CHIMIA

CHIMIA 2016, Volume 70
ISSN 0009-4293
www. chimia.ch

SCS
Swiss Chemical
Society

Supplementa to Issue 7-8/2016

SCS Fall Meeting 2016

Oral Presentation Abstracts Session of Catalysis Science & Engineering

September 15, 2016
University of Zurich, Irchel Campus
http://scg.ch/fallmeeting/2016

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In situ Studies on the Behavior of Metal/Oxide Catalysts during the Water-gas Shift Reaction

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In this talk, it will be shown how a series of *in-situ* techniques {X-ray diffraction (XRD), pair-distribution-function analysis (PDF), X-ray absorption spectroscopy (XAS), environmental scanning tunneling microscopy (ESTM), infrared spectroscopy (IR), ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)} can be combined to perform detailed studies of the structural, electronic and chemical properties of metal/oxide catalysts used for the production of hydrogen through the water-gas shift reaction (WGS, $CO + H_2O \rightarrow H_2 + CO_2$) [1-4]. Under reaction conditions most WGS catalysts undergo chemical transformations that drastically modify their composition with respect to that obtained during the synthesis process [1,2]. The active phase of catalysts which combine Cu, Au or Pt with oxides such as ZnO, CeO_2, TiO_2, CeO_x/TiO_2 and Fe_2O_3 essentially involves nanoparticles of the reduced noble metals. The oxide support undergoes partial reduction and is not a simple spectator, facilitating the dissociation of water and in some cases modifying the chemical properties of the supported metal. Therefore, to optimize the performance of these catalysts one must take into consideration the properties of the metal and oxide phases. IR and AP-XPS have been used to study the reaction mechanism for the WGS on the metal/oxide catalysts [3,4]. Data of IR spectroscopy indicate that formate species are not necessarily involved in the main reaction path for the water-gas shift on Cu-, Au- and Pt-based catalysts. Thus, a pure redox mechanism or associative mechanisms that involve either carbonate-like (CO_3, HCO_3) or carboxyl (HOCO) species should be considered. In the last two decades, there have been tremendous advances in our ability to study catalytic materials under reaction conditions and we are moving towards the major goal of fully understanding how the active sites for the production of hydrogen through the WGS actually work.

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Parahydrogen-based hypersensitive NMR/MRI toolkit for catalysis

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When parahydrogen is used in catalytic hydrogenations instead of normal H_2, the NMR signals of reaction products and intermediates can be enhanced by 10000-fold and more, owing to the phenomenon of parahydrogen-induced polarization (PHIP). This can clearly facilitate the detection of reaction products and short-lived intermediates not detectable by conventional NMR. Previously, this major advantage has been explored in the context of H_2 activation by transition metal complexes and clusters in solution. Many such catalysts activate H_2 via the formation of metal dihydrides, which is key to PHIP observation as the latter requires incorporation of both H atoms of an H_2 molecule into the same reaction intermediate or product.

To extend PHIP studies from homogeneous to heterogeneous catalysis, it was thus essential to retain the proper H_2 activation mechanism for the hydrogenation reaction. Initially, this was achieved by immobilizing a suitable transition metal complex on a solid support. Our recent results show that several immobilized Rh and Ir complexes can produce PHIP effects both in liquid phase and in gas phase hydrogenations of alkenes and alkynes. Further extension to other types of single-site and/or molecularly defined heterogeneous hydrogenation catalysts is not only possible, but is also highly desirable, and is currently in progress.

In contrast, for supported metal catalysts (e.g., Pt/Al_2O_3) the Horiuti-Polanyi hydrogenation mechanism is intrinsically non-pairwise, and no PHIP effects were expected. Despite that, they were successfully observed both in liquid-solid and in gas-solid heterogeneous hydrogenations of unsaturated substrates catalyzed by various supported metal catalysts as well as several metal oxides and bulk unsupported metals. Thus, PHIP effects are quite common in heterogeneous hydrogenations, providing a remarkable possibility to develop a hypersensitive NMR-based tool for catalytic research. Indeed, the unique chemical specificity of NMR spectroscopy and the non-invasive nature of MRI, combined with the major signal enhancement provided by PHIP, can give access to new knowledge about the mechanisms of important chemical reactions and the dynamic processes in operating reactors. Examples include the application of PHIP to the mechanistic and kinetic studies of heterogeneous hydrogenations of various unsaturated compounds, and MRI of operating gas-solid catalytic reactors. Another promising direction of research is the extension of PHIP to reactions other than hydrogenation of double and triple C-C bonds, as exemplified by the PHIP study of the catalytic oligomerization of unsaturated hydrocarbons and hydrofesulfurization of thiophene. Applications of PHIP to homogeneous catalytic processes are far from being exhausted either. Metal-free catalysts such as frustrated Lewis pairs (FLP) are considered as alternative catalysts for cheaper and greener industrial catalytic hydrogenations. Observation of PHIP effects upon parahydrogen activation by FLP provides a novel powerful instrument for the detailed mechanistic studies of their functioning. Finally, the interest to this field of research extends far beyond catalysis alone, as catalytic PHIP-based enhancement can be extremely useful for providing signal enhancement in various practical applications of NMR and MRI, including biomedical studies of metabolism in vivo.

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A closure to the controversy around hydrogen spillover: a nanolithography and single nanoparticle spectro-microscopy approach

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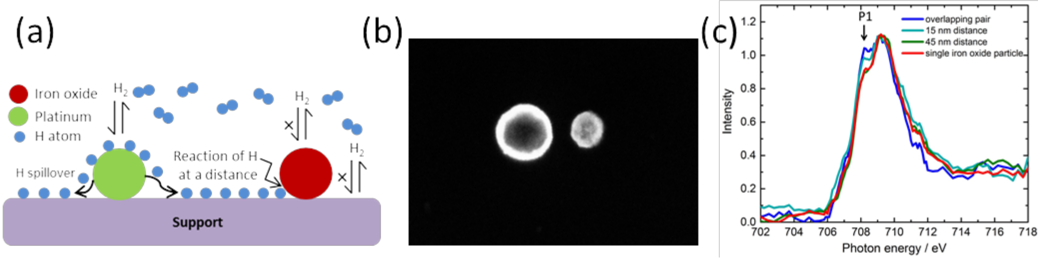
We employ enhanced precision of top-down nanofabrication [1, 2] and single-particle *in-situ* X-ray absorption spectromicroscopy [2] to visualize hydrogen spillover, which is a critical phenomenon in heterogeneous catalysis [3]. Depending on the nature of the support, hydrogen spillover may occur in hydrogen catalysed reactions, which involve dissociative chemisorption of hydrogen onto a catalytic metal particle followed by migration of hydrogen atoms over the support. This eventually leads to the reaction of the hydrogen atoms with a species away from the hydrogen-splitting catalyst (Fig. 1a). Evidence of the occurrence of hydrogen spillover on non-reducible supports such as alumina is disputed, but has often been assumed to explain catalytic phenomena, while its occurrence on a reducible support like titania is generally accepted. Direct experimental proof of its existence does not exist due the lack of well-defined model systems and the inability to observe the effect directly.



We develop novel model surfaces using extreme ultraviolet (EUV) lithography [1] and electron beam lithography (EBL) [2, 4] to achieve nanometer precision over particle size and its positioning. X-ray photoemission electron microscope (X-PEEM) at the Swiss Light Source (SLS) enables in-situ spectromicroscopy on individual iron particles prepared with nanofabrication [2, 4]. Fifteen pairs of nano-sized iron oxide and platinum particles at varying distances from each other starting at 0 nm to 45 nm are positioned on the same support with an accuracy of one nanometer, previously not achievable. The SEM image in Fig. 1b shows one of the pairs with a 25 nm distance. All pairs along with an iron oxide particle without any platinum in its proximity are probed simultaneously to visualize chemical reduction by hydrogen spillover. The spectra showed that hydrogen spillover on non-reducible alumina support depends on the distance from the catalyst and is relevant only at distances below 15 nm (Fig. 1c), occurring only on special sites. Maximum reduction occurs in the iron oxide particle overlapping with platinum, indicated by the highest intensity in the Fe L2,3 edge spectrum (P1 in Fig. 1c). As the distance from platinum increases, less reduction takes place and the pairs at higher distances, along with the iron oxide particle without platinum in its vicinity, have coinciding spectra which implies no spillover. Spillover on reducible titania support, which occurs via coupled electron-proton transfer, is uniform all over the support irrespective of distance. For the first time, distance dependence of hydrogen spillover has been experimentally visualized, and the hydrogen diffusion and migration mechanisms are elucidated by DFT calculations.

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Photoelectrochemical Water Splitting from Earth-Abundant CuO Thin Film Photocathode: Enhancing Performance and Photo-stability through Deposition of Overlayers

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Cupric oxide (CuO) is a promising absorber material for the fabrication of scalable, low cost solar energy conversion devices, due to the high abundance and low toxicity of copper. It is a p-type semiconductor with a band gap of around 1.5 eV, absorbing a significant portion of the solar spectrum. One of the main challenges in using CuO as solar absorber in an aqueous system is its tendency towards photocorrosion, generating Cu_2O and metallic Cu. Although there have been several reports of CuO as a photocathode for hydrogen production, it is unclear how much of the observed current actually corresponds to H_2 evolution, as the inevitability of photocorrosion is usually not addressed.

In this research, we investigated the effect of the deposition of overlayers onto CuO thin films for the purpose of enhancing its photostability as well as performance for water splitting applications. CuO thin film was fabricated by galvanic electrodeposition of metallic copper onto gold-coated FTO substrates, followed by annealing in air at 600 ^{o}C. Photoelectrochemical measurement of the bare CuO film using 0.5 M Na_2SO_4 / 0.1 M K_2HPO_4 (pH 5) under simulated AM 1.5 sunlight showed a current density of *ca.* 1.5 mA cm^{-2} (at 0.4 V_{RHE}), which photocorroded to Cu metal upon prolonged illumination. This photocorrosion could be suppressed by deposition of 50 nm-thick TiO_2, deposited by atomic layer deposition. In addition, we found that insertion of an n-type CdS layer, deposited by chemical bath deposition, between the CuO and TiO_2 layers was able to enhance significantly the photocurrent compared to without the CdS layer. A maximum photocurrent of 1.7 mA cm^{-2} (at 0 V_{RHE}) and relatively positive onset potential (*ca.* 0.9 V_{RHE}) was observed using the photocathode stack FTO/Au/CuO/CdS/TiO_2/Pt. Structural, electrochemical, and photostability characterizations of the photocathode as well as results on various overlayers will be presented.

Why Size Matters and Favors CO Activation on Larger Ru Nanoparticles: A Molecular Understanding from First Principles

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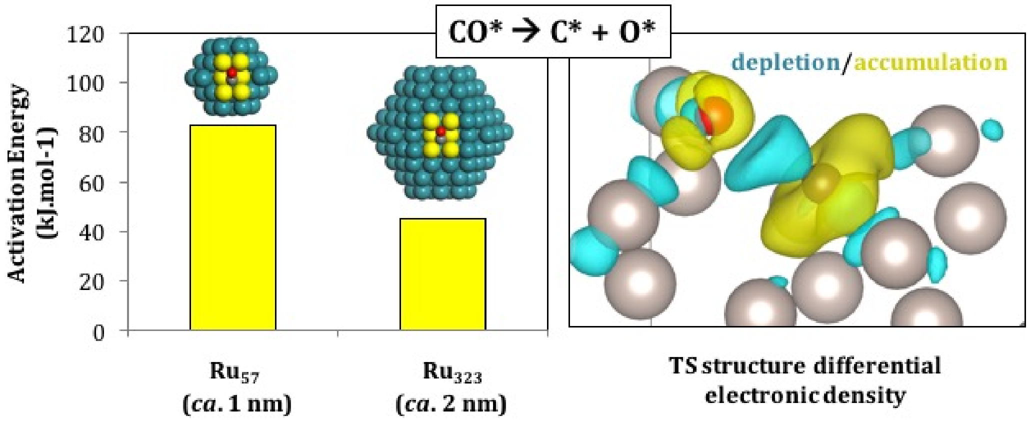
The activation of the strong CO bond during Fischer-Tropsch Synthesis has long been ascribed to special step-edge sites present on the surface of metal nanoparticle catalysts.[1-3] Accordingly, CO activation rate has been correlated with the abundance of such metal ensembles, which is supposedly low on small clusters (smaller than 5 nm).[4]

In this contribution, by using *ab initio* density functional theory (DFT) calculations on Ruthenium (Ru) nanoparticle models of realistic sizes (1-2 nm) to we evaluate the direct CO activation over a collection of step-edge metal sites on different coordination environments. According to our calculations, C-O bond cleavage is easier over more saturated step-edge Ru sites. We ascribe this effect to the saturation-dependent nature of electron back donation from the metal to the hybrid CO-metal π-symmetry bands on η^2–bound transition-state structures for CO dissociation. We also show that some of the step-edge sites can activate CO with affordable energy barriers even at high coverage conditions under real catalytic conditions.



These findings provide a molecular understanding on the cleavage of strong bonds by step-edge sites, which are believed to be the active sites for several relevant chemical transformations involving CO, NO and N_2. The approach presented here goes beyond the ideal slab models typically used on computational heterogeneous catalysis by exploring the reactivity of metal nanoparticle with realistic size and shapes and by evaluating the substrate-metal bonding contributions to understand the bond activation process with DFT calculations.

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Modelling the Phosphorous Dynamics of Vanadyl Pyrophosphate Catalysts

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Maleic anhydride (MA) is an important intermediate in chemical industry. It is produced by heterogeneous catalytic oxidation of n-butane in air. Mainly tubular fixed bed reactors are used for this strong exothermal reaction. The catalyst consists of vanadium phosphorous oxides (VPO) and is employed as pelletized full-body shapes. Even after many years of investigation, reaction mechanism and nature of the active sites are not fully understood. An important subject is the slow loss of phosphorous shifting conversion and MA-selectivity in commercially unattractive regions. In order to prevent this phosphorous loss, it is industrial practice adding several ppm of an organic phosphorous compound together with water to the reactor feed [1]. Dynamic experiments in an industrial-scale pilot reactor showed various partially opposed effects on different time scales. From these experiments a kinetic model was derived that accounts for any observed interactions between TMP and water on the VPO surface. The kinetic model was integrated in a two-dimensional, heterogeneous reactor model (gPROMS) which could be successfully applied describing well the temperature profiles and product compositions up to 500 h time on stream.

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On purpose CO production via methane oxychlorination over heterogeneous catalysts

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Selective oxidation of methane into carbon monoxide is an appealing approach to valorise the emerging vast natural-gas reserves, as the latter is a key intermediate in the manufacture of commodities such as alcohols, acids, isocyanates, and esters (Fig. 1a).[1] Particularly, this process could be advantageously coupled to the well-established CO conversion into formic acid and/or methanol, which are highly attractive energy carriers.[2] In the present study, we developed a continuous gas-phase catalytic process for the highly selective transformation of CH_4 into CO (Fig. 1a). Therein, CH_4 is reacted with oxygen in the presence of hydrogen chloride over a catalysts enabling the C-H bond functionalization to proceed *via* oxychlorination chemistry, which ischaracterized by significantly lower energy barrier compared to direct oxidation. Chloromethanes ($CH_{4-n}Cl_n$) formed in the latter reaction are oxidized *in situ* on the catalyst surface to produce CO, regenerating HCl, which effectively acts as a reaction mediator (Fig. 1a). In order to identify a mild-oxidizing catalyst, the redox propensity of which can be further controlled by the surface chlorination, a systematic evaluation of different catalyst families was conducted. Vanadium phosphate (VPO) and titanium oxide (TiO_2) appeared to be the optimal catalysts for this process, resulting in exceptionally high CO yields of 30 and 34% at 97 and 90% selectivity, respectively (Fig. 1b). A remarkable CO conversion was only possible when HCl was present in the feed (Fig. 1b), demonstrating its pivotal role in the activation of methane.

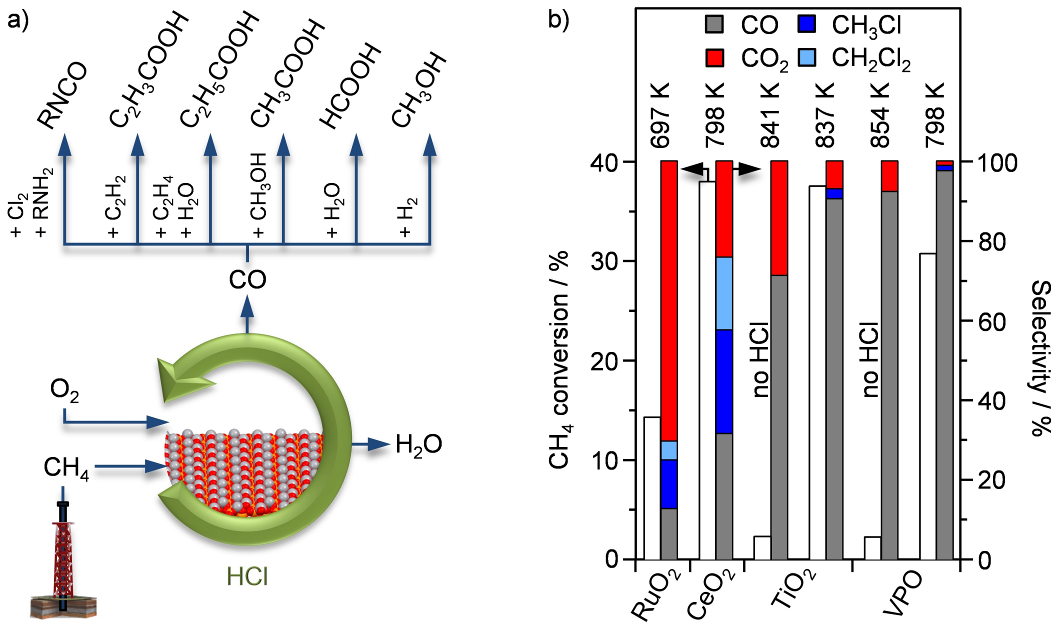

Figure 1 a) Natural gas valorization *via* HCl-mediated selective conversion of CH_4 into CO. b) Performance of different catalysts.

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Rational design of ceria-based supported noble metal catalysts for low temperature CO oxidation using transient X-ray absorption spectroscopy.

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Rational design of more powerful catalysts requires identification of active intermediates and determination of the structure of active sites. However, this is difficult especially for heterogeneous catalysts because of a large structural heterogeneity of catalytic surfaces. Ceria (CeO_2) is a well-known oxygen storage material which is often used as a support for noble metal catalysts to improve their activity for water-gas-shift reaction, CO oxidation, and three-way catalysis. During low temperature CO oxidation on ceria supported platinum nanoparticles, the reaction most probably occurs at the Pt-CeO_2 interface where CO is provided by platinum and reactive oxygen is provided by ceria[1]. Using state-of-the-art X-ray spectroscopic methods, we recently showed that the reduction of Ce^{4+} to Ce^{3+} is involved in the catalytic cycle of CO oxidation and is part of the rate determining step[2]. Furthermore, we could distinguish between a short-lived active Ce^{3+} species and a longer-lived Ce^{3+} spectator species.

Based on this knowledge, we started a rational design of more active catalysts by introducing dopants (Zr, Nd, Co, Sn, Ti, Bi) into the ceria structure in order to accelerate the reduction step of active cerium atoms. The best homogeneous solid solutions were obtained using Zr or Sn as dopants which was confirmed with XRD and EDX analyses. Platinum nanoparticles of 1.9 nm size with a narrow size distribution were deposited on the surface using a uniform colloidal solution[1]. The narrow size distribution of the platinum nanoparticles was important for comparing the activity of the catalysts normalized to the number of active Pt atoms at the metal-support interface.

As expected, both Sn and Zr dopants significantly increase the reducibility and oxygen storage capacity of ceria, however, only Sn improves the activity of the catalyst for low temperature CO oxidation. To understand this phenomenon, we used transient X-ray absorption spectroscopy at the Ce L_3-edge. We correlated the overall rate of carbon dioxide formation to the rates of Ce^{3+} oxidation and Ce^{4+} reduction during fast switching between CO+O_2 and CO atmospheres. Moreover, we analyzed the reactivity of tin under the same conditions at the Sn K-edge. The identification of true catalytic intermediates and the active sites with transient X-ray absorption and emission techniques will be discussed. The influence of dopants on the catalytic activity of ceria-based supported metal catalysts will be explained.

Acknowledgment: This work was supported by the Swiss National Science Foundation (project number 200021_140750)

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TiO$_2$ nanocontainers and nanospheres as photocatalysts for CO$_2$ reduction and photoelectrochemical water splitting: Structural modification.

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CO$_2$ gas is one of the major factors of the climate imbalance. The reduction of CO$_2$ by photocatalysis is proposed to convert CO$_2$ gas into more valuable molecules (such as CH$_4$, CH$_3$OH etc.) because solar energy, being an alternative, cheap and environmentally friendly source of energy, can be used as power supply[1]. For this process, titanium dioxide-based materials with various structures are commonly used as photocatalysts[2,3]. Furthermore, the photocatalytic water splitting using the TiO$_2$-based materials could be a great option for hydrogen production to obtain clean and renewable energy sources[4].

In this project, the TiO$_2$ nanocontainers and nanospheres (Figure 1 (A), (B)) with different crystalline structures are investigated because the crystalline phase, the size and the shape of TiO$_2$ may have an influence on its band gap energy and consequently on its photocatalytic properties[5]. Moreover the embedment of silver nanoparticles into the TiO$_2$ material is explored. Indeed, the presence of silver islands may enhance its photoactivity[6].

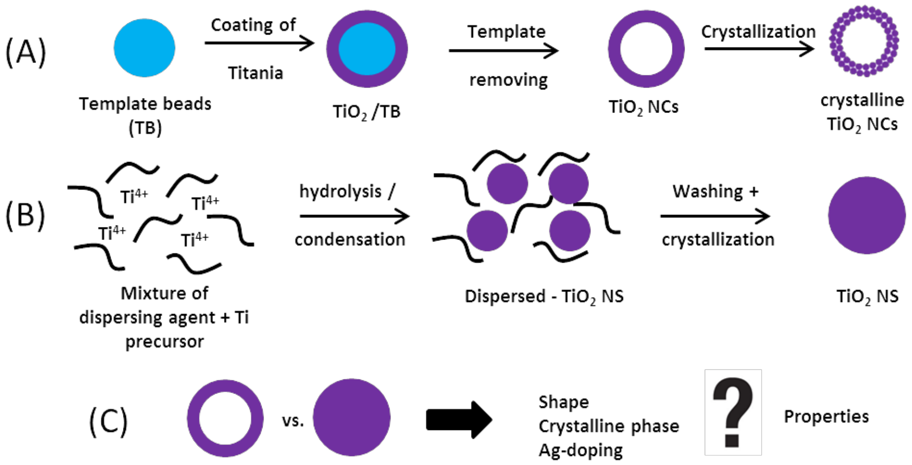

Figure 1: Synthesis of (A) TiO$_2$ nanocontainers, (B) TiO$_2$ nanospheres and (C) the study objectives

The objective of this study (Figure 1 (C)) is the correlation between the morphology of the TiO$_2$-based materials and their photocatalytic properties for the CO$_2$ reduction and the photoelectrochemical water splitting.

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Understanding of the role of Fe in highly active and stable Ni-Fe dry reforming catalysts

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One major drawback of Ni-based dry reforming ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$) catalysts is the rapid deposition of coke, leading to catalyst deactivation.[1,2] Recently, the alloying of Ni with transition metals has been proposed as a concept to decrease the coking tendency of Ni, albeit often contradictory results have been obtained. To this end, Ni-Fe catalysts embedded in a thermally stable $Mg_xAl_yO_z$ matrix have been developed. The formation of alloyed Ni-Fe nanoparticles was confirmed via TEM-EDX, XRD and XAS measurements. The catalytic performance of monometallic Ni and Fe as well as the bimetallic catalysts was evaluated at 650 °C. Bi-metallic catalysts, in particular, Ni_4Fe_1 (2.6 h^{-1} of TOF_{CH4}) showed a high activity and stability when compared to monometallic Ni (1.8 h^{-1} of TOF_{CH4}) and Fe (0.4 h^{-1} of TOF_{CH4}) catalysts that showed a fast deactivation and a low catalytic activity, respectively. *In situ* XAS measurement revealed the formation of FeO in bimetallic Ni-Fe under DRM conditions, whereas Ni was maintained in its metallic state, Ni^0, both for Ni and Ni-Fe catalysts. The formation of a layer of FeO on an Ni-enriched Ni-Fe alloy was confirmed by probing the diffusion dynamics of Ni-Fe films and DFT calculations. Furthermore, using combined in-situ XAS and XRD experiments, we could demonstrate that FeO removes carbon deposited via a redox mechanism ($C + FeO \rightarrow CO + Fe$).

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Chemical layer deposition of porous alumina overcoats increases activity and stability in liquid phase catalytic conversion of biomass-derived chemicals

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Biomass-derived chemicals represent an attractive sustainable alternative to petrochemicals. However, the competitiveness of these processes has been limited by the low stability of metal catalysts under the severe conditions used during biomass upgrading.[1] In order to prevent metal leaching and sintering, we developed a chemical layer deposition (CLD) overcoating technique based on the control over aluminum alkoxide surface reactions kinetics and stoichiometry. After deposition of 30 cycles of an alumina overcoat onto alumina supported copper nanoparticles, imaging using high angle annular dark field scanning transmission electron microscopy (HAADF STEM) revealed a conformal porous overcoat. This porosity was was characterized and quantified by nitrogen physisorption. The overcoat suppressed irreversible catalyst deactivation during the liquid-phase hydrogenation of furfural. While a significant loss of activity due to mass transfer limitations and metal coverage by the overcoat was observed by O’Neill *et al.* when using atomic layer deposition (ALD),[2] most of the surface metal sites remained accessible with CLD as confirmed by chemisorption, illustrating the benefits of overcoats porosity that can be targeted by tuning synthesis parameters. Current work is focused on tuning this porosity for the synthesis of shape selective catalyst overcoats.

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