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Electrochemical Hydrogen Oxidation/Evolution Kinetics – New Insights into an Old Field

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The hydrogen oxidation/evolution reaction (HOR/HER) is a central reaction in both fundamental electrocatalysis and in electrochemical energy conversion devices, viz., in H_2/air fuel cells as well as in water electrolyzers. The most active catalyst for this reaction is platinum, and in acidic electrolytes its kinetics are so large, that their quantification by the commonly used rotating disk electrode (RDE) technique turned out to be compromised by unaccounted for mass-transport resistances. This will be outlined in this presentation, showing that the true HOR/HER kinetics of Pt in acidic electrolytes are about two orders of magnitude larger than previously assumed [1]. This explains why ultra-low loadings of platinum in H_2/air fuel cell anodes or in water electrolyzer cathodes are sufficient to sustain very high rates at very low overpotentials.

A mechanistically very interesting aspect of the HOR/HER reaction is that early *ab-initio* models predicted that its kinetics on platinum are independent of pH [2], which recently was shown to not be the case, as the HOR/HER kinetics on Pt are ≈100-fold lower in alkaline compared to acidic electrolytes [3]. The so far proposed explanations for this effect are an increased H/metal bond strength [3, 4], a change of the reaction mechanism from H^+ to H_2O activation requiring more oxophilic catalyst surfaces [5], and/or a change of the water configuration at the metal/electrolyte interface [6]. The consistency of these hypotheses with the HOR/HER kinetics on different metal electrodes will be discussed. One other fundamental question of interest is whether the hydrogen oxidation/evolution reaction on palladium catalysts actually occurs on metallic palladium (as assumed in calculations [3]) or on palladium-hydride, a question which we will try to address by means of *operando* X-ray absorption studies [7].

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Magic at the interface: model multicomponent electrodes with controlled interfacial geometry for the electrocatalytic reduction of CO_2

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Combining the electrochemical reduction of CO_2 (eCO_2RR) with carbon-neutral energy sources is a potentially sustainable strategy for recycling carbon emissions. In particular, reducing CO_2 to CO would provide a versatile building block for the production of liquid fuels and plastics by well-established processes in industry. However, the application of this reaction requires the development of more efficient electrocatalysts.[1] Cu-In and Cu-Sn catalysts have shown high selectivity for CO evolution at moderate overpotentials, but their further development requires the rationalization of the synergistic effect observed in these multicomponent systems. Oxidic species that are stable under reaction conditions are crucial to the eCO_2RR over bulk In and Sn electrodes,[2,3] and recent findings indicate that the presence of $In(OH)_3$ plays a pivotal role in maintaining a high selectivity for CO over Cu-In catalysts.[4] Consequently, we hypothesize that bifunctional sites located at the interfaces between Cu surfaces and In and Sn (hydr)oxides are particularly favorable for CO evolution. In this context, we have developed a photolithography-based microfabrication process for creating model electrodes with controlled oxide-on-metal interfaces (**Figure 1**). By establishing quantitative relationships between the geometry and the CO evolution activity of the model electrodes, with further support from surface analytical techniques including operando studies, we aim to unveil the role of interfacial sites in the reduction of CO_2 to CO and to develop new descriptors for the rational optimization of this family of multicomponent catalysts.

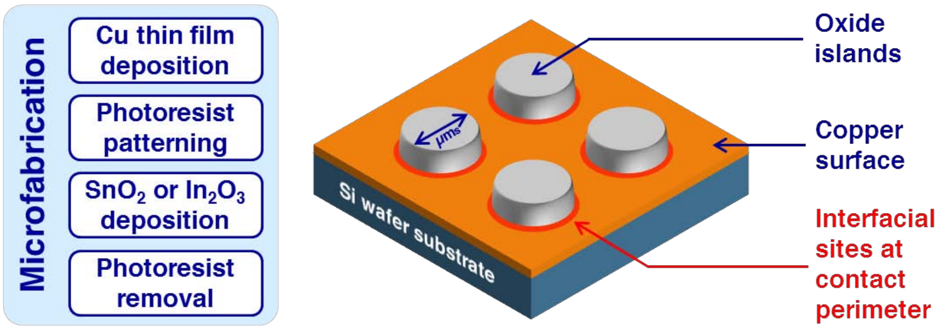

Figure 1 Main process steps for the fabrication of microstructured multicomponent model electrodes and a schematic representation of the resulting geometry. Interfacial sites are located at the contact perimeters between the circular oxide islands and the underlying smooth metal surface.

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Design of ionic polymer catalysts for the synthesis of carbonates from CO_2 and epoxides

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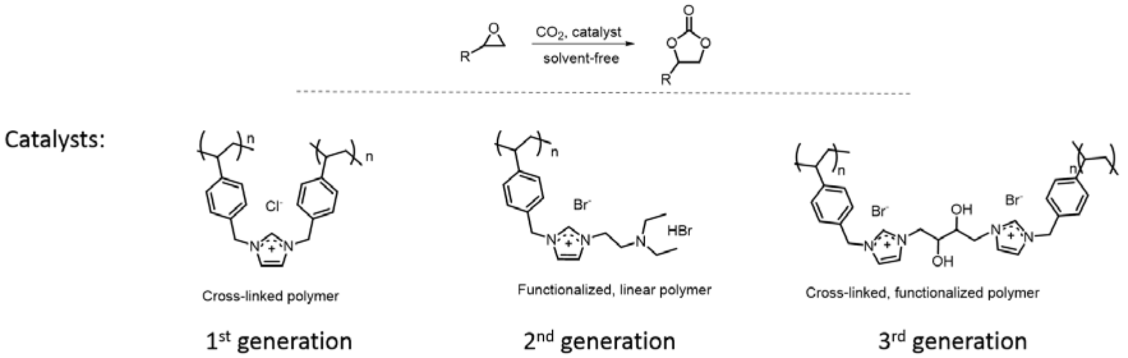
The synthesis of cyclic carbonates from epoxides and CO_2 (CCE reaction) is an atom-efficient, scalable reaction of industrial importance. It is an important example of a catalytic reaction highlighting the utilization of CO_2 as a building block. Numerous catalysts (both metallic and metal-free)[1] have been proposed for this reaction, and in particular, ionic liquids and ionic polymers have emerged as a class of potent catalysts in this transformation. In our group, we have prepared imidazolium-based polymers (Fig. 1) incorporating functional groups that are potent catalysts for the CCE reaction.[2-4]



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Surface structure and reactivity of perovskite oxynitride materials

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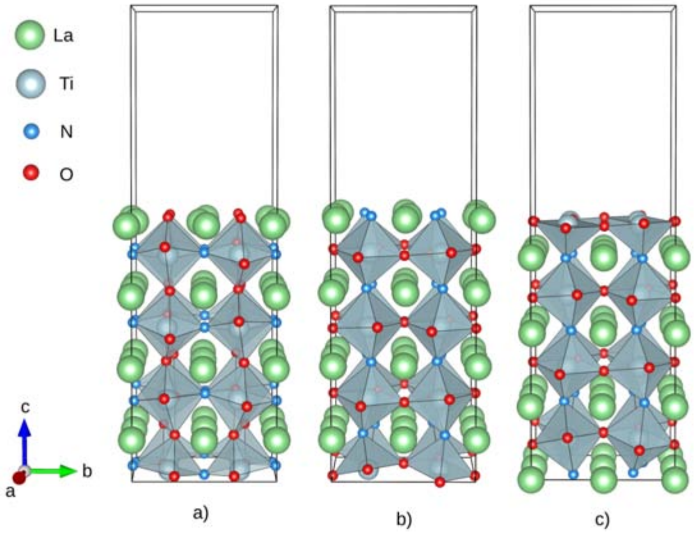
Owing to their reduced band gap compared to pure oxides, perovskite oxynitrides are a promising class of materials for photocatalytic water-splitting electrodes. While the bulk structure of these materials has been investigated both experimentally and theoretically, our knowledge about their surface structure is still very limited, despite that fact that it will dictate potential reaction mechanisms.

Based on our density functional theory (DFT) results we determine the anion arrangement in the bulk and at the surface to be different, as it is driven by bonding and electrostatic considerations respectively. From our calculations we can extract the preferred surface orientations and their terminations and will discuss them both in terms of the chosen synthesis route and as a function of their environment. We will then compare the photo-electrochemical performance of different perovskite oxynitride materials and discuss the potential of strain in thin-film configurations to induce polarity and suppress recombination losses.

Our calculations lead to a deeper understanding of the surface structure and hence the reactivity of this promising class of materials and will be instrumental in optimising them for applications in photocatalytic water splitting.



a) LaO (0.980 J/m^2), b) LaN (0.542 J/m^2) and c) TiO_2 (0.654 J/m^2) terminations of the (001) surface for the energetically most preferential bulk anion order.

Microstructural self-regeneration of $LaSrTiNiO_{3-\delta}$: fast recovery from sulfur poisoning

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Poisoning by sulfur is a common problem for Ni catalysts as well as solid oxide fuel cells (SOFCs). It is widely accepted that the deactivation in SOFCs is due to the poisoning of Ni sites active for the water gas shift reaction (WGS, $CO + H_2O \rightarrow CO_2 + H_2$). This reaction provides additional H_2 for oxidation when the cell is operated on syngas feeds [1]. Current SOFC materials cannot easily be regenerated after sulfur poisoning. Some perovskite type metal oxides (PMO) exhibit the remarkable reversible segregation of catalytically active metals from and reincorporation back into the PMO host lattices. This was found to be highly efficient in inhibiting sintering of metal particles during redox cycling [2,3]. This redox stability was applied on Ni to develop a water gas shift active and regenerable SOFC anode material. It can be shown that after reduction at 800 °C Ni is selectively reduced and segregated to the $LaSrTiNiO_{3-\delta}$ (LSTN) surface where it forms catalytically active, metallic Ni particles of few tens nm in size (Fig. 1-a) [3]. After reoxidation Ni is fully reincorporated into the perovskite lattice as shown by Ni K-edge XANES (Fig. 1-b). Catalytic data for the WGS reaction obtained over a number of redox cycles and Ni particle size analysis show the excellent redox stability of this material and demonstrate inhibition of Ni particle sintering. For comparison, redox cycling of an impregnated material (Ni/LST) leads to sintering and severe loss of catalytic activity over a few redox cycles (Fig. 1-c). Exposure of LSTN to H_2S caused an expected loss of catalytic activity (Fig. 1-d), which again can be completely restored within two redox cycles.

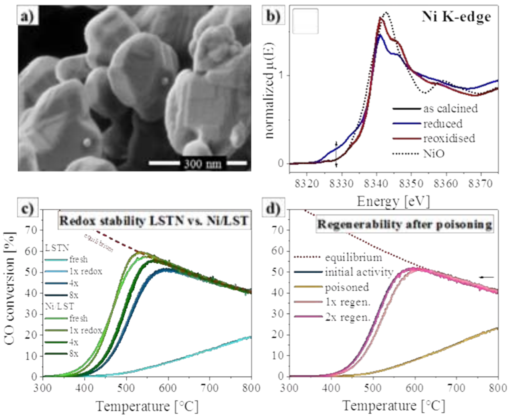

Figure 1. a) SEM image of reduced LSTN - segregated Ni particles on LSTN crystallites. b) Ni K-edge XANES of calcined, reduced and reoxidised LSTN. c) CO conversion for pre-reduced LSTN and Ni/LST over 8 redox cycles and d) after H_2S poisoning and over two oxidative regeneration cycles.

From a material and methodological point of view it is demonstrated that the structural reversibility exhibited by some PMOs can be exploited to completely regenerate S-poisoned catalysts which otherwise would suffer from deactivation by particle sintering. This function can be potentially applied to a variety of Ni catalyzed reactions suffering from similar deactivation phenomenon.

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Directed Evolution of Artificial Metalloenzymes: Genetic optimization of the catalytic activity

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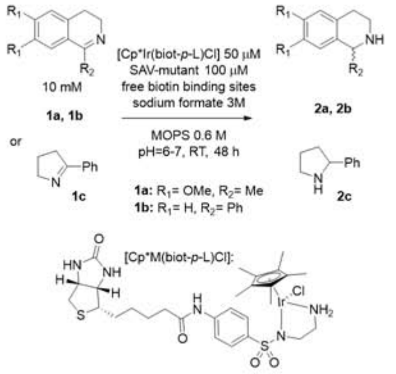
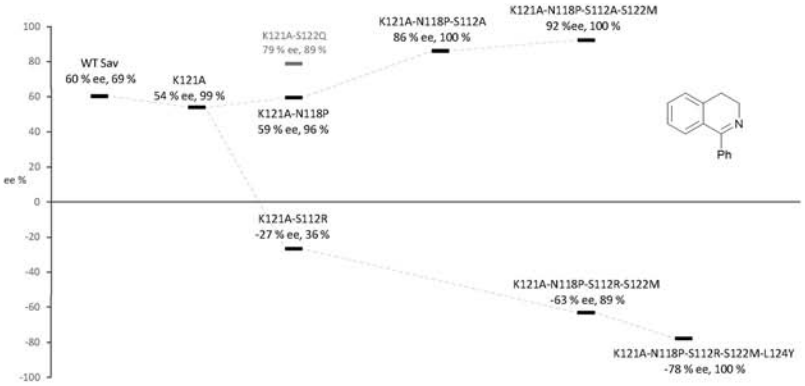
Artificial metalloenzymes (ArMs) are hybrid catalysts created by a non-covalent incorporation of an organometallic cofactor within a host protein scaffold.[1,2] This system, based on biotin-streptavidin technology, combines attractive features both of enzymatic and organometallic catalysis under near physiological conditions.[3,4] With the aim of performing catalysis *in vivo*, we have selected the transfer hydrogenation of cyclic imines as a model reaction.Herein we demonstrate the potential of directed evolution of artificial transfer hydrogenases (ATHase). Building upon a streamlined protocol[5], Sav mutants contained in *E. coli* cell free extracts were treated with diamide[6] and screened in the presence of the iridium cofactor. After identification of a successful "hit", the results were reproduced; the corresponding mutant was overexpressed, purified using an iminobiotin column and confirmed by screening.





This simplified process significantly speeds up the screening protocol and allows for the identification of improved Sav mutants for ATHase of cyclic imines. Guided by the protein crystal structure, we have performed four rounds of mutation and selection. As a result, two Sav isoforms with improved activities and yielding opposite enantiomers in the reduction of 1-phenyl-3,4-dihydroisoquinoline were obtained. X-ray analysis confirmed the presence of introduced mutations, namely K121A-N118P-S112A-S122M (96 % ee, full conversion) and K121A-N118P-S112R-S122M-L124Y (-82 % ee, full conversion). These mutants also show improved reaction rates in comparison with the use of Sav wild type.

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Zeolites for Clean Air

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The use of zeolites as adsorbents and catalysts in petrochemical processes is well established now for several decades. More recently, spurred by developments in automotive catalysis (DOC, SCR), their unique properties including temperature stability and hydrophobicity, combined with tailored pore geometries have been exploited in numerous environmental applications as catalysts, adsorbents and as exceptional support materials. Examples of these include: decomposition of N_2O from nitric acid tail gas by Fe-zeolites, adsorption of VOCs in composite matrices and as novel oxidation catalysts in conjunction with platinum group metals that can operate in high dust environments. These unique materials, used alone or combined with other chemical functionalities enable a large scope of end uses. The utility of such zeolite properties can be rationalized and explored leading to high performance materials by design.

Supported Crystalline Monodisperse Ga_2O_3 Nanoparticles with Tunable Size for the Catalytic Dehydrogenation of Propane

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Crystalline colloidal monodisperse Ga_2O_3 nanoparticles with tunable sizes ranging from 2.5 to 5.2 nm have been prepared from gallium acetylacetonate and oleylamine. Concentrated toluene solutions of these nanoparticles were impregnated onto various supports to give catalysts active for propane dehydrogenation (PDH) with selectivities and activities higher than those of a benchmark catalyst prepared from gallium nitrate. Importantly, this synthesis method allows characterizing Ga_2O_3 nanoparticles prior to their deposition on supports and it leads to active, well-defined supported Ga_2O_3 PDH catalysts amenable for a more direct evaluation of support and particle size effects on catalytic properties.

Conventional synthesis routes for gallium oxide-based catalyst catalysts typically use aqueous gallium nitrate solutions for impregnation of supports, followed by calcination.[1] This approach usually gives ill-defined catalysts with a broad distribution of metal sites. Identification of the catalytically active sites in such systems is very challenging, if not impossible. Here, we report the synthesis of crystalline, ligand-capped Ga_2O_3 nanoparticles with controllable size that form a stable colloidal solution in an organic solvent (toluene). The synthetic methodology to such size-tunable nanoparticles has been developed previously for the preparation of solution-processable gallium oxide quantum dots for optoelectronic applications.[2] We demonstrate that this method serves as a convenient entry to establish a structure-activity relationship for Ga-based catalysts that includes particle-support interactions, particle size effect and the nature of Ga sites.

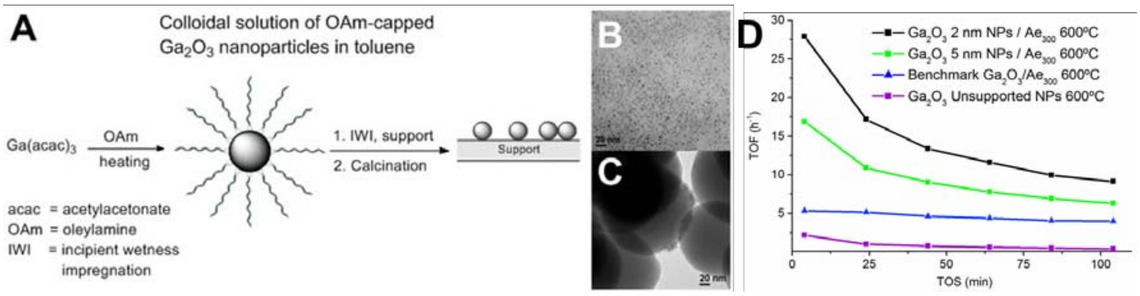

Figure 1. *Synthesis of ligand-capped colloidal Ga_2O_3 nanoparticles and their impregnation onto supports (A). TEM images show Ga_2O_3 nanoparticles in a colloidal solution (B) and the same NPs after impregnation and calcination onto silica nanospheres (C). Catalytic performance for propane dehydrogenation at 550 ºC (WHSV= 7.2 h^{-1}) (D).*

By introducing synthetic protocols from quantum dots chemistry to catalysis, we have successfully produced stable colloidal solutions containing crystalline gallium oxide nanoparticles with controllable sizes. Depositing these nanoparticles onto various supports gives catalysts that are active for propane dehydrogenation. Our results show that colloidal routes allow to prepare catalysts with higher activity and selectivity per total gallium when compared to the benchmark systems obtained through a *conventional* route, i.e. the impregnation of aqueous solutions of $Ga(NO_3)_3$ on the support. The colloidal approach uses pre-formed, well-defined gallia NPs and therefore allows for a more direct and systematic evaluation of the catalyst performance, an important step towards the development of structure-activity relationships in gallia systems.

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Rational design of Pd/Na-ZSM-5 catalysts for complete methane oxidation

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Stabilization of metal nanoparticles in a constrained internal space of a support has attracted considerable attention in the recent years [1], allowing to reduce the production costs by decreasing the amount of the active metal. In this work, we have exploited this approach in order to prepare active and stable methane oxidation catalysts, which currently lack low-temperature activity and long-term stability due to metal nanoparticle sintering [2], for possible utilization in catalytic converters to treat the exhaust of natural gas fueled vehicles. Moreover, we defined the activity and stability descriptors for the novel fully sodium exchanged Pd/Na-ZSM-5 catalysts using various zeolite post-modification techniques.

Dealuminated ZSM-5 zeolites were obtained by leaching the parent material (Clariant SM-27, Si/Al=12) with HCl, HNO_3 and oxalic acid. Mesoporous ZSM-5 was obtained by consecutive base and acid leaching. The thus treated zeolites were then exchanged with salts of Pd and Na to achieve 1 wt. % palladium and to fully exchange the acid sites of the zeolite. The stability of the catalysts was evaluated in a quartz glass plug-flow reactor with a feed of 1 vol.% CH_4, 4 vol.% O_2 and 5 vol.% H_2O (bal. N_2) at 420°C and GHSV = 80,000 h^{-1}.

Transmission IR spectra (Fig. 1b) of acid washed Pd/Na-ZSM-5 revealed different Al extraction mechanisms by the acids. Whereas HCl caused unselective surface and bulk dealumination of the framework (as evidenced by the increase of the peaks corresponding to the terminal Si-OH at 3743 cm^{-1} and H-bonded Si-OH groups at 3520 cm^{-1}), oxalic acid caused only surface dealumination [3]. Both HNO_3 and oxalic acid significantly reduced the amount of extra-framework aluminum (EFAL, 3664 cm^{-1}). The better performance of the samples washed by HNO_3 and oxalic acid (Fig. 1a) suggests that EFAL species passivate Pd/Na-ZSM-5 catalysts. Generation of a small amount of mesopores (nanocages) by desilication together with the control of aluminum speciation yielded a highly active and stable catalyst. Microscopic investigation confirmed that this was achieved by trapping palladium particles within the nanocages of the zeolite (Fig. 1c,d).

The results show that achieving high performance of Pd/Na-ZSM-5 requires, besides the complete Na exchange, control of Al speciation and pore structure of the zeolite.

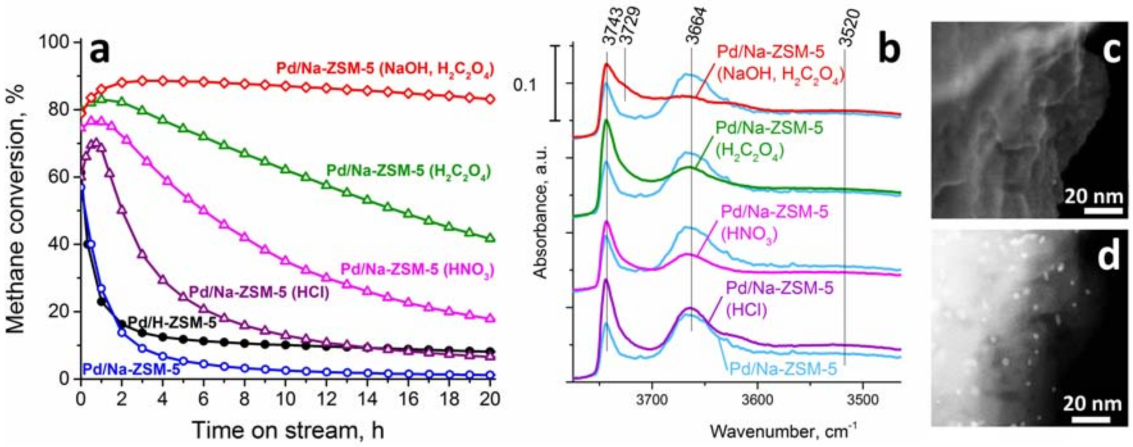

Figure 1. (a) Catalytic performace, (b) transmission IR spectra of various Pd/Na-ZSM-5. (c) Secondary electron and (d) transmission electron microscopy images of base-acid leached Pd/Na-ZSM-5.

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Deactivation of Fluid Catalytic Cracking Catalysts, a Three-Dimensional View of Structural Changes

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Since its commercial introduction three-quarters of a century ago fluid catalytic cracking has proven to be one of the most important conversion processes in the petroleum industry. In this process porous composites composed of zeolite and clay crack the heavy fractions in crude oil into transportation fuel and petrochemical feedstocks. Yet, over time the catalytic activity of these particles decreases. Here we report on resonant ptychographic and fluorescence tomography measurements complemented by electron microscopy to elucidate the structural changes that lead to catalyst deactivation. In combination, acquired tomograms reveal zeolite amorphization and distinct structural changes to the particle exterior as the driving forces behind catalyst deactivation. Amorphization of zeolites, in particular, close to the particle exterior results in a reduction of catalytic capacity. A concretion of the outermost particle layer into a dense amorphous silica-alumina shell further reduces the mass transport to the active sites within the composite. The results provide a complementary explanation to currently suggested deactivation mechanisms driven by feed and reactor impurities.

Rational design of sulfur-tolerant ruthenium catalysts for dry biomass derived CO methanation

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The process of methane production from dry biomass, called wood-to-Synthetic Natural Gas (SNG), consists of 4 main steps: biomass gasification, syngas cleaning to remove catalyst poisons such as H_2S, COS and C_4H_4S using “cold” gas cleaning technologies, methanation and upgrading to remove H_2O and CO_2.[1] To make SNG cost-competitive, the concept of integrating gas cleaning with methanation, which utilizes the ability of ruthenium-based catalysts to be regenerated under oxidizing atmosphere after sulfur poisoning is explored.[2]

However, a complete recovery of the catalytic activity after the regeneration cannot be achieved so far, probably because of a combination of several reasons. Firstly, Al_2O_3 support of the nanoparticles can “store” some of the sulfur poisons in the form of sulfate, which prevent efficient regeneration.[2] Secondly, TEM and XAS analysis evidences particle sintering upon recycling of originally 1 nm particle in Ru/Al_2O_3.

Here, we show that silica largely improve the regeneration process, because it is less prompt to sulfur storage (Fig. 1a). *Operando* XAS at the sulfur K-edge (Fig. 1b) and DRIFTS (Fig. 1c) showed that sulfate species formed on SiO_2 are unstable and could be removed by subsequent treatment with H_2. However, sintering still remains an issue. In addition, DRIFT spectroscopy revealed altered CO adsorption profile for the regenerated catalyst, implying that structural and/or electronic properties of the catalyst are changed after a poisoning-regeneration cycle.

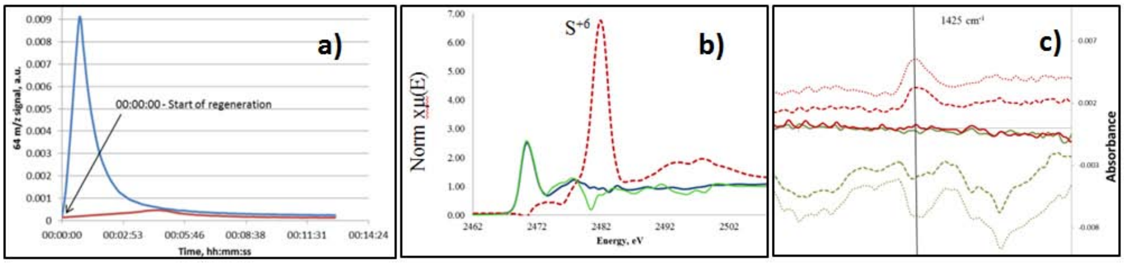

Figure 1: a) SO_2 detected at the reactor outlet for Ru/Al_2O_3 (red) and Ru/SiO_2 (blue) b) Sulfur K-edge XAS spectrum of Ru/SiO_2 catalyst taken during methanation with poisoning (blue), regeneration in 1% O_2 (red) and subsequent methanation (green); c) DRIFTS spectrum of Ru/SiO_2 showing sulfate (ca. 1425 cm^{-1} band)[4] formation (1% O_2 regeneration after catalyst poisoning, red) and decomposition (1% H_2, green) onSiO_2 surface

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Development of Coke- and sintering-resistant Ni/SiO_2-based dry reforming catalyst by depositing a thin layer of Al_2O_3 via ALD

S. Kim[1], A. Armutlulu[1], P. M. Abdala[2], D. Hosseini[1], C. R. Müller[2]*, C. Copéret[2]

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The dry reforming of methane, DRM ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$), is a promising process to convert two greenhouse gases into a synthesis gas (H_2/CO), that is a key intermediate for liquid fuels synthesized via the Fischer-Tropsch process [1]. Due to its comparatively low price (when compared to noble metals) and high activity, Ni-based catalysts are attractive for DRM. The main deactivation mechanisms of Ni-based dry methane reforming (DRM) catalysts are sintering and coke deposition, the extent of coke deposition being critically affected by the size of the Ni particles [2, 3]. Thus, by controlling and stabilizing the Ni particle size Ni-based DRM catalysts that possess a high and stable activity can be realized. In this work, we have developed Al_2O_3-coated, SiO_2-supported Ni DRM catalysts using atomic layer deposition (ALD). Catalysts with different Al_2O_3-shell thicknesses were prepared. Coating of Ni nanoparticles with an Al_2O_3 shell increases appreciably the catalysts' resistance to sintering and coke formation when compared to unmodified SiO_2-supported Ni.

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