Structure-Reactivity Relationships in Single-Site Catalysis for Sustainable Chemistry
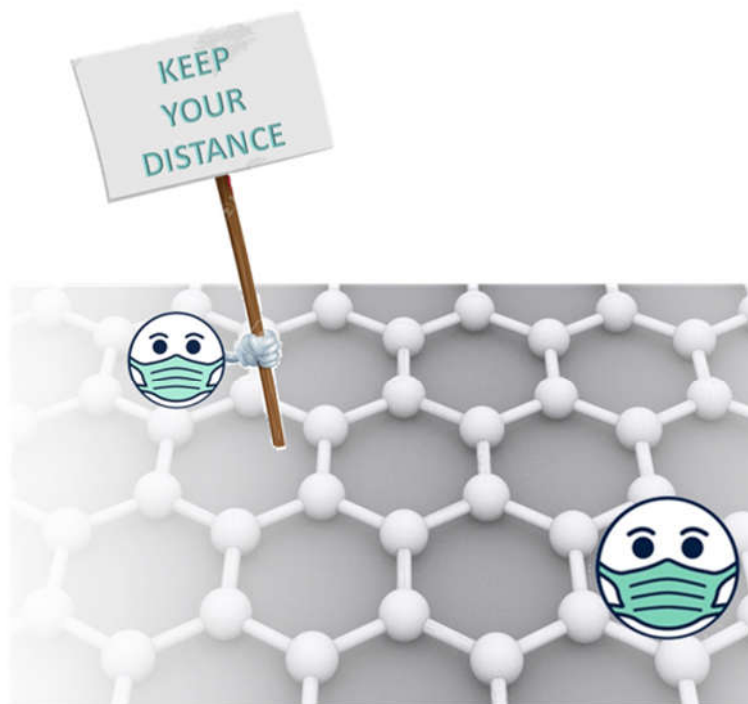
Open Online Workshop *via*
https://workshop.catalysis.de/

9:00 am – 3:30 pm
23rd of March 2021

Single-Site Catalysis for Sustainable Chemistry

Structure-Reactivity Relationships in Single-Site Catalysis for Sustainable Chemistry

Single-site catalysts (SSC) have been investigated for a variety of reactions in the past. However, currently they are gaining increasing attention in catalysis. This is due to several reasons: SSC´s enable maximum utilization of active (metal) ions, which is especially important for the practical use of scarce and/or costly noble-metal catalysts. Moreover, by interaction with the neighboring atoms, their electronic properties, and consequently their catalytic activity may be altered, which is similar to molecular organometallic catalysts. Therefore, SSC´s provide a potential means to implement the advantages of homogeneous complex catalysts, such as well-defined spatial environment and electronic structure into heterogeneous catalysis.

In this workshop, the potential of SSC´s for sustainable and environmentally benign catalytic reactions (e. g. CO_2 valorization, renewable H_2 production, biomass conversion) as well as for efforts to increase selectivity in catalysis will be highlighted. Three invited presentations from outside LIKAT as well as five oral and poster presentations each from LIKAT *Topic 01 - Structure-Reactivity Relationships* will be presented.

You are welcome to join on https://workshop.catalysis.de/.

Scientific Program

9:00 am   Prof. Angelika Brückner
Welcome
Leibniz Institute of Catalysis, Rostock

9:10 am   Prof. Feng Shi

L1   Catalytic amination of alcohol and carbon dioxide with joint-research between homo- and heterogeneous catalysis
Lanzhou Institute of Chemical Physics, China

9:50 am   Prof. Xinjiang Cui

L2   Catalytic dehydrogenation with well-defined heterogenous catalysts
Lanzhou Institute of Chemical Physics, China

10:30 am   Break

10:40 am   Dr. Ali M. Abdel-Mageed

L3   Active Site and Reaction Mechanism During CO Oxidation on Cu-Single Atom Catalyst Supported Metal-Organic Framework
University of Ulm, Germany

11:20 am   Sebastian Cisneros

L4   Highly efficient single-site ruthenium-based catalysts for CO_2 methanation
Leibniz Institute of Catalysis (Department Brückner), Rostock

11:50 am   Jawaher Mosrati

L5   High activity of isolated Single Cu-atom catalyst (SAC) supported on CeO_2-TiO_2 revealed by Operando spectroscopy
Leibniz Institute of Catalysis (Department Wohlrab), Rostock

12:20 am   Lunch Break

1:00 pm   Junhao Huang

L6   Atomically dispersed Pd on few-layer polymeric carbon nitride for (photo)catalytic applications
Leibniz Institute of Catalysis (Department Strunk), Rostock

1:30 pm

L7

Dr. Dan Zhao

Non-oxidative propane dehydrogenation over catalysts with supported ZnO_x species: Effects of host matrix and ZnO_x speciation

Leibniz Institute of Catalysis (Department Linke), Rostock

2:00 pm

L8

Dr. Abel Salazar

Synergetic Bimetallic Oxidative Esterification of 5-hydroxymethylfurfural (HMF) over Bimetallic Co/Ru Catalysts

Leibniz Institute of Catalysis (Department Mejia/Kragl), Rostock

2:30 pm

Poster Session

all LIKAT Topic 01 - Structure-Reactivity Relationships

P1

Ahn Binh Ngo - Department Brückner

Deep insight into the effect of formaldehyde on NH_3-SCR of NO_x over different V_2O_5-WO_3/TiO_2catalysts by operando spectroscopy

P2

Dr. Christoph Kubis - Department Brückner

In-situ FTIR/NMR spectroscopic characterization of transition metal single-site complexes for homogeneously catalyzed carbonylation reactions

P3

Moritz Lang - Department Strunk

Supported TiO_2 on SBA-15 – Electronic properties in dependence of structural influences

P4

Kevin Lindenau – Department Beweries

Mechanistic insights into dehydrocoupling of amine boranes using dinuclear zirconocene complexes

P5

David Decker - Department Beweries

Highly E-selective transfer-semihydrogenation of alkynes with ammonia borane and a Co(II) PNN pincer catalyst

3:30 pm

End of Workshop

Catalytic amination of alcohol and carbon dioxide with joint-research between homo- and heterogeneous catalysis

L1

*Feng Shi**

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The catalytic alkylation of amines is one of the fundamental reactions, building key intermediates for the synthesis of polymers, dyes, pharmaceuticals and bio-active compounds. Traditionally, the reaction of amines with organic halides presents the state-of-the-art procedures, suffering from environmental problems, high cost of the starting materials and low selectivity to the desired products. To address the drawbacks vise supra, the alcohols are considered as green alkylation agents and numerous developments have been achieved using both homogeneous and heterogeneous catalysis. Although these advances, it is still highly desirable to explore new, green and sustainable alkylating regents.[2] In this context, the catalytic alkylation of amines applying CO_2/H_2 and glycerol attracts increasing interests. We will present our recent achievements on these topics.

Joint-research between homo- and heterogeneous catalysis for the amination
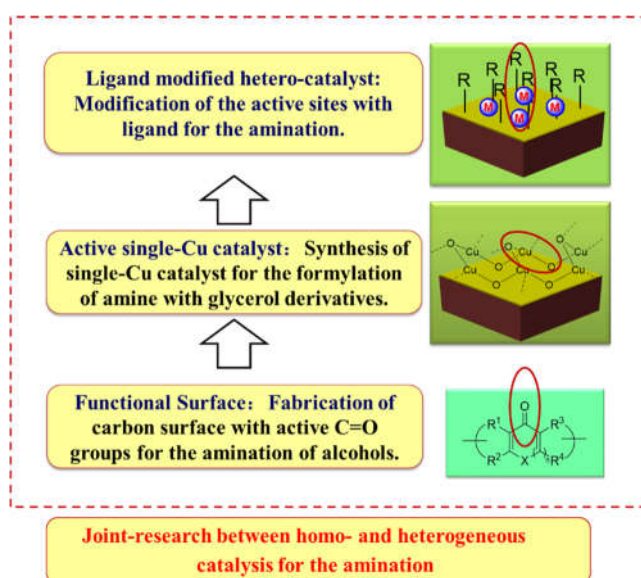
The glycerol was firstly used as the reducing, methylating and carbonyl resources.[3,4] The nitroarene can be reduced to the corresponding amines in the presence of CuNiAlOx catalyst where the glycerol can transform into high valued 1,3-dihydroxypropan-2-one directly. Although high yields of the amines were obtained, the transformation of glycerol was complicated with low yield of 1,3-dihydroxypropan-2-one. Further investigation found that the single site Cu catalyst displayed excellent transformation of glycerol with high utilization rate of carbon source and the desired formylated amines were achieved in high yields.[5]

In addition, the CO_2/H_2 was studied as methylating and formylating regents in the presence of amines. Using CuAlOx catalyst, the methylated amines were obtained in 80-95% yields. To selectively produce the methylated/formylated amines, the surface ligands were fabricated and resulting catalysts displayed controllable activity on this transformation.[6,7]

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Catalytic dehydrogenation with well-defined heterogenous catalysts

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The catalytic dehydrogenation of N- and O-containing compounds is one of the pivotal reactions, building key intermediates such as aldehydes, ketones and imines. In addition to affording valuable chemical products, the catalytic dehydrogenation of N- and O-containing compounds could potentially lead to practical hydrogen carriers for energy storage. However, catalysts able to efficiently catalyze the dehydrogenation of N- and O-containing compounds are mainly based on well-defined molecular catalysts such as Ir,[1] Ru, [2], Co and Fe[3] complexes.

Despite the excellent performance of these homogeneous catalysts on a laboratory scale, their large-scale implementation is limited by their high cost, stability and complex recycling protocols. In this respect, heterogeneous catalysts have intrinsic advantages that overcome these limitations and a number of promising catalysts have been developed. I will display recent works using well-defined heterogeneous catalysts on this reaction[4,5] (Figure 1).
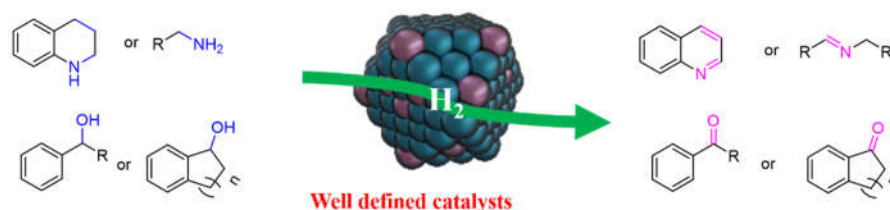
Figure 1. The dehydrogenation of N- and O-containing compounds.

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Active Site and Reaction Mechanism During CO Oxidation on Cu-Single Atom Catalyst Supported Metal-Organic Framework

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The design of single-atom based catalysts has been an ultimate goal for many years for the catalyst architecture. In addition to the desire to maximize the cost-efficiency of using precious metals, single-atom catalysts are highly interesting also from a fundamental point of view because of the well-defined nature of the active site compared to dispersed metal nanoparticles.[1] Identification of the active site is a precondition for a comprehensive understanding of the mechanism of catalytic reactions, and thus for a systematic control of their activity and selectivity. With their high porosity and exceptionally large surface areas, the structurally well-defined metal–organic frameworks (MOFs) represent a robust and very selective platform for the atomic dispersion of metals, and thus stabilizing individual metal atoms into their frameworks.[2]

Recently, we reported a single-atom catalyst (SAC), Cu/UiO-66, prepared by the covalent attachment of individual Cu atoms to the structural defect sites at the zirconium oxide clusters of the MOF UiO-66. Catalytic performance tests showed that these SAC-catalysts are highly active and stable during CO oxidation under technically relevant gas mixtures (O_2/CO = 20 and temperature up to 350°C).[3] Here, we expanded on our studies to understand the reaction mechanism on these catalysts, by combining insights from operando spectroscopies (X-ray absorption spectroscopy (XAS), electron paramagnetic resonance (EPR) and diffuse reflectance FTIR), and activity / kinetic isotope effect (KIE) studies during CO oxidation together with DFT computations of different reaction pathways.

These studies revealed that the reaction cycle starts by the creation of an O-vacancy defect site at the interface between Cu single atoms and Zr oxide clusters, forming an F-center. Then O_2 is activated on this O-vacancy, followed by CO adsorption on Cu^{1+}, and subsequent reaction with the atomic oxygen. The reaction cycle starts over again by recreation of the F-center (i.e., vacancy creation) by reaction with CO. KIE measurements, in good agreement with detailed DFT calculations, revealed that the removal of interface active oxygen by reaction with CO adsorbed on Cu single sites is the rate limiting step in this reaction.

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Highly efficient Ru sites for CO2 methanation: from single sites to sub-nanometer clusters

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The upgrading of CO_2 to high energy density fuels upon the use of Ru based catalysts is one interesting and relevant catalytic process to investigate. On the one hand, Ru is known as highly active in CH_4 production, which is the basis of power to gas (P2G) processes for the successful incorporation of renewable electricity into the commercial grid.[1] On the other hand, the fundamental understanding of CO_2 methanation could help to improve the efficiency in the development of catalysts for more complex reactions, e.g. methanol or olefine production from CO_2.[2,3] The challenge for the successful implementation of heterogeneous catalytic processes that rely on precious metals lies, however, in developing catalysts with low metal loading, enhanced activity, and no detriment in their selectivity. That means, the metal utilization must be maximized while keeping the nature/structure of the active centres. This could be accomplished if stable sub-nanometre (<1 nm) sites, eventually atoms, can be dispersed on the support,[4,5] instead of relatively large (>2 nm) metal nano-clusters.[6] With this motivation, we have applied the sol-gel route to synthesize Ru based catalysts with Ru loading from 1 down to 0.6 wt.% on TiO_2 and TiO_2-CeO_2 supports, respectively. Our catalytic results obtained from reaction experiments at differential conditions in a plug flow reactor (PFR) have demonstrated these catalysts to outperform the methanation activity of the, as far as we know, most active reported Ru/TiO_2 (P-90) catalyst[7] by ca. 2-4 times (mass normalized basis) at 190 °C and without detriment in the selectivity upon increasing the temperature up to 350 °C. Furthermore, both EPR and DRIFTS characterizations in _operando_ conditions indicate that Ru sites might consist of very well dispersed entities strongly interacting with the support(s). We are performing additional measurements using complementary methods such as NAP-XPS and low temperature CO adsorption to gain more insights about the structure of the active centres responsible of such an astonishing catalytic behaviour.
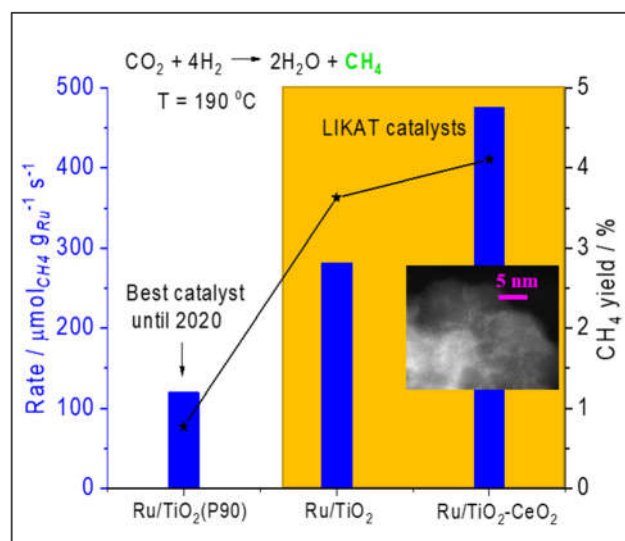
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High Activity of Isolated Single Cu-atom Catalyst (SAC) Supported on CeO$_2$-TiO$_2$ Revealed by Operando Spectroscopy

L5

Jawaher Mosrati,[1] _Ali M. Abdel-Mageed,_[2] _Thanh Huyen Vuong,_[1] _Reni Grauke,_[1] _Stephan Bartling,_[1] _Hanan Atia,_[1] _Udo Armbruster,_[1] _Sebastian Wohlrab,_[1] _Jabor Rabeah,_[1] _Angelika Brückner_[1]

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Single-atom catalysts (SACs) with atomically dispersed metals have attracted considerable interest in the field of heterogeneous catalysts due to their 100% metal atom efficiency and superior catalytic activity compared with conventionally supported nano-catalysts. CO oxidation reaction over Cu-based catalysts, which is of great interest not only from a fundamental point of view but also for practical applications including catalytic converters and air purification[1,2], has attracted great attention due to high activity, selectivity, low price, and availability of Cu. However, the focus on the design of highly active and stable supported single atom Cu catalysts has gained little attention.

Therefore, the aim of this work was to develop highly active and atomically dispersed Cu catalysts (Cu-SAC) on CeO$_2$-TiO$_2$ for CO oxidation reaction at moderate to low temperature. To this end, different Cu catalysts with different Cu loading (0.06, 0.26, 0.86 wt.%; Cat1, Cat2, and Cat3, respectively) supported on Ce40/Ti100 (molar ratio 40:100) were prepared by sol-gel method and tested for CO oxidation. To derive reliable structure-reactivity relationships, _operando_ Electron Paramagnetic Resonance (EPR), FTIR spectroscopy in diffuse reflectance mode (DRIFTS) as well as near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) have been performed under reaction conditions. The catalytic test results indicate the Cu-mass normalized conversion rates of SACs (Cat1 and Cat2) are significantly higher than the most obtained over supported Cu catalysts which contain a higher Cu loading[3]. In this way, the rate of Cat3 is also low due to the formation of Cu clusters.
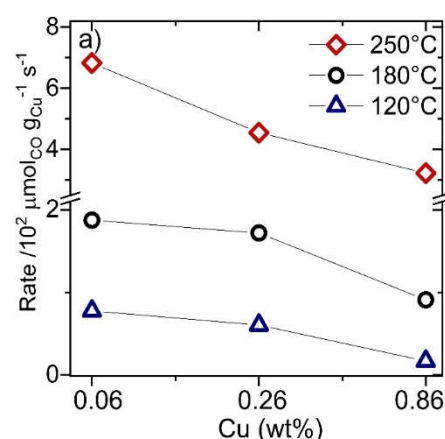
Figure.1. Rate of CO conversion normalized on the Cu mass.

Operando spectroscopic investigations show that increasing Cu interactions with CeO$_2$ greatly enhances the redox activity of Cu^{2+}/Cu$^+$ and Ce^{4+}/Ce^{3+}, as evidenced by EPR, DIRTFS and NAP-XPS. More active sites and oxygen vacancy defects for the CO adsorption and molecular oxygen activation are the primary factors for excellent catalytic performance.

This work provides some insights into the design of highly active and stable Cu-SACs for possible industrial applications in the future.
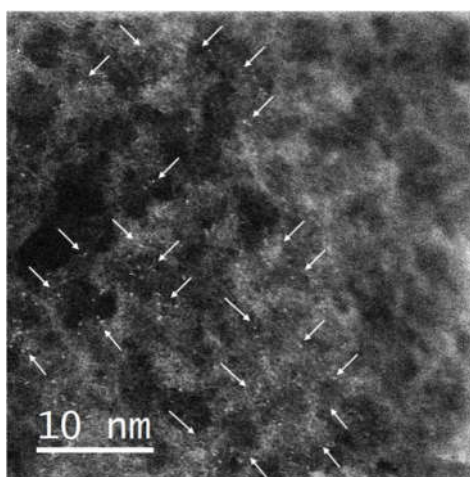
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Atomically dispersed Pd on few-layer polymeric carbon nitride for (photo)catalytic application

L6

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The Suzuki coupling reaction is an important method to construct C-C bonds and has been broadly applied in fine-chemical synthesis.[1] Homogeneous Palladium catalysts were confirmed to possess a relatively high efficiency for the Suzuki reaction, but challenges with the recovery of the costly and toxic palladium catalyst were found.[2] The alternative strategy of supported Pd nanoparticles has also faced limitations because of insufficient activity and poor chemoselectivity.[3] Single-atom catalysts (SACs) that integrate the merits of homogeneous and heterogeneous catalysts may provide an option to overcome the obstacles.[4] Herein, we have developed abundant surface sites for anchoring Pd atomic species on a few-layer polymeric carbon nitride through a wet impregnation method, producing an efficient and stable Pd/CN catalyst for the Suzuki-coupling reaction. IR spectroscopy was used to characterize the supported metal and to investigate the reaction mechanism. We chose CO as probe molecule for the in-situ DRIFTS measurements to study the electronic and coordination structure of the surface metal sites, in order to distinguish the Pd single atom from clusters. In-situ ATR-IR measurement was conducted to detect the reactants and intermediate species on the surface metal sites to get an in-depth mechanistic understanding. Besides, for comparison, a Pd cluster catalyst was synthesized using a calcination method with H_2 treatment. We evaluate the metal dispersion of both Pd single atom and clusters catalyst via H_2 and CO pulse chemisorption technology to explore the relationship among the surface metal size, metal loading, and metal density. This work provides insights into the electronic and coordination structures of single-atom catalysts at the molecular level and contributes to the understanding of the structure-reactivity relationships.

Fig. 1. HAADR-STEM image of the 0.5 wt% Pd/CN catalyst; arrows indicate location of single atoms.

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Non-oxidative propane dehydrogenation over catalysts with supported ZnOₓ species: Effect of host matrix and ZnOₓ speciation

L7

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The non-oxidative dehydrogenation of propane (PDH) to propene is one of the most important on-purpose technologies for producing propene.[1,2] The commercial catalysts with supported Pt and CrOₓ species have some shortcomings related to high-cost and toxicity, respectively. Herein, we present environmentally friendly ZnO-Silicalite-1(ZnO-S-1) catalysts which were prepared by a simple method containing physically mixing and following *in-situ* treatment by H_2 under reaction conditions.
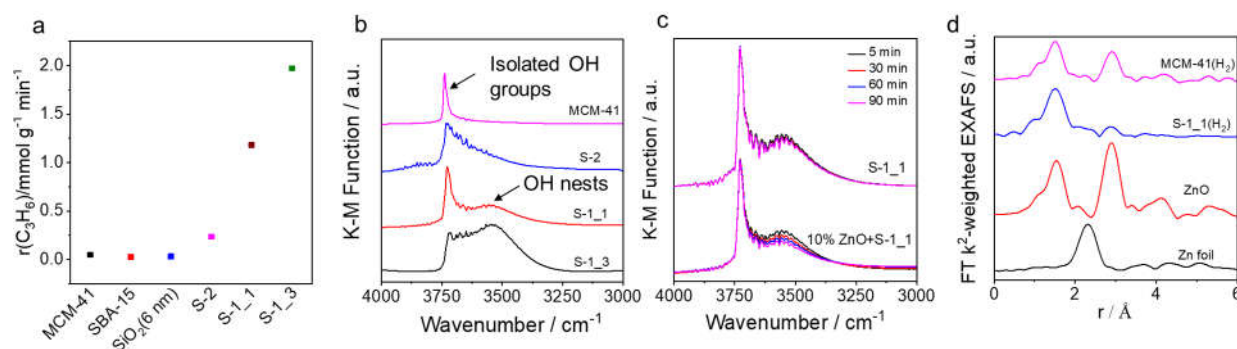
Figure 1 (a) The rate of propene formation over different ZnO and SiO_2-based material mixtures after H_2 treatment, reaction conditions: 550 °C, 40 ml/min, C_3H_8:N_2=2:3. (b) The DRIFTs of SiO_2-based support at 550 °C. (c) *In-situ* IR spectra of S-1_1 and ZnO-S-1_1 mixture at 550 °C in 50 vol% H_2. (d) The EXAFS spectra of as-prepared samples and reference materials.

All ZnO-zeolite mixtures show higher activity (0.24, 1.18 and 1.97 mmol/g/min for S-2, S-1_1 and S-1_3, respectively) than ZnO-meso-SiO_2-based materials (~0.05 mmol/g/min) (Figure 1a). To explore the reason(s) behind this, we applied *in-situ* DRIFT spectroscopy. Mesoporous SiO_2 materials only possess isolated OH groups at about 3720 cm⁻¹(Figure 1b); while zeolites possess isolated OH groups and OH nests (at about 3540 cm⁻¹). To explore the function of different OH groups, *in-situ* DRIFTs tests with bare S-1_1 and a mixture of ZnO and S-1_1 were carried out in 50 vol% H_2 at 550°C (Figure 1c). The intensity of the OH nest band in the spectrum of ZnO-S-1_1 decreased with time on H_2 stream. No changes in the spectrum of bare S-1_1 could be observed. This result suggests OH nests anchor active Zn species. Their structure was determined from EXAFS studies (Figure 1d). In comparison with reference ZnO material, the first and second shell scatterings at 1.5 and 2.9 Å correspond to O and Zn neighbors as in ZnO, respectively. While no substantial contribution from the second Zn shell was identified in the spectrum of S-1_1(H₂) which was prepared upon reductive treatment of ZnO and S-1_1. On the basic of fitting results, binuclear Zn-oxo species were concluded to be stabilized on the surface of S-1 zeolite. In summary, the defective OH groups on zeolite provide anchoring sites for binuclear Zn-oxo species which are active sites in PDH.

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Synergetic Bimetallic Oxidative Esterification of 5-Hydroxymethylfurfural under Mild Conditions

L8

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5-Hydroxymethylfurfural (HMF) has become a benchmark chemical as it can be obtained by the processing of renewable biomass, making its downstream modification an important topic both in industry and academia.[1,2] Finding catalytic processes for the selective derivatization of HMF is challenging due to its reactivity, hence mild conditions are needed. Selective oxidative esterification of HMF was achieved on batch and flow conditions under mild conditions using oxygen (from air) as oxidant. A synergetic effect between the used catalysts, cobalt oxide over nitrogen-doped carbon, and ruthenium over carbon catalysts was observed by catalytic and electron paramagnetic resonance measurements. Improvement of the conversion rates was achieved using a perfluoroether as solvent, proving that oxygen diffusion is the limiting factor in the system.
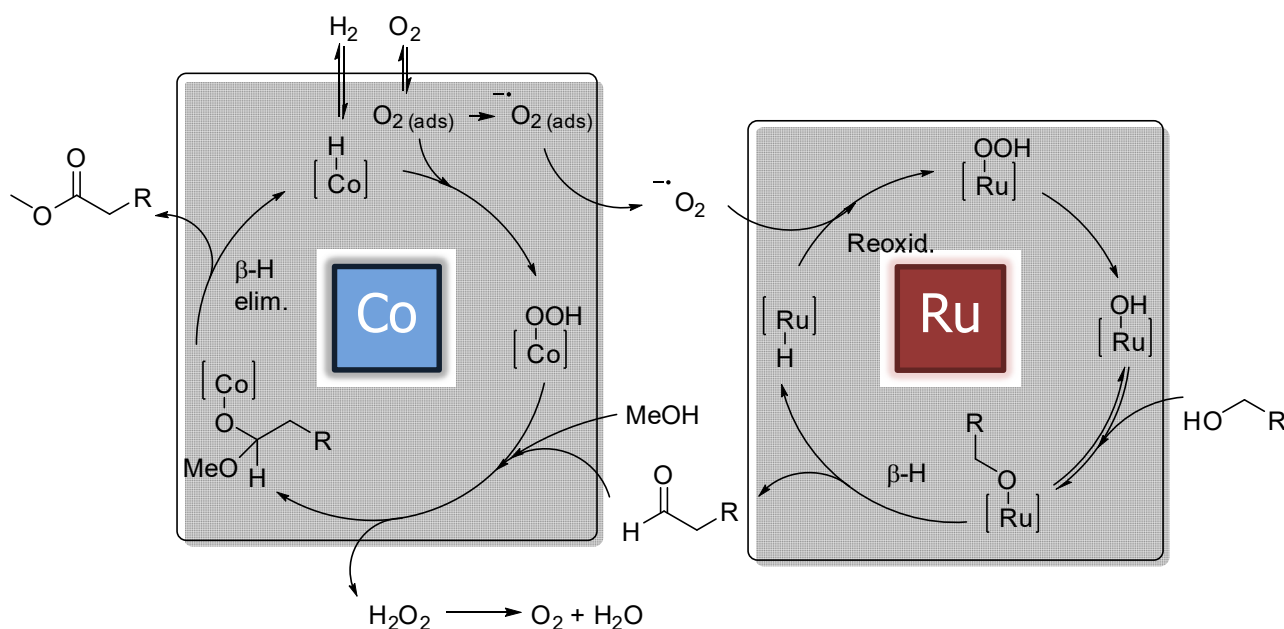

Figure 1. Synergetic Bimetallic Oxidative Esterification of HMF.

The catalytic system was brought to flow conditions. For which a new series of nitrogen-doped carbon-supported bimetallic Co/Ru heterogeneous catalysts were prepared and characterized by XRD, XPS and N_2 Physisorption. Under optimized conditions the flow reactor showed a 15-fold increase on the productions of dimethyl-2,5-furandicarboxylate compared to batch conditions.

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Deep insight into the effect of formaldehyde on NH_3-SCR of NO_x over different V_2O_5-WO_3/TiO_2 catalysts by operando spectroscopy

P1

Anh Binh Ngo, _Thanh Huyen Vuong, Hanan Atia, Ursula Bentrup, Vita A. Kondratenko, Evgenii V. Kondratenko, Jabor Rabeah, Udo Ambruster, Angelika Brückner*_

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Selective catalytic reduction of nitrogen oxides (NO_x) by ammonia (NH_3-SCR) is the state-of-the art technology for the abatement of these harmful substances to the environment. The challenges of this technology are to improve the conversion of NO_x at low temperature and restrict the negative effects from other components in the flue gas such as H_2O, SO_2, phosphorous and heavy metals.[1] However, from the uncompleted combustion of fuel, formaldehyde is also formed, the effect of which has been widely neglected so far and this is the aim of this work. Therefore, it was the aim of this work to investigate the mechanism of formaldehyde conversion in NH_3-SCR of NO_x on different V_2O_5-WO_3/TiO_2, depending on their composition and surface properties by combining catalytic tests within situ FTIR and EPR experiments.

Our study was first carried out on a commercial V_2O_5-WO_3/TiO_2 catalyst (1 wt. % V, 6 wt. % W). These results showed many negative effects of formaldehyde. HCHO reacts with NH_3 and forms HCN as the main product. This undesired reaction lowers NO_x conversion and N_2 selectivity. By in situ FTIR spectroscopy it was found that HCHO and NH_3 react on the surface of catalyst to intermediate $HCONH_2$ which liberates HCN.[2] Subsequently, catalysts of different composition, WO_3/TiO_2 (W-Ti), V_2O_5/TiO_2 (V-Ti) and V_2O_5-WO_3/TiO_2 (V-W-Ti), were analyzed to explore the effect of the different catalyst components on the reaction of HCHO. On the most active V-W-Ti catalyst HCHO caused the highest decline of NO_x conversion in the whole temperature range and released the highest amount of HCN. In situ FTIR results indicated that the high surface acidity of V-W-Ti promotes NH_3 adsorption and formation of $HCONH_2$. In contrast, on W-Ti and V-Ti catalysts, the amount of NH_3 ads is not large enough, HCHO rather interacts with lattice oxygen of the catalysts to form $HCOO^-$ which then decomposed or was oxidized to CO and CO_2. In addition, results from in situ EPR experiments revealed that the high redox activity of V-W-Ti also accelerates the rate of conversion of HCHO to $HCONH_2$, facilitating the formation of HCN and simultaneously reducing the amount of NH_3 for the SCR reaction. These results may support further studies to restrict the negative effect of HCHO in NH_3-SCR technology.

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In-situ FTIR/NMR spectroscopic characterization of transition metal single-site complexes for homogeneously catalyzed carbonylation reactions

P2

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Alkene hydroformylation is a homogeneously catalyzed multistep reaction which kinetics is influenced by the structure of substrates and ligands and their concentrations.[1,2] In catalysis a general approach in order to study aspects of reaction mechanisms is combining kinetic measurements with *in situ* spectroscopic investigations into catalytic relevant species. The composition of catalyst complexes in rhodium catalyzed hydroformylation is very sensitive to actual reaction conditions. Identification and quantification of catalytically relevant complexes are requirements for kinetic and mechanistic considerations but also essential for industrial process optimization. Established analytical techniques for *in situ* studies are HP FTIR- and NMR-spectroscopy. Chemometric algorithms can be of great benefit for the analysis of spectroscopic data in order to extract pure component spectra and concentration profiles.[3,4] The interpretation of vibrational spectra is often favourably supported by DFT calculations. In the presentation results from *in situ* spectroscopic and kinetic studies on alkene hydroformylation using a single site phosphite-modified rhodium catalyst are presented.[5,6] Molecular structures of all relevant rhodium complexes in the catalytic system were elucidated by HP FTIR- and NMR-spectroscopy, isotopic labelling, as well as DFT calculations.

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Supported TiO$_2$ on SBA-15 for Photocatalysis – understanding the electronic processes

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Photocatalytic activity has been reported for various TiO$_2$ containing materials.[1] Especially supported titania on silica in sub monolayer loadings are considered to perform particularly well.[2] Previous experiments displayed a dependency of activity and selectivity on the titania loading due to the presence of tetrahedrally coordinated single sites for low loadings.[3] The aim of this work is to further investigate silica supported titania species with respect to their electronic properties and photoactivity.

The oxidation of 2-Propanol was chosen as a photocatalytic model reaction for various TiO$_2$/SBA-15 catalysts. The activity strongly correlates with the amount of titania. Experiments probing the electronic behavior are promising to provide a deeper insight into the actual processes facilitating the photocatalytic reaction. As methods of choice laser-induced transient absorption and transient photoluminescence spectroscopy were selected. Initial measurements indicate differences in electron transitions and dynamics. Exemplarily the transient absorption spectra of silica supported titania is shown in Figure 1. The dynamics seem to be similar, while the spectra show a clear difference. Photoluminescence spectroscopy seems to be sensitive to different phenomena. Here the slow dynamics of the photoluminescence strongly vary between different samples.
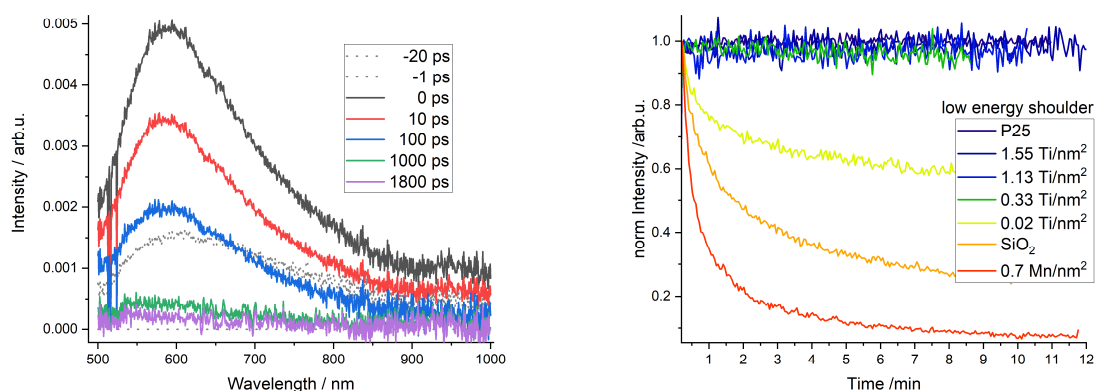

Figure 2. Transient Absorption Spectra for 1.13 Ti/SiO$_2$ at various times and slow PL dynamics of various samples.

Connecting those results with the photocatalytic behavior might help understanding the exact reaction pathway and lead the way to designing more efficient photocatalysts.

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Mechanistic insights into dehydrocoupling of amine boranes using dinuclear zirconocene complexes

P4

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The atom-efficient catalytic formation of bonds between main group elements such as boron and nitrogen is of great interest in the fields of organometallic and materials chemistry as it could provide an entry point to new main group compounds and materials.[1] Up to now, a plethora of early and late transition metal complexes are known to serve as catalysts for the dehydrocoupling of primary and secondary amine boranes.[2] Coordinatively and electronically unsaturated early transition metal complexes, especially those of group 4 metals are very interesting in this context as these are known to possess unique, high reactivities with N-H and B-H bonds. Examples for the use of group 4 metallocene systems that consist of metallocene dihalide and organolithium reagents were reported in the past,[3] however, in these systems the elucidation of the mechanistic details is complicated by the presence of the strong base.
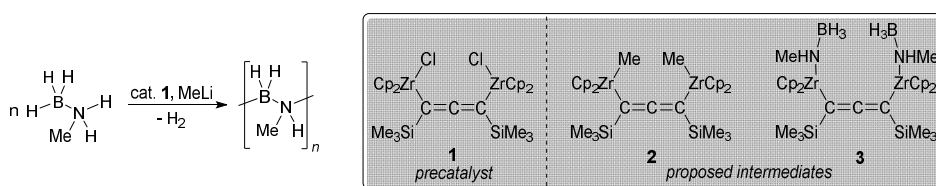
Scheme 3: A dinuclear zirconocene allenediide bridged precatalyst (**1**) for dehydropolymerisation of $H_3B \cdot NMeH_2$.

Catalytic dehydrocoupling of $H_3B \cdot NMe_2H$ using the in situ system $Cp_2Zr(Cl)(\mu\text{-}Me_3SiC_3SiMe_3)$ $Zr(Cl)Cp_2$ (**1**)/MeLi was studied as a model for previously reported dehydropolymerisation of $H_3B \cdot NMeH_2$.[4] NMR and UV-Vis spectroscopic monitoring of the activation of the precatalyst with MeLi shows that this reaction proceeds slowly and stepwise via a singly methylated species. NMR spectroscopic monitoring of the catalytic reaction as well as speciation experiments indicate that dinuclear Zr(III) alkyl and hydride complexes, formed by decomposition of the allenediide ligand in **1**, are important intermediates in the catalytic process. Overall, our findings suggest that the in situ system **1**/MeLi comprises several interconvertible Zr species that catalytically convert the amine borane via different pathways and all contribute to the macroscopically observed activity of the system.

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Highly *E*-selective transfer-semihydrogenation of internal alkynes with ammonia borane and a Co(II) PNN pincer catalyst

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Alkenes are versatile building blocks for a broad range of applications in organic chemistry that can be synthesized by semi-hydrogenation of alkynes. The selective formation of *E*- or *Z*-alkenes however still represents a major challenge, especially when considering functional or aliphatic substrates. While *Z*-selective hydrogenation can be conveniently achieved using a multitude of catalyst systems, including the Lindlar catalyst as the most prominent example, *E*-selectivity is more difficult to obtain and one of the most common routes still is Birch-reduction using alkali metals in ammonia, producing stoichiometric amounts of waste. The use of suitable hydrogen transfer reagents instead of gaseous hydrogen is a practical and safe alternative.[1]

We present two Co(II) PNN complexes[2] as active catalysts in the dehydrogenation of ammonia borane and the semihydrogenation of different substituted internal alkynes in methanol at exceptionally low catalyst concentration in less than 30 minutes. This mild system shows an excellent *E*-selectivity due the isomerization of the initially formed *Z*-alkene. Furthermore, labeling experiments with deuterated ammonia borane and methanol showed that H-transfer to the substrate occurs from the B-H bond of $H_3B \cdot NH_3$ and the O-H of MeOH. A reliable method to determine the end point of the reaction is the monitoring of the H_2 evolution, which takes place due to the dehydrogenation of the ammonia borane mediated by the catalyst during the transfer semihydrogenation, using a gas burette.[3]
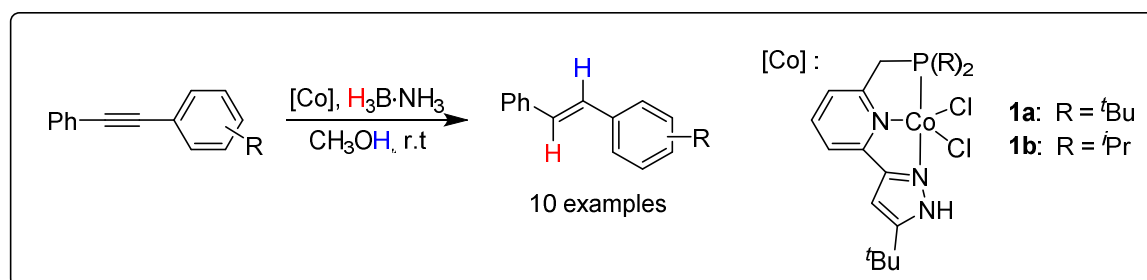

Figure 4. Transfer semihydrogenation of internal alkynes using a cobalt(II) catalyst.

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