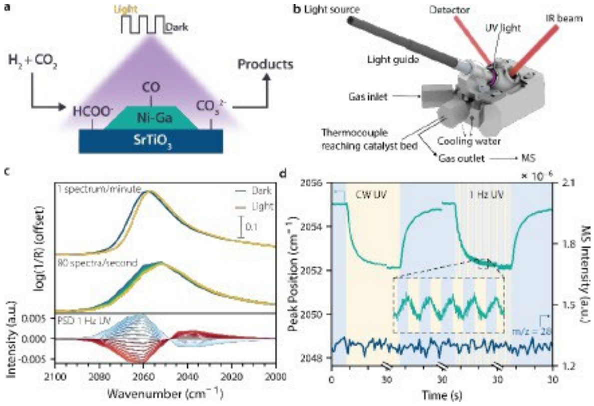

Figure 1: a, Resonant catalysis concept; b, Stimulando set-up; c, Light-induced changes confirmed with PSD analysis are tracked by steady-state and rapid-scan IR spectroscopy; d, Reversible peak position shifts under continuous (CW) and pulsed light (1 Hz) by rapid-scan IR spectroscopy (ms time resolution) with operando MS activity analysis.

Significance

The results provide valuable insights for adjusting light stimulation parameters, such as intensity, duty cycle and wavelength, paving the way to more effective stimulation to enhance performance.

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A Journey from Rapid- to Step-Scan IR: Revealing Early Isotopic-Exchange Dynamics in CO_2 Hydrogenation on Cu/ZrO_2

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Introduction

Studying reaction mechanisms in heterogeneous catalysis under realistic conditions and on short timescales remains a major challenge.[1,2] In this work, we introduce a new approach that combines time-resolved operando transmission infrared spectroscopy (TR-IR) with steady-state isotopic transient exchange (SSITE) to decipher the CO_2 hydrogenation mechanism over a Cu/ZrO_2 catalyst. Previous studies [3,4] have proposed that Cu-bound formates are key intermediates in this reaction. Our aim is to highlight the isotopic exchange dynamics of these species to better understand their involvement in the catalytic cycle.

Results & Discussion

The TR-IR/SSITE tests were carried out for CO_2 hydrogenation reaction over a 5,8 $_{wt}$% Cu/ZrO_2 catalyst at 220 °C and 3 bars, using alternating 20% $\mathbf{^{12}CO_2}$/60% H_2/He and 20% $\mathbf{^{13}CO_2}$/60% H_2/He-Kr gas feeds. The catalyst pellet (1.21 cm², ~10 mg) was loaded in an IR cell with an internal dead volume inferior to 0.5 cm^3. The evolution of gas phase and surface adsorbed species were monitored using a Pfeiffer QMS 200 mass spectrometer and Bruker Vertex 70V FTIR spectrometer (MCT detector), respectively. IR spectra were first collected in rapid-scan mode with 4 cm^{-1} resolution (122 ms). The spectra recorded under $\mathbf{^{12}CO_2}/H_2$ exhibit characteristic IR bands of carbonate, methoxy, and formate species adsorbed on the catalyst surface, which undergo the expected red shift when switching to $\mathbf{^{13}CO_2}/H_2$. We applied a deconvolution methodology based on fitting the direct spectra under chemically coherent constraints (13 IR bands), enabling precise reconstruction of difference spectra (see Figure). Analysis of the first-second exchange reveals that IR bands at 1570 cm^{-1} and 1353 cm^{-1}, assigned to formates adsorbed on ZrO_2 and Cu, respectively, display markedly different kinetics: Cu-bound formates exchange 10 times faster (0.045 μs^{-1} vs. 4.6 10^{-3} μs^{-1}), underlining their pivotal role in the CO_2 hydrogenation mechanism. The same approach was applied to spectra collected using the newly developed isotopically-triggered step-scan IR method (8 cm^{-1} and 2.5 ms). A comparison with the rapid-scan results will be presented during the congress.

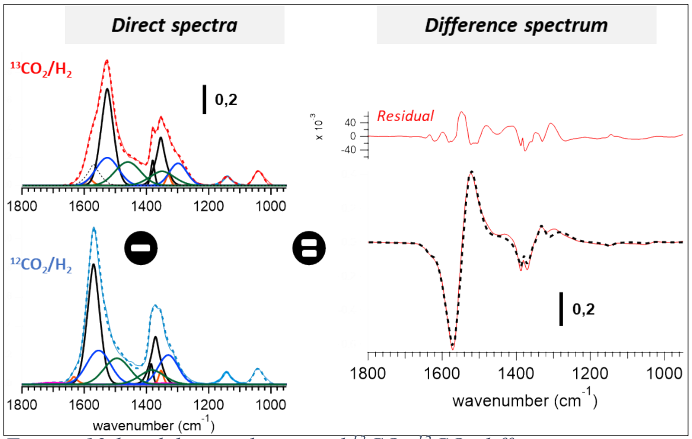

Figure: 13-band deconvolution and $^{13}CO_2$-$^{12}CO_2$ difference spectra on Cu/ZrO_2 at 220 °C, 3 bar. (dashed lines = fits)

Significance

The TR-IR/SSITE approach, combined with our deconvolution methodology, provides a powerful tool to probe the dynamics of heterogeneous catalytic reactions and to examine individual reaction steps at the molecular level under realistic steady-state conditions on short timescales.

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Operando Insights into the Effect of Ceria Incorporation on the Oxygen Evolution Reaction Performance of Iridium-Based Catalysts

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Introduction

Proton-exchange membrane water electrolyzers (PEMWE) are emerging as a key technology for sustainable, electrocatalytic green hydrogen production. The high conversion rates of PEMWE allow efficient energy storage from renewable sources and ensure a dynamic energy supply despite seasonal variations. However, PEMWE advancement is hindered by the large overpotentials required for the acidic oxygen evolution reaction (OER) at the anode. Although Ir- based catalysts remain the most active and stable under the harsh conditions of low pH, high potential, and high oxygen concentration, their scarcity and insufficient long-term durability limit large-scale deployment [1,2]. Recent studies, including our previous work, have shown that above ~1.6 V vs. RHE, rutile IrO_2 undergoes a shift in its degradation mechanism as lattice oxygen begins to interact with active sites, leading to performance loss [3]. Enhancing the catalytic activity and stability of these noble-metal oxides is therefore essential to reduce precious metal loading and enable GW-scale PEMWE systems.

Results & Discussion

In this work, we investigate the incorporation of abundant and cost-effective Ce into IrO_2 for improved performance and stability at lower Ir content. $Ir_xCe_{1-x}O_2$ (x=0.2, 0.5, 0.8) samples were prepared by flame spray pyrolysis (FSP) method. XRD and Raman spectroscopy confirmed the coexistence of metallic and oxidic Ir species. *Ex situ* XAS revealed a shift of the Ir white line to lower energies compared to rutile IrO_2, pointing to the presence of lower oxidation states of iridium inside $Ir_xCe_{1-x}O_2$ samples. After electrochemical conditioning by potential cycling, XAS, XPS, and TEM analyses showed distinct structural evolution across the series: $Ir_{0.8}Ce_{0.2}O_2$ underwent noticeable particle sintering, whereas lower-Ir formulations maintained well-dispersed nanoparticles. Additionally, XPS results revealed that $Ir_{0.5}Ce_{0.5}O_2$ exhibited the highest degree of metallic Ir oxidation to higher Ir valence states. Simultaneously recorded Cyclic Voltammetry (CV) and Fixed Energy X-ray Absorption Voltammetry (FEXRAV) profiles as shown in Figure 1a reveal cycle-dependent changes in both electrochemical activity and X-ray absorption response, highlighting the dynamic evolution of the $Ir_{0.5}Ce_{0.5}O_2$ catalyst under operando conditions. RDE measurements demonstrated that $Ir_{0.5}Ce_{0.5}O_2$ and $Ir_{0.8}Ce_{0.2}O_2$ achieve lower overpotential at 10 mA cm^{-2}, along with enhanced stability relative to commercial IrO_2, confirming enhanced Ir utilization. Moreover, highest Ir mass activity at 1.53 V vs. RHE was obtained for $Ir_{0.5}Ce_{0.5}O_2$. While increasing Ir content above a 0.5 molar ratio did not further boost activity, likely due to Ir sintering induced by potential cycling, reducing Ir content to 0.2 resulted in significant activity loss. To further elucidate the potential-dependent behavior of the catalysts, operando XAS measurements were conducted under chronoamperometric (CA) conditions. As shown in Figure 1b, the white-line position of the $Ir_{0.5}Ce_{0.5}O_2$ catalyst increases progressively with applied potential, reflecting its strong Ir response. Figure 1c compares the potential dependent white-line shifts of all Ir-Ce compositions, while Figure 1d presents the corresponding currents recorded during CA measurements. The operando results reveal clear composition-dependent trends; $Ir_{0.2}Ce_{0.8}O_2$ exhibits the highest average Ir oxidation state to the applied potential, correspondingly to low OER activity. $Ir_{0.5}Ce_{0.5}O_2$ shows the most pronounced Ir redox flexibility and reversibility together with the highest currents, indicating an optimal balance between oxidation dynamics and catalytic performance. $Ir_{0.8}Ce_{0.2}O_2$ demonstrates a moderate Ir redox response coupled with high current output. These findings highlight that tuning the Ir-Ce ratio enables control over redox dynamics and OER activity.

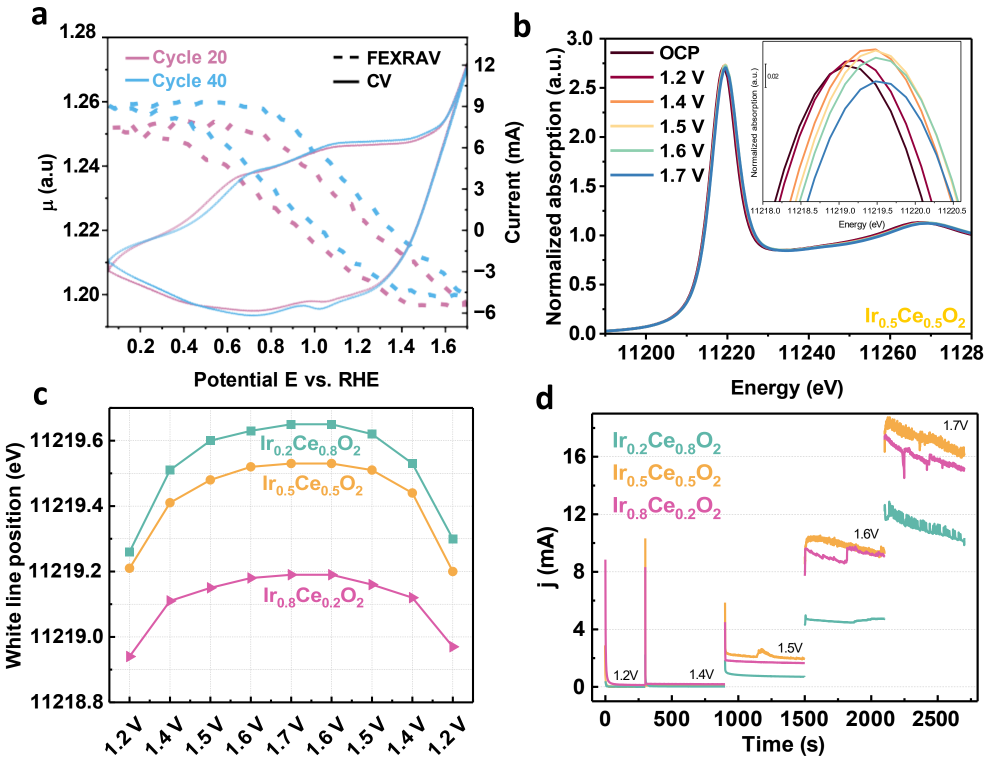

Figure 1. (a) Operando comparison of CV and FEXRAV signals at selected cycles (20 and 40). Solid lines represent the electrochemical current density, while dotted lines show the corresponding FEXRAV µ-intensity as a function of potential (vs. RHE) b) Operando Ir L_3-edge XANES spectra showing the white-line evolution of $Ir_{0.5}Ce_{0.5}O_2$ under increasing applied potentials (vs. RHE), with an inset showing an enlarged view of the white line region. (c) Potential-dependent white-line shifts for $Ir_xCe_{1-x}O_2$ compositions (d) Chronoamperometric i-t curves recorded during the operando XAS measurements.

Significance

By unraveling the influence of Ce on the chemical and electronic structure of IrO_2 during OER using operando XAS, this study aims to develop more efficient and durable catalysts tailored for sustainable H_2 production, ultimately optimizing catalyst design for real-world electrolyzer applications.

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Crystallite size dependent oxidation captured using operando magnetometry

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Introduction

Iron, cobalt and nickel catalysts are known for their industrial use in the Fischer-Tropsch CO hydrogenation, CO_2- and/or steam-assisted reforming reactions as well as CO and CO_2 methanation reactions. In these processes, catalyst deactivation typically occurs *via* sintering and/or carbon deposition; however, oxidation of the catalytically active phase may also occur by e.g. water or CO_2 in the product or feed [1,2,3]. This observation is particularly interesting because the oxidation of the corresponding bulk phases is typically not thermodynamically feasible at the relevant conditions of the abovementioned reactions. Therefore, oxidation is thought to be crystallite size dependent, which is possible due to the high surface energy contributions of nano-sized crystallites [4]. This work aims to investigate the size-dependent oxidation of ferromagnetic catalysts (model systems and industrially relevant catalysts) using *operando* magnetometry [5]. Reaction environments were simulated via co-feeding of water at different levels.

Results & Discussion

For all three systems studied, crystallite size dependent oxidation has been observed using the operando magnetometer. An example of the lower oxidation threshold of smaller supported nickel particles (3.6 vs. 7.5 nm) as function of water to hydrogen partial pressures is shown in Figure 1 as indicated via loss of magnetization. Importantly, it could be shown that size dependent oxidation agrees with thermodynamic prediction taking differences in the surface energies between the starting metal (or metal carbide) phases and the resulting oxide phases into account, highlighting the universality of this concept. With the nickel-based catalysts we were further able to distinguish surface and bulk oxidation.

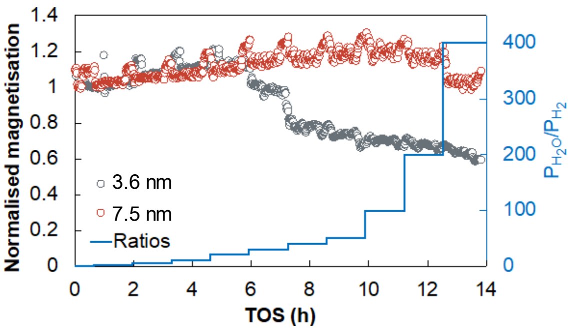

Figure 1. Oxidation threshold tests of differently sized nickel nano particles as function of water to hydrogen ratio

Significance

The results of this study allow to predict catalyst stability threshold as function of reaction conditions. They further inform catalyst design with respect to choice of optimum crystallite size.

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Operando Raman and MES-DRIFTS study on the role of gold and vanadium in ceria-based oxidation catalysts

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Introduction

V and Au dispersed on ceria have remarkably different impacts on ceria performance for toluene oxidation, which follows the Mars-van Krevelen mechanism [1-3]. Au/CeO_2 is more active than CeO_2, whereas VO_x/CeO_2 is less active and selective to CO_2, as it produces benzaldehyde and CO. *Operando* Raman and concentration-modulation excitation spectroscopy (c-MES) DRIFTS bring complementary insights into the mechanism, the nature of the active site, catalyst state, adsorbed hydrocarbon and oxygen species.

Results & Discussion

c-MES-DRIFT-MS experiments were performed with the catalysts reported in [2] at 200-300 °C alternating between He or O_2/He and toluene/He with or without O_2. The time-resolved spectra were transformed to the phase domain to selectively identify the active species. Fig. 1 shows that toluene is molecularly adsorbed on CeO_2 surface and activated by H subtraction from the methyl group by lattice O^{-2}, forming benzyl species ($C_6H_5CH_2^-$), $\nu_{(CH_2)} = 2800$ cm^{-1} [4]. This intermediate can be stepwise oxidized to benzoxyl and benzoate. Subsequent decarboxylation and oxidation of the aromatic ring produces formate and aldehyde-like species, which are finally oxidized to CO_2 and water. Aromatic ring activation seems to be the rate-limiting step, since the oxidation proceeds readily after the decarbonylation. VO_x acidic sites hamper H abstraction from the methyl group, Au particles would facilitate the activation of molecular oxygen, in agreement with the formation of peroxide/superoxide species observed by o*perando* Raman.

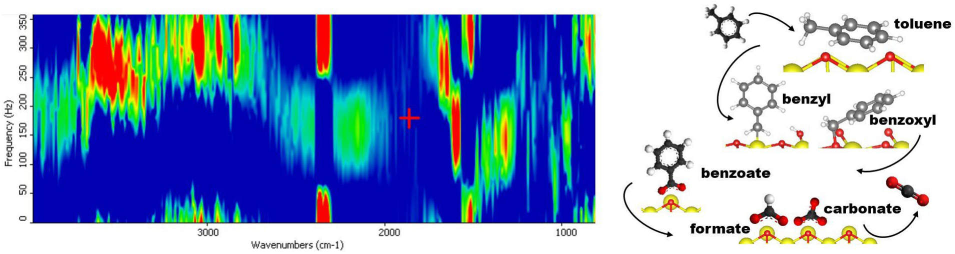

Figure 1. Proposed reaction mechanism of toluene oxidation on surface CeO_2.

Significance

Modulated and *operando* spectroscopy coupled with advanced spectral analysis provide molecular insights into the reaction mechanisms that explain toluene oxidation on ceria-based catalysts and facilitate the rational design of optimized catalytic systems.

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Determining surface coverage on working Ni/SiO$_2$ catalysts by transient operando XANES at Ni K-edge

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Introduction

Developing better catalytic materials requires a deep understanding of their function. The key concepts here are *active sites* and *surface coverage* – the fraction of surface sites occupied by reaction intermediates. Surface coverage is directly linked to and, in fact, often determines catalytic activity, selectivity, and stability. Characterizing the active sites and quantifying the coverage under reaction conditions remains a major challenge. Existing techniques are either semi-quantitative or lack necessary specificity for active sites.[1] Operando hard X-ray absorption spectroscopy (XAS) combined with transient gas switching is potentially a powerful technique to solve this challenge.[2]

Results & Discussion

Recently we studied the coverage of surface intermediates over supported Ni/SiO$_2$ nanoparticles during CO$_2$ methanation. Combining in situ FTIR spectroscopy and isotope labelling, we found that *CO groups (*i.e.*, surface carbonyls, **Fig. 1a**) are the dominant surface species and the key reaction intermediates. The determined surface coverage was low, however, involving only ≈1.2% of Ni atoms in the particles (≈6% of surface atoms).[3] More recently, at ROCK beamline (SOLEIL), we performed meticulous transient gas switching experiments ($H_2 \leftrightarrow CO_2 + H_2$) followed by XAS over the same catalysts. Excellent signal quality (**Fig. 1b**) and fast scanning enabled extraction of a distinct new spectral component (S2 on **Fig. 1c**) via MCR-ALS analysis. This component represents active surface Ni atoms undergoing reversible changes during methanation. The evolution of S2 fraction correlates precisely with methane formation (**Fig. 1d**). Moreover, the spectral shape of S2 with a pronounced pre-edge feature at 8333 eV (1s→3d) is different from expected Ni phases (NiO, NiCO$_3$, etc.) and indicates formation of non-centrosymmetric reactive complexes on the catalyst surface.[4] Finally, the fraction of S2 (≈1.0–1.8%) matched the fraction of involved Ni atoms derived from isotope labelling and FTIR analysis.

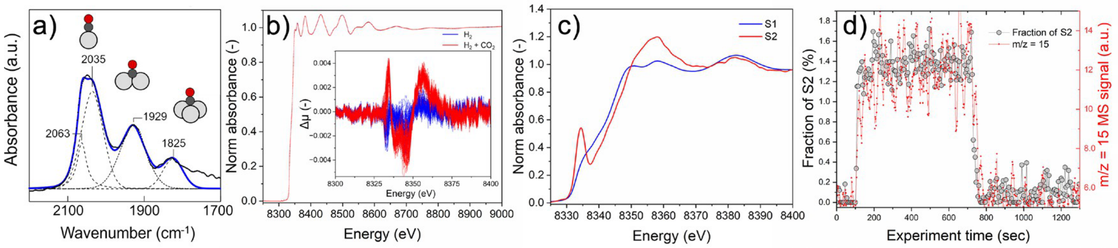

Figure 1. a) In situ FTIR spectrum of surface carbonyls recorded during CO$_2$ hydrogenation over Ni/SiO$_2$ catalyst at 220 °C; b) In situ XAS spectra and corresponding difference spectra (inset) recorded upon switching from H$_2$ to H$_2$+CO$_2$ flow at 220 °C and 1 bar over the same catalyst; c) Pure spectra obtained by MCR-ALS analysis; d) Correlation between the fraction of S2 (grey) and methane MS signal (red).

Significance

Similar results were obtained for Co- and Ru-based methanation catalysts, highlighting the potential of transient hard X-ray XAS as a quantitative probe for active sites and surface coverage.

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PLENARY TALK

Spatiotemporal Analysis of Nanoparticle Surface Dynamics: Prospects for Atomic-Level *Operando* Characterization of Catalysts with Electron Microscopy

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During heterogeneous catalysis, nanoparticle surface structures can undergo significant change and may sometime form multiple transient and dynamic structures which complicates the task of identifying active sites. There are many outstanding questions regarding the role of atomic-scale dynamic meta-stability (i.e., fluxional behavior) in catalysis. This is similar to the challenge of understanding the role of molecular conformations for catalytic functionality in enzymes. The structures constantly undergo thermally induced stochastic change but many of the structural changes may not impact catalysis. The challenge is to understand structural changes that are catalytically functional from spectator changes. Observations of atomic level structural dynamics under *operando* conditions can be performed in the transmission electron microscope (1). We have conducted *operando* measurements on Ru/SiO_2 and Pt/CeO_2 catalyst during CO oxidation. For the supported Ru catalyst, we find that RuO_2 layers formed under some reaction conditions and once thought to be the source of ruthenium catalysts' high activity, are effective spectator species, which diminish the activity of the catalyst by reducing the surface area available for more active surface structures (2). For the Pt/CeO_2 system, we were able to show that atomic level structural dynamics correlates directly with turnover frequency (3) showing that fluxionality is directly involved in catalytic functionality in this case. Recent developments in electron detectors and artificial intelligence have made it possible to track the fluxional behavior on nanoparticle surfaces with spatiotemporal resolutions of 1 Å and 10 ms (at moderate electron dose). Though this timescale is much longer than typical molecular timescale (usually considered to be in the range of picoseconds to nanoseconds) is similar to typical turnover frequencies in heterogeneous catalysis (0.1 – 100). Under some conditions, such as Pt in CO, very pronounced fluxional behavior is observed on the Pt surface even at room temperature (4). These observations highlight the importance of developing suitable descriptors for atomic-level structural dynamics such as those based on Markovian behavior or persistent homology (5). Differentiating functional structural dynamics from spectator dynamics will be a challenge for the interpretation of such observations.

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Decoupling Metal-Support Interactions

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Introduction

Metal-support interactions (MSI) are key in the performance of heterogeneous catalysts.[1] They can induce electronic or geometric effects and provide interfacial sites with different activity. This research probes MSI, decoupling the MSI-related effects. X-ray absorption spectroscopy (XAS) with modulation-excitation (ME) is applied on (un)promoted nickel-based catalysts, serving as test system with CO_2 methanation as model reaction.

Results & Discussion

A 10 w% Ni/SiO_2 catalyst was promoted by depositing 15 mol% of ZrO_2 or CeO_2. TEM revealed that the promoters are in close contact with Ni nanoparticles. Activity measurements indicate that the methane selectivity improves in the order Ni/SiO_2<CeO_2–Ni/SiO_2<ZrO_2–Ni/SiO_2, with enhancements up to a factor of two. To gain insight into this promotional effect, operando, time-resolved XANES measurements were performed at the ROCK beamline[2] (Figure 1). The spectra showed no significant difference, suggesting promotion does not lead to electronic modifications of the Ni phase.

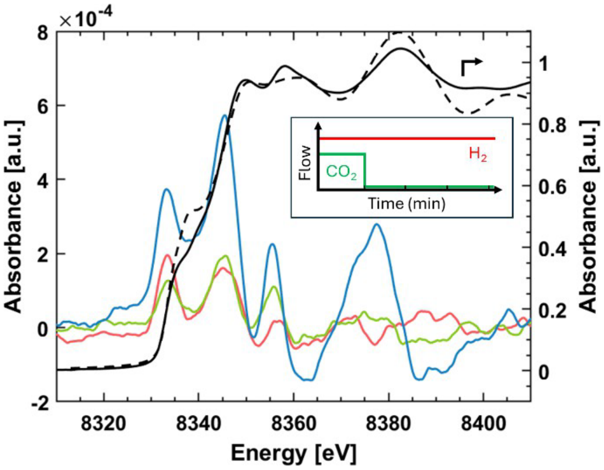

Figure 1: In-phase demodulated spectra after PSD for Ni/SiO_2 (red), ZrO_2-Ni/SiO_2 (green) and CeO_2-Ni/SiO_2 (blue), plotted with the XANES spectrum of Ni-foil (full line) and simulated XANES (dashed line); applied modulation (inset).

To distinguish between geometric effects and interfacial contributions, a ME experiment was conducted and combined with phase-sensitive detection (PSD) to probe the active sites. The in-phase demodulated spectra of Ni/SiO_2, ZrO_2–Ni/SiO_2 and CeO_2–Ni/SiO_2 (Figure 1), are similar in shape, pointing to a comparable underlying process. However, the higher amplitude observed for CeO_2–Ni/SiO_2 suggests that this process is more abundant on that material. First analysis of the PSD profiles with experimental difference spectra show no correspondence. This observation indicates that the process occurring during modulation is likely non-redox in nature, with adsorption of gas-phase species possibly playing a key role. It remains to be determined whether this arises from geometric factors, e.g. selective coverage of specific Ni crystal planes by the promoting phase, or from the formation of active interfacial sites. Further interpretation is supported by DFT-based calculations of interfacial energies, adsorption energies and simulated XANES spectra.

Significance

This work is methodologically significant as it extends the sensitivity of ME-XAS to detect adsorption events through DFT-based calculations and XANES simulations. Decoupling of the different contributions to MSI will allow for a more informed design of catalysts.

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Design of copper sites in Cu-SSZ-13 to control HCN formation and conversion during NH$_3$-SCR in the presence of HCHO

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Introduction

Secondary emissions formed during the combustion of alternative fuels have attracted scientific interest in recent years, as their interaction with state-of-the art catalysts is still not completely understood. Especially HCHO and HCN have been shown to deactivate traditional NH$_3$-SCR catalysts, yet their influence on the active sites remains not fully elucidated. While the deactivation was observed for all investigated SCR systems [1], Cu-SSZ-13 exhibits a peculiar response to the presence of HCHO and HCN: it is the only catalyst that shows a decrease in SCR activity in the low temperature region and at the same time demonstrates the potential to prevent the generation of HCN emissions in the presence of HCHO. By means of systematic *in situ/operando* spectroscopic investigations, this study aims to understand the impact of HCHO presence on the structure and activity of different Cu sites during the SCR of NO$_x$ with NH$_3$.

Results & Discussion

To investigate the interaction of HCHO and HCN with the active site of Cu-SSZ-13 catalysts, a series of samples with different Cu-loadings and Si/Al-ratios was prepared [2]. While a loss in NH$_3$-SCR activity was observed for all investigated catalysts, at temperatures above 350 °C a site selective response was detected. Samples containing a high concentration of Z$_2$Cu species were associated with pronounced HCN emissions even at higher temperatures, whereas samples containing ZCuOH species exhibited a drastic decrease in HCN formation with rising temperatures.

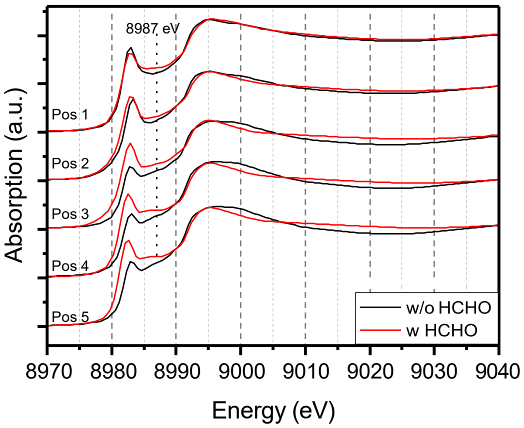

Figure 1: Spatially resolved XANES of Cu-SSZ-13 during steady state SCR conditions in absence (black line) and presence (red line) of HCHO at 300 °C. Position 1 / 5 – beginning / end of the catalyst bed.

Spatially resolved *operando* XAS measurements revealed the presence a partially reduced Cu sites in the presence of HCHO in comparison to SCR conditions in the absence of HCHO (Figure 1). Additionally, the feature appearing around 8979 eV in the XANES profile was attributed to the formation of mobile Cu-CN species based on DFT calculations. Further detailed characterization by *in situ* DRIFTS and DRUVS validated the coordination of cyanide ligands to the active site.

Significance

Adjustments in the Cu-SSZ-13 composition allow tuning of the structural properties of Cu-sites to diminishing HCN emissions. In this regard, an increased number of ZCuOH sites is expected to contribute to HCN conversion above 350 °C. Hence, the findings in this study provide guidance for the further development of Cu-SSZ-13 catalysts aimed at minimizing highly toxic HCN emissions and mitigating the overall impact of HCHO in the exhaust of synthetic fuel and bio-fuel combustion engines.

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Metal-support interactions govern restructuring dynamics in bimetallic Pt oxidation catalysts

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Introduction

Supported bimetallic alloy catalysts (BACs) often restructure and deactivate under oxidizing conditions, limiting practical use.[1] For example, PtM (M= transition metal) BACs are highly active for oxygenation reactions, but rapidly deactivate due to oxidation and segregation of the more oxophilic metal. Suppressing and ultimately controlling this oxidation process could lead to the practical deployment of PtM BACs for total and partial oxidations.

Results & Discussion

We report a ternary metal-support interaction (MSI) between PtCu nanocrystals and a reducible Mn_2O_3 support that alters the PtCu restructuring dynamics. Operando X-ray spectroscopic measurements reveal that on nonreducible Al_2O_3, PtCu deactivates through the expected segregation of Cu to form surface Cu oxide clusters (**Fig 1A-C**). Reducible Mn_2O_3 instead promotes PtO formation upon O_2 exposure while Cu oxidation is suppressed **(Fig 1D-F**). Theoretical calculations attribute this to strong Pt-Mn interfacial charge transfer, which increases Pt oxophilicity and lowers the driving force for electron withdrawal from Cu. The resulting PtO supplies reactive oxygen for catalysis, and the preserved mixed-metal surface sustains both activity and stability, which is supported by kinetic and DRIFTS experiments.

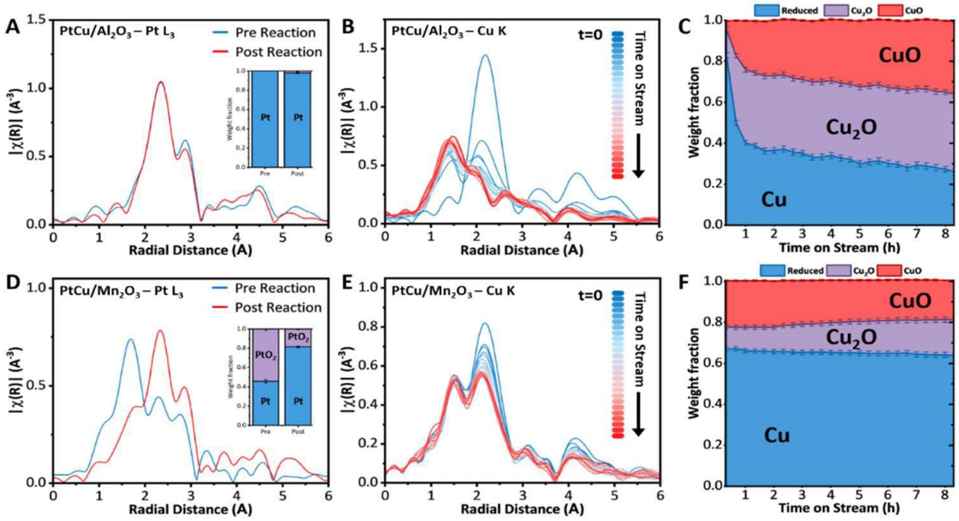

Fig 1. Operando XAS of PtCu catalysts during propene oxidation. *(A,D) Pt L_3-edge EXAFS; (B,E) Cu-edge K EXAFS. Insets and (C,F) show Pt and Cu weight fractions before, during, and after reaction. Top row = PtCu/Al_2O_3. Bottom row = PtCu/Mn_2O_3.*

Significance

These results identify metal-oxide support reducibility as a fundamental descriptor of restructuring in bimetallic nanoparticle catalysts and a practical MSI design lever for stabilizing bimetallic surfaces and controlling performance for oxidation reactions.

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Unraveling Structure–Activity Relationships in Pd–Zn/C Catalysts for CO_2 Hydrogenation to Methanol

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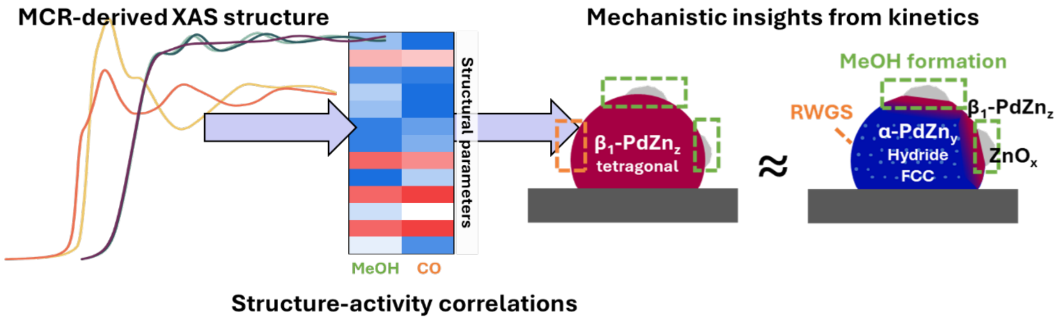
Introduction

Pd–Zn bimetallic catalysts are emerging as promising alternatives to Cu-based systems for CO_2 hydrogenation to methanol. However, progress has been limited by methodological "blind spots" in earlier studies, where characterization techniques insensitive to structural disorder obscured the roles of coexisting bimetallic (α- and β_1-PdZn) and zinc oxide (disordered vs. crystalline) phases.

Results & Discussion

In this work, we establish a comprehensive structure–function map for the Pd–Zn catalytic system. By systematically varying metal loading and pre-treatment conditions, we generated a representative library of catalysts with tunable phase compositions supported on inert graphitic carbon. Using in situ X-ray Absorption Spectroscopy (XAS) combined with multivariate curve resolution (MCR), we deconvoluted the distinct spectral signatures of all major structural components, including amorphous species present under reaction conditions. Statistical analyses, supported by kinetic measurements, enabled us to assign catalytic functions to each phase.



Our results show that methanol and CO are produced through parallel pathways on different active sites. Methanol synthesis requires interfacial sites formed between tetragonal β_1-$PdZn_z$ alloy and adjacent disordered ZnO_x, whereas crystalline ZnO plays a minimal role. CO formation occurs on general (bi)metallic surfaces. The Pd-rich, hydride-forming α-$PdZn_y$ phase is identified as a spectator under methanol-forming conditions; in contact with zinc oxide, it readily transforms into β_1-$PdZn_z$, shifting selectivity toward methanol.

Significance

This refined active-site model highlights the synergistic roles of ordered β_1-PdZn and disordered ZnO_x, offering clear design principles for next-generation methanol synthesis catalysts. More broadly, the combined in situ/operando XAS and statistical methodology provides a robust framework for identifying active phases in complex catalytic systems.

Operando Raman Spectroscopy with Online UV-Vis Analysis of Carbon-based Catalysts under Harsh Reaction Conditions

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Introduction: Phosgene synthesis is a critical industrial process for manufacturing isocyanate precursors, used for polyurethanes, polycarbonates, antioxidants, agrochemicals, and pharmaceutical production. Commonly deployed carbon-based catalysts suffer from deactivation via extensive chlorination, causing weakened C-C bonds and chlorinated volatile organic compounds that block active sites.[1] To fundamentally address this challenge and gain mechanistic insights into carbon-chlorine (Cl_2) interactions, we employed *operando* Raman spectroscopy, with simultaneous product gas analysis using an online UV-Vis transmission probe and Mass Spectrometry (MS). We probed various carbon structures, varying in graphitization and strain, through multiple cycles of alternating reactive (25% Cl_2) and inert (He) atmospheres at 200 °C to study Cl_2 activation, structural stability and reversibility of Cl_2 uptake/release.

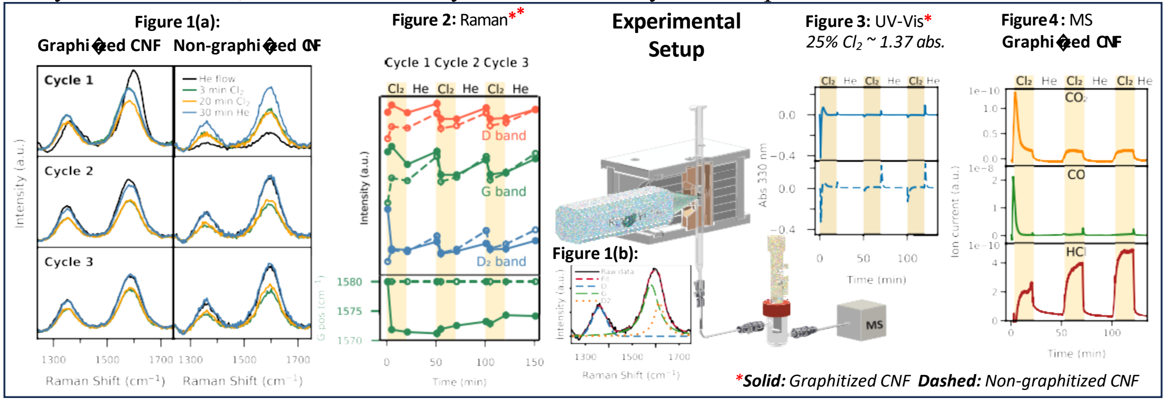

Figure 1: *(a) Raman spectra of graphitized (left) and non-graphitized (right) carbon nanofibers (CNFs) through 3 cycles of alternating Cl_2 and He (b) Sample peak fitting of D, G and D2 bands.* ***Figure 2:*** *(a) D, G and D2 intensities (b) G band positions – at 3 min Cl_2, 20 min Cl_2, 30 min He per cycle,* ***Figure 3:*** *UV-Vis of molecular Cl_2 (catalytic data - blank) showing Cl_2 consumption of graphitized (solid) and non-graphitized (dashed) CNFs .* ***Figure 4:*** *MS: CO_2, CO and HCl*

Results & Discussion: Our *operando* spectroscopy results reveal distinct initial structural responses of CNFs leading to an irreversible surface rearrangement after high Cl_2 consumption on first exposure (UV-Vis, Figure 3). For the graphitized CNFs, initial Cl_2 exposure led to a decrease of the well-ordered graphitic phase, evidenced by a decrease in G band intensity. A concurrent red shift (~9 cm^{-1}, Figure 2b) indicates a possible volume expansion from C-Cl chemisorption overshadowing any electronic (doping) effects.[2] Simultaneously, the D2 band intensity decreased, attributable to Cl_2-mediated surface etching and oxidation, releasing CO_2, CO and HCl (MS, Figure 4). In stark contrast, the non-graphitized CNF (of similar size) exhibited an instantaneous, sharp increase in intensity of all bands at their characteristic positions. The resulting active phase following these initial structural transitions in both materials remained stable and reversible to different degrees – with both the defect (D, D2) and graphitic (G) band intensities consistently recovered (Figure 2a) upon Cl_2 desorption (Figure 3) during subsequent cycles.

Significance: This research provides a framework of thinking for the rational design of carbon materials, thereby guiding property optimization to elucidate the Cl_2 activation pathway, minimize volatile byproducts and sustain reversible catalytic function extending across several cycles.

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Elementary surface reaction kinetics unveil distinctly different active sites of ZnO-ZrO₂ catalysts in CO₂ and CO hydrogenation to methanol reactions

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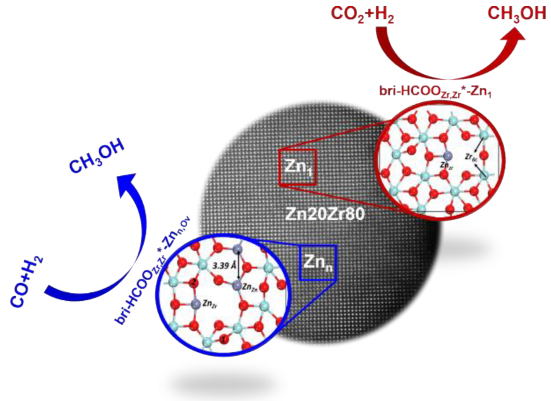
Introduction

The active site of a solid catalyst varies sensitively with the catalyzed reaction. Herein, using experimentally measured elementary surface reaction kinetics of the formate hydrogenation reaction over a $ZnO-ZrO_2$ catalyst under working conditions by operando temporal in situ DRIFTS spectroscopy, in combinations with comprehensive structural characterizations and theoretical simulations, we unveil the distinctly different active sites in catalyzing the CO_2 and CO hydrogenation to methanol reaction.

Results & Discussion



Schematic illustration of the active site-active formate pair on the Zn20Zr80 Catalysts in the CO_2 or CO hydrogenation to methanol reaction

A $ZnO-ZrO_2$ catalyst with an atomic Zn:Zr ratio of 1:4 was found to catalyze the CO_2 and CO hydrogenation to methanol reactions at an apparent barrier of about 82 and 55 kJ/mol, respectively. Zn^{2+} cations with different local environments were found present on the $ZnO-ZrO_2$ surface, including Zn_1 single atoms exclusively with a Zn-O-Zr local structure and Zn_n clusters with both Zn-O-Zr and Zn-O-Zn local structures. The -Zr-O-Zr- structure bonded to the Zn_n clusters was more easily to be reduced than that bonded to the Zn_1 single atoms. Using operando temporal in situ DRIFTS spectroscopy to experimentally measure elementary surface reaction kinetics of the formate hydrogenation reaction over a $ZnO-ZrO_2$ catalyst under working conditions, in combinations with comprehensive theoretical simulations, we successfully identified the bridge-formate species at the Zn_1 single atom site with an apparent hydrogenation barrier of about 62 kJ/mol as the active site-active species pair for catalyzing the CO_2 hydrogenation to methanol reaction while the bridge-formate species at the Zn_n clusters with an apparent hydrogenation barrier of about 115 kJ/mol as the spectator, whereas the bridge-formate species at the Zn_n cluster bonded to an in situ formed -Zr-V_o-Zr- structure with an apparent hydrogenation barrier of about 68 kJ/mol as the active site-active species pair for catalyzing the CO hydrogenation to methanol reaction while the bridge-formate species at the Zn_1 single atom site with an apparent hydrogenation barrier of about 122 kJ/mol as the spectator. Following these findings, a Zn_1/ZrO_2 single atom catalyst was fabricated to be more active than the ZnO-ZrO_2 catalyst in catalyzing CO2 hydrogenation reaction to methanol.

Significance

These results provide a reliable and effective methodology of elementary surface reaction kinetics for identifications of the active site-active species pair of working catalysts in complex reactions and unveil how sensitively the active site structure varies with the catalyzed reaction.

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Time-resolved XAFS/XRD combined technique for *Operando* simultaneous measurements

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Abstract

The simultaneous acquisition of multiple structural parameters via synchrotron-based combined techniques represents a novel advancement in materials characterization. This work introduces a novel setup integrating time-resolved X-Ray Absorption Fine Structure (XAFS) and X-Ray Diffraction (XRD). The apparatus employs dedicated detectors for each technique, grid ion chambers for XAFS and a curved Mythen detector without the impact of gaps for XRD. The channel-cut monochromator cooled with liquid nitrogen was used to get monochromatic light with the photon energy changing rapidly. The setup achieves a time resolution on the order of ~20 ms. This beamline will allow for coordinated measurements of local and long range structural changes in chemical transformations and phase transitions using both techniques. We demonstrate the capability of this technique to track structural evolution in CO_2RR catalyst by monitoring the formation pathways.

Poster Abstracts

Unraveling Structure-Activity Relationships in Pd-Cu Catalysts for CO_2 Hydrogenation to Higher Alcohols

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Introduction

The selective hydrogenation of CO_2 to higher alcohols (HA) is a promising route to sustainable fuels and chemicals, but current catalysts show limited performance.[1] Pd-Cu catalysts are promising systems for HA synthesis[2]. However, it is still unknown how Pd-Cu bimetallic phases evolve during pretreatment and under reaction conditions, and how this affects product selectivity. In this work, we investigate how composition and reduction temperature influence phase formation, surface intermediates, and performance in Pd-Cu/SiO_2 catalysts for CO_2 to HA.

Results & Discussion

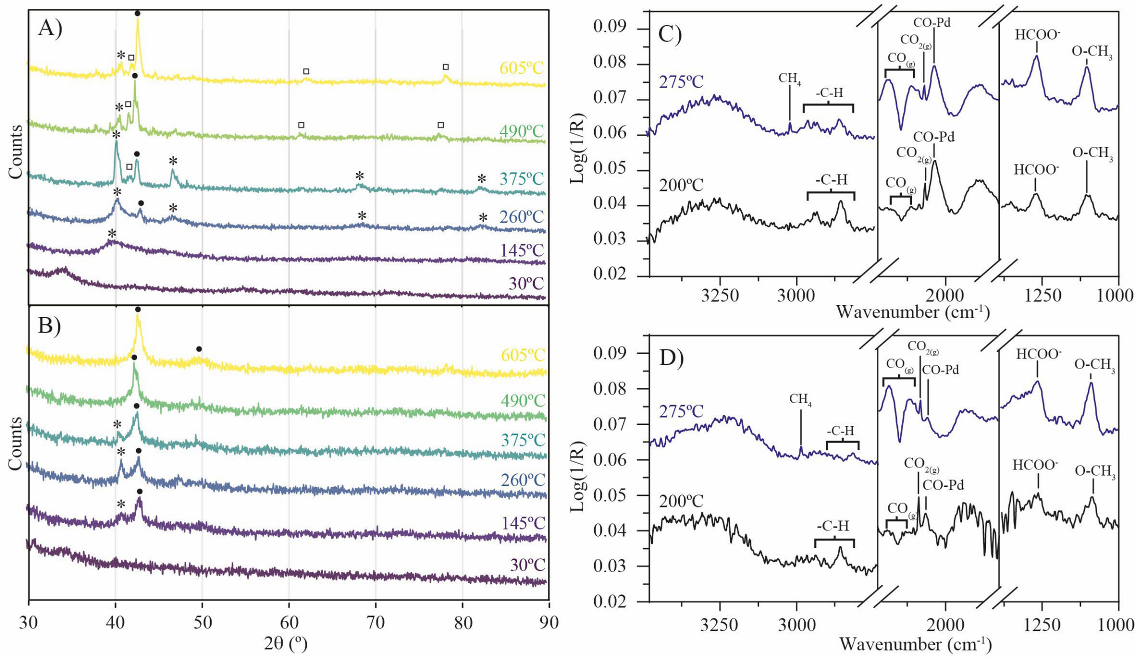

Figure 1. A) In-situ XRD of Pd_xCu_y/SiO_2 (Pd-rich) and B) Pd_xCu_y/SiO_2 (Cu-rich) catalyst. (*) Pd, (□) A1 PdCu phase, (●) B2 PdCu phase. C) DRIFTS spectra of Pd-rich catalyst and D) Cu-rich catalyst.

A series of Pd-Cu/SiO_2 catalysts of different composition were characterized *in situ* during reduction by X-ray diffraction (XRD) (Figure 1 A-B). Pd-rich samples first formed metallic Pd, then a transient A1 (FCC) phase, before transforming into ordered B2 (BCC). In contrast, Cu-rich catalysts directly formed the B2 phase. Operando DRIFTS revealed composition-dependent surface chemistry: Pd-rich catalysts (Figure 1 C) exhibited stronger C-H stretching bands (2700–3100 cm^{-1}) associated with methoxy and formate intermediates and strong CO adsorption bands (2100–1900 cm^{-1}), compared to Cu-rich catalysts (Figure 1 D). These results demonstrate that reduction pre-treatments and Pd-Cu ratios dictate alloy phase evolution and intermediate formation, which correlate with product selectivity.

Significance

By correlating phase evolution and surface chemistry with catalytic performance, this work identifies structure-function relationships that govern CO_2 hydrogenation pathways.

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Selective dehydration of isobutanol on H-FER: *operando* IR, multivariate analysis and kinetic modeling

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Introduction

Acidic ferrierite (H-FER) is able to dehydrate isobutanol to linear butenes with high selectivity, but the reaction mechanism explaining such selectivity remains elusive.[1] This work aims to elucidate the reaction mechanism and provide kinetic rate constants for the main reaction.

Results & Discussion

The measurements were performed in a custom-made IR cell operating as a closed batch *operando* reactor and allowing to measure simultaneously the gas phase composition and the species adsorbed on the catalyst (Fig. 1A). Isobutanol dehydration on HFER was followed along temperature ramps from 40 to 260°C. Intermediates and products were identified and quantified by MCR-ALS analysis of the surface spectra (Figure 1B) and by fitting gas spectra (Figure 1B') with known references. The high selectivity to linear butenes was confirmed, and 2-butanol was found as an intermediate adsorbed at the HFER surface, suggesting that the key reaction step is the isomerization of the alcohol to the linear isomer. The validity of the proposed mechanism was confirmed by microkinetic modelling of both surface *and* gas phase concentration profiles (Figure 1C), which also showed that the rate limiting step is the alcohol isomerization step. This is the first experimental confirmation of previous computational predictions on a comparable system.[2]

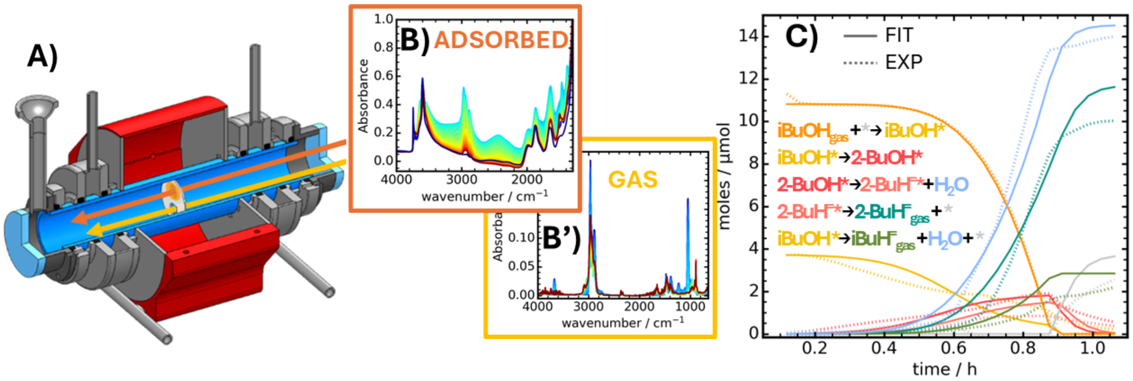

Figure 1: A) Scheme of the closed-batch FTIR operando cell. B) Spectral evolution of the spectra of HFER and the adsorbed species. B') Spectral evolution of the gas phase C) Result of the microkinetic model and included reactions.

Significance

This work demonstrates the potential of closed-batch *operando* IR for identifying reaction intermediates and enabling kinetic modeling of both gas-phase and surface concentrations in catalytic reactions. Applied to the selective dehydration of isobutanol on HFER, it provides the first experimental evidence that the key reaction step is the isomerization of isobutanol to 2-butanol.

Aknowledgements. We acknowledge Agence Nationale de la Recherche under France 2030 (contract ANR-22-PEBB-0009) for support in the context of the MAMABIO project (B-BEST PEPR).

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Probing Ultrafast Dynamic Processes in Photocatalysts via Time Resolved X-ray Absorption Spectroscopy

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Introduction

Achieving efficient solar-to-hydrogen conversion relies on a detailed understanding of the dynamic charge transfer processes in photocatalytic materials. By integrating advanced spectroscopic tools with kinetic measurements under operando conditions, we bridge the gap between photoinduced electronic processes and catalytic reaction pathways. In this study, we employ time-resolved operando X-ray absorption spectroscopy (XAS), leveraging its wide temporal range from picoseconds to microseconds, to probe charge-transfer dynamics in state-of-the-art Pt/TiO_2 photocatalysts.

Results & Discussion

This study examines how the crystalline phase of TiO_2 governs H_2 evolution, using picosecond laser-pump X-ray-probe Ti K-edge XAS to probe the underlying dynamics. Under photoexcitation, TiO_2 exhibited the transient formation of Ti^{3+} electron traps, with lifetimes that vary significantly across different TiO_2 polymorphs (anatase, rutile and brookite). Brookite exhibited the longest-lived Ti^{3+} species suggesting effective charge separation and enhanced charge transfer to Pt consistent with its superior performance. Pt/TiO_2 heterostructures were further examined to assess changes in Ti K-edge dynamics. Pt introduces an additional electron decay pathway, shortening Ti^{3+} polaron lifetimes and indicating efficient electron extraction at the Pt/TiO_2 interface.

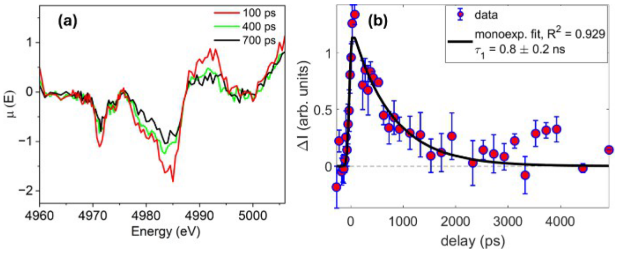

Figure 1: Ti K-edge difference spectra at specific delay and kinetic trace at 4982 eV

Significance

This investigation provides key insights into how TiO_2 phase selectivity and metal-semiconductor interfacial engineering govern charge separation, transport, and recombination. Ultimately, our work supports the rational design of more efficient and durable photocatalytic systems for sustainable hydrogen production.

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Operando X-ray Diffraction of Co/TiO_2 Catalysts: Impact of TiO_2 Polymorphs on the Cobalt Active Phase during CO_2 Hydrogenation

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Introduction

Co-based catalysts are receiving renewed interest for their performance in CO_2 hydrogenation, particularly on reducible TiO_2 supports [1,2]. However, the nature of the active Co phase, and how the type of support (e.g., TiO_2 polymorph) affects it, remains debated [3]. Here, we prepared 10 wt.% Co/TiO_2 catalysts on pure anatase (Co/A) and rutile (Co/R) and used *operando* XRD to track their structural evolution during reduction and under high-pressure CO_2 hydrogenation conditions.

Results & Discussion

After reduction at 250 °C, CoO reflections were observed on both anatase and rutile, while after reduction at 450 °C Co^0 reflections appeared in the XRD plots (Figure 1A&B). Co^0 reflections appear earlier on anatase, indicating a higher CoO reducibility than on rutile. Under CO_2 hydrogenation reactions, CoO reflections vanished and Co^0 emerged on anatase, whereas CoO remained stable on rutile, in accordance with the corresponding TPR data (Figure 1C). Thus, the TiO_2 polymorph strongly influences the stability of Co species, thereby providing means to tweak catalytic performance.

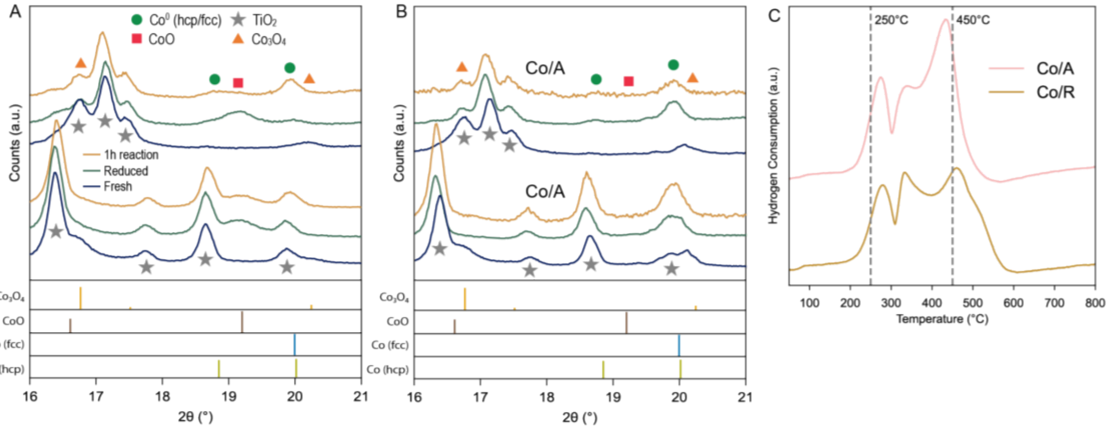

Figure 1.(a&b) Operando X-ray diffraction (XRD) patterns of Co/A (top) and Co/R (bottom), (a) is with 250 °C reduction, (b) is with 450 °C reduction. Blue XRD plots are of the as-synthesized catalysts, green XRD plots of the reduced catalysts, and yellow XRD plots of the catalysts after 1 h of CO_2 hydrogenation. Reference diffractograms are plotted beneath the figures (c) Reduction profiles of Co/A and Co/R, vertical lines indicate the chosen reduction temperatures.

Significance

These results reveal that the TiO_2 polymorph controls the active Co species during CO_2 hydrogenation, which in turn influences the catalytic performance. Furthermore, it shows that *operando* XRD is a strong technique to study support effects and helps understand catalytic phenomena.

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High-Field EPR Spectroelectrochemistry – Development and Application

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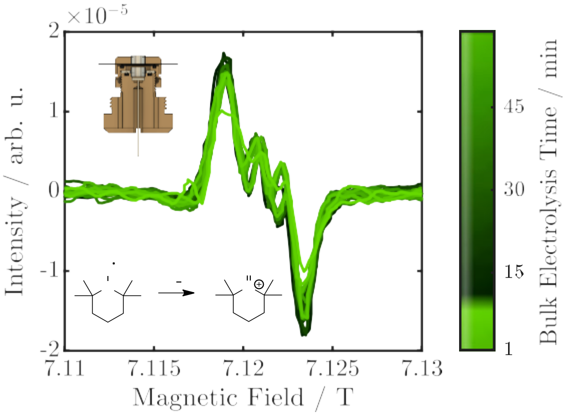
Introduction

Inspired by cofactors, modern catalysts often feature transition metal centers,[1] whose redox processes can be probed by cyclic voltammetry[2] and characterized by EPR spectroscopy.[3] For integer spin species, high-field EPR is essential to access transitions silent at X-band (9.5 GHz).[3] Integer-spin species such as chromium(II), manganese (III) are highly relevant for 3d transition metal catalysis. To enable in situ and operando studies under these conditions, we present a high-field EPR spectroelectrochemical (HFEPR-SEC) cell operable between 180 and 360 GHz.

Results & Discussion

We present the development of an HFEPR sample holder compatible with both high-field EPR measurements and electrochemical experiments. Unlike conventional EPR, high-field EPR operates without a resonator,[3] necessitating a fundamentally different sample holder geometry. In our design, the working electrode serves a dual function as both electrode and microwave mirror. The custom three-electrode setup behaves as a Randles circuit, as confirmed by Electrochemical Impedance Spectroscopy. High-quality cyclic voltammograms of various transition metal complexes were successfully recorded. Successful HFEPR measurements were performed on TEMPO at room temperature and in frozen solution, as well as on transition metal complex solutions at cryogenic temperatures. As a proof of concept, in situ EPR measurements were conducted during the bulk electrolysis of TEMPO at room temperature. The oxidation process could be monitored spectroscopically, as evidenced by a decrease in signal intensity corresponding to the loss of the paramagnetic species.



HFEPR spectra of TEMPO measured at room temperature and 200 GHz during continuous electrochemical TEMPO-oxidation.

Significance

As a new method, HFEPR-SEC enables the investigation of catalysts and their reactive intermediates during catalytic reactions. By combining electrochemistry with high-field EPR, it allows in situ characterization of paramagnetic species, including those of integer spin. This approach offers powerful new opportunities for mechanistic studies by providing valuable insights into electronic structure changes during catalytic reactions.

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Operando transient EPR spectroscopy unravels active Fe^{2+} ions in zeolites with unprecedented site-selectivity

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Introduction

Catalysts based on Fe-exchanged zeolites represent a major class of materials for the removal of NO_x and N_2O from exhaust gases and for the partial oxidation of hydrocarbons. While they are active for these reactions, the nature of the active site(s) remains debated because of the heterogeneous distribution of Fe ions and the tendency of Fe to adopt various coordination environments depending on exchange position. Here, we use modulated excitation electron paramagnetic resonance spectroscopy (ME-EPR) to identify Fe^{2+} ions in specific exchange positions of the framework that are responsible for the activation of N_2O, during reaction.

Results & Discussion

Spectroscopic identification of active sites during reaction suffers from the need to disentangle complex signals of species likely not involved in the reaction. EPR spectroscopy is capable of providing site-selective information on the coordination environment of Fe ions.[1,2] Coupled to transient experiments such as modulated excitation (ME),[3] it can deliver information on the nature of the active sites that is beyond what was obtained so far. We have analyzed Fe-zeolite catalysts (MFI, FER, CHA, BEA) comprising Fe species with a different degree of agglomeration (monomers in different environments and clusters) upon exposure to repeated pulses of N_2O in Ar (ME-EPR), while measuring product evolution by mass spectrometry. The EPR spectra obtained in N_2O at 400°C clearly show that N_2O oxidizes all types of Fe species to Fe^{3+}. However, it is by repeatedly adding/cutting-off N_2O in the ME-EPR approach that only specific Fe^{3+} sites can be observed to reversibly activate N_2O and break the N_2-O bond. Signals of species not involved in this process remain silent to the phase sensitive analysis and can be considered spectators. The species visible after phase sensitive analysis coincide consistently and solely with Fe coordinated in the so-called beta-exchange positions of the zeolite topologies. From a structural perspective, while all frameworks are characterized by the same type of species, the beta-exchange position in BEA framework exhibits a distinct zero field splitting, revealing a clear difference in the coordination environment that cannot be obtained by other techniques under reaction conditions.

Significance

This work demonstrates that the transient nature of the ME experiments allows the extraction of key mechanistic details that would remain otherwise hidden in steady-state experiments. The modulated excitation approach is even more important for a technique highly sensitive to the local environment of different Fe species, such as EPR spectroscopy.

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Operando Electrochemical K-edge XAS Captures Near-Surface Electrolyte Composition and Transient Molecular Catalyst Structures

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Introduction

Electrochemistry can drive reactions and separations needed for sustainable energy conversion, chemical production, and waste resource recovery.[1] The interfacial composition of electrolyte with electrodes, electrocatalysts, and membranes dictates observed reactivity;[2] inherently, interfaces are microscopically complex, and difficult to reproduce and characterize through *ex-situ* methods. We have observed that activity and stability of the molecular nitrate reduction catalyst Co(DIM) (cobalt 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene) is strongly dependent on aqueous electrolyte composition,[3] but we are unable to assert specific electrolyte-dependent mechanisms because transient Co(DIM) intermediates are unknown. In this work, we use *operando* K-edge XAS to describe transient Co(DIM) species as a function of applied electrode potential and electrolyte composition.

Results & Discussion

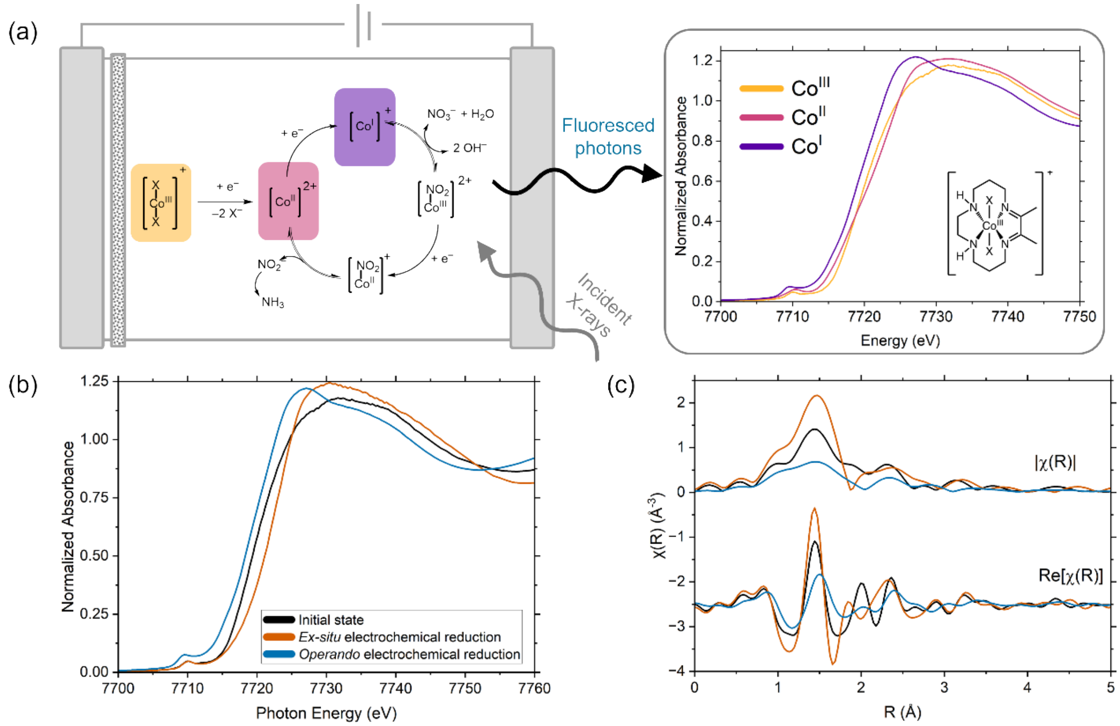

Figure 1. (a) Conceptual schematic for *operando* Co K-edge XAS measurements of Co(DIM) under an applied electrochemical potential. Backside illumination of a graphite foil working electrode in a flow cell enables total-fluorescence yield (TFY) XAS of aqueous Co(DIM) in its initial and reduced states. (b-c) Normalized absorbance (b) and k^2-weighted R-space EXAFS of Co(DIM) in its initial state (black) and in its reduced states, *ex-situ* (red) and *operando* (blue). Stark differences between the *ex-situ* and *operando* rising edge energy and coordination environment highlight the unique ability of *operando* XAS to illuminate transient, catalytically-relevant intermediate species.

A two-chamber flow electrochemical cell with a graphite foil working electrode enabled backside illumination of aqueous Co(DIM) solutions and total-fluorescence yield (TFY) XAS (Figure 1a).

Alongside variation of supporting electrolyte concentration, identity, and pH at open circuit, we investigated reduced species both *ex-situ* and *operando*. Figure 1b shows stark differences between *ex-situ* and *operando* reduction in the rising edge; notably, the *ex-situ* reduced species appears less electron-dense about Co than the initial state. EXAFS shows that Co–N/Co–O single scattering [R_{eff} = 1.92 Å] amplitude intensifies in *ex-situ* measurements but diminish in *operando* measurements (Figure 1c). These data support a mechanism by which a six-coordinate $\mathrm{Co^{III}}$(DIM) bearing two bromo ligands is initially reduced to a four-coordinate $\mathrm{Co^{I}}$(DIM) that is nominally the active catalyst for nitrate reduction. However, $\mathrm{Co^{I}}$(DIM) is susceptible to bromo, aquo, or hydroxo ligand reassociation in water. Ligand reassociation is competitive with binding of nitrate, explaining our previous observations of catalytic activity dependence on electrolyte composition.

Significance

This work augments our understanding of Co(DIM)'s uniquely active and ammonia-selective mechanism of nitrate reduction electrocatalysis. Direct observation of coordination number and ligand identity revises the previously accepted catalytic mechanism that relied on molecular structural intuition from electroanalysis and computation. The interaction of Co(DIM) with its electrolyte motivates catalyst, electrolyte, and reactor engineering to extract maximal nitrate reduction activity.

The techniques developed in this study highlight nascent opportunities for *operando* X-ray spectroscopy of homogeneous and molecular electrochemical species. In this study, we analytically deconvolute contributions of mixtures of Co(DIM) species in a single spectrum. We have recently extended our *operando* reactor and workflow to a model system of iron hexacyanoferrate, which serves as a probe molecule to describe local electrolyte composition. We anticipate these measurements will support the growing appreciation of local electrolyte's deterministic role in electrocatalysis reactivity.[4,5]

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NAP-XPS Equipment for *Operando* and *In Situ* Studies

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Introduction

Material science plays a vital role in the discovery and optimization of solutions for many key applications such as energy storage, catalysis, electronics, and pharmaceuticals. However, advancements in this field are limited by the available tools and the conditions they can withstand.[1] More precisely, it is difficult to study materials in situ (in conditions close to their working environments) or operando (while they are functioning), even though these techniques would give a more complete and realistic overview of the mechanisms at play.

Recent instrumental technology developments can help address these challenges. For example, electron energy analyzers were limited to ultra-high vacuum (UHV) measurements. However, thanks to the development of a differentially pumped lens system[2], x-ray photoelectron spectroscopy (XPS) can be carried out at pressures up to 1 bar[3]. Advanced NAP-XPS systems have taken advantage of this and enable the study of in situ and operando material surfaces.

Results & Discussion

This poster demonstrates how NAP-XPS tools, such as the EnviroESCA[4], provide new insights into redox reactions. Case studies of plasma-induced process (plasma-driven redox reactions of copper oxide and silver)[5–7] and of other operando investigations (iron and platinum oxides redox behaviors and electrochemical interface analysis)[8] will be presented.

Significance

NAP-XPS systems enable operando studies of plasma and electrochemical processes, providing insights into critical redox mechanisms for catalysis, energy storage, and material synthesis.

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Employing K-Promotion in Cu-In Catalysts to Control Phase Separation and CO_2 Activation for Low-T RWGS

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Introduction

The reverse water-gas shift (RWGS) reaction is a key route for CO_2 hydrogenation to CO[1], providing an important intermediate for downstream fuel and chemical synthesis. Developing catalysts that are highly selective and active at low temperature is critical for improving process efficiency and enabling integration with renewable H_2. Cu-In bimetallic catalysts are promising because of their high CO selectivity and favorable thermal stability[2]. Here, we investigate potassium promotion as a catalyst design strategy to tune the structure of silica-supported Cu-In catalysts and reveal how potassium governs the phase evolution, CO_2 activation, and RWGS performance under low-temperature conditions.

Results & Discussion

A systematic variation of K loading establishes a clear structure-performance relationship in Cu-In/SiO_2 catalysts. An optimal K loading of 5 wt.% delivers the best RWGS performance, reaching a CO yield of 15.1 % and a CO formation of 353.9 µmol gcat^{-1} s^{-1} at 350°C, while maintaining stable operation for 72h. Under high pressure conditions (2-3 MPa), the catalyst preserves nearly 100% CO selectivity, effectively suppressing methanation and methanol formation.

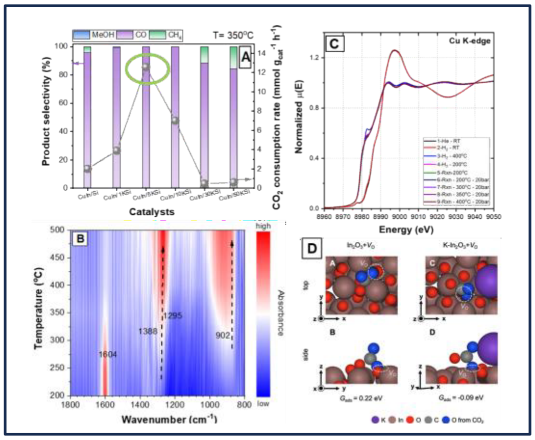

Fig. (A) RWGS activity and selectivity over Cu-In catalysts with various K loadings; (B)in-situ DRIFTS and (C) in-situ XAS Cu K-edge of Cu-In/5KSi under RWGS; (D) DFT-optimized structures of adsorbed CO_2 on $In_2O_3+V_O$ and $K–In_2O_3+V_O$ with calculated G'_{ads}s.

Operando and complementary characterization reveal that potassium strongly influences catalyst structure. At low loadings, Cu-In alloy formation dominates, whereas at optimal K loading (5 wt.%) promotes a phase-separated architecture consisting of CuO and In_2O_3-rich domains. Operando Cu K-edge XAS shows that Cu remains predominantly reduced under reaction conditions, while subtle deviations from purely metallic Cu indicate persistent electronic and interfacial interactions with the In-containing phase. In situ DRIFTS identifies carbonate and formate surface intermediates, consistent with enhanced CO_2 activation on 5 wt.% K added catalyst. Density functional theory shows that potassium strengthens CO_2 adsorption on oxygen-deficient In_2O_3 surfaces and stabilizes vacancy-assisted CO_2 activation pathways. Together, the results indicate that K promotion balances Cu-based H_2 activation with vacancy-rich In_2O_3 sites for CO_2 activation, leading to superior low-temperature RWGS performance.

Significance

These findings show that potassium is not only an electronic promoter but also a structural modifier that controls phase separation and interfacial functionality in Cu-In catalysts. By linking operando spectroscopy with catalytic performance and theory, this work provides a new mechanistic insight into how alkali promotion governs the bifunctional RWGS catalysis and offers practical design principles for highly selective low-temperature CO_2-to-CO conversion catalysts.

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Introducing *Stimulando* Time-Resolved Infrared Spectroscopy to Study Intermittent Light-Stimulated CO_2 Hydrogenation

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Introduction

Resonant catalysis predicts that applying an intermittent stimulus, such as light, at high frequencies comparable to turnover frequencies (TOFs) can enhance activity by orders of magnitude and improve selectivity.[1] However, experimental evidence is so far rather limited due to a poor understanding of how such stimulation affects catalysts and reaction intermediates. Here, time-resolved "*stimulando*" infrared (IR) spectroscopy was used to observe catalyst materials under operating conditions and during light stimulation in the CO_2 hydrogenation over Ni-Ga-based catalysts as a model probe reaction (Fig. 1a, 1b).

Results & Discussion

Light-induced changes in surface species were tracked using steady-state and rapid-scan IR spectroscopy (Fig. 1c). Both analytical methods revealed a reversible decrease in CO and formate coverage under UV illumination. Furthermore, rapid-scan IR with millisecond time resolution demonstrated that the surface coverage of CO under light irradiation decreased with faster kinetics compared to the increase in CO surface coverage in the dark (Fig. 1d). Despite the observed changes in surface coverage of both CO and formates, the CO_2 hydrogenation performance was not significantly affected under the conditions studied herein.

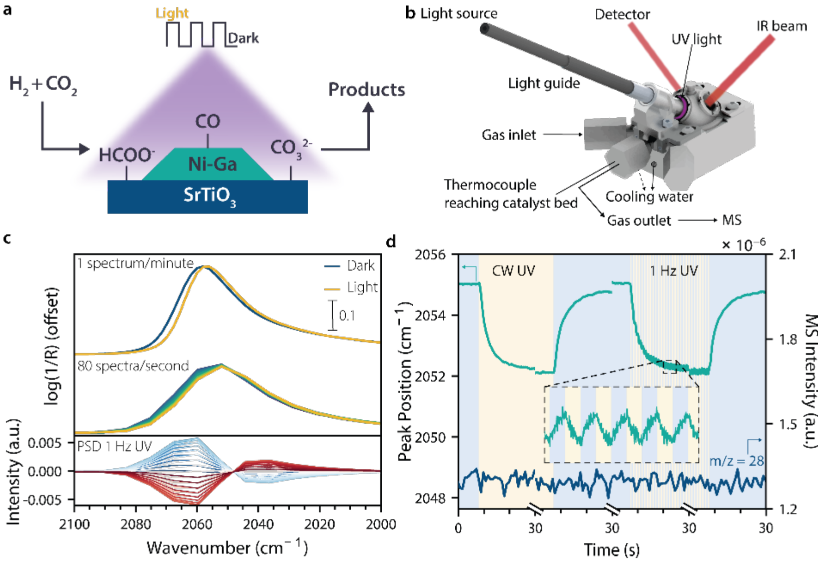

Figure 1:a, Resonant catalysis concept; b, Stimulando set-up; c, Light-induced changes confirmed with PSD analysis are tracked by steady-state and rapid-scan IR spectroscopy; d, Reversible peak position shifts under continuous (CW) and pulsed light (1 Hz) by rapid-scan IR spectroscopy (ms time resolution) with operando MS activity analysis.

Significance

The results provide valuable insights for adjusting light stimulation parameters, such as intensity, duty cycle and wavelength, paving the way to more effective stimulation to enhance performance.

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Engineering a Membrane Assembly Electrode Device for a Durable and High-rate Ethylene Synthesis via CO Electroreduction

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Introduction

The urgency to mitigate greenhouse emissions has significantly propelled CO_2 capturing and upscaling research, focusing on electrochemical conversion using intermittent renewable energy for minimizing CO_2 emissions. The need for efficient, on-demand CO_2-derived fuel production is crucial for enhancing operational resilience in resource-constrained environments. In our research, optimizing a compact membrane electrode assembly (MEA) system for the electrosynthesis of ethylene (C_2H_4), leveraging advanced electrochemical technologies to convert captured CO_2 into a high-energy fuel.

Results & Discussion

We report Cu-based electrolyzers to upscale carbon monoxide (CO) to C_2H_4 (**Figure 1**). Our zero-gap MEA electrolyzer is specifically designed for *operando* X-ray absorption spectroscopy (XAS) measurements, enabling real-time monitoring of the chemical and structural dynamics during electrochemical operation. This innovative design allows us to maintain optimal operational conditions while precisely assessing the dynamic changes occurring within the Cu-based system. We achieved a faradaic efficiency (FE) of C_2H_4 exceeding 80% while maintaining device degradation below 0.5 mV/hr at current densities over 100 mA/cm^2, using large-scale 25-cm^2 electrolyzers. Our approach emphasizes engineering MEAs featuring in-house synthesized Cu nanocatalysts with stabilized Cu(100) facets, which are known to enhance C_2H_4 selectivity. The high energy resolution fluorescence detected (HERFD) XAS measurements will inform our optimization strategies by providing insights into how variations in working conditions and MEA engineering influence performance and stability. Ultimately, we explore enhancing energy efficiency for C_2H_4 production up to 45% by optimizing the anode and the configuration.

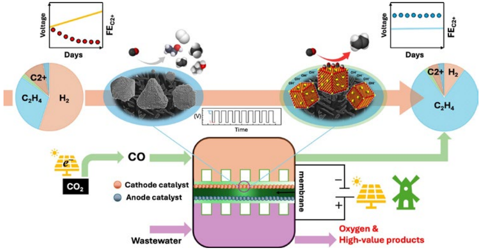

Figure 1. Scheme of MEA zero-gap electrolyzer with an engineered cathode selectively making C_2H_4 from CO.

Significance

This research advances sustainable energy solutions by optimizing ethylene production from captured CO_2, addressing the urgent need to reduce greenhouse gas emissions. Our innovative zero-gap MEA electrolyzer design, enabling real-time operando measurements, enhances catalyst efficiency and durability, ultimately transforming CO into valuable fuels for use in resource-limited environments.

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Regulating aldol-condensation activity using Pt single atoms

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Introduction

Single atoms supported on metal oxides typically exist in cationic state, acting as Lewis acid sites that interact with adjacent oxygen atoms of the support to form Lewis acid-base pairs theoretically.[1] However, the role of Lewis acid-base properties in catalytic processes remains largely not-utilized and unexplored. Gaining insight into these interactions could unlock new catalytic pathways, particularly for bifunctional or cooperative catalysis, when both redox and acid-base properties are crucial. [2, 3]

Results & Discussion

Aldol condensation of carbonyl compounds such as acetone has been extensively studied on metal oxide catalysts such as TiO_2. [4, 5] It is well established that Lewis acid-base pairs serve as active sites for this reaction, whereas meal surfaces, such as reduced Cu, are >10-fold less active. [4] Our findings align with this general observation - reduced Pt, whether in the 2D raft or nanoparticle form, is not active for aldol condensation. Instead, aldol condensation activity originates from Lewis acid-base sites, in the form of Pt-O-Fe containing cationic Pt single atoms. Combining kinetics results, operando characterization, and computational studies, we confirmed that the Pt-O-Fe sites in Pt single-atom catalysts uniquely enhanced the adsorption of acetone, enabled the enolate stabilization, and shifted the rate-determining step toward C-C bond formation

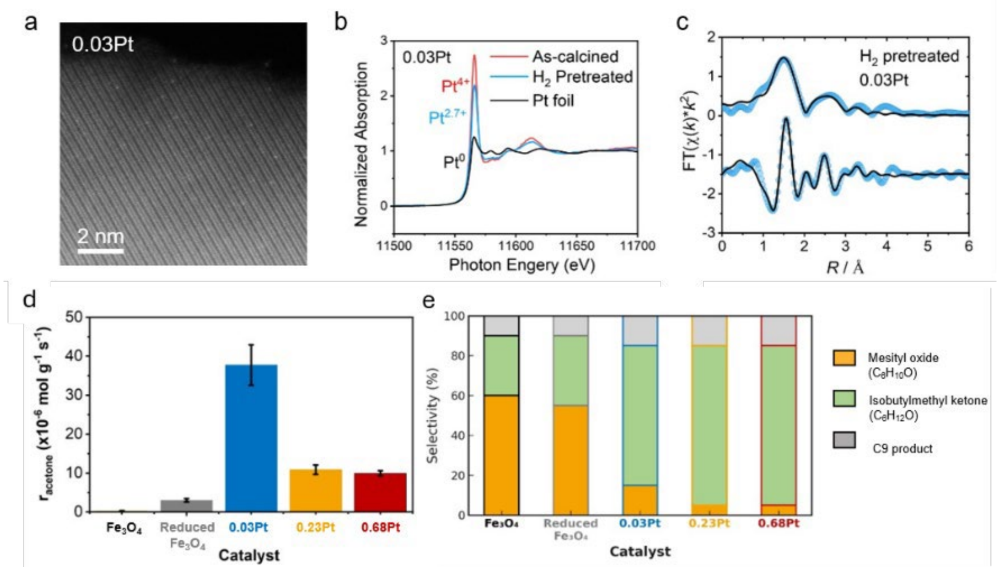

Figure 1. Characterization of Pt single atom catalyst (0.03Pt) on Fe_3O_4 support (a-c) and its performance in aldol-condensation of acetone in comparison with metallic Pt structures (0.23Pt and 0.68Pt)

Significance

Grafting Pt atoms on iron oxide surface fundamentally redefines the metal–support electronic interplay, with direct consequences for electron transfer processes, intermediate stabilization, and elementary step energetics during chemical transformation.

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CO_2 and CO adsorption induced structural variation in supported Pd and PdAu bimetallic nanocluster systems

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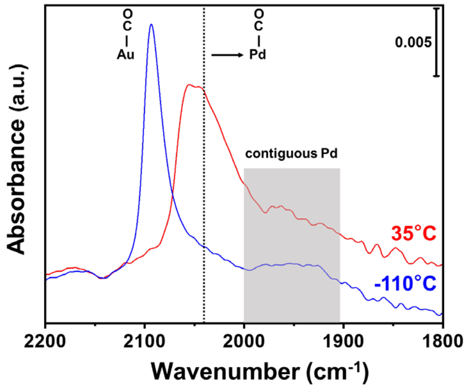
Introduction

Diluting Pd in less active metals (PdM_x, M = Au, Ag, Cu…etc) has been shown to be an effective strategy to modulate the selectivity and activity of various catalytic reactions including direct H_2O_2 synthesis[1]. Although PdAu is an effective direct H_2O_2 synthesis catalyst and has been studied extensively, the relation between surface composition and catalytic properties remains unclear. In addition, how promoters such as CO_2 interact with the catalyst is also under debate. This work aims to address (1) the effect of CO_2 on surface composition of $PdAu_x/SiO_2$ particles during direct H_2O_2 synthesis reactions, and (2) the effect of CO adsorption on surface composition as a function of Pd content (pure Pd to $PdAu_{15}$), and particle size (3 nm vs 11 nm). The surface composition was probed by in-situ CO adsorption diffuse reflectance infrared spectroscopy (DRIFTS) and in-situ and operando X-ray absorption (XAS) measurements during H_2O_2 synthesis. To probe CO induced Pd migration, the DRIFTS spectra were collected under various temperatures ranging from cryogenic to room temperature in gas phase. Finally, further atomic level insight regarding the adsorbate-adsorbent interaction will be complemented by density functional theory and Monte Carlo simulations.

Results & Discussion

The CO-DRIFTS shown below indicate that CO could induce Pd migration to the surface even at room temperature. In addition, the introduction of CO_2 increases H_2O_2 selectivity and suppresses the formation of hydride phase of Pd/SiO_2. Combining CO-DRIFTS and operando XAS results of various samples (Pd content and size), the effect of adsorbates will be presented.



Reduced $PdAu_{15}/SiO_2$ (~3 nm) in-situ gas phase CO-DRIFTS collected under 35 and -110 °C. The gas phase CO was flushed by N_2 flow for 5 minutes.

The CO adsorption bands of $PdAu_{15}/SiO_2$ collected at 35°C are drastically different compared with those at -110°C, suggesting enrichment of Pd on the surface.

Significance

Our findings suggest that the interpretation of IR spectrum must consider the CO induced Pd migration and the presence of CO_2 suppresses the formation of hydride phase during direct H_2O_2 synthesis.

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Spectroelectrochemical Understanding of the Electronic Nature of Mixed-Dimensional Excitonic Systems

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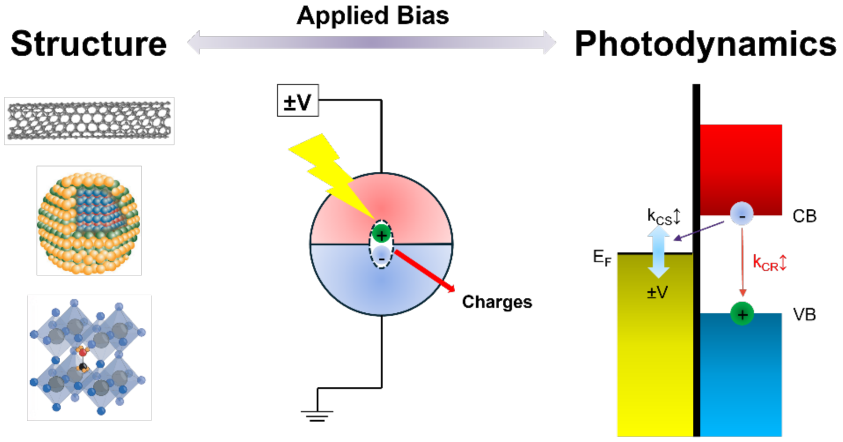
Introduction

Optoelectronic heterointerfaces with mixed dimensionality, integrating zero-, one-, and two-dimensional (0D, 1D, 2D) excitonic semiconductors, have emerged as a powerful platform for tailoring photodynamics through controlled exciton confinement and interfacial engineering. However, they often suffer from poorly designed interfaces with unwanted recombination channels through traps and energy-level misalignments, hindering photoinduced charge generation and undermining device performance and operational stability.[1,2]

Previous Results and Research Plan

Previous studies on photoinduced charge separation dynamics in optoelectronic heterojunctions involving 1D semiconducting single-walled carbon nanotubes (s-SWCNTs) and organic electron-accepting materials have shown efficient charge separation and long-lived charge carriers that persist for more than 1.5 μs.[3,4] However, some heterojunctions show inconsistent interfacial photodynamic properties, such as charge separation rate and yield, with Marcus Theory, the relationship between band energetics and photoinduced charge separation rates. We hypothesize that different interfacial molecular interactions induce discrepancies between interfacial and bulk energetics, such as band offsets and interfacial trap states, and they critically contribute to this inconsistency. To resolve this, using spectroelectrochemistry (SEC), we will systematically study donor/acceptor optoelectronic heterojunctions between s-SWCNTs and other low-dimensional semiconductors, such as quantum dots (QDs, 0D), transition metal dichalcogenides (TMDCs, 2D), and 2D metal halide perovskites (MHPs, pseudo-2D), as our model systems. SEC has been well established for photodynamic characterization under applied bias, and it can reveal hidden electronic characteristics of excitonic systems, including accurate interfacial band offsets via steady-state SEC and possible trap-mediated photodynamics via time-resolved SEC.



Significance

New fundamental models for understanding the complex interplay among chemical structures, interfacial coupling, and photoinduced charge separation dynamics will be developed to disentangle the intertwined structure-property relationship that governs photodynamics in mixed-dimensional optoelectronic systems.

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Elucidating Rhenium Surface Dynamics on TiO_2 under High-Pressure CO_2 Hydrogenation Conditions

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Developing efficient catalysts for green methanol synthesis via CO_2 hydrogenation remains challenging due to poor CO_2 activation at low temperatures. Re/TiO_2 catalysts overcome this kinetic limitation, enabling significant methanol production at temperatures as low as 150 °C and pressures up to 330 bar—milder than conventional Cu/ZnO/Al_2O_3 systems.[1] Their superior performance arises from sub-nanometer Re clusters that selectively promote methanol formation (Figure 1a) and from the redox flexibility of Re species, allowing coexistence of cationic and metallic Re sites. This duality facilitates reactive Re–hydride and Re–carbonyl intermediates that drive CO_2 conversion toward methanol with high selectivity.[1,2]

A systematic evaluation of Re/TiO_2 catalysts with Re loadings between 3 and 50 wt% was conducted under CO_2 hydrogenation conditions (300 bar, 35–200 °C). Remarkably, methanol formation was detected at temperatures as low as 35–50 °C, reaching >60% selectivity—performance not previously reported for CO_2 hydrogenation catalysts. Increasing Re loading above ~24 wt% enhanced methanol selectivity at low temperatures (<100 °C), whereas higher temperatures promoted CH_4 formation at the expense of methanol. TEM (Figure 1b) and XRD (not shown) analyses of the 48 wt% Re/TiO_2 sample revealed no large Re aggregates, indicating that high metal dispersion can be maintained even at elevated loadings. *Operando* DRIFTS during CO_2 hydrogenation showed distinct linear Re–CO bands (2075 and 2035 cm^{-1}) (Figure 1c), confirming the presence of low-nuclearity Re species analogous to those observed in low-loaded systems. These results, together with *in-situ* XAS studies, suggest that the enhanced low-temperature activity originates from highly dispersed, redox-flexible Re sites capable of stabilizing reactive carbonyls.

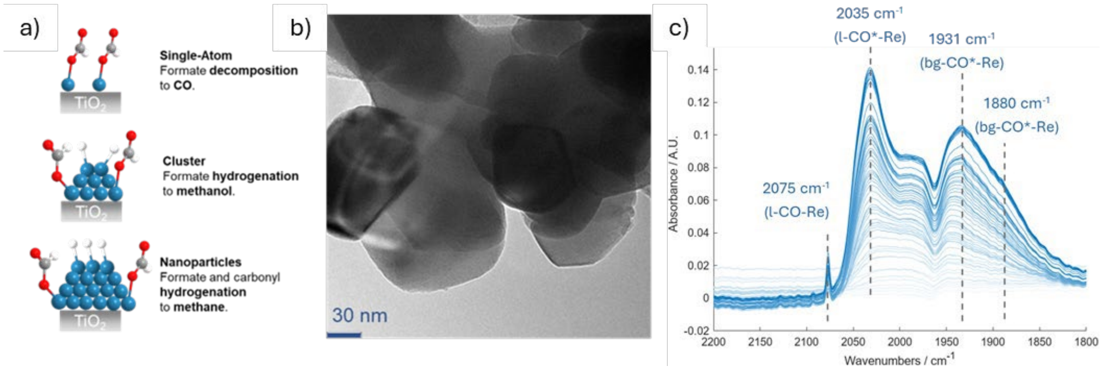

Figure 1. a) Schematic illustration of the proposed size-dependent catalytic behavior of Re/TiO_2 catalysts. b) TEM micrograph of a 48 wt% Re/TiO_2 catalyst after calcination in air at 350 °C under atmospheric pressure, showing no visible Re aggregation. c) Time evolution *operando* DRIFT spectra of the carbonyl region under CO_2 hydrogenation conditions (10 bar, H_2:CO_2=3, T=50°C).

Significance

These findings demonstrate an unprecedented ability of Re/TiO_2 catalysts to activate CO_2 and produce methanol at near-ambient temperatures, providing new insights into structure–activity relationships that redefine the boundaries of low-temperature CO_2 hydrogenation.

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Operando Spectroscopy Insights into Washcoated Monoliths for CO Oxidation

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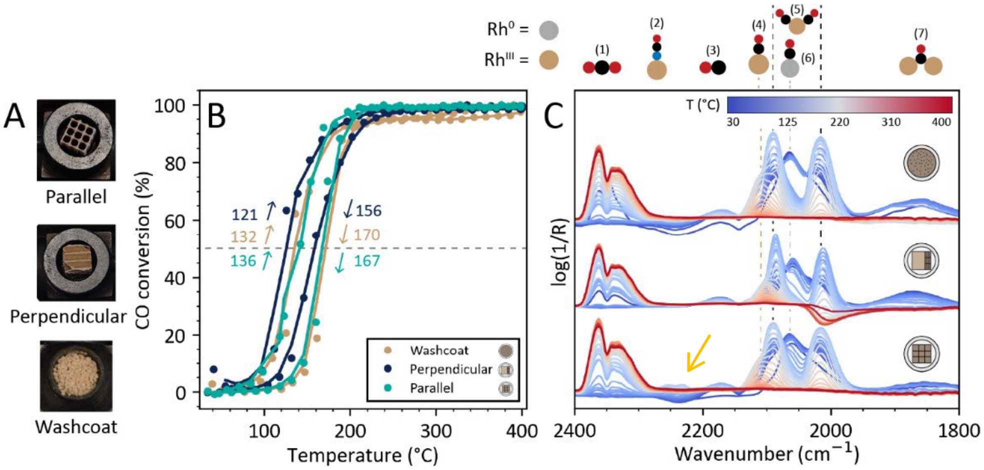
Introduction

Monolithic catalysts washcoated with platinum-group metals (PGMs) are essential for exhaust aftertreatment and have potential for application in steam methane reforming (SMR).[1] To understand their behavior under working conditions, methods are required to characterize such shaped catalyst materials. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) with CO as a probe molecule can be used to study metal oxidation state, dispersion, and metal–support interactions.[2] However, DRIFTS is typically applied to powders rather than intact structured catalysts. Here, we used operando DRIFTS to study CO oxidation on Rh/Al_2O_3 washcoated monolith cores (3×3 channels), revealing an overall more reduced Rh state and the presence of N impurities in the monolith compared to powder washcoats.



Operando DRIFTS during CO oxidation on washcoated monoliths and washcoat. The arrow indicates the NCO intermediate band that only appeared in the monolith with the channels oriented parallel to the gas flow.

Results & Discussion

Operando DRIFTS was performed on monolith cores in different orientations and on a washcoat prepared from the same catalyst slurry. The catalysts showed comparable CO oxidation activity with T_{50} = 121–136 °C. However, the IR spectra of the monoliths oriented parallel to gas flow showed a band typical of CO-Rh^0 persisting at higher temperature, and a band at 2250–2230 cm^{-1} near the light-off temperature. This band was assigned to an NCO intermediate, typical in NO reduction by CO,[3] and likely arose from residual NO_x due to incomplete removal of nitric acid used for pH adjustment during catalyst manufacturing. Recalcination suppressed this feature, supporting the assignment. These findings show that operando DRIFTS on intact monoliths is possible and can reveal effects of structure and preparation that can go undetected when using powder analogues.

Significance

Characterizing structured catalysts under realistic conditions exposes how subtle preparation differences impact catalyst surface chemistry and catalytic performance.

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Technological Advances for Temperature-Dependent Electrochemical Studies Using *In Situ* TEM

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Introduction

Transmission electron microscopy (TEM) is a powerful technique used to characterize materials at the nano- and atomic scale. No other method achieves the same level of structural and chemical resolution, making TEM indispensable for understanding the atomic and chemical makeup that governs material behavior. Using specially designed *in situ* holders with the TEM enables more relevant environments to be introduced while observing nano- and atomic-scale behaviors. With this capability, researchers can now directly observe nanoscale phenomena, including electrocatalytic surface area loss[1], corrosion propagation in steel[2], nucleation and growth of nanomaterials[3], and battery shorting[4,5].

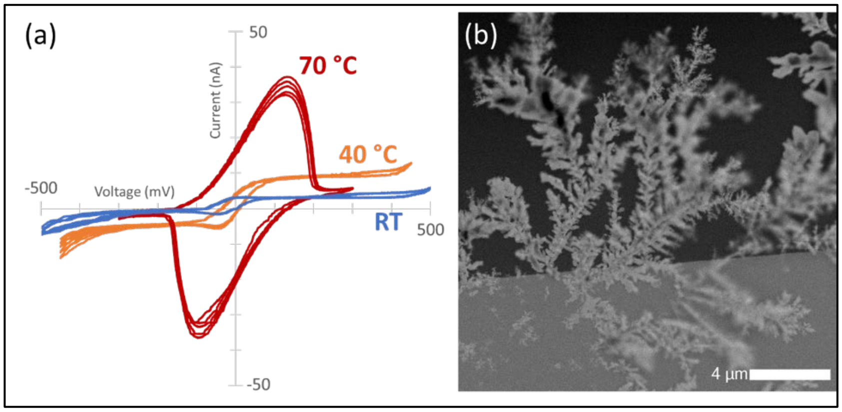

Figure 1. (a) Chemical redox cycling of 50 mM ferric and 50 mM ferrous chloride at room temperature (blue), 40 °C (orange) and 70 °C (red) within a closed-cell TEM system (b) TEM micrograph of silver dendrites formed in real time on the platinum working electrode by chronoamperometry. This type of dynamic is what batteries undergo when they are charged and discharged, and observation of this dynamic will support innovations increasing battery lifetime and enhancing safety.

Results & Discussion

In this presentation, examples of how the temperature, both below and above room temperature, affect the kinetics of electrochemical reactions as well as the morphological structures of the materials will be showcased (Figure 1). In addition, examples of temperature-dependent phenomena, such as the crystallization of water to ice and the nucleation and growth of gold (Figure 2) will be discussed, with diffraction, energy-dispersive X-ray spectroscopy (EDX), and electron energy loss spectroscopy (EELS) analyses as a complement.

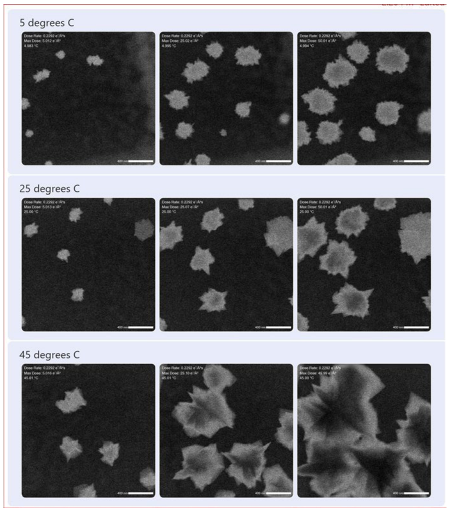

Figure 2. Demonstrating the effect of temperature while holding total dose constant on morphology as gold nucleates and grows in a solution of gold chloride.

Significance

Temperature has a major impact on material behavior and, until now, it has been impossible to study materials at more extreme yet realistic temperatures *in situ* in a liquid environment within the TEM. Now, it is possible to study temperature dependence on batteries that will operate in cold climates, electrocatalysts at elevated temperatures, and the formation of different nanomaterials that at high temperatures, which will drive more efficient research and development of new materials.

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Performance of binuclear transition metal ion sites in the activation of molecular oxygen form selective methane oxidation

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Introduction

Selective oxidation of methane to methanol represents one of the possibilities for minimizing the emissions of methane, which is a greenhouse gas with high global warming potential. Further, this reaction is one of the key steps in the transformation of CO_2 and hydrogen into synthetic fuels. Recently developed systems based on binuclear transition metal ions sites capable of splitting molecular oxygen and forming highly active α-oxygen species ($[M^{4+}=O^{2-}]^{2+}$, M = Fe, Co, Mn, Ni) [1,2]. These binuclear sites can be prepared in zeolite matrices of various topologies (FER, *BEA, MOR) containing local structure and Al organization allowing the formation of binuclear sites [3,4] There are two unique properties of these sites: (a) they are able to oxidize methane to methanol even at room temperature, (b) methanol is released from the zeolite without any effluent. This opens the possibility of producing progressive catalytic material for efficient methane oxidation.

Results & Discussion

Nevertheless, due to the fact that this highly important reaction occurs in (quasi)catalytic pulse regime and desorption of the methanol product is the rate determining step dramatically affecting selectivity of the whole reaction, the detail information on the state of the active site and on the observation species as well as side reactions is essential. To obtain this information, operando FTIR spectroscopy of the catalysts (Fe- and V-FER zeolites) was employed to monitor reactivity of the active site, formation and reactivity of the α-oxygen species and release of the product of methane oxidation. It was found that interaction of α-oxygen species with oxygen molecule (reflected in the shift of the α-oxygen species band around 880 cm^{-1}) represents the key for the formation of methanol, while DFT study indicates that methoxyle species which cannot be released directly from the active site are formed when to α-oxygen species are facing each to other. Further, operando spectroscopy enabled to optimize conditions for the splitting of molecular oxygen to α-oxygen species.

Significance

The results of the FTIR operando study enabled to understand mechanism of the activation of molecular oxygen over binuclear transition metal ion site in the zeolite matrix, the interaction of the activated oxygen (α-oxygen species) with methane and to competitive reactions of α-oxygen species which are essential for the selectivity of the methane oxidation and activity of the system.

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Using *operando* XAS to identify correlations between structure and activity in Ga-based propane dehydrogenation catalysts

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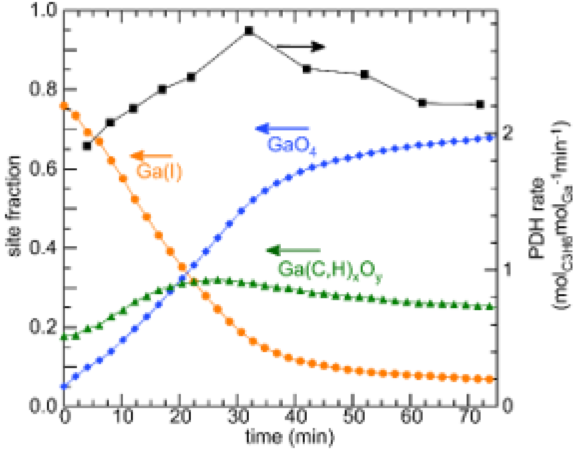
Introduction

Non-oxidative propane dehydrogenation (PDH) produces >20 MMT propylene annually, with demand projected to reach ~160 MMT by 2030.[1] Ga-based alumina catalysts are used industrially due to their high selectivity (>90%), but they suffer from deactivation, and the nature of the active Ga site(s) remains debated. Here, we interrogate Ga speciation in a model Ga/γ-Al_2O_3 catalyst under PDH conditions using *operando* XAS.

Results & Discussion

We first establish criteria for assigning Ga electronic structure and coordination from XAS by investigating the XAS of a wide range of Ga references. Then, we apply these criteria to identify and quantify Ga species formed during a PDH reaction catalyzed by Ga/γ-Al_2O_3. The clear spectroscopic signatures enable direct correlation between Ga speciation and PDH activity, as well as an estimated count of the active sites.



During 1 hr. of PDH reaction catalyzed by H_2-treated Ga/γ-Al_2O_3, a major fraction of Ga(I) sites convert into four-coordinate Ga(III)O_4 and four coordinate Ga(R,H)$_xO_y$ species. The reaction rate, measured simultaneously, linearly correlates with the fraction of Ga(R,H)$_xO_y$ species.

For instance, during high temperature H_2 pre-treatment, Ga(III)O_4 species reduce into Ga(I). Rapidly changing the atmosphere from H_2 (1 bar) to propane (0.2 bar, balanced in He), causes Ga(I) to partially oxidize into Ga(III)O_4 and a third species, whose XANES resembles that of spectroscopically similar Ga(III)H_xO_{4-x} and/or Ga(III)C_xO_{4-x} sites. The propane dehydrogenation rate, measured simultaneously, correlates linearly with the cumulative site fraction of Ga(III)(C/H)$_xO_{4-x}$ sites, suggesting these species are the resting state of a dominant PDH catalytic cycle, while the other major species are not active sites.

Significance

These results demonstrate a complex and dynamic Ga site distribution in a catalyst under reaction conditions. In addition, the active sites are a minor fraction of the total Ga, whereas less or inactive Ga are a major fraction of sites under reaction conditions. This highlights the importance of correlating structure with activity and avoiding prematurely assigning activity to species that exist under reaction conditions.

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Understanding nano Ceria formation from operando post treatment

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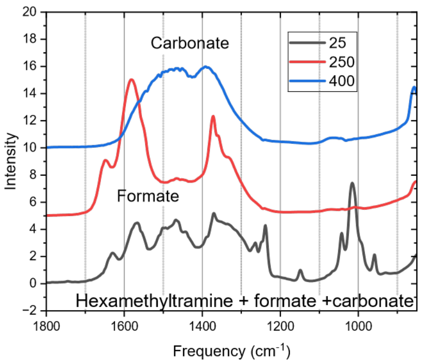
Introduction

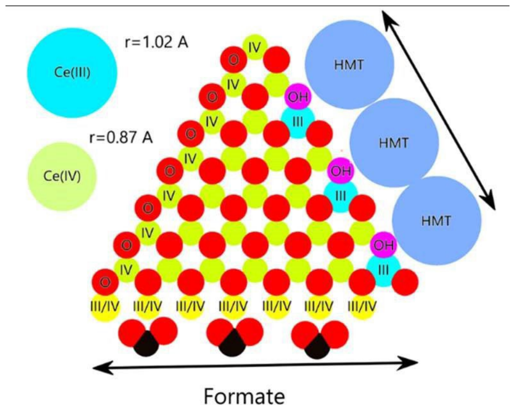
The process of formation[1] of nano ceria from HMT and Ce(III)$(NO_3)_3$ has been understood by operando measurement of the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), during heating of the as-synthesized crystallites of ceria. The synthesis (formulas below) mixture contains CeO_2 with hydroxyl groups that can form hydrogen bonds with the HMT. The formaldehyde also reacts with newly formed ceria to form chemisorbed formate. These two species stabilize a reduced ceria surface that helps control the formation of small nanoparticles. [2]

$C_4N_6H_{12} + 6H_2O \rightarrow 4NH_3 + 6CH_2O$ (1) HMT hydrolyzes

$Ce(III)(NO_3)_3 + 3H_2O + 3NH_3 \rightarrow Ce(OH)_3 + 3NH_4NO_3$ (2) cerium nitrate transforms to cerium hydroxide

$4Ce(OH)_3 + O_2 \rightarrow 4CeO_2 + 6H_2O$ (3) cerium hydroxide oxidizes to ceria with some hydroxyl groups





The surface hydroxides and chemisorbed formate stabilize Ce^{+3} ions that are highly coordinated with longer bonds with neighbors causing compressive surface stress. The core of nano-ceria experiences negative pressure (tension), stabilizing overall lattice expansion.[2]

Results & Discussion

The as-synthesized crystallite has reduced surface ceria that is stabilized by the above absorbed species. When the sample is heated the HMT desorbs and decomposes and provides formaldehyde (also observed with simultaneous operando mass spectra measurements) that forms chemisorbed formate at 200 °C and the formate decomposes to CO and CO_2 that forms adsorbed carbonate on the surface at 400 °C. Operando diffraction measurements show that the lattice expansion is significantly reduced after desorption.

Significance

The operando heat ramp allows us to verify the synthesis species and to understand how reduced surface of nano ceria is produced by the above synthesis.

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The Nuclearity and Reactivity of Highly Dispersed, Cationic Platinum in Medium-Pore Zeolites during Reaction and Thermal Treatments

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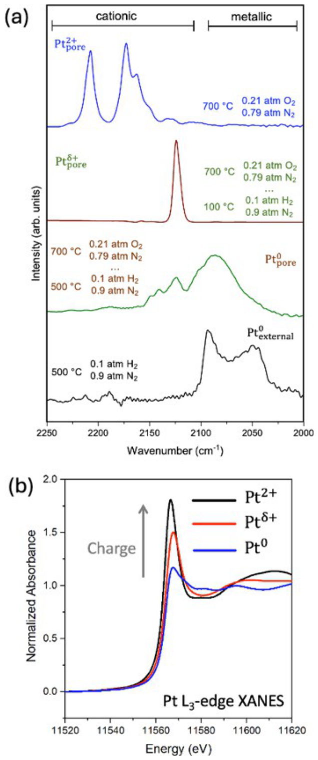
Introduction

Zeolite-supported Pt catalysts are widely applied in petrochemical processing, undergoing periodic regeneration steps that result in Pt migration, agglomeration, and (re)dispersion. Extensive research has focused on understanding Pt stabilization in zeolite micropores and the transformations that control the nature of the metal under reaction conditions [1,2]. A specific challenge is determining the nature of species that exist during the Pt agglomeration and redispersion processes that occur during pre-treatments, operation, and regeneration. A portion of Pt in working catalysts likely exists in such highly dispersed intermediate states, and often are undetected.

Results & Discussion

We now report characterization of isolated, stable $Pt^{\delta+}$ species, shown spectroscopically to exist as an intermediate during interconversion of Pt^{2+} and Pt^0 states, supported by HZSM-5. By treating aqueous ion-exchanged Pt/HZSM-5 samples in various gas environments at controlled temperature, both the state and location of Pt can be controlled (see CO FTIR figure at right and our publications [2,3]. The observed red shift of the band after reduction at 100 ºC corresponds to an increase in the electron density on $Pt^{\delta+}$ relative to Pt^{2+}, consistent with the XANES results in panel (b); reduction in white line intensity is consistent with the intermediate charge of this species. Operando EXAFS analysis recorded during hydrogenation catalysis (not shown) reveals distinct local chemical environments and binding to the zeolites, which is associated with unique reaction kinetics.



(a) CO-adsorption FTIR (DRIFTS) spectra highlighting the dramatically different chemical and electronic states of Pt in HZSM-5 subjected to different post-exchange treatments after initial ion exchange. From [2,3]. (b) Measuring charge on a previously unstudied dispersed, stable, Pt species in HZSM-5: Pt L_3 XANES contrasting the white-line of $Pt^{2+}_{pore}$and Pt^0_{pore} with that of the newly measured $Pt^{\delta+}_{pore}$.

Significance

Temperature and composition of the gas-phase environment during thermal treatments and reactions control Pt speciation in Pt-ion-exchanged HZSM-5. An intermediate $Pt^{\delta+}$ state was stabilized, isolated, and characterized by operando XANES/EXAFS and CO-adsorption DRIFTS, with the data demonstrating that this intermediate state is distinct from the previously investigated Pt^{2+} and Pt^0 states in ethylene hydrogenation systems. These findings shed light on how Pt speciation helps to explain metal migration and stabilization in the zeolite matrix during catalysis.

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Operando Insights into the Effect of Ceria Incorporation on the Oxygen Evolution Reaction Performance of Iridium-Based Catalysts

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Introduction

Proton-exchange membrane water electrolyzers (PEMWE) are emerging as a key technology for sustainable, electrocatalytic green hydrogen production. The high conversion rates of PEMWE allow efficient energy storage from renewable sources and ensure a dynamic energy supply despite seasonal variations. However, PEMWE advancement is hindered by the large overpotentials required for the acidic oxygen evolution reaction (OER) at the anode. Although Ir- based catalysts remain the most active and stable under the harsh conditions of low pH, high potential, and high oxygen concentration, their scarcity and insufficient long-term durability limit large-scale deployment [1,2]. Recent studies, including our previous work, have shown that above ~1.6 V vs. RHE, rutile IrO_2 undergoes a shift in its degradation mechanism as lattice oxygen begins to interact with active sites, leading to performance loss [3]. Enhancing the catalytic activity and stability of these noble-metal oxides is therefore essential to reduce precious metal loading and enable GW-scale PEMWE systems.

Results & Discussion

In this work, we investigate the incorporation of abundant and cost-effective Ce into IrO_2 for improved performance and stability at lower Ir content. $Ir_xCe_{1-x}O_2$ (x=0.2, 0.5, 0.8) samples were prepared by flame spray pyrolysis (FSP) method. XRD and Raman spectroscopy confirmed the coexistence of metallic and oxidic Ir species. *Ex situ* XAS revealed a shift of the Ir white line to lower energies compared to rutile IrO_2, pointing to the presence of lower oxidation states of iridium inside $Ir_xCe_{1-x}O_2$ samples. After electrochemical conditioning by potential cycling, XAS, XPS, and TEM analyses showed distinct structural evolution across the series: $Ir_{0.8}Ce_{0.2}O_2$ underwent noticeable particle sintering, whereas lower-Ir formulations maintained well-dispersed nanoparticles. Additionally, XPS results revealed that $Ir_{0.5}Ce_{0.5}O_2$ exhibited the highest degree of metallic Ir oxidation to higher Ir valence states. Simultaneously recorded Cyclic Voltammetry (CV) and Fixed Energy X-ray Absorption Voltammetry (FEXRAV) profiles as shown in Figure 1a reveal cycle-dependent changes in both electrochemical activity and X-ray absorption response, highlighting the dynamic evolution of the $Ir_{0.5}Ce_{0.5}O_2$ catalyst under operando conditions. RDE measurements demonstrated that $Ir_{0.5}Ce_{0.5}O_2$ and $Ir_{0.8}Ce_{0.2}O_2$ achieve lower overpotential at 10 mA cm^{-2}, along with enhanced stability relative to commercial IrO_2, confirming enhanced Ir utilization. Moreover, highest Ir mass activity at 1.53 V vs. RHE was obtained for $Ir_{0.5}Ce_{0.5}O_2$. While increasing Ir content above a 0.5 molar ratio did not further boost activity, likely due to Ir sintering induced by potential cycling, reducing Ir content to 0.2 resulted in significant activity loss. To further elucidate the potential-dependent behavior of the catalysts, operando XAS measurements were conducted under chronoamperometric (CA) conditions. As shown in Figure 1b, the white-line position of the $Ir_{0.5}Ce_{0.5}O_2$ catalyst increases progressively with applied potential, reflecting its strong Ir response. Figure 1c compares the potential dependent white-line shifts of all Ir-Ce compositions, while Figure 1d presents the corresponding currents recorded during CA measurements. The operando results reveal clear composition-dependent trends; $Ir_{0.2}Ce_{0.8}O_2$ exhibits the highest average Ir oxidation state to the applied potential, correspondingly to low OER activity. $Ir_{0.5}Ce_{0.5}O_2$ shows the most pronounced Ir redox flexibility and reversibility together with the highest currents, indicating an optimal balance between oxidation dynamics and catalytic performance. $Ir_{0.8}Ce_{0.2}O_2$ demonstrates a moderate Ir redox response coupled with high current output. These findings highlight that tuning the Ir-Ce ratio enables control over redox dynamics and OER activity.

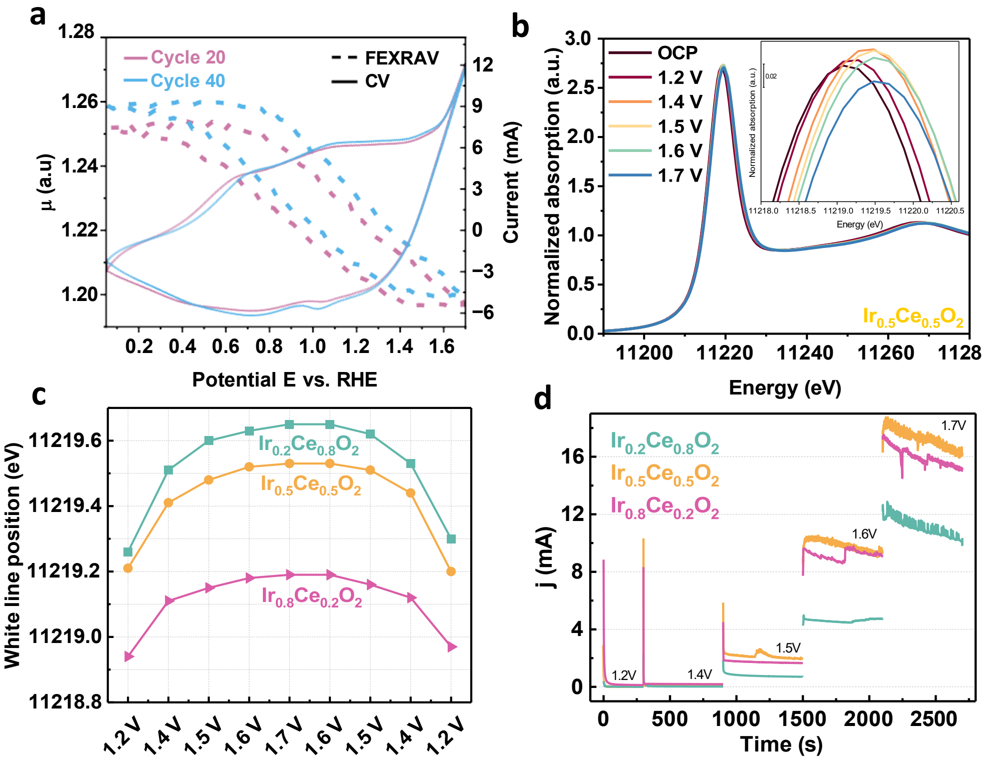

Figure 1. (a) Operando comparison of CV and FEXRAV signals at selected cycles (20 and 40). Solid lines represent the electrochemical current density, while dotted lines show the corresponding FEXRAV μ-intensity as a function of potential (vs. RHE) b) Operando Ir L_3-edge XANES spectra showing the white-line evolution of $Ir_{0.5}Ce_{0.5}O_2$ under increasing applied potentials (vs. RHE), with an inset showing an enlarged view of the white line region. (c) Potential-dependent white-line shifts for $Ir_xCe_{1-x}O_2$ compositions (d) Chronoamperometric i-t curves recorded during the operando XAS measurements.

Significance

By unraveling the influence of Ce on the chemical and electronic structure of IrO_2 during OER using operando XAS, this study aims to develop more efficient and durable catalysts tailored for sustainable H_2 production, ultimately optimizing catalyst design for real-world electrolyzer applications.

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Operando-Guided Low Temperature CO_2 Capture and Conversion

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Introduction

Despite the existence of various strategies for CO_2 conversion, its viability remains low, due to the purification steps between its capture and conversion, required to have an efficient process. To overcome this issue, CO_2 capture and utilization can be integrated in-situ, exploiting dual functional materials (DFMs) [1]. Currently, alkali metal containing oxides (e.g. K/Al_2O_3) are exploited to capture CO_2, and active catalyst element(s) (e.g. Cu) are incorporated to convert it to CO, CH_4, C_{2+} products. High temperatures (ca. 450°C) are required for optimal catalytic performances. Lowering this temperature is key to improving the process viability and sustainability. In this work, two complementary approaches are investigated for this goal, i.e. alternative methods to standard thermal heating and rational design of next-generation catalysts.

Results & Discussion

Microwave (MW) heating is a material-selective, fast and controlled method. We demonstrate for the first time CO_2 capture and reduction (CCR) under MW heating. The initial investigation shows that the potassium strongly absorbs MWs, enabling the efficient heating of the material without additional susceptors. Under MW heating the catalytic performances at 350 °C remained relatively stable compared with 450°C, whereas a pronounced decline was observed under thermal heating, suggesting an improvement in low-temperature activity. A customized setup with access ports enables operando characterization. As a first demonstration, operando thermal imaging (Figure 1) revealed pronounced temperature heterogeneities, directly linked to catalytic reactivity.

Previous studies (space- and time-resolved DRIFTS, XAFS, XRD) highlighted the unique state of K, which becomes amorphous under reaction conditions, allowing CO_2 capture, Cu dispersion and interaction with the trapped CO_2 to fully convert it. These insights guide the rational design of next-generation catalysts for CCR. A highly dispersed capture element wets a high-surface-area support, on which active catalyst element(s) are incorporated. The project preliminary results show that a new material was synthesized with comparable productivity (ca. 0.2 mmol g_{cat}^{-1}) to previously achieved systems, but operating far below 200 °C. To deeply understand this material functioning and how to optimize its performances, further operando investigation is planned.

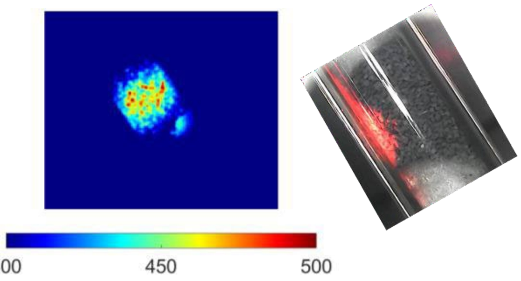

Figure.1 IR thermal camera (left) and optical (right) imaging of $Cu\text{-}K/Al_2O_3$ at 450°C under microwave heating. The temperature scale is given in [°C]. The bed length is 0.5 cm.

Significance

The present study highlights the central role of operando insights. In fact, it is the operando understanding of the DFM – its amorphous state and interaction with MWs, that made it possible to lay the groundwork for CCR at lower temperatures and to design next-generation catalysts with improved performance.

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The Disappearing Surface Nitrides: *Operando* Evidence for Hidden Redox Dynamics in Fe/MgO during Ammonia Decomposition

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Introduction

Ammonia decomposition is a promising route for carbon-free hydrogen production, yet the surface state of Fe-based catalysts remains highly dynamic and strongly dependent on the surrounding gas environment.[1] In our previous *operando* soft X-ray study, Fe/MgO under 1.0 mbar NH_3 at elevated temperature displayed coexisting NH_x adsorbates and iron nitride species on the catalyst surface. However, when the atmosphere was switched away from NH_3, the surface nitrogen signal nearly vanished, raising a key mechanistic question: does the apparent loss of surface nitrides simply reflect nitrogen removal, or does it reveal a hidden surface reaction coupled to the support?

Results & Discussion

To address this question, we designed *operando* gas-switching experiments and followed the response of N, Fe, O, and Mg on Fe/MgO using XPS/AES and AEY-NEXAFS. N 1s XPS shows that surface NH_x and nitride-related features present under NH_3 collapse after switching to He or UHV at reactive temperature. At the same time, Fe 2p XPS and Fe $L_{3,2}$-edge AEY-NEXAFS indicate oxidation of Fe^0/$Fe^{\delta+}$ toward Fe^{2+}, while O 1s, Mg 1s, Mg KLL, and Mg K-edge signatures show coupled evolution of oxide/hydroxide-derived Mg-O environments. Taken together, the data are consistent with a support-coupled surface equilibration process: hydroxylated MgO/$Mg(OH)_2$ species act as an internal oxidizing reservoir, consuming reduced Fe/nitride surface states and stabilizing Fe^{2+} in $Mg_xFe_{1-x}O$-like environments. Rather than being merely inert, He and UHV expose a latent redox equilibrium that is masked under NH_3 reaction conditions.

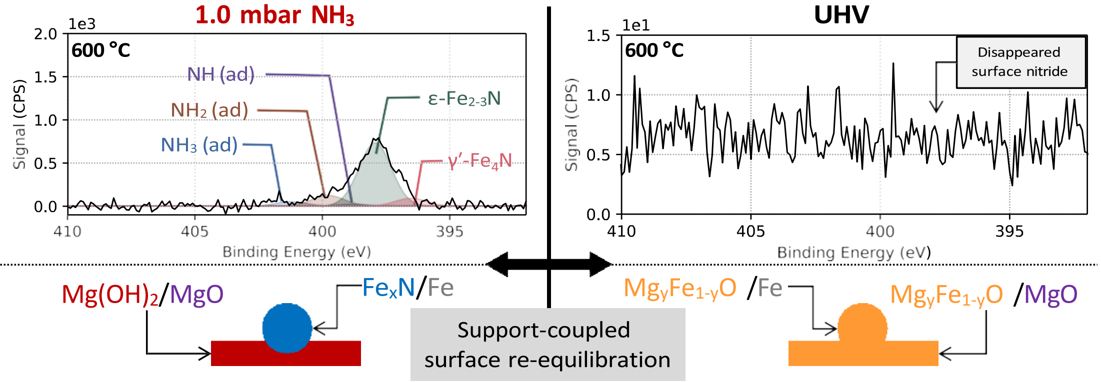

Figure 1. Disappearance of surface nitrogen upon *operando* gas-phase switching on Fe/MgO. Surface N 1s XPS under 1.0 mbar NH_3 shows NH_x adsorbates and iron nitride species, whereas after switching to UHV at constant temperature no detectable surface NH_x/nitride signal remains. The combined *operando* observations are consistent with support-coupled surface re-equilibration involving Fe oxidation and Mg-Fe-O reorganization.

Significance

These results show that gas-phase switching can actively perturb coupled metal-support-hydroxyl equilibria and thereby reshape the apparent surface speciation of ammonia decomposition catalysts. More broadly, this work highlights that *operando* interpretation of nitride-bearing Fe catalysts must account not only for adsorbate and nitride dynamics, but also for hidden support-assisted redox processes that emerge when the gas chemical potential is changed.

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Pulsed operando DRIFTS/GC to study the nature of the hydrocarbon pool on zeolites during the methanol-to-olefins reaction

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Introduction

The methanol-to-olefins (MTO) process is an attractive alternative chemical transformation to fuels and chemicals.[1] MTO is characterized by a hydrocarbon pool mechanism consisting of multiple catalytic cycles within the pores of a zeolite and by a product distribution highly dependent on zeolite topology. Carbenium ions confined within the pores of the zeolite catalyst are considered key intermediates and are typically identified by ^{13}C-NMR,[2] UV,[3] and IR spectroscopies.[4] In this work, direct relationships between species within ZSM-5 and product distribution are obtained under reaction conditions using a pulsed methodology with short CH_3OH (CD_3OD) pulses and diffuse reflectance infrared spectroscopy (DRIFTS) combined with online gas-chromatography (GC).

Results & Discussion

At each CH_3OH pulse (10 s; 0.17 bar) over ZSM-5 followed by 10-min Ar flow, activity increases and selectivity develops following the MTO product distribution typical of this topology. The pulsed method clearly identifies carbenium ions such as polymethylbenzenium ion (MB, 1620 cm^{-1}) and alkyl-substituted cyclopentenyl ions (1513 cm^{-1}) within the pores of ZSM-5, which is otherwise challenging under continuous CH_3OH flow. MB clearly correlates to production of ethene and propene. When sequences of CH_3OH pulses are alternated to sequences of CD_3OD pulses, ethene concentration decreases in each pulse while that e.g. of C_4 fraction increases significantly. Simultaneously, the vibrational signals of the carbenium species shift to lower energy and GC peaks to lower retention times due to isotope exchange. The product concentrations and DRIFTS signals return to the expected behavior in the subsequent CH_3OH cycles. The formation of the hydrocarbon pool continues in the CD_3OD pulses, but CD_3OD impacts products selectivity differently from CH_3OH.

By correlating the vibrational shift of the MB ion and the chromatographic shifts of the products upon deuterium exchange under reaction conditions, the production of ethene in ZSM-5 can be unambiguously associated to an aromatic catalytic cycle that has MB as precursor. C_{3+} hydrocarbons are instead associated to a different mechanistic origin, that can be reconciled with the olefin catalytic cycle.

Significance

The pulse methodology enables observation of hydrocarbon species within the porosity of the zeolite that would be otherwise difficult by IR spectroscopy. Deuterium exchange is a key analytical tool to help understanding the hydrocarbon pool mechanism under reaction conditions.

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Thin Film Operando Sample Environment for X-ray HERFD, Emission and Fluorescence Spectroscopy

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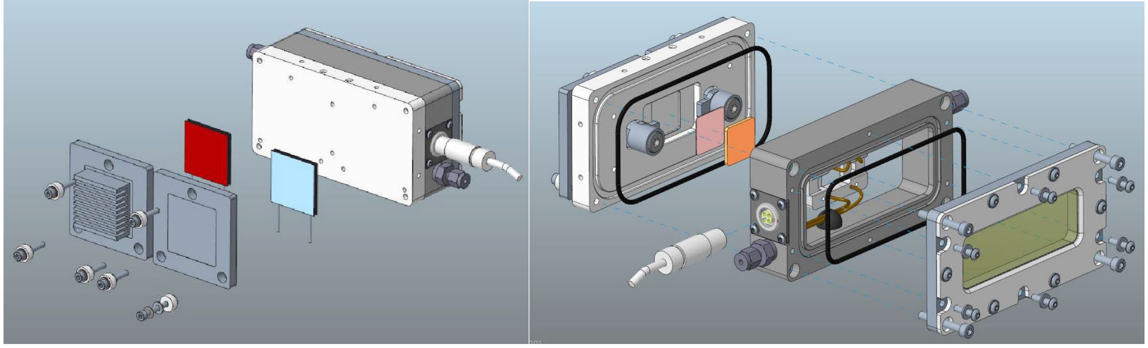
Introduction

A new sample environment has been developed at Diamond Light Source for the study of thin films in a gas environment at temperature. The cell has inlet and outlet ports for gases/vacuum, two Peltier modules for heating and/or cooling and spring-loaded contacts connected to a potentiostat allowing a two or four-point probe on the surface of the film. Uneven heating gives rise to a thermal gradient that can induce a Seebeck voltage from thermoelectric materials. A large front window was included for XES, HERFD and X-ray Fluorescence measurements on I20-Scanning at Diamond Light Source.[1]



Results & Discussion

We have tested this new sample environment on a Ni foil for calibration and on a metal-organic framework (MOF) that has shown to have good thermoelectric properties, Cu-HHTP.[2] We measured the Seebeck voltage produced from the MOF whist increasing the temperature difference across the film and then exposed the sample to dopant molecules (O2 and H2O saturated He) following the effect on the thermoelectric properties simultaneously. Using X-ray High energy resolution fluorescence detection (HERFD-XANES) we saw how changes to the MOF architecture can affect thermal and electric conductivity and thus the thermoelectric performance.

This sample environment combines complementary potentiostatic measurements with thin film samples, under operando conditions, and has led to a new method to study thin films and thermoelectric materials with X-ray Spectroscopy.

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Figure 1: Exploded view drawing of the thermoelectric cell for thin films at Diamond Light Source

SWIFT – Spectroscopy WithIn Fast Timescales: The New Flagship Operando Beamline coming to Diamond-II.

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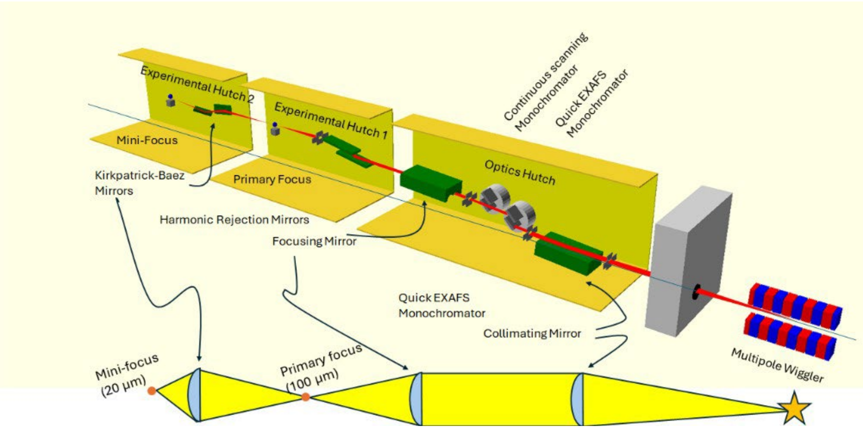
SWIFT is a high flux core-level spectroscopy beamline with a design that strikes an impressive balance between time and spatial resolution, enabling processes to be followed on timescales of tenths of milliseconds and sample heterogeneities to be investigated down to 20 µm in scale. These features will enable science and engineering insights to be obtained that hitherto have been impractical to achieve, with economically important applications spanning manufacturing, energy, environmental management, chemical, aerospace and tourism. This new beamline will increase the relevance of XAS in these areas and will be of significant benefit to both academia and industry. SWIFT will contribute significantly to research in catalysis, batteries, nuclear materials, the environment, cultural heritage, enzymes, and will incorporate significant elements of AI and Big Data.

SWIFT is an essential development to maintain and enhance the capacity and capabilities for X-ray spectroscopy at Diamond-II, as the X-ray spectroscopy community will lose a beamline in the upgrade, and the core-EXAFS beamline (B18) is more than 3 times oversubscribed. However, the case for SWIFT is not only about capacity but also crucially about capability and being able to drive new research and innovation. The addition of SWIFT to the portfolio of X-ray Absorption Spectroscopy (XAS) instruments on Diamond-II will offer transformative capabilities for the study of materials in a wide range of disciplines including high flux, time resolution and ability to make spatially resolved measurements.

In short, SWIFT will be an essential piece of the research landscape and will be an essential tool for operando X-ray spectroscopy.



SWIFT beamline optical layout.

When Water Turns Poison: Operando Modeling of Ni-Ga Catalyst Deactivation

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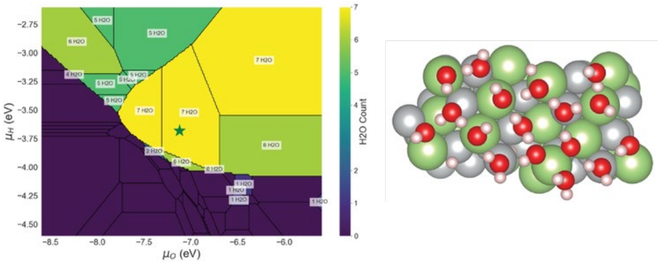
Introduction

Recent advances in *operando* spectroscopy have transformed our understanding of catalysis, showing that surfaces continuously adapt under reaction conditions. Yet, experiments alone cannot reveal the role of metastable states, atomistic detail of active sites, and the processes that drive catalyst deactivation[1]. *Operando* modeling[2] provides a complementary perspective by explicitly accounting for temperature, pressure, and reactant environment, allowing theory to resolve which states are accessible under operating conditions and how they evolve with the environment.



Phase diagram of the grand canonical ensemble of Ni_5Ga_3 (111) with the number of water molecules per phase. The green star denotes the chosen reaction conditions. The top view of the system under reaction condition is shown.

Results & Discussion

Using grand canonical sampling and DFT calculations, we investigated Ni-Ga model catalysts, ranging from supported clusters of varied size and shape to different Ni_5Ga_3 facets, under CO_2 hydrogenation conditions (200°C, 1 atm, 1:3 CO_2:H_2). Incorporating these conditions, we treat the surface as a dynamic statistical ensemble, revealing equilibrated states and their sensitivity to the environment. Across all models, operating conditions place the system near phase boundaries; between hydride-rich and hydride-poor conditions and between alloying and dealloying. While active sites can form after catalyst activation, under reaction conditions the equilibrated surface becomes poisoned by water, driving deactivation. The activity-stability balance is strongly structure sensitive: whereas stepped Ni_5Ga_3 surfaces show high activity, they are prone to water poisoning. Flat facets resist water poisoning yet display lower activity. This trade-off points toward particle size control and morphology as key levers to tuning performance.

Significance

These insights highlight how *operando* modeling complements spectroscopy by distinguishing transient and metastable species from equilibrated structures under operating conditions. In doing so, *operando* modeling may identify opportunities to steer surface transformations toward improved catalytic performance.

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This work is part of the Advanced Research Center Chemical Building Blocks Consortium, ARC CBBC, which is co-founded and co-financed by the Dutch Research Council (NWO) and the Netherlands Ministry of Economic Affairs and Climate Policy.

Operando XRD During High-Temperature Electrolysis at the Stanford Synchrotron Radiation Lightsource: Enabling Real-Time SOEC Analysis

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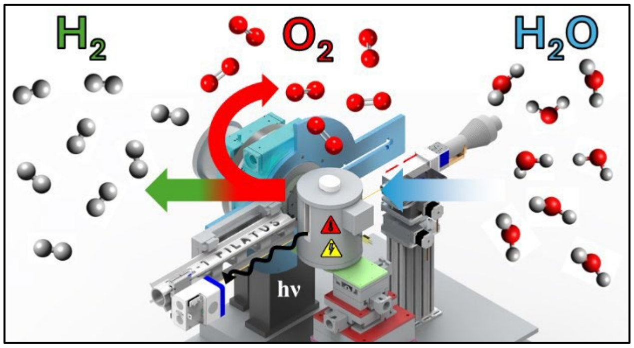
Introduction

Understanding structural evolution under realistic operating conditions is essential for improving materials used in high-temperature electrolysis (HTE). Solid oxide electrolysis cells (SOECs) operate under extreme thermal and chemical environments, where phase instability, cation segregation, and microstructural degradation limit long-term performance. To address these challenges, we have developed an *operando* X-ray diffraction (XRD) capability at beamline 2-1 of the Stanford Synchrotron Radiation Lightsource, enabling real-time tracking of structural changes in functioning electrochemical cells [1]. In parallel, we are developing high-entropy A-site–doped $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) materials designed to enhance structural stability and mitigate degradation pathways in SOEC electrodes.

Results & Discussion

The *operando* XRD platform integrates a custom high-temperature furnace, controlled gas environment, and precision electrochemical cell assembly, allowing continuous diffraction measurements during key stages of SOEC operation, including thermal ramp, reduction, and electrolysis under humidified conditions. Initial measurements reveal that early-stage thermal treatment plays a critical role in secondary phase formation and can strongly influence long-term structural stability. We demonstrate how this capability enables direct observation of lattice evolution, phase transitions, and subtle structural distortions during operation—features that are inaccessible through *ex situ* characterization. These measurements provide a framework for investigating degradation mechanisms in conventional SOEC electrode materials. Building on this, we introduce a class of high-entropy A-site–doped LSCF compositions, where multiple cations are incorporated on the A-site to increase configurational entropy and suppress phase segregation. The *operando* platform is uniquely suited to probe these materials when applied in a SOEC device, allowing us to directly compare their structural response under electrochemical bias and reactive atmospheres with that of conventional LSCF.



← Schematic of the operando XRD setup at beamline 2-1 of the Stanford Synchrotron Radiation Lightsource, enabling real-time structural characterization of SOECs under operating conditions. Figure taken from [1].

Significance

These results demonstrate a powerful integration of advanced *operando* characterization with the design of next-generation electrode materials. When combined, this will enable direct, real-time observation of structural evolution in both conventional and high-entropy LSCF systems under device-relevant conditions, providing new insight into the mechanisms governing degradation and stability in SOECs. Furthermore, the combined methodology offers a comprehensive pathway to rationally design more durable, high-performance electrodes for hydrogen production technologies.

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In-Situ DRIFTS Investigation of the Evolution of Surface Species in the Direct Conversion of Methane to Methanol over H-Ferrierite

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Introduction

The direct conversion of methane to methanol (DCMM) presents a promising pathway for sustainable methane utilization.[1] Zeolite and zeotype catalysts, particularly those functionalized with transition metals, have shown significant potential in facilitating this transformation.[1] While previous studies have primarily focused on oxidation mechanisms in aqueous and/or multi-step reaction conditions[2], our research investigates the feasibility of direct CH_4 oxidation under dry conditions using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

Results & Discussion

Building on our prior work demonstrating stepwise CH_4 oxidation to CH_3OH using modified zeolites[3,4], this study focuses on achieving direct conversion under mild conditions. In-situ DRIFTS experiments revealed that H-FER efficiently activates CH_4 in the presence of N_2O, producing surface methoxy species (CH_3-O-). Combined analyses by NH_3-TPD, solid-state NMR, and pyridine-sorption IR both Brønsted acid sites (Si-OH-Al) and extra-framework aluminum (EFAl) species act as active centers. The Brønsted sites are the domainally active sites. Moreover, the intrinsic pore confinement of FER provides a spatially restricted environment that suppresses overoxidation, thereby improving methoxy selectivity. Among all tested samples, H-FER-550 exhibited the highest activity due to the coexistence of strong Brønsted acidity and moderate EFAl content. The proposed mechanism involves CH_4 and N_2O co-adsorption, activation, and subsequent methoxy formation on acid sites.

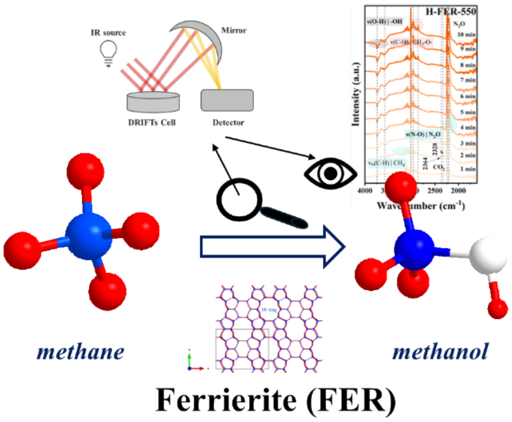

Figure 1 *In Situ DRIFTS Investigation of Surface Species in Dry CH_4 Oxidation to Methanol over H-Ferrierite*

Significance

This study provides direct spectroscopic evidence that Brønsted acid sites drive CH_4 activation and methoxy formation on H-FER. The proposed mechanism, likely dominant also in DCMM processes, offers valuable insights into the design of bifunctional or metal-modified zeolite catalysts for efficient low-temperature methane valorization.

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Operando EPR investigation of anionic vacancies: semiconductor physics and heterogeneous catalysis

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Introduction

Point defects are of extreme importance in determining the physical and chemical properties of materials. Among these, anionic vacancies are particularly crucial for semiconductors, as they can induce a completely different magnetic, optical and electric properties, compared to an ideal vacancy-free material. This is largely due to the introduction of intra-bandgap states and electron-donor behaviour associated with vacancies formation. At the same time, anionic vacancies in heterogeneous catalysts have an important role in many chemical reactions, such as CO_2 to MeOH conversion [1-3] and NH_3 oxidation.[4]

Results & Discussion

As for many point defects, the detection of anionic vacancies is often not trivial. EPR is a powerful method for their investigation, as vacancies often act as electron trapping sites (F-centers) and become paramagnetic. Here we present a general view on oxygen vacancies from a semiconductor physics perspective and the implications for catalysis, based on *operando* EPR and contact-free microwave conductivity measurements on a series of reducible oxides (In_2O_3, CeO_2, ZrO_2 and others). The results are complemented by *operando* XAS and XRD analysis. It is shown how the formation of oxygen vacancies can lead to an increase of n-type conductivity, decrease of p-type conductivity and how these properties are related to catalytic activity.

The investigation of nitrogen vacancies in carbon nitrides is also presented, as an example of a combination of *operando*, CW and pulse EPR methods (ESEEM and RIDME), together with DFT, providing a deep understanding of their reaction-induced structural changes and their effect on the catalytic behaviour and deactivation of the material.[5]

Significance

This study proposes a general model of the catalytic behavior of reducible oxides, connecting it to their semiconductor properties. It also demonstrates the power of *operando* EPR and microwave conductivity measurement methods, which provided the experimental validation of the model.

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FTIR and XAS Operando for Mechanistic Insights into the *In-Situ* Restructuring of Coordinated Copper in Post-Metalated MOFs during Photocatalysis

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Anthony Beauvois,[5] Guillaume Clet,[1]Georges Mouchaham,[3] Guillaume Maurin,[4]
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Introduction

MOFs provide tunable platforms for photocatalysis, where the structure–activity relationship essential to understand, especially in Cu-functionalized systems, where coordination and redox behavior strongly influence performance. We previously observed that Cu^{2+} in UiO-66$(COOH)_2$ undergoes light-induced in-situ restructuring process unlike pristine UiO-66-Cu[1], inferred from *operando* FTIR through the evolution of surface anhydrides during photocatalytic FAc dehydrogenation, yet the role of free carboxylates on its activity was not addressed. Furthermore, no real-time evolution of Cu oxidation states was demonstrated. To address this, UiO-66 derivatives with varied BDC/BTCA ratios (x:y) were synthesized (Fig.1A) and post-metalated with Cu^{2+} to assess the influence of free carboxylates on their activity as well as its in-situ restructuring process. Then complementary *operando* FTIR and XAS were employed, enabling real-time monitoring of framework evolution and Cu oxidation-state dynamics under real time conditions respectively for fully understanding the underlying mechanism.[2]

Results & Discussion

The formation of anhydride species was monitored by *operando* FTIR due to the change in the Cu coordination (Fig. 1B), occurring simultaneously with changes in Cu oxidation state, as revealed by *operando* XAS (Fig.1C). The increase in photocatalytic activity observed with higher COOH content in the samples (Fig.1D) was directly linked to this *in-situ* restructuring process. Then a linear correlation between the *in-situ* restructuring and the sample activity was established (Fig. 1D, inset).

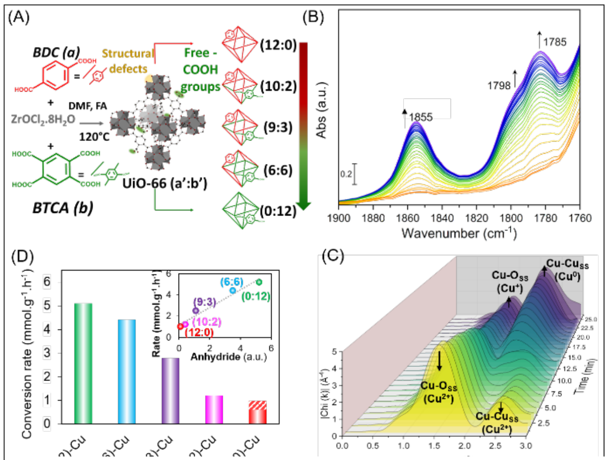

Figure 1. (A) Scheme of the synthesis procedure of differen samples. (B) Performance of different samples in photocatalytic FAc dehydrogenation. (C) Evolution, versus reaction-time, of the IR surface spectra of the (0:12)-Cu sample during the FAc dehydrogenation in the anhydride vibrational region and (D) the Cu K- edge EXAFS spectra of (0:12)-Cu sample during the photocatalytic reaction; inset: activity versus anhydride of the various samples.

Significance

These insights highlight the crucial role of Cu coordination and its *in-situ* restructuring, underscoring the value of *operando* spectroscopy in guiding the design of highly efficient catalysts for H_2 generation.

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Kinetic Relevance of Oxide Support Redox Processes for Supported Vanadia Catalysts during Methanol Oxidation with Transient *Operando* DR UV-Vis-MS Spectroscopy

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Introduction: Alcohol oxidation with supported vanadia catalysts has been widely studied and regarded as a model system in heterogenous catalysis. An intriguing feature of ~10^3 variation in turnover frequency was observed for methanol oxidation with redox and non-redox oxide supports[1]. For ethanol oxidation by VO_x/CeO_2, *operando* investigations revealed the redox participation of CeO_2 while contradictory findings were reported for surface VO_x involvement[2,3]. Here, the redox kinetics of surface VO_x on oxide supports (CeO_2, TiO_2, ZrO_2, Nb_2O_5, Al_2O_3, and SiO_2) was investigated with *operando* concentration modulation excitation (c-ME) DR UV-Vis-MS spectroscopy during methanol ODH to allow spectral enhancement of weak signals with modulation excitation spectroscopy (MES) via phase sensitive detection and CH_3OH- temperature programmed surface reaction (TPSR).

Results & Discussion: *In situ* Raman spectroscopy confirmed that surface VO_x sites were molecularly dispersed below monolayer coverage (<8 V/nm^2). *Operando* DR UV-Vis-MS spectroscopy during CH_3OH-TPSR, demonstrated the reduction of surface $V^{5+}O_x$ to $V^{4+/3+}O_x$ sites while the redox supports (CeO_2, TiO_2, ZrO_2, Nb_2O_5) were found to supply lattice oxygen to re-oxidize the reduced surface $V^{n+}O_x$ sites at higher temperatures whereas non-redox supports (Al_2O_3 and SiO_2) did not. For VO_x/CeO_2, Ce^{4+}/Ce^{3+} redox species appeared at 200-450 ^{0}C during CH_3OH-TPSR. For VO_x/TiO_2, *operando* concentration modulation excitation (c-ME) DR UV-Vis-MS spectroscopy, while switching O_2 on/off, revealed the reduction of surface V^{5+} sites to $V^{4+/3+}$ in a feed of CH_3OH/Ar that re-oxidized in a CH_3OH/O_2/Ar feed and a slow Ti^{4+}/Ti^{3+} redox cycle (Fig. 1).

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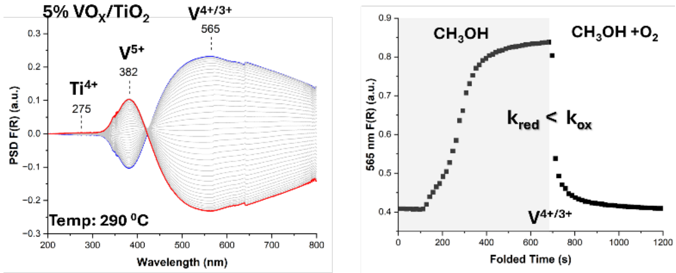

(1a) Phase Domain Spectra

(1b) Apparent Kinetics

Figure 1(a). Phase domain spectra during O_2 switching MES on 5%VO_x/TiO_2, and 1(b) apparent kinetics of the $V^{4+/3+}$ species formation and consumption during reduction and re-oxidation steps.

Significance: Application of *operando* DR UV-Vis-MS with MES has provided key fundamental information about the kinetic relevance of the redox processes of oxide supports during alcohol oxidation by supported vanadia catalysts (CeO_2> TiO_2 ~ZrO_2> Nb_2O_5).

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Investigating Relationships Between Gas-Phase Reactive Intermediate Speciation and Product Yields during Heterogeneous Catalytic Reactions

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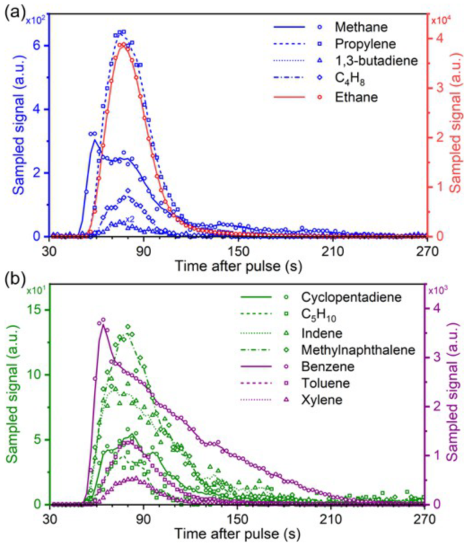
Introduction

Operando and in situ characterization of chemical events occurring on solid catalyst surfaces has become an essential aspect of reaction mechanism development. For many heterogeneous reactions, there is evidence that additional information is uniquely available by considering the composition of reactive species in the gas phase, which are not commonly measured in catalysis studies.[1,2,3.] During reactions, we study the time-resolved composition of reactive intermediates and relate these to overall reaction outcomes, including product yields.

Results & Discussion

Here, we present results that explore the interconnected roles of the surface, catalyst pores, and the near-surface gas phase in heterogeneous catalytic systems. The near-surface region (defined as a region hundreds of microns to millimeters above a surface) and reactor effluents are interrogated primarily through molecular-beam time-of-flight mass spectrometry with near-universal species detection (including radical and highly reactive closed shell species). These techniques are complemented by diffuse reflectance FTIR spectroscopy, which selectively probes adsorbate compositions during reactions. A primary focus of this presentation involves new studies of the mechanisms of alkane and alkene aromatizations with zeolite-based catalysts. A significant recent expansion of our work involves development of a temporally resolved approach for tracking the complete chemical composition of a reaction products/intermediates in response to reactant pulses. Use of energy-tunable VUV-synchrotron photoionization spectrometry allows for confirmation of the identities and transient behavior of key reactive species, such as dienes, whose formation is central to formation of aromatics. The figure at right shows representative results.



Representative individual time traces collected in response to a single pulse of ethane over a bed of Pt/HZSM-5 of (a) $C_{1\text{-}4}$ observed species; and (b) C_{5+} observed species. 500°C, 600 Torr

Significance

The measurement of reactive gas-phase intermediate generation rates and their transient behavior provides a new perspective and source of data to elucidate the mechanisms of complex, and even deactivating, heterogeneous chemical systems.

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Reducibility of unsupported and Al_2O_3-supported RuO_2 catalysts: when Ru-oxide challenges Ru-metal in hydrogenation

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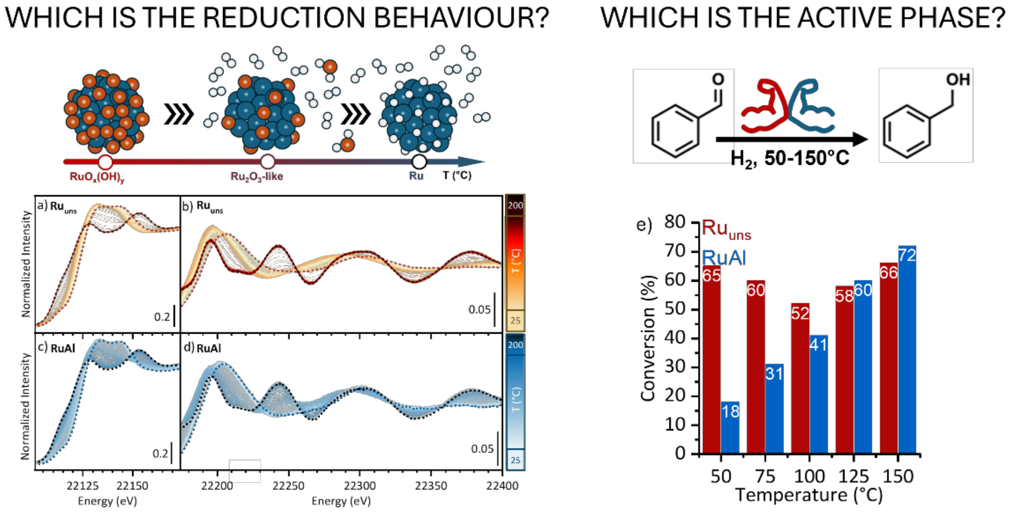
Introduction

High reducibility of Ru-based catalysts can be achieved with deposition precipitation synthesis, at the cost of increasing the complexity of the Ru phase, including defective and hydrated phases, hence a challenge for characterization. To tackle this challenge, H_2-TPR was coupled to operando synchrotron techniques (XRD, PDF, XAS) and chemometric analysis (PCA/MCR) to characterize the reduction behavior of two industrial catalysts: 5wt% Ru/Al_2O_3 (RuAl) and unsupported $RuO_x(OH)_y$ (Ru_{uns}). Catalytic performance was tested with benzaldehyde hydrogenation.

Results & Discussion

PCA/MCR analysis of synchrotron experiments (Fig1 a-d) revealed a two-step reduction pathway coherent with H_2-TPR data, involving a defective Ru_2O_3-like intermediate, characterized by both Ru–Ru bond contraction and lattice expansion, consistent with oxygen vacancy formation.[1,2] Importantly, catalytic tests (Fig1 e) showed that an amorphous, hydrated $RuO_x(OH)_y$ phase can outperform metallic Ru in benzaldehyde hydrogenation under mild conditions (50 °C).



Evolution of the normalized Ru K-edge XAS spectra of (a-b) Ru_{uns} and (c-d) RuAl during the H_2-TPR experiment in the (a-c) XANES and (b-d) EXAFS regions. The first and last spectra are reported with dotted lines; e) Effect of the reaction temperature in the hydrogenation of benzaldehyde over Ru_{uns} and RuAl catalysts.

Significance

These findings deepen the understanding of the reduction mechanisms of Ru oxidic precursors and challenge the conventional view that only metallic Ru is catalytically active, highlighting the potential of structural disorder and redox flexibility in Ru-based catalyst design.

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Elevating Cobalt to Noble Heights: understanding Co-Re catalyst outstanding TOF in Methanol Steam Reforming through *in-situ* DRIFTS

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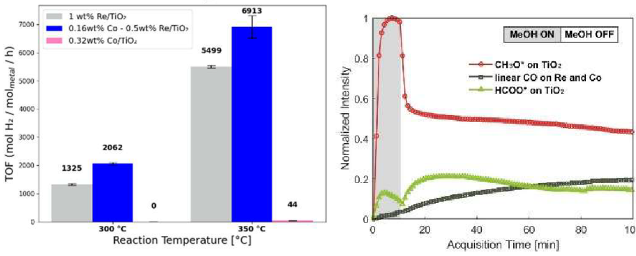
Introduction

Methanol steam reforming (MSR) is a promising route for on-demand hydrogen generation owing to the relatively facile C–H bond activation and high H/C ratio of methanol. While highly dispersed platinum-group metals show excellent intrinsic activity and water-gas shift (WGS) performance, their low temperature application is hindered by the high activation barriers, when supported on reducible oxides [1]. To overcome this limitation, a bimetallic cobalt-rhenium catalyst supported on TiO_2 demonstrated high TOF of Co and Re while lowering the apparent activation energy, with Co exhibiting a nearly 150-fold increase in TOF compared to Co/TiO_2.

Results & Discussion

A series of bimetallic rhenium-transition metals on TiO_2 at 1:1 molar ratio have been synthesized through sequential impregnation on a 0.5 wt% Re/TiO_2, with cobalt exhibiting a remarkable enhancement of catalytic activity and reduction in apparent activation energy upon the addition of only 0.16 wt%. The bimetallic catalyst outperformed both 1 wt% Re/TiO_2 and 0.32 wt% Co/TiO_2, achieving a turnover frequency more than 150 times greater than the monometallic cobalt catalyst. The observed activity is attributed to improved dispersion and reducibility of cobalt and to an optimized electron transfer when both metals coexist on the TiO_2 surface. *In-situ* DRIFTS revealed how the transition from physiosorbed methanol to methoxy on TiO_2 occurs at lower temperature when cobalt is present and highlighted two competing pathways involving formate and methoxy decomposition, with the latter being the most reactive species. Both intermediates form on the TiO_2 surface at low temperature without the need of metal sites, while their decomposition proceeds only via surface migration to nearby Re and Co centers. Co/TiO_2 does not show carbonyl associated with methoxy decomposition at 300°C, in line with the catalytic activity. Interestingly, the sharp peak at 2025 cm^{-1}, attributed to linearly adsorbed *CO on Re, increases in intensity relative to the broad band at 1930 cm^{-1} (bridged carbonyls) when both Co and Re are present. This suggests overlapping *CO vibration on the two metals [2] and confirm the contribution of Co to the overall observed catalytic activity.



Left: Comparison of TOF (mol H_2/mol$_{metal}$ /h) for 1 wt% Re/TiO_2, 0.16 wt% Co – 0.5 wt% Re/TiO_2 and 0.32 wt% Co/TiO_2. Right: time evolution of surface species during in-situ DRIFTS at 300°C

Significance

The results demonstrate that tailored bimetallic catalysts can rival the prevailing platinum group metals benchmarks, with *in-situ* DRIFTS highlighting the enhanced C-H bond cleavage of CH_3O* species and revealing the main reaction pathways dictating the selectivity in MSR.

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Operando X-ray spectroscopy of transition metal oxides interfaces

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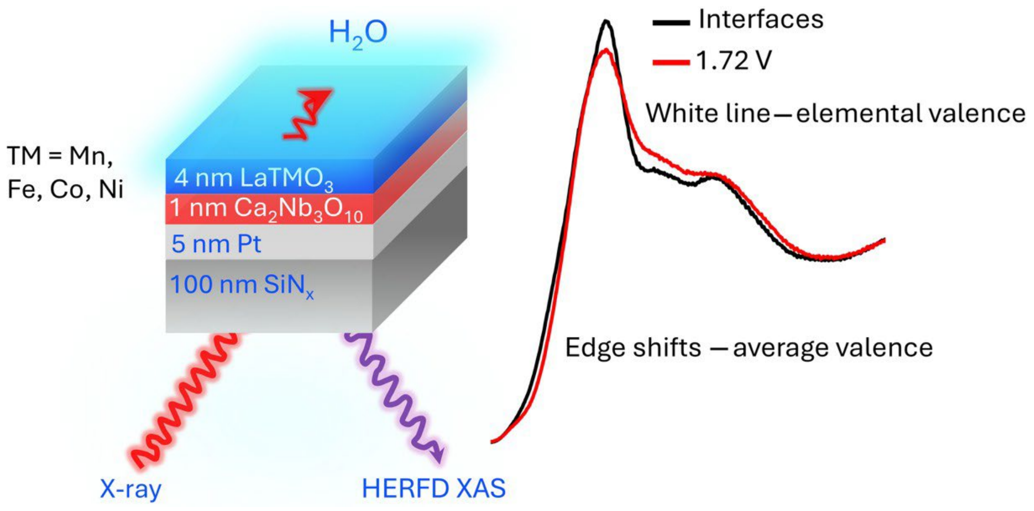
We study how electrochemistry reshapes transition-metal electronic structure at oxide–electrolyte interfaces by performing operando HERFD-XAS and 1s2p RIXS on few-nanometer epitaxial $LaTMO_3$ (TM = Mn, Fe, Co, Ni) thin films, grown by PLD to precisely control lattice strain and coordination.

The results establish three general principles:

(1) Electrolyte contact fundamentally modifies the interfacial electronic structure. The dry-state catalysts do not represent the active state.

(2) In monometallic oxides 3d electron counts remain constant, while metal–oxygen covalency increases with applied potentials.

(3) In bimetallic oxides edge shifts track the average oxidation state of both metal ions, while the white line intensity determines the element-specific valence state under applied potentials.



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Operando electronic structure of RuO$_x$ at the interface

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Introduction

Elucidating the electronic structure of amorphous ruthenium (hydro)oxides especially at the electrocatalytic solid–liquid interface redox conditions is still a major challenge.[1,2] Ex situ Ru K-edge HERFD-XAS of RuO_2 and RuO_xH_y shows nearly identical edge positions,[3] making it challenging to obtain detailed electronic-structure information. Oxygen K-edge and *operando* HERFD-XAS at Ru L_3 edge provides the great advantage of performing such studies due to directly probes the valence state with enhancing energy resolution.

Results & Discussion

We propose that the local symmetry of RuO_xH_y is very similar to that of crystalline RuO_2. To examine this, we used the Bethe–Salpeter equation (OCEAN code) to simulate the O K-edge XAS, introducing a negative charge into the RuO_2 model to increase the Ru 4d occupancies. Interestingly, the simulated O 1s XAS spectra exactly reproduce the experimental results (Figure 1b). This indicates that the valence state of Ru in RuO_xH_y is closer to +3 rather than +4. Furthermore, we show that the average Ru valence does not exceed +5 in 0.1 M $HClO_4$ solution even under high anodic potential of 1.6 V vs. RHE.

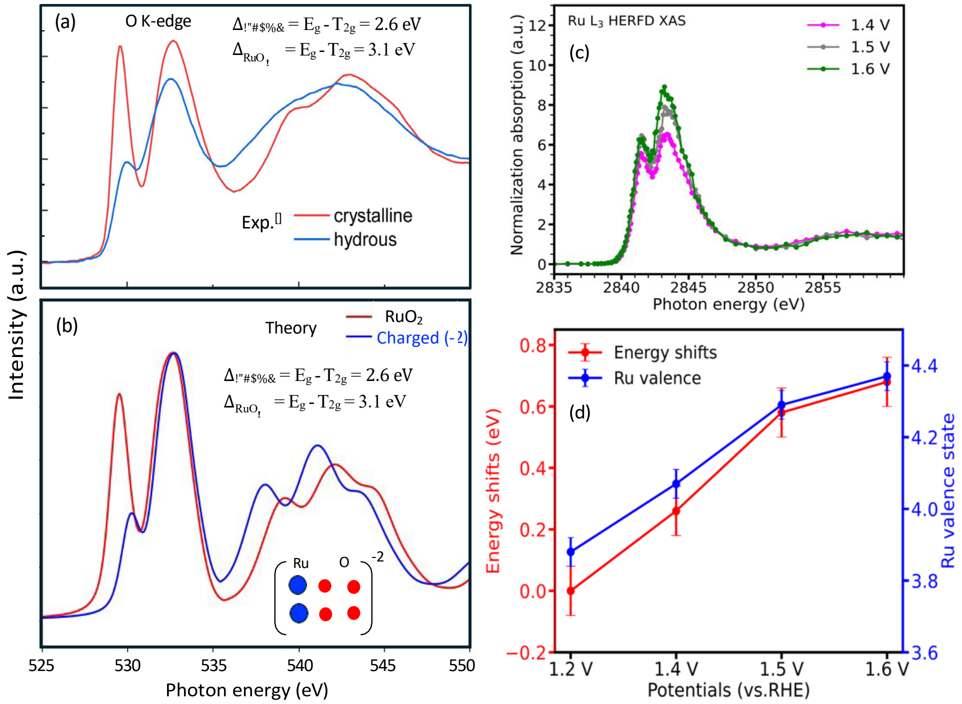

Figure 1. (a) experimental ex situ O 1s XAS of RuO_2 (crystalline) and ruthenium (hydro)oxide (hydrous) reprocured by ref.[3], (b) theoretical O 1s XAS simulation of RuO_2 and charged RuO_2. (c) Operando Electrocatalytic Ru L_3 HERFD XAS of RuO_xH_y on Au/SiN_x membrane in 0.1 M $HClO_4$ electrolyte, (d) corresponding energy shifts and Ru average valence state.

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Operando MES-Raman and MES-DRIFTS study of CO oxidation on highly dispersed CeOx on Cu_2O nanocubes

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Introduction

Inverse catalysts consist of oxide species supported on metals, leading to strong oxide–metal interactions. These interactions can stabilize active sites and significantly alter catalytic reactivity. In this work, we prepared inverse $CeO_x/Cu@Cu_2O$ catalysts, featuring highly dispersed ceria clusters on Cu_2O nanocubes. Structural characterization by HRTEM and *in situ* XRD confirmed controlled Cu oxidation states that promote formation of the active CeO_x/Cu^{+1}-Cu^0 interface. Catalytic tests showed that ceria incorporation markedly enhances CO conversion, reaching a T_{50} of 75ºC [CO(1%)/O_2(5%)/Ar; Q=100 mL/min, 50 mg catalyst]. Reference measurements showed that pure CeO_2 is inactive for CO oxidation within this temperature range, while pure Cu_2O nanocubes only oxidize CO above ~150 °C. These results highlight the crucial role of Cu–Ce interfacial sites in activating CO and enhancing overall oxidation performance. We have probed the nature of the active sites, the catalyst state, and the adsorbed intermediates in operando Raman and DRIFT concentration-modulation excitation spectroscopy (c-MES) experiments to investigate intermediate species potentially bound to interfacial sites.

Results & Discussion

Combining *operando* Raman-MS with DRIFT-MS while systematically varying CO and O_2 concentration (c-MES-PSD experiments) enables us to correlate the formation of surface intermediates with catalytic activity and to identify rate-relevant species. Isothermal experiments were performed from 50 to 125 °C. Time-resolved modulated spectra were processed using the phase-sensitive detection (PSD) method, which separates static spectator signals from true reactive intermediates. MES-Raman monitored the characteristic F_2g mode of CeO_2 at 463 cm^{-1}, corresponding to Ce–O lattice vibrations, along with a defect-induced band at ~600 cm^{-1}. This defect band changed synchronously with CO introduction, indicating consumption of lattice oxygen during CO oxidation. Raman signals of Cu_2O were observed, including the band at 150 cm^{-1} (fundamental lattice mode) and the more intense band at 216 cm^{-1} (first-order lattice vibration), but no CuO-related features appeared. Importantly, the Cu_2O Raman features were only weakly influenced by reactant modulation. Phase-resolved DRIFT spectra displayed bands evolving synchronously with CO feed. Two well-defined features corresponding to CO species bound to Cu^+ sites were detected at 2106 cm^{-1}, assigned to geminal CO (symmetric mode), and at 2135 cm^{-1}, associated with linearly adsorbed CO. These rapidly disappeared upon switching the feed to O_2. Additionally, carbonate/carboxylate species were identified at ~1650 and ~1300 cm^{-1}.

Significance

Modulated concentration and advanced analysis of *operando* Raman and DRIFT spectra provides molecular-level insight into the mechanism of CO oxidation over CeO_2 clusters supported on $Cu@Cu_2O$ nanocubes. The combined results demonstrate that both components of the catalyst dynamically participate in the reaction and highlight the important role of interfacial Cu–CeO_x sites in generating highly active reaction centers.

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MES-FTIR at high pressure to investigate the CO_2 hydrogenation on Pd/CeO_2 nano fibers

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Introduction

Pd(1%)/CeO_2 nanofibers were synthesized by electrospinning of precursor solutions containing PVP, cerium acetylacetonate, and Pd acetate, followed by drying and controlled calcination to obtain ceramic, highly porous fibers. CO_2 hydrogenation was investigated on this hierarchical micro–meso–macroporous structure, which is expected to be advantageous for catalytic applications. Modulation excitation FTIR spectroscopy in a pressurized transmission reaction cell was applied to obtain relevant information about the reaction mechanism closer to the real reaction conditions. We employed a home-made, low-volume, stainless-steel cell fitted with CaF_2 windows sealed using Kalrez O-rings. The cell withstands temperatures up to 270 °C and pressures up to 15 atm.

Results & Discussion

SEM and TEM images revealed continuous nanofibers with diameters of 150–170 nm, rough surfaces, and a homogeneous dispersion of small Pd nanoparticles (< 1 nm). The catalytic activity of the Pd(1%)/CeO_2 nanofibers for CO_2 direct hydrogenation to methanol was measured in the range 200-250 ºC at 30 atm in a conventional plug flow reactor. MES experiments were performed by modulating between $H_2 + CO_2$ and H_2 + Ar at 225 °C under 1, 4, and 6 atm using a flow-through electronic valve for gas switching synchronized with the FTIR spectrometer. Reactant gases were supplied through high-pressure mass-flow controllers, and a back-pressure regulator was used to maintain the desired operating pressure. At lower pressures, the reverse water–gas shift (RWGS) reaction dominates, whereas increasing pressure enhances methanol selectivity. Our preliminary MES-PSD results indicate that a specific formate species. monodentate formate (m-HCOO), likely bound to the ceria support in close interaction with the metal particles, becomes increasingly favored with pressure. This shift in surface speciation may reflect a change in the reaction pathway, promoting hydrogenation of the intermediate toward methanol formation.

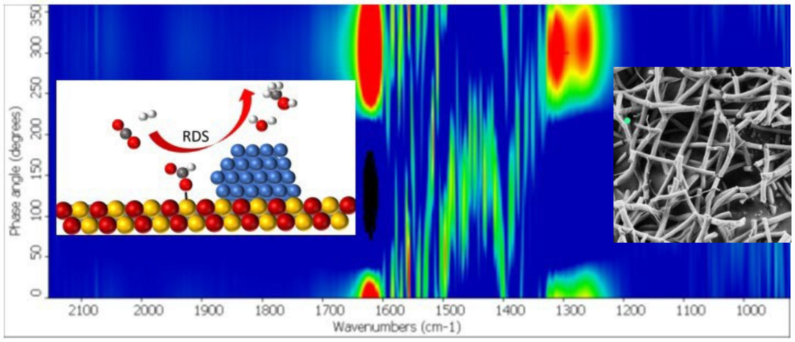

Figure 1. 2D-Phase resolved FTIR spectra. Insets show a SEM image of the nanofiber catalyst and scheme showing the key role of monodentate formates.

Significance

Operando MES-FTIR experiments under high pressure to reduce the gap with real operating conditions.

Following Redox Chemistry Across Space and Time

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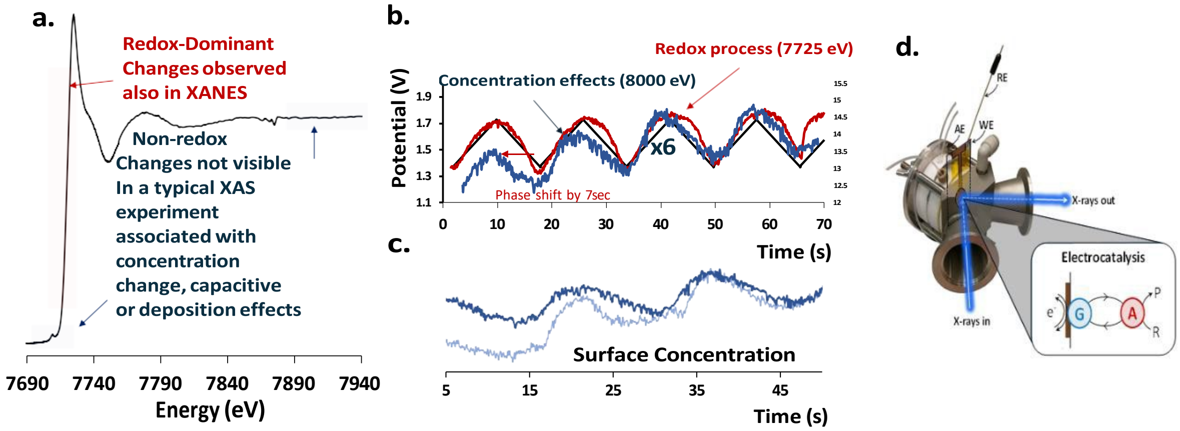
Introduction

One of the greatest challenges of the 21st century will be securing cheap and renewable sources of energy. One of the most promising approaches to this challenge is to design catalysts from earth-abundant materials capable of implementing key chemical reactions, including splitting water into hydrogen and oxygen ($H_2O \rightarrow 2H^+ + O_2$); and both the oxidation ($H_2 \rightarrow 2H^+$) and reduction ($2H^+ \rightarrow H_2$) of hydrogen among many others. In studying catalysts, we often focus on the "nature of the active site" which for classical heterogeneous catalysts works well- but not all catalysts work by surface sorption processes alone.

Results & Discussion

In this work we will explore how X-ray experiments (both XAS(2) and imaging(3))can be used to probe systems over different timescales. Utilising underlying electrochemical change coupled to single wavelength x-ray absorption we can separate the different timescales of deposition and oxidative electrochemical processes. Using X-ray imaging we can follow the movement of redox process through mm-mm of deposited material. The redox events between substrate and catalyst and the speed of these processes appear to play a key role in both engineering product selectivity and catalyst stability.



Separation of Distinct Electrochemical processes with Single Wavelength X-ray Absorption Spectroscopy.

Significance

The techniques we show demonstrate the capacity to separate distinct electrochemical processes as well as their timescales with both XAS and X-ray imaging.

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Operando HERFD-XANES and VtC-XES Probes Atomic and Electronic Structure Evolution

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Introduction

Operando HERFD-XANES and VtC-XES are shown to offer ultrahigh sensitivity to resolve geometric symmetry, ligand environments and electronic structures, overcoming the limitation of conventional in situ techniques in capturing subtle atomic/electronic changes. Herein, we apply these methods to quantify reversible angle distortion of CoPc in CO_2RR, demonstrating their unmatched power in probing catalyst structural dynamics.

Results & Discussion

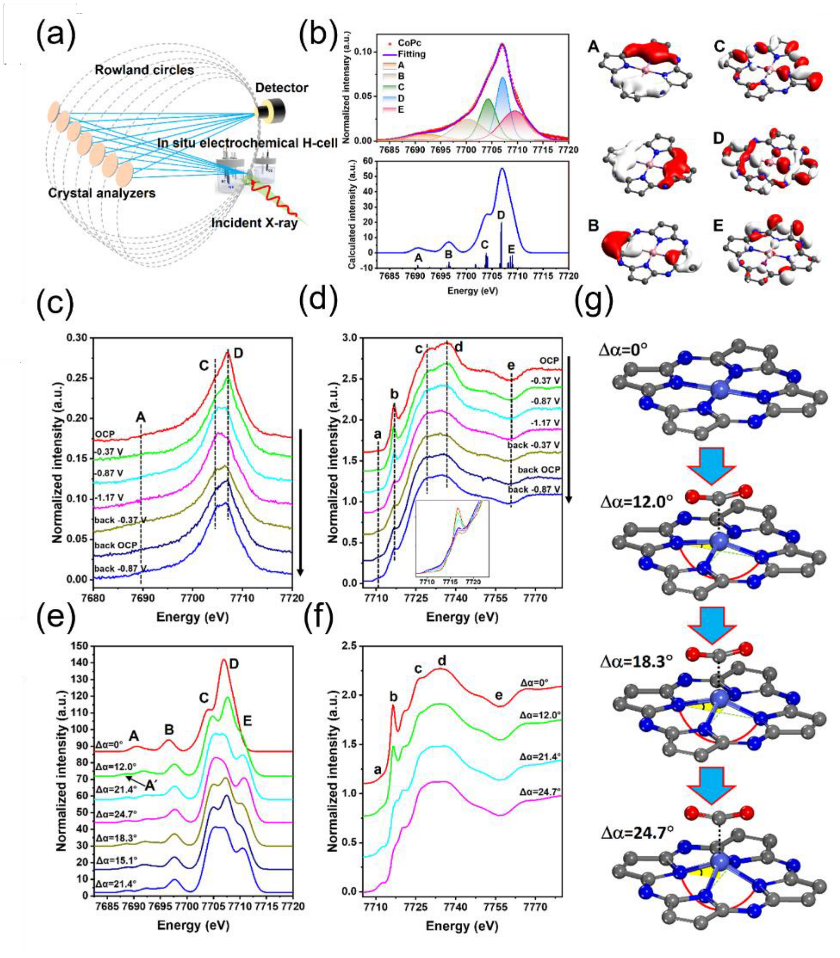

Fig. (a) Schematic of the operando XES measurement setup using a seven-crystal Johann-type spectrometer. (b) Experimental (top) and theoretical (bottom) VtC-XES spectra of CoPc. Experimental VtC-XES (c) and HERFD-XANES spectra (d) of CoPc under CO_2RR conditions at various working potentials. Calculated VtC-XES (e) and HERFD-XANES spectra (f) of CoPc using various models. (g) Optimized models with different Δα used for theoretical simulations, with yellow triangle indicating the distortion angle.

The operando HERFD-XANES and VtC-XES collectively link CoPc's structural dynamics to CO_2RR performance via high-resolution spectral signals. Figure (a) depicts the operando XES setup with a seven-crystal Johann-type spectrometer. Seven Rowland circles integrate crystals, sample and detector to enlarge solid angle, enhancing signal-to-noise ratio for dilute atomic sites under real CO_2RR conditions. Figure (b) shows experimental and theoretical VtC-XES spectra of CoPc. Five deconvoluted features match well with DFT calculations. A at 7690.5 eV corresponds to N 2s→Co 1s transitions, while D at 7707 eV arises from Co-ligand-N/C interactions, validating subsequent analyses. Figure (c) presents experimental VtC-XES at different potentials. OCP spectra show weak $K\beta_{2,5}$ splitting. Negative potentials intensify C at 7704.4 eV and weaken D, with reversibility upon potential cycling.

Figure (d) displays experimental HERFD-XANES. The pre-edge peak at 7710.5 eV strengthens while the 1s→4pz shoulder diminishes. Feature c/d intensity ratio varies with potential reversibly. Feature e's stable position confirms unchanged Co-N bond length. Figure (e) shows calculated VtC-XES for models with varying $\Delta\alpha$. Theoretical spectra match experiments, with increasing $\Delta\alpha$ amplifying $K\beta_{2,5}$ splitting and inducing Feature A'. Feature C's CO_2 p character correlates with CO FE. Figure (f) presents calculated HERFD-XANES that reproduce experimental features. The stable first trough energy across $\Delta\alpha$ confirms distortion only involves bond angles, validating Co's deviation from N_4 plane with constant Co-N length. Figure (g) depicts optimized models with $\Delta\alpha$. Increasing $\Delta\alpha$ pulls N atoms out of the original plane, forming obtuse N-Co-N angles. Co offsets upward, modulating Co 3d orbitals. The $\Delta\alpha=21.4°$ model shows optimal Co-CO_2 interaction, matching highest CO FE and lowest *COOH barrier.

These results demonstrate operando high-resolution X-ray spectroscopy's power in capturing subtle structural changes. Reversible N-Co-N angle distortion tunes CoPc's electronic structure, offering key insights for high-performance single-atom catalyst design.

Significance

This work resolves the long-standing challenge of capturing subtle atomic and electronic changes that traditional in situ techniques miss. Operando HERFD-XANES and VtC-XES offer ultrahigh sensitivity to clarify geometric symmetry and ligand environments, quantifying reversible angle distortion of symmetric materials and revealing distortion-governed structural dynamics. The identified structure-performance relationship guides high-efficiency catalyst design, inspiring broader application of high-resolution operando spectroscopy in single-atom material systems for next-generation heterogeneous catalyst development.

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Decoupling Dynamic Metal Site Evolution in Mo-Based MFI Catalysts for Methane Dehydroaromatization via Operando Spectroscopy

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Jiyun Hong, [2,3] Simon R. Bare, [2,3] Gagandeep Singh Dhillon, [4] Kyle P. Robinson[1]

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Introduction

Methane dehydroaromatization (MDA) over Mo/MFI catalysts involves dynamically evolving metal species whose structure, location, and interactions govern performance. Decoupling these contributions remains challenging due to their simultaneous transformation. Here, we use Operando and in situ X-ray absorption spectroscopy (XAS), combined with temperature-programmed analysis and data-driven methods, to resolve co-evolving Mo species and elucidate their roles across catalyst systems.

Results & Discussion

First, we investigate Mo/MFI catalysts across a range of Mo loadings using in situ TPR-XANES coupled with principal component analysis (PCA) and multivariate curve resolution–alternating least squares (MCR-ALS) (Figure 1). This approach enables the extraction of distinct spectral components corresponding to isolated, micropore-confined Mo species and externally located, aggregated Mo-oxide domains. The resulting decomposition provides direct insight into their independent reduction pathways and establishes a quantitative, location-based framework for comparing catalysts with varying compositions.

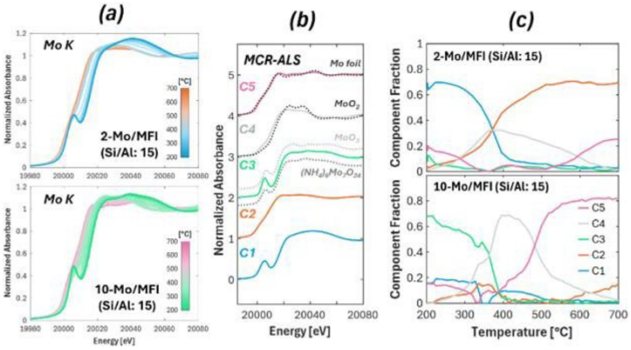

Figure 1. **(a)** *In-situ* Mo K-edge XAS of 2- and 10 wt.% Mo/MFI (Si/Al: 15) from 200 to 700 °C under H_2. **(b)** Extracted components from PCA/MCR-ALS of combined datasets. **(c)** MCR-ALS component profiles vs. temperature.

We extend operando XAS to Fe-promoted systems to examine how metal-metal interactions influence Mo speciation and performance. Using $Fe_2(MoO_4)_3$/ZSM-5 as a model precursor, activation leads to Fe_2O_3 formation and MoO_x migration into zeolite channels. In contrast, separately introduced oxides hinder Mo migration, increasing external Mo species. These differences result in improved benzene selectivity for pre-associated Fe-Mo systems.

Significance

These results demonstrate that operando spectroscopy, combined with advanced analysis and catalyst design, enables decoupling of overlapping metal site transformations. By resolving spatial distribution and metal-metal interactions, this work provides a framework for linking catalyst structure to performance in MDA and related systems.

Towards Integrated Ammonia Synthesis and Separation: Unraveling Active Sites in Functional Nanoporous Materials

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Introduction

Aluminum-based metal-organic frameworks (Al-MOFs) were applied to ammonia (NH_3) synthesis to enable effective NH_3 adsorption and separation under ambient conditions (25-100 °C, 1 bar). To understand the adsorption mechanism, Monte Carlo simulations and in situ spectroscopies combined with temperature-programmed analyses were performed. The results revealed that pore-surface functional groups and framework geometry, rather than surface area alone, critically govern NH_3 interactions.

Results & Discussion

NH_3 adsorption and separation were investigated using CAU-10 series materials with functionalized pore topologies to enhance physisorption under mild conditions. CAU-10-OH exhibited high NH_3 uptake (0.89-3.65 mmol g^{-1}) at 25-100 °C and 1 bar, as measured by breakthrough curves and online NH_3 synthesis/separation system (**Figs. 1-2**). Monte Carlo simulations and *in situ*/operando spectroscopies revealed that pore topology and functional groups critically govern adsorption [1, 2]. Hydroxyl-functionalized CAU-10-OH showed rapid NH_3 uptake at low pressures due to enhanced adsorbent-adsorbate interactions, and its framework and adsorption/separation ability retained after 15 cycles (> 200 h). Packed-bed simulations demonstrated that CAU-10-OH could replace cryogenic separation, achieving uptakes of 1.92-3.18 mmol g^{-1}. These findings provide insights into the rational design of MOFs for green NH_3 synthesis and gas separation.

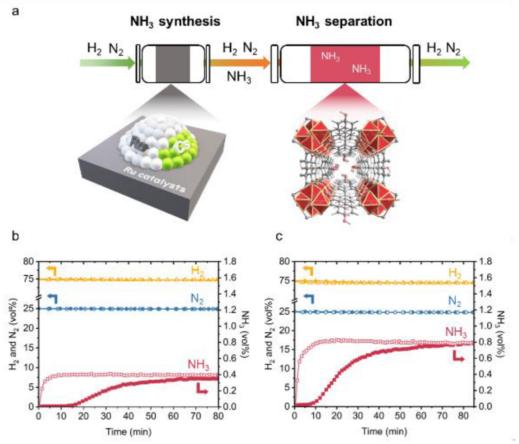

***Figure 1.** Integration of NH_3 synthesis with Al-MOFs for NH_3 adsorption and separation.*

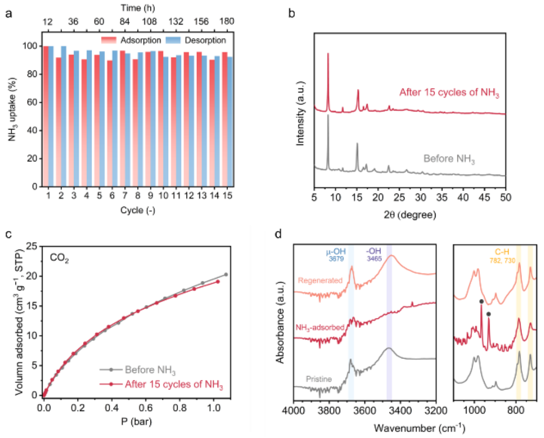

***Figure 2.** Cycling performance, structural characterization, and in situ DRIFT spectra of Al-MOFs during NH_3 adsorption and separation.*

Significance

These findings greatly advance our understanding of NH_3 adsorption and desorption mechanisms on CAU-10 materials, enabling the rational design of MOFs for green NH_3 synthesis and other efficient gas adsorption and separation applications.

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Operando Spectroscopic Identification of Active Species in Chloroaluminate Ionic Liquids for Low-Temperature Polyolefin Deconstruction

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Introduction

Converting waste polyolefins has been challenge in developing circular plastics economies.[1] Chloroaluminate ionic liquids enable selective transformation of polyolefins into gasoline-range alkanes through tandem cracking-alkylation at remarkably low temperatures (<100 °C),[1,2] offering significant advantages over conventional pyrolysis processes that require elevated temperatures (> 400 °C) and suffer from severe coking deactivation[3]. The identity of catalytically active species in chloroaluminate systems has been elusive. While $Al_2Cl_7^-$ anions have been conventionally proposed as active sites, kinetic analysis revealed that initial polyethylene conversion rates are not proportional to $Al_2Cl_7^-$ concentrations, suggesting involvement of more complex speciation. In this work, we studied the dual roles of chloroaluminate species and alkyl chloride additives in generating carbenium ion-based mechanisms that drive interconnected cracking and alkylation cycles under operando conditions.

Results & Discussion

This study employs a comprehensive operando spectroscopic approach to identify active species and elucidate their structural dynamics during low-temperature polyolefin deconstruction. We combine ^{27}Al magic-angle spinning nuclear magnetic resonance spectroscopy (^{27}Al MAS NMR), *in situ* Raman spectroscopy, and Al K-edge X-ray absorption near edge structure (XANES) spectroscopy to monitor chloroaluminate speciation under reaction conditions. ^{27}Al MAS NMR investigations reveal that while $Al_2Cl_7^-$ represents the predominant anionic species, small concentrations of $AlCl_3$ generated through $Al_2Cl_7^-$ dissociation ($Al_2Cl_7^- \rightleftarrows AlCl_3 + AlCl_4^-$) serve as the true catalytic initiators. *In situ* Raman spectroscopy demonstrates that tert-butyl chloride (TBC) additives react with these transient $AlCl_3$ species to form $AlCl_3$-TBC adducts, which function as carbenium ion precursors. The characteristic Raman bands at 350-400 cm^{-1} corresponding to Al-Cl stretching vibrations shift upon TBC coordination, providing direct spectroscopic evidence for adduct formation. Al K-edge XANES spectroscopy reveals systematic changes in aluminum coordination environments during reaction progression. The pre-edge features at 1563-1565 eV, diagnostic of tetrahedral $AlCl_4^-$ coordination, intensify as $AlCl_3$-TBC adducts convert to generate tert-butyl carbenium ions paired with $AlCl_4^-$ anions. These operando measurements definitively establish that carbenium ions remain associated with $AlCl_4^-$ counterions throughout the catalytic cycle, forming iC_4^+-$AlCl_4^-$ ion pairs as the most abundant reactive intermediates (MARI).

Kinetic control experiments using linear hexadecane (n-C_{16}) as molecular probes, combined with density functional theory calculations, elucidate the mechanistic pathway. The initial tert-butyl carbenium ions activate C-H bonds in polyethylene and iso-alkanes via hydride transfer mechanisms, generating secondary carbenium ions that propagate through β-scission (cracking) and electrophilic addition (alkylation) pathways. The operando spectroscopic data reveal that this tandem process maintains steady-state carbenium ion concentrations while continuously regenerating active $AlCl_3$ species through the catalytic cycle.

Temperature-dependent operando measurements (60-90 °C) demonstrate that the equilibrium $Al_2Cl_7^-$ ⇄ $AlCl_3$ + AlCl $^-$ shifts toward increased $AlCl_3$ concentrations at elevated temperatures, correlating directly with enhanced catalytic activity. The spectroscopic evidence establishes that successful polyolefin deconstruction requires precise balance between $AlCl_3$ availability for carbenium ion initiation and sufficient $Al_2Cl_7^-$ concentrations to maintain ionic liquid stability and prevent aluminum precipitation.

Figure Operando Raman spectroscopy reveals chloroaluminate speciation dynamics during polyolefin deconstruction; Time-resolved *in situ* Raman spectra during tandem LDPE cracking-alkylation with iC_5 and TBC additive, showing progressive weakening of $Al_2Cl_7^-$ band (310 cm^{-1}) and strengthening of $AlCl_4^-$ band (350 cm^{-1}); Correlation between LDPE conversion and chloroaluminate speciation; and Chloroaluminate speciation stability during consecutive $n\text{-}C_{16}$ conversion cycles, confirming steady-state equilibrium maintenance after initial active species generation.

Significance

These operando spectroscopic findings resolve the longstanding question of active site identity in chloroaluminate catalysis and provide molecular-level insights essential for rational design of next-generation ionic liquid catalysts for sustainable polymer valorization.

References

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Operando Raman Spectroscopy of the Deactivation Process of Aniline Synthesis Catalysts under Industrial Relevant Reaction Conditions

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Introduction

Aniline synthesis is a key step in the production chain of isocyanate precursors that are used in the manufacture of polyurethanes, polycarbonates, agrochemicals and pharmaceuticals. [1] Copper-silica catalysts are generally used in aniline synthesis. For aniline synthesis via gas-phase nitrobenzene (NB) hydrogenation, catalyst deactivation is attributed to coke formation, metal sintering, metal migration or a combination of these factors.[2] In this work, we probe the structure–composition–performance relationship of copper-based catalysts through several cycles of reaction and regeneration – at 300 °C – using *operando* Raman spectroscopy with online gas infrared (IR).

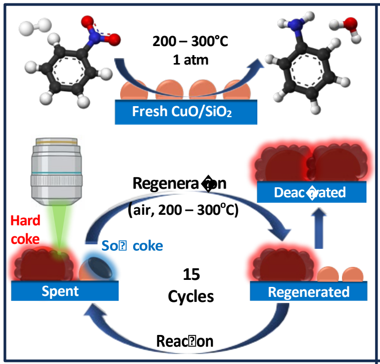

Figure 1

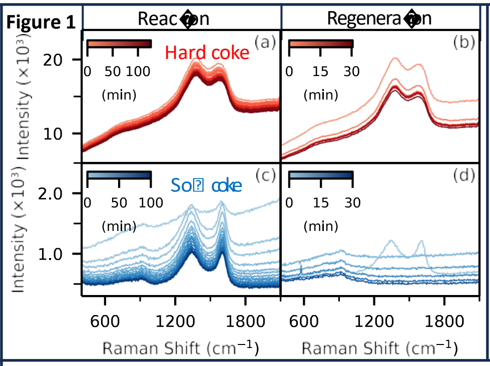

Figure 2

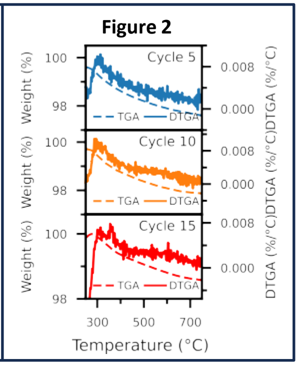

Figure 1: Raman spectroscopy tracking specific catalyst spots to distinguish soft coke (blue) and hard coke (red) formed during the reaction (a ,c) and regeneration (b, d) phases of various cycles. Figure 2: Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric (DTGA) profiles of coke burn-off for spent catalysts after 5, 10, and 15 reaction cycles.

Results & Discussion: During multi-cycle catalytic operation, we tracked the evolution and burn-off of two distinct coke species using Raman spectroscopy (Figure 1). At one spot, we observed soft (reversible) coke that burns off almost instantaneously upon regeneration (Figure 2b), while at another spot harder (persistent) coke resists burn-off and accumulates (Figure 2a). DTGA of coke burn-off revealed a progressive increase in the proportion of hard coke through repeated reaction-regeneration cycles, evidenced by the emergence of a distinct peak (~ 355ºC) and a broad shoulder extending beyond 400ºC (see cycle 15 profile in figure 2). Transmission Electron Microscopy (TEM) showed significant metal migration and sintering during early cycles, and in later cycles encapsulation of the sintered copper particles and coverage of the silica support in coke-like species was observed as well, with partial metal re-dispersion after regeneration. We hypothesize the encapsulation of the active metal and support prevents copper redispersion upon regeneration and ultimately leads to catalyst deactivation as cycling progresses. Simultaneous activity measurements with online gas IR revealed a 10% drop in nitrobenzene conversion after 12 cycles, which is consistent with the observed structural changes with cycling. This methodology can be extended to systematically decouple the individual roles and understand the complex interplay between the competing deactivation drivers by testing various model catalyst systems.

Significance: The insights from our *operando* Raman spectroscopy studies can provide clear strategies for tuning both catalyst properties (e.g., stabilizing active copper, mitigating coke formation) and process conditions (e.g., regeneration temperature/duration, NB: H_2 ratios), to develop robust catalysts with extended operational lifetimes and increased process efficiency.

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Operando/In-situ XANES Measurements of Frictional Oil/Metal Interfaces

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Introduction

Tribology research on engine systems to develop lower frictional surfaces has attracted much attention. To clarify the friction mechanism on engine-oil/friction-metal interface, we have developed a friction tester to achieve the *operando/in-situ* measurements of the X-ray absorption near edge structure (XANES) using the total electron yield (TEY) method [1]. In the present study, we will discuss the chemical reactions of oil molecules at the frictional oil/metal interfaces.

Results & Discussion

Figure 1 (a) shows the photo of the friction tester installed in the measurement chamber of BL-6.3.2 at the Advanced Light Source (ALS). The tester composed of a rotating-ring and counter block which are made from SUS440C steel. The ring touched an oil-soaked sponge, which contained 100-μL liquid oil. Consequently, the ring and the counter block were always wet with the oil in the vacuum chamber. Soft X-ray beams irradiate at the ring, and the sample current at the oil/ring interface can be measured as TEY. Figure 1 (b) and (c) shows the *operando/in-situ*-measured XANES spectra in the FeL and CK regions, respectively. In the FeL-XANES, FeL peaks can be well observed after 2-min rotation, through the thinner oil layer during the ring-rotation. In CK-XANES, evolution of the π* peak near 285 eV can be clearly observed by the frictional ring-rotation. Such the CK-XANES profile agrees to unsaturated aliphatic acids [2]. Hence, this observation indicates the double-bonds formation at the frictional oil/metal interfaces. Such the double-bonds formation in the oil molecules at the frictional oil/metal interface suggests that degradation of oil could be affected by the double bonds.

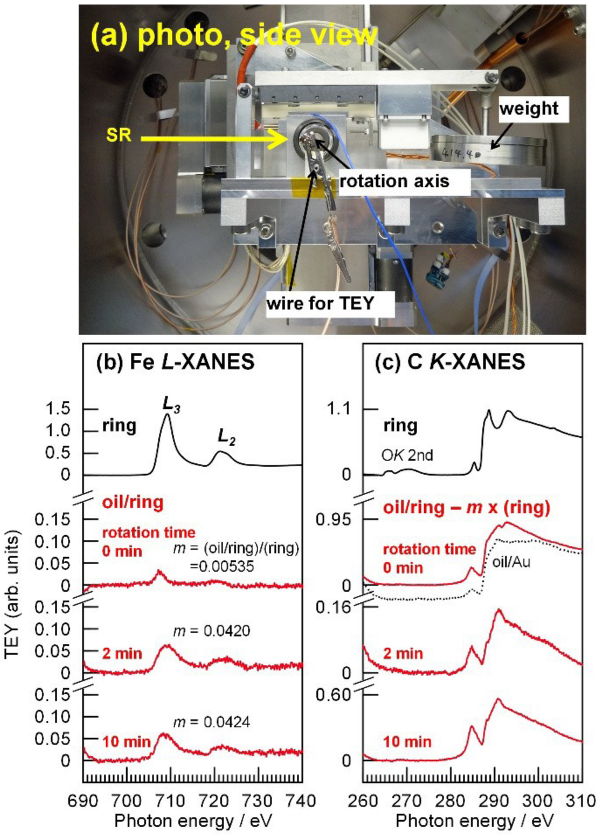

Fig. 1 Photo of the friction tester (a) and *in -situ* measured XANES in the Fe*L* (b) and C*K* (c) regions of the original ring and the oil/ring interface rotated for 0, 2, and 10 min.

Significance

Formation of unsaturated double-bonds at the frictional oil/ring interface was observed from the *operando/in-situ* XANES measurements of frictional oil/metal interfaces.

References

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Track the structure evolution of catalysts for CO_2 hydrogenation to alcohols

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Introduction

The reaction of CO_2 hydrogenation has been heavily studied due to its significance in converting abundant CO_2 to valuable chemicals.[1,2] For this reaction, the grand challenge is how to design active structures with high selectivity. To address this challenge, one needs to know the nature of active structure, which is currently lacking. Motivated by this, we studied Cu/ceria and ZnFeOx catalysts for CO_2 hydrogen to methanol and higher alcohols, respectively.

Results & Discussion

In studying Cu/ceria for CO_2 hydrogenation to methanol (Fig. 1, left), we tracked the structure change of Cu/ceria by applying multiple operando and in-situ techniques including XAS, XPS, neutron scattering, STEM, and DRIFTS. It is found that the formation rate of methanol coincides with the formation of a unique Ce^{3+} species. The formed Ce^{3+} sites are bound to hydrides, carbonate species, and interfacial active Cu sites. The Cu-ceria interaction in this complex moiety is weak and can be easily disturbed with reaction environment variations, leading to dynamic changes at the interface upon the hydrogenation of active carbonate intermediates.

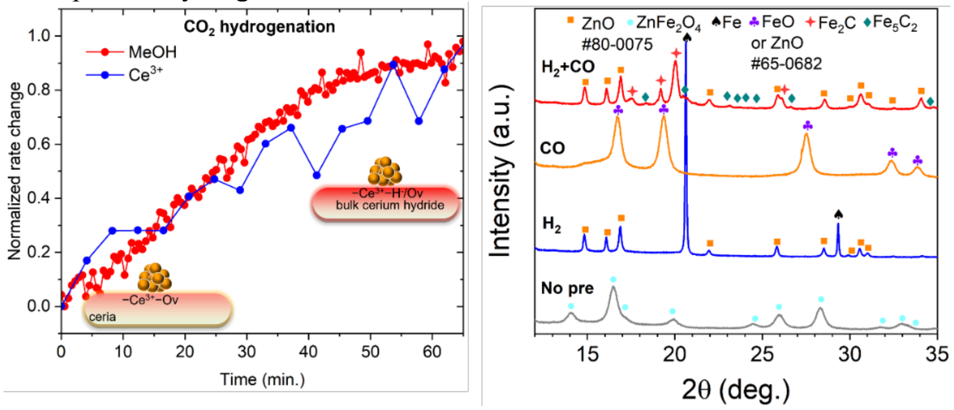

Figure 1. (Left) The correlation between the change of Ce species and methanol formation. (Right) Speciation of pretreated ZnFeOx catalyst.

In investigating ZnFeOx catalyst for CO_2 hydrogenation to higher alcohols, it is found that by changing the pretreatment condition, the selectivity and yield of C_{2+} oxygenates can be changed. To determine the species that lead to a high yield of C_{2+} oxygenates, we studied pretreated (Fig. 1, right) and reacted ZnFeOx catalysts by combining operando and in-situ XRD, XAS, XPS, DRIFTS, and Mössbauer spectroscopy. The formation of C_{2+} oxygenates is correlated with ZnO/FeCx interfaces.

Significance

These results obtained from this work help design active species or structures for selective CO_2 hydrogenation to valuable chemicals.

References

1. X. Jiang, X. Nie, X. Guo, C. Song, J. G. Chen, *Chem. Rev.* 120 (2020), 7984.
2. RP. Ye, J. Ding, W. Gong, *et al. Na.t Commun.* 10 (2019), 5698.

Operando QXAFS Study of Oxygen Evolution Reaction Electrocatalysis of Cobalt-based oxides

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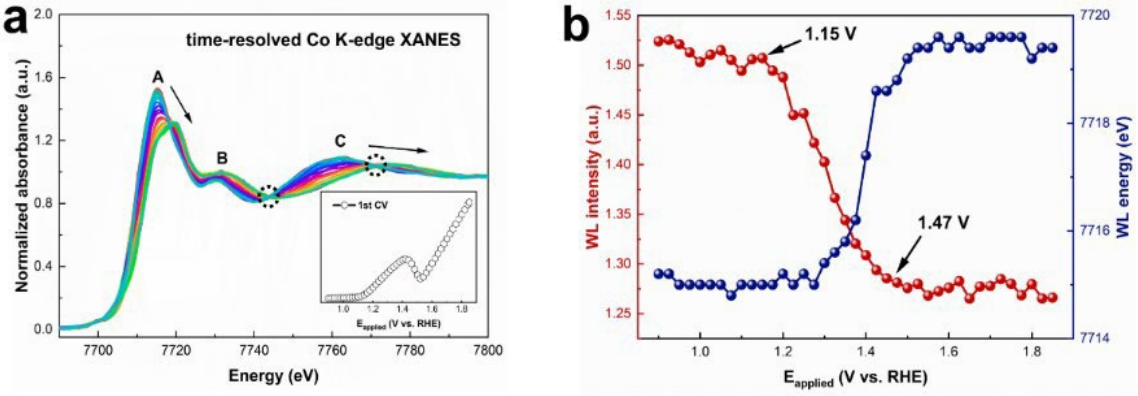
Introduction

In this study, we explore the distinct reconstruction behaviors of two cobalt-based molybdate polymorphs, α-CoMoO4 and β-CoMoO4, with wolframite-type structures. α-CoMoO4 undergoes a gradual surface reconstruction, forming amorphous cobalt oxyhydroxide, consistent with the lattice oxygen oxidation mechanism (LOM). In contrast, β-CoMoO4 rapidly transforms into CoOOH through an acid group dissociation (AGD) mechanism involving the dissociation of $MoO_4{}^{2-}$ groups. Real-time tracking of the phase transition by cyclic voltammetry (CV) and quick-scanning X-ray absorption fine structure (QXAFS) reveals detailed kinetic insights into these processes.

Results & Discussion

To investigate the rapid reconstruction behavior of β-CoMoO4 during the initial CV cycle, we employed QXAFS to track the dynamic evolution of the cobalt valence state and local structure with increasing anodic potentials. The following figures are the results of *operando* quick-scanning XAFS tracking of the irreversible reconstruction. (a) Time-resolved *operando* Co K-edge XANES spectra of β-CoMoO4 during the first CV cycle between 0.9 and 1.85 V. The inset is the corresponding first CV curve. (b) The intensities and energy positions of the white line (WL) with the oxidation potentials. QXAFS analysis of the second and subsequent CV cycles indicated that the structure was almost preserved, confirming that the reconstruction process was completed within the first CV cycle.



Significance

We utilized QXAFS and CV to track the reconstruction kinetics of these wolframite cobalt-based oxide polymorphs. The research results indicate that β-CoMoO4 can complete its reconstruction within a single CV cycle. These findings highlight the rapid and efficient reconstruction kinetics of β-CoMoO4 under the OER conditions.

References

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Operando VIII Schedule

ALL ORAL SESSIONS IN MERRILL HALL

Sunday, May 10

Plenary Session 7:00-8:15 PM

Session Chair: Janos Szanyi

7:00-7:15 PM | Simon R. Bare – *SLAC National Accelerator Laboratory*

Introduction and Welcome

7:15-8:15 PM | Plenary Talk: Davide Ferri – *Paul Scherrer Institute*

Seizing Materials Structure in the Act by Multi-Modal Spectroscopy

Monday, May 11

Plenary and Keynote Session 8:30-10:00 AM

Session Chair: Fan Yang

8:30-9:30 AM | Plenary Talk: Peter Crozier – *Arizona State University*

Spatiotemporal Analysis of Nanoparticle Surface Dynamics: Prospects for Atomic-Level *Operando* Characterization of Catalysts with Electron Microscopy

9:30-10:00 AM | Keynote Talk: Jungwon Park – *Seoul Nation University*

Operando Atomic-Scale Characterization of Catalysts in Liquid

10:00-10:30 AM | Coffee Break

Reactor Dynamics Session 10:30-11:50 AM

Session Chair: Linxiao Chen

10:30-10:50 AM | Lucy Costley-Wood – *University College London*

Mapping Reactive Zones in Magnetic Induction Reactors by XRDCT

10:50-11:10 AM | Donato Decarolis – *Diamond Light Source*

Understanding Localized Heat Transfer in Autothermal Reactions

11:10-11:30 AM | Aubrey Hepstall – *Georgia Institute of Technology*

Operando Analysis of Mechanocatalytic Reaction Environments

11:30-11:50 AM | Alireza Javanmard – *Penn State University*

Transient Pseudo-Random Binary Sequence (PRBS) *Operando* Reactor with Real-Time Adsorbate Monitoring for Mechanistic Identification

Dynamic Modulation Spectroscopy 1:00-2:50 PM

Session Chair: Maarten Nachtegaal

1:00-1:30 PM | Keynote Talk: Matteo Monai – *Utrecht University*

Introducing Stimulando Time-Resolved Infrared Spectroscopy to Study Intermittent Light-Stimulated CO_2 Hydrogenation

1:30-1:50 PM | Charlotte Vogt – *Technion*

From Modulation to Emergence: Dynamic Response Spectroscopy and the Nonlinear Dynamics of Catalytic Interfaces

1:50-2:10 PM | Arnaud Travert – *Universite de Caen Normandie*

Modulation Excitation Spectroscopy Beyond Phase-Sensitive Detection

2:10-2:30 PM | Miguel Banares – *CSIS Instituto de Catalisis*

Operando Raman and MES-DRIFTS Study on the Role of Gold and Vanadium in Ceria-Based Oxidation Catalysts

2:30-2:50 PM | Servaas Lipps – *University of Ghent*

Interpreting Non-Redox Responses in Modulation-Excitation XAS

2:50-3:20 AM | Coffee Break

Operando Spectroscopy 3:20-4:20 PM

Session Chair: Anatoly Frenkel

3:20–3:40 PM | Jingyi Chen – *University of Arkansas*

Understanding the Phase Transition of Nickel Hydroxide Using In-Situ X-Ray Absorption Spectroscopy

3:40-4:00 PM | Marcus Baer – *Helmholtz Zentrum Berlin*

Operando Studies of Energy Conversion Devices by HAXPES

4:00-4:20 PM | Merve Kurt – *Karlsruhe Institute of Technology*

Operando Insights into the Effect of Ceria Incorporation on the Oxygen Evolution Reaction Performance of Iridium-Based Catalysts

Session Chair: Adam Hoffman

4:20-6:00 PM | Poster Blitz

7:00-9:00 PM | Poster Session – Located in Nautilus Hall

Tuesday, May 12

Plenary and Keynote Session 8:30-10:00 AM

Session Chair: Phil Christopher

8:30-9:30 AM | Plenary Talk: Charlie Sykes – *Tufts University*
Single-Atom Alloy Catalysts: Born in a Vacuum, Tested in Reactors, and Understood in Silico

9:30-10:00 AM | Keynote Talk: Elad Gross – *Hebrew University*

High Spatial Resolution Operando IR Nanospectroscopy Reveals Structure-Reactivity Correlation in Pd Nanoparticles

10:00-10:30 AM | Coffee Break

Oxide Catalysts 10:30-11:50 AM

Session Chair: Javier Ruiz Martinez

10:30-10:50 AM | Christian Hess – *TU Darmstadt*

Identifying Active Sites in Selective Oxidation Catalysts Using Combined *Operando* and Transient Analysis: from Supported to Bulk Systems

10:50-11:10 AM | Israel Wachs – *Lehigh University*

Redox Dynamics of Supported VO_x/CeO_2 During Methanol Oxidation Monitored with *Operando* UV-Vis-MS Spectroscopy

11:10-11:30 AM | Weixin Huang – *Univ. of Science Tech. of China*

Elementary Surface Reaction Kinetics Unveil Distinctly Different Active Sites of ZnO-ZrO_2 Catalysts in CO_2 and CO Hydrogenation to Methanol Reactions

11:30-11:50 AM | Michael Claeys – *University of Cape Town*

Crystallite Size Dependent Oxidation Captured Using *Operando* Magnetometry

Session Chair: Jiyun Hong

5:00- 6:00 PM | Poster Blitz

7:00-9:00 PM | Poster Session – Located in Nautilus Hall

Wednesday, May 13

Metal Ions in Zeolites 8:30-10:00 AM

Session Chair: Christian Hess

8:30-9:00 AM | Keynote Talk: Coleman Kronawitter – *University of California, Davis*

Reversible Changes to Active Sites during Co-Reactions of Ethane, Carbon Dioxide, and Hydrogen Measured through *Operando* X-ray Absorption Spectroscopy

9:00-9:20 AM | Simon Barth – *Karlsruhe Institute of Technology*

Design Of Copper Sites in Cu-SSZ-13 to Control HCN Formation and Conversion During NH_3-SCR in the Presence of HCHO

9:20-9:40 AM | Dhruba Deka – *Pacific Northwestern National Laboratory*

Linking Cu Ion Speciation to SCR Reactivity in Cu-CHA Catalysts via *Operando* EPR Spectroscopy

9:40-10:00 AM | Daniel Cano-Blanco – *Paul Scherrer Institute*

Fe Monomers at Work: *Operando* Multi-spectroscopy Approach Identifies the Fe^{2+}/Fe^{3+} Pair Enabling N_2O-Assisted CH_4 Oxidation in Fe-Zeolites

10:00-10:30 AM | Coffee Break

Supported Metals 10:30-11:50 AM

Session Chair: Coleman Kronawitter

10:30-10:50 AM | Liqun Kang – *Max Planck Institute*

Seeing Nitrogen Differently: A New *Operando* Picture of Fe and FeCo Catalysts in Ammonia Decomposition

10:50-11:10 AM | Nikolay Kosinov – *Eindhoven University*

Determining Surface Coverage on Working Ni/Sio2 Catalysts by Transient *Operando* XANES at Ni K-Edge

11:10-11:30 AM | Melissandre Richard – *University of Lille*

A Journey from Rapid- to Step-Scan IR: Revealing Early Isotopic-Exchange Dynamics in CO_2 Hydrogenation on Cu/ZrO_2

11:30-11:50 AM | Sumant Phadke – *Paul Scherrer Institute*

Unraveling Structure–Activity Relationships in Pd–Zn/C Catalysts for CO_2 Hydrogenation to Methanol

Metal-Support Interactions and Dynamics 1:00-3:00 PM

Session Chair: Charlotte Vogt

1:00-1:20 PM | Anatoly Frenkel – *Stonybrook University*

Reaction–Driven Redispersion: A Low-Temperature Route to Catalyst Stability

1:20-1:40 PM | Linxiao Chen – *University of North Texas*

In-Situ Support-Wetting of Metal Cluster Regulates Catalytic Activity

1:40-2:00 PM | Jeong Park – *Korea Advanced Institute of Science & Technology*

Operando Microscopic and Spectroscopic Investigation of Metal–Oxide Interfaces in Mixed and Bimetallic Nanocatalysts

2:00-2:20 PM | Marlon da Silva – *Laboratório Nacional de Luz Síncrotron-CNPEM*

Spatio-Temporal Insights into Supported Pd Nanoparticles Dynamics Using Full-Field Hyperspectral XAS imaging

2:20-2:40 PM | Steven Chavez – *University of California, Los Angeles*

Metal-Support Interactions Govern Restructuring Dynamics in Bimetallic Pt Oxidation Catalysts

2:40-3:00 PM | Anastassiya Khan – *SLAC National Accelerator Laboratory*

Revealing Methanation-Induced Sintering in Rh/Tio_2 Catalysts via *Operando* X-Ray Thermometry

3:00-3:30 AM | Coffee Break

Liquid Environments 3:30-5:30 PM

Session Chair: Elad Gross

3:30-3:50 PM | Arun Asundi **–** *SLAC National Accelerator Laboratory*

Operando XAS Characterization of Aerobic Oxidation Catalysts for Plastic Deconstruction

3:50-4:10 PM | Vaishnavi Ganesh – Utrecht University

Operando Raman Spectroscopy with Online UV-Vis Analysis of Carbon-based Catalysis under Harsh Reaction Conditions

4:10-4:30 PM | Angel Garcia-Esparza **–** *SLAC National Accelerator Laboratory*

Access to Study the Electrode-Electrolyte Interface with Modulation Excitation X-Ray Spectroscopy

4:30-4:50 PM | Christoph Kubis – *Leibnitz Institute*

In-Situ / *Operando* Spectroscopic Investigations on Kinetic and Mechanistic Aspects of Homogeneously Catalyzed Hydroformylation

4:50-5:10 PM | Maarten Nachtegaal – *Paul Scherrer Institute*

Operando XAS in Flow: Identification of Active Sites for the Conversion of Methane to Oxygenates in Water

5:10-5:30 PM | Javier Ruiz-Martinez – *King Abdullah University of Science and Technology*

In situ MAS NMR Reveals Insights into Hierarchical Zeolite Formation during Post-Synthetic Base Leaching

Thursday, May 14

Plenary and Keynote Session 8:30-10:00 AM

Session Chair: Miguel Banares

8:30-9:30 AM | Plenary Talk: Bingjun Xu – *Peking University*

Understanding Cu-Catalyzed CO_2 Electrochemical Reduction via *Operando* Spectroscopies: Mechanism, Cation Effect and Devices

9:30-10:00 AM | Keynote Talk: Fan Yang – *Shanghai Tech University*

Dynamic Catalytic Sites for Selective CO/CO_2 Conversion

10:00-10:30 AM | Coffee Break

Frontiers in operando spectroscopy 10:30-11:50 AM

Session Chair: Matteo Monai

10:30-10:50 AM | Hanya Spoelstra – *Utrecht University*

Exploring Carbon Growth Dynamics during Catalytic Methane Pyrolysis with *Operando* Raman Spectroscopy

10:50-11:10 AM | Damian Vico van Berkel – *Delft University*

Far-IR Spectroscopy as a Direct Coordination Environment Probe in Catalysis

11:10-11:30 AM | Yu Wang – *Shanghai Syn. Radiation Facility*

Time-Resolved XAFS/XRD Combined Technique for *Operando* Simultaneous Measurements

11:30-11:50 AM | Gabriele Deplano – *Max Planck Institute*

Operando Spectroscopic Investigation to Explain Reactivity in LPMO-Mimic Cu Complexes in Solution

Operando VIII Poster Presenters

May 11-12, 2026

May 11, 2026

	Name	Affiliation	Poster Title
1	Mikhail Agrachev	ETH Zurich	Operando EPR investigation of anionic vacancies: semiconductor physics and heterogeneous catalysis
2	Margareth Baidun	Delft University	When Water Turns Poison: Operando Modeling of Ni-Ga Catalyst Deactivation
3	Allueva Alava / Matteo Monai will present	Utrecht University	Unraveling Structure-Activity Relationships in Pd-Cu Catalysts for CO_2 Hydrogenation to Higher Alcohols
4	Daniel Cano Blanco	Paul Scherrer Institute	Operando transient EPR spectroscopy unravels active Fe^{2+} ions in zeolites with unprecedented site-selectivity
5	Qijun Che	SLAC	Operando X-ray spectroscopy of transition metal oxides interfaces
6	Luke Keenan	Diamond Light Source	Thin-Film Operando Sample Environment for X-ray HERFD, Emission and Fluorescence Spectroscopy
7	Shih-Yuan Chen	AIST	Towards Integrated Ammonia Synthesis and Separation: Unraveling Active Sites in Functional Nanoporous Materials
8	Pietro De Angeli	Delft University	Elevating Cobalt to Noble Heights: understanding Co-Re catalyst outstanding TOF in Methanol Steam Reforming through in-situ DRIFTS
9	Jan den Hollander / Vaishnavi Ganesh will present	Utrecht University	Spectroscopy Insights into Washcoated Monoliths for CO Oxidation

10	Mohamad El Roz / Marco Daturi will present	University of Caen	FTIR and XAS Operando for Mechanistic Insights into the In-Situ Restructuring of Coordinated Copper in Post-Metalated MOFs during Photocatalysis
11	Sheima Khatib	Virginia Tech	Decoupling Dynamic Metal Site Evolution in Mo-Based MFI Catalysts for Methane Dehydroaromatization via Operando Spectroscopy
12	Niko Hansen	UC Davis	Investigating Relationships Between Gas-Phase Reactive Intermediate Speciation and Product Yields during Heterogeneous Catalytic Reactions
13	Jonathan Hanson / Siu-Wai Chan will present	Brookhaven National Lab	Understanding nano-Ceria formation from operando post-treatment
14	Rosalie Hocking	Australian Synchrotron	Following Redox Chemistry Across Space and Time
15	Paolo Lazzarini	University of Turin	Reducibility of unsupported and Al_2O_3-supported RuO_2 catalysts: when Ru-oxide challenges Ru-metal in hydrogenation
16	Yuanyuan Li	Oak Ridge National Lab	Track the structure evolution of catalysts for CO_2 hydrogenation to alcohols
17	Haoyi Li	SLAC	Engineering a Membrane Assembly Electrode Device for a Durable and High-rate Ethylene Synthesis via CO Electroreduction
18	Ivan Lopez Luque	Delft University	Elucidating Rhenium Surface Dynamics on TiO_2 under High-Pressure CO_2 Hydrogenation Conditions
19	Raquel Portela	ISP, CSIC	Operando MES-Raman and MES-DRIFTS study of CO oxidation on highly dispersed CeOx on Cu_2O nanocubes

20	Hyun Suk Kang	Tarleton State University	Spectroelectrochemical Understanding of the Electronic Nature of Mixed-Dimensional Excitonic Systems
21	Ezgi Erdem	SLAC	Employing K-Promotion in Cu-In Catalysts to Control Phase Separation and CO_2 Activation for Low-T RWGS
22	Honghong Shi	PNNL	Regulating aldol condensation activity using Pt single atoms
23	Miaomiao Wen	Chalmers University	In Situ DRIFTS Investigation of the Evolution of Surface Species in the Direct Conversion of Methane to Methanol over HFerrierite
24	Dean Miller	SLAC	Operando Electrochemical K-edge XAS Captures Near-Surface Electrolyte Composition and Transient Molecular Catalyst Structures
25	Kaan Yalcin / Coleman Kronawitter	UC Davis	The Nuclearity and Reactivity of Highly Dispersed, Cationic Platinum in Medium Pore Zeolites during Reaction and Thermal Treatment
26	Mathias Kiefer	SLAC	Operando XRD During High-Temperature Electrolysis at the Stanford Synchrotron Radiation Lightsource: Enabling Real-Time SOEC Analysis
27	Yuying Huang	Shanghai Advanced Research Institute	Operando QXAFS Study of Oxygen Evolution Reaction Electrocatalysis of Cobalt-based Oxides
28	Ruichao Xu	National Synchrotron Radiation Laboratory	Operando HERFD-XANES and VtC-XES Probes Atomic and Electronic Structure Evolution

May 12, 2026

1	Luke Keenan	Daimond Light Source	SWIFT – Spectroscopy Within Fast Timescales: The New Flagship Operando Beamline coming to Diamond
2	Hung-Ling Yu / Abir Podder will present	University of Virginia	CO_2 and CO adsorption-induced structural variation in supported Pd and PdAu bimetallic nanocluster systems
3	Floor Brzesowsky	Utrecht University	Introducing Stimulando Time-Resolved Infrared Spectroscopy to Study Intermittent Light-Stimulated CO_2 Hydrogenation
4	Jiri Dedercek	J. Heyrovský Institute, Czech Academy of Sciences	Performance of binuclear transition metal ion sites in the activation of molecular oxygen for selective methane oxidation
5	Claudia Franke	University of Stuttgart	High-Field EPR Spectroelectrochemistry – Development and Application
6	Emilie Gerouville	SPECS	NAP-XPS Equipment for Operando and In-Situ Studies
7	Qijun Che	SLAC	Operando electronic structure of RuOx at the interface
8	Neelesh Kumar	Lehigh University	Kinetic Relevance of Oxide Support Redox Processes for Supported Vanadia Catalysts during Methanol Oxidation with Transient Operando DR UV-Vis-MS Spectroscopy
9	Letizia Lanza	Delft University	Operando-Guided Low-Temperature CO_2 Capture and Conversion
10	Luca Maggiulli / Davide Ferri will present	Paul Scherrer Institute	Pulsed operando DRIFTS/GC to study the nature of the hydrocarbon pool on zeolites during the methanol-to-olefins reaction

11	Jennifer McConnell	Cornell University	Technological Advances for Temperature-Dependent Electrochemical Studies Using In-Situ TEM
12	Yasuji Muramatsu	University of Hyogo	Operando/In-situ XANES Measurements of Frictional Oil/Metal Interfaces
13	Aruna Nair	SLAC	Probing Ultrafast Dynamic Processes in Photocatalysts via Time-Resolved X-ray Absorption Spectroscopy
14	Arnaud Travert	Université de Caen Normandie	Selective dehydration of isobutanol on H-FER: operando IR, multivariate analysis and kinetic modeling
15	Vaishnavi Ganesh	Utrecht University	Operando Raman Spectroscopy with Online UV-Vis Analysis of Carbon-based Catalysis under Harsh Reaction Conditions
16	Sungmin Kim	PNNL	Operando Spectroscopic Identification of Active Species in Chloroaluminate Ionic Liquids for Low-Temperature Polyolefin Deconstruction
17	Liqun Kang	Max Planck Institute	The Disappearing Surface Nitrides: Operando Evidence for Hidden Redox Dynamics in Fe/MgO during Ammonia Decomposition
18	Raquel Portela	ISP, CSIC	MESFTIR at high pressure to investigate the CO_2 hydrogenation on Pd/CeO_2 nanofibers
19	Bas den Hartigh/ Matteo Monai & Bert Weckhuysen to present	Utrecht University	Operando X-ray Diffraction of Co/TiO2 Catalysts: Impact of TiO2 Polymorphs on the Cobalt Active Phase during CO2 Hydrogenation

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