

Fritz-Haber-Institut der Max-Planck-Gesellschaft
Boreskov Institute of Catalysis SB RAS



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Fourth German-Russian Seminar on Catalysis



Bridging the Gap between Model and Real Catalysis

5-8 September, 2016

Kloster Banz, Germany

Abstracts

Novosibirsk-2016

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The main topics are: in situ studies of catalytic reactions, (photo) electrochemistry, nanoparticles and catalysis

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The scientific program of seminar includes six plenary lectures (40 min) and presentations (20 min).

The main topics are:

- in situ studies of catalytic reactions
- (photo) electrochemistry
- nanoparticles and catalysis

Plenary Lectures
PL-1 ÷ PL6

Metal Particle Size Effects: An Interference of Activation and Adsorption Factors

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High metal dispersion improves utilization of noble metal. On the other hand, reactivity of the surface atoms may depend significantly on the size of metal particles, since changes in the metal particle size lead to alterations of the relative ratio between edges, corners and terrace atoms, as well as changes in the electronic structures. Therefore, turnover frequency (TOF), defined as the activity per unit of exposed surface, demonstrates not only independence on size (structure insensitivity) but also structure sensitivity (particle size effect). As a result, the overall activity of the catalyst becomes a function of metal dispersion (fraction of exposed atoms) and the particle size effect, which requires careful management of metal particle size for achieving optimal performance and/or minimizing noble metal loading.

The discussion of the relationship between particle size and TOF will be based on the concept proposed by Van Santen et al. [1], which rationalizes the relationship of TOF of catalytic reactions on transition-metal particle size. The concept emphasizes the dependence of the rate-limiting activation stage and the geometry of the appropriate surface active site. In this lecture particular focus will be given on the chemisorption of the reacting molecules on metal nanoparticle surface and the impact of this stage on TOF. This lecture will concentrate on the impact of chemisorption on the reactivity of metal surface atoms neglecting metal-support interface phenomena. It will be shown that in the case of small metal particles (< 3-4 nm) adsorption and strong structural modification of the nanoparticle surface may dominate the activation stage and the observed TOF significantly deviate from “TOF – particle size relationship” predicted by the theory [1].

Interference between activation and adsorption factors will be demonstrated by the experimental results for oxidation and hydrogenation processes over supported Pt and Pd catalysts.

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The Dynamics of Active Metal Catalysts Revealed by *In Situ* Electron Microscopy

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Conventional high-resolution imaging by electron microscopy plays an important role in the structural and compositional analysis of catalysts. However, since the observations are generally performed under vacuum and close to room temperature, the obtained atomistic details concern an equilibrium state that is of limited value when the active state of a catalyst is in the focus of the investigation. Since the early attempts of Ruska in 1942 [1], in situ microscopy has demonstrated its potential and, with the recent availability of commercial tools and instruments, led to a shift of the focus from ultimate spatial resolution towards observation of relevant dynamics.[2] In order to enable the observation of catalysts in their active state, we have recently adapted an environmental scanning electron microscope for the investigation of surface dynamics on active catalysts and implemented commercially available sample holders for in-situ studies of catalysts in their reactive state inside a transmission electron microscope. Using these tools we are now able to cover a pressure range from 10^{-4} mbar to 10^3 mbar and a spatial resolution ranging from the mm to the sub-nm scale.

Presently we are investigating the behaviour of metal catalysts during hydrocarbon partial oxidation and decomposition reactions as well as structural dynamics during oscillatory red-ox reactions. The observations are performed in real-time and under conditions in which the active state of the catalyst can be monitored. The latter is of utmost importance, since the key requirement is to observe relevant processes and dynamics that are related to catalytic function. The ability to directly image the active catalyst and associated morphological changes at high spatial resolution enables us to refine the interpretation of spatially averaged spectroscopic data that was obtained under otherwise similar reaction conditions, for example during near-ambient-pressure in situ XPS measurements.[3] In the case of metal catalysed chemical vapour deposition growth of graphene, we are able to observe growth of graphene domains in real time and to study the effect of catalyst surface termination, atmosphere and temperature in a very flexible way.[4]

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***In Situ* Approach for Mechanistic Studies of Heterogeneous Catalytic Reactions**

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The *in situ* approach is a methodology that combines the investigation of catalysts by different techniques directly during reaction with the simultaneous measurement of catalytic activity/selectivity. This approach is actively developed since the end of the twentieth century when a row of modern techniques such as XANES, EXAFS, X-ray photoelectron spectroscopy (XPS), polarization-modulation Infrared reflection absorption spectroscopy etc. was adapted for measurements under elevated pressure [1-4]. At the beginning of the 21st century, this approach was referred to by some authors as the *operando* study. The main advantage of this methodology is a possibility to study the electronic and atomic structure of catalytically active sites and surface intermediates and to correlate these data with catalytic performance. The understanding of the structure–activity/selectivity relationships and the identification of surface intermediates and the main routes of catalytic transformations provide the deep insight into mechanisms for catalytic reactions.

In this contribution, we demonstrate the potential of IR absorption spectroscopy, XANES, XPS, and X-ray diffraction (XRD) techniques for the *in situ* mechanistic studies of heterogeneous catalytic reactions. We present the results of an *in situ* study of the self-sustained reaction-rate oscillations in the oxidation of methane over a nickel foil at atmospheric pressure by XRD and mass-spectrometry as well as the results of an *in situ* study of the self-sustained reaction-rate oscillations in the oxidation of propane over a nickel foil at elevated pressure by XANES and XPS combined with mass-spectrometry and gas chromatography. In both cases, we found that the oscillations originate due to periodical oxidation and reduction of nickel [5]. Ni in the metallic state is several times more active than NiO. We also present the results of *in situ* studies of the selective oxidation of methanol and ethanol over a monolayer V₂O₅/TiO₂ catalyst [6,7]. In this case, we used *in situ* XANES, XPS, and IR absorption spectroscopy. The obtained results were complemented with kinetic measurements in a flow reactor. In fact, we examined the product distribution depending on the reaction temperature using gas chromatography. After that, we studied *in situ* the surface intermediates simultaneously with analysing gas phase by IRAS. In additional experiments, the chemical state of vanadium and titanium cations was examined by XPS and XANES. On the basis of obtained results, the mechanism for the selective oxidation of methanol to dimethoxymethane and methyl formate as well as the mechanism for the selective oxidation of ethanol to acetaldehyde and acetic acid were developed.

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Measuring an Electrocatalyst's Vital Signs: The Need for *In Operando* Studies

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Batteries, fuelcells, photocells and many other applications are powered by fundamental electrochemical processes. Compared to surface science under UHV conditions, electrochemical systems combine a wide variety of additional effects. These range from the presence of an electrolyte and a multi-component environment to reaction conditions such as finite temperature, pressure, and electrode potential. Due to this complexity our knowledge of the ongoing processes is mostly limited to the macroscopic regime. However, nowadays interface-sensitive experiments together with theoretical modeling are able to provide deeper insights into structures and processes at the atomic level. This fundamental knowledge makes the development and/or design of improved (electro)catalysts possible.

Following a general overview of electrochemistry, I will compare the concepts of surface science and electrochemistry in detail, addressing both their similarities and differences. Using apparently simple electrocatalytic reactions as model systems, the effects of the reactive surrounding as well as environmental parameters will be successively explored [1,2]. It turns out that pure and perfect catalyst models, which are often used in literature, are in many cases insufficient.

Finally, these concepts will be extended from single crystals to the nanoregime, where nanostructured surfaces and particles are often used for electro-catalytic reactions. Taking transition metal alloys as an example, we will show that nanoparticles are not rigid objects but often change their morphologies and compositions under reaction conditions [3-5]. Thus, understanding the dynamic nature of these catalysts is crucial in our efforts to further extend our ability to rationally design multi-component (electro-)catalysts.

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About Active Sites and Spectators in Heterogeneous Catalysis

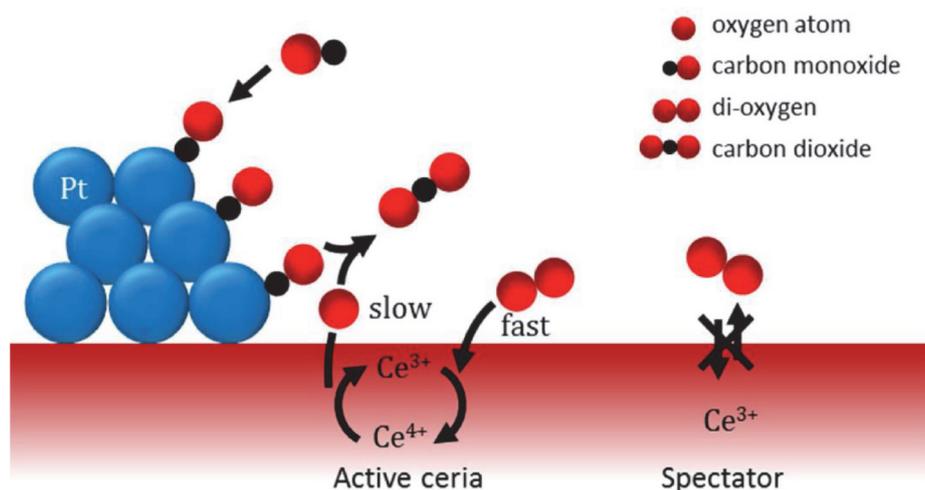
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The focus of my talk will address the difficulty to measure the structure of catalytically active sites in heterogeneous catalysis. Most catalysts have large structural heterogeneity and the identification of what constitutes the active site is very complex. In supported metal catalysts, the support cannot be assumed to be an inactive component. Ceria is a well-known support that is able to store and release oxygen. For that reason, it finds application in reactions that involve redox reactions. Upon oxygen release, part of Ce^{4+} reduces to Ce^{3+} . The ceria oxygen-storage capacity and the presence of Ce^{3+} are often related to catalytic performance, however quantitative descriptions are lacking. By building on recently developed spectroscopic tools based on x-ray absorption and emission spectroscopy on the one hand and electron spectroscopy on the other, we have been able to quantify the role of Ce^{3+} in the oxidation of carbon monoxide over Pt/CeO₂. Transient measurements with high time resolved x-ray emission spectroscopy showed the existence of Ce^{3+} as spectator and as active intermediate in the reaction. The consequences of these observations on the relationship between oxygen storage capacity and the presence of Ce^{3+} on catalytic performance will be discussed.



Simplified scheme of the role of Ce^{3+} in the carbon monoxide oxidation over Pt/CeO₂

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Soft and Hard X-ray Ambient Pressure Photoelectron Spectroscopic Characterization of the BiVO₄/Potassium Phosphate Interface for Water Splitting Applications

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The material requirements for water splitting photoelectrodes are quite stringent. The material must absorb a large fraction of solar photons, have conduction band and valence band positions that straddle the water oxidation and reduction potentials, and be stable for years under illumination in aqueous electrolyte solution [1]. Due to their potential long term stability in aqueous solution, ease of synthesis, and low cost of production, semiconducting metal oxide materials have recently garnered much attention for use as photoelectrodes for photoelectrochemical water splitting [1]. Most studies have focused on binary semiconducting oxide materials [1, 2, 3]. To date, no binary oxide material has met all the criteria listed above. This has driven researchers to expand the materials database and investigate more complex multinary oxides [1].

Among the multinary semiconducting metal oxides being explored for solar water splitting, bismuth vanadate, BiVO₄, is currently viewed as one of the most promising candidates. The monoclinic scheelite phase of BiVO₄ has a band-gap of 2.4 eV which implies that 11 % of the solar spectrum can be absorbed. Recent reports of >5 % solar to hydrogen conversion efficiency under AM 1.5 illumination makes it the most successful oxide photoanode to date [4, 5]. An additional attractive feature is that thin films of BiVO₄ can be produced with cheap, convenient methods, for example, through spray pyrolysis [6, 7].

Ambient pressure X-ray photoelectron spectroscopy has proven itself a useful technique for in-situ characterization of solid/electrolyte interfaces [8, 9]. With soft X-rays (AP-XPS) water adsorption from the gas phase at pressures up to a few Torr can be studied providing information about the early stages of solid/electrolyte interface formation [6]. The tender X-ray form (AP-HAXPES) can be used to directly interrogate a solid surface under an electrolyte film that is tens of nanometers thick [7]. We have used both photon energy regimes to study the BiVO₄/potassium phosphate buffer solution interface (BiVO₄/K-Pi). Our AP-XPS measurements on BiVO₄(010) single crystal surfaces indicate that the surface is fully hydroxylated by ~0.5 Torr, in direct contrast to density functional theory calculations. We have also investigated the open-circuit behaviour of the thin-film BiVO₄/bulk-like K-Pi

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electrolyte interface when illuminated with a solar-simulator. Upon illumination we observe changes in the BiVO₄ consistent with the production of a small amount of H⁺ and significant restructuring of the electrolyte near the interface. These results provide fundamental information about the general behaviour of water splitting photoelectrodes under illumination.

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Oral Presentations

OP-1 ÷ OP-36

Synchrotron and Neutron Studies of Operating Electrochemical Interfaces

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The operation of all electrochemical energy-related systems, such as supercapacitors, batteries, fuel cells, etc. depends largely on the processes occurring at electrochemical interfaces at which charge separation and chemical reactions occur. Evolution of structure and composition at the interface between electrodes and electrolytes affects all the device functional parameters including power and long-term performance stability. The analytical techniques capable of exploring the interfaces are still very limited, and more often only ex situ studies are performed. This sometimes leads to loss of important pieces of the puzzle hindering the development of novel technologies, as in many cases intermediates and electrochemical reaction products cannot be “quenched” for post process analyses. Techniques capable of operando probing of electrochemical interfaces by photons and neutrons have become an extensively growing field of research. The presentation sums up highlighting approaches, developing ideas and our recent finding on the adaptation of x-ray photoelectron- and absorption-, vibrational spectroscopies, x-ray and neutron diffraction reflectometry in electrochemical studies.

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Standardized Electrochemical Measurements of Catalysts for the Oxygen Evolution Reaction

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Electrochemical water splitting for hydrogen production is widely seen as a key technology in a sustainable energy scenario [1, 2]. In this context, the electrochemistry of oxygen is of greatest significance [3]. Specifically, the oxygen evolution reaction (OER) is of profound interest as it is the kinetically more sluggish half reaction in water electrolysis.

A considerable amount of research has been directed at replacing catalysts for OER based on pricey precious metals. However, it seems that a breakthrough is not yet reached and a deep understanding of structure-function relationships is not yet established. A contributing factor to this gap in knowledge might be the fact that a lot of data in the literature is not easily comparable. One of the standard techniques to evaluate new electrocatalysts for OER is the rotating disk electrode technique (RDE [4]). There is, however, no commonly accepted standardized protocol to conduct these measurements and, in consequence, drawing conclusions from a set of different studies is not straightforward.

We will present our efforts in establishing a standardized protocol for the electrochemical evaluation of catalysts for OER in alkaline media. Based on existing attempts at standardization [5], we defined a series of measurements that allows for the evaluation of activity and, most importantly, stability of electrocatalysts. The between-lab reproducibility of a nickel cobalt oxide standard electrode using the proposed sequence is presented. Factors that influence the electrochemistry of OER catalysts such as binders and support material are discussed. An argument is made that rotating disk electrode experiments should only serve as the starting point of characterization. Further analysis both before and after electrochemical measurements as well as in-operando techniques are required to understand a given system in more depth. Examples for such additional structural analysis (SEM) and spectroscopic analysis (Raman spectroscopy) are presented.

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The Electronic Structure of Iridium Oxides Active in Water Splitting

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Iridium oxide based electrodes are promising candidates for electrocatalyzing the oxygen evolution reaction (OER) in acidic media. To gain a deeper understanding of their electronic structure, we combined X-ray photoemission spectroscopy (XPS) and the near-edge X-ray absorption fine structure (NEXAFS) of benchmark catalysts with theoretical calculations. Our investigations reveal a pre-edge feature in the O K-edge of the catalytically more active X-ray amorphous IrO_x, along with additional intensity at higher binding energies in the Ir 4f spectrum when compared to rutile-type IrO₂. We identify the former as O 2p hole states (formally O¹⁻) and the latter as formally Ir^{III} species.[1]

Using CO oxidation, we found that the additional oxygen species identified in amorphous IrO_x are extremely electrophilic, oxidizing CO to CO₂ at room temperature. The exceptional reactivity of these formally O¹⁻ species is suspected to play a critical role in the OER by reacting with OH/H₂O to form the OOH intermediate, which likely explains the exceptional OER activity of amorphous IrO_x. Like in biological water splitting, the electrophilic oxygen in IrO_x seems to be an optimal precursor site for the nucleophilic attack of (preadsorbed) water during the O–O bond formation process. The creation of electrophilic oxygen in photosystem II is enabled by the easy accommodation of different oxidation states of the coordinated Mn ions. Likewise flexibility in the oxidation state for iridium is needed for electrophilic oxygen formation in iridium, which is apparently found in IrO_x. [2]

To follow the formation of such highly defective amorphous iridium oxide surfaces on metallic iridium during the OER and as a function of the applied potential, we have developed an electrochemical cell based on the proton exchange membrane Nafion[®][3] compatible with the Near-Ambient-Pressure XPS setup of the ISS beamline at the synchrotron BESSYII/HZB.

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The Role of Ir-Oxohydroxides for the Oxygen Evolution Reaction

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A successful transition towards renewable energy sources (RES) requires efficient energy storage solutions in order to ensure a stable power supply. In this regard, chemical energy storage through H₂-production has been identified as the most adaptable technological solution.^[1] Proton exchange membrane (PEM)-based electrolyzer setups for water splitting allow for the production of high-purity H₂ at high pressures. However, PEM create a highly acidic, corrosive environment, which threatens the stability of the electrocatalytic electrode coatings. This is especially crucial for the efficiency-limiting anodic oxygen evolution reaction (OER). So far, Ir-based materials remain the only candidates for stable, high-current-density OER-catalysis under acidic conditions.^[2] Due to Ir-scarcity, reduction of Ir-loadings and stability against corrosion remain key-targets of OER-catalyst design. Recent findings by P. Strasser et al. emphasized the relevance of XRD-amorphous Ir-oxohydroxide-species, both highly active and relatively stable under acidic OER-conditions.^[3] Crystalline rutile-IrO₂ prepared at higher temperatures exhibited dramatic activity loss. This highlights the importance of the nature of the prepared Ir-phase for OER-performance. In order to study the superior electrocatalytic properties of the little understood class of amorphous Ir-oxohydroxides, we designed a hydrothermal synthesis procedure. We found a strong influence of synthesis conditions on the chemical nature of the produced Ir-oxohydroxides and used this family of compounds to establish functional links between structural characteristics and observed OER-performance.

XRD-analysis showed that the oxidic compounds produced by hydrothermal treatment of hydrolyzed Ir-precursors are amorphous and thermogravimetric analysis confirmed the strongly hydrated oxohydroxide form of Ir. Assessment of OER-performance was conducted using linear sweep voltammetry (LSV) for activity and galvanostatic measurements for stability. For electrode loadings below 100 $\mu\text{g}_{\text{Ir}}\cdot\text{cm}^{-2}$, our best samples outperformed the benchmarks recently reported by McCrory et al.^[4]

Mixed Ir-oxidation states have been evoked as a key feature of high-performance Ir-based OER-electrocatalysts.^[5] We could assign a mixed Ir^{III/IV}-oxidation state to the sample bulk via temperature-programmed reduction. The analysis of XPS spectra obtained at the BESSY synchrotron radiation source was rendered possible by a thorough theoretical model, which predicts the particular energy loss features of Ir-oxides, allowing for rational Ir-speciation.^[6] The results confirmed a mixed Ir^{III/IV}-oxidation in the near-surface region. Our theoretical model also allowed for the analysis of the NEXAFS of the O K-edge. Characteristic resonance features were assigned to formally O^I-species stabilized in Ir^{III/IV}-oxohydroxides. The electrophilic nature of these species was revealed using a stoichiometric titration reaction at room temperature based on CO as a probe molecule. Thus we could show

how the amount of available reactive $O^{\cdot-}$ -species is conditioned by the synthesis parameters and correlates with OER-performance. In an analogy to preactivated oxygen described for biological OER in photosystem II,^[7] this suggests that the superior electrocatalytic performance of Ir-oxohydroxides stems from their ability to accommodate formally $O^{\cdot-}$ -species, which could constitute sites for the nucleophilic attack of a second oxygen species, leading to the O-O-bond formation under OER-conditions. These findings are an important step towards a rational understanding of the superior OER-performance of XRD-amorphous $Ir^{III/IV}$ -oxohydroxides and pave the way towards rational electrocatalyst design in view of cost-effective acidic OER-electrocatalysis.

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Catalytic Properties of Titanium Dioxide Nanotubular Film Obtained by Anodization of Titanium Foil

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Nanostructural modifications of titanium dioxide are of great research interest, particularly in the development of promising functional media for renewable energy sources, efficient photoelectric transducers, memristor memory cells, photocatalysts for the removal of organic impurities, and others [1]. The optical gap width of the stoichiometric TiO₂ (> 3.1 eV) determines its photocatalytic activity under the action of the near UV radiation, which constitutes only several percents in the solar spectrum. In order to shift the spectral response to the visible region and enhance the catalytic activity, it is reasonable to decrease the optical gap width of the material, in particular due to generation of structural vacancies in the oxygen sublattice. The aim of this work was to synthesize a photocatalyst that is active under visible light and is based on nanotubular titanium dioxide film with nonstoichiometry and structural vacancies near the interface with titanium foil.

Nanotubular titanium dioxide film was synthesized on a Digma setup consisting of electrochemical cell, thermostat and power supply. The anodic oxidation was carried out with a substrate made of a 100 μm thick titanium foil BT1-0. Primary anodization was performed in a 1% solution of hydrofluoric acid in ethylene glycol. This was followed by etching of the titanium substrate in a solution of acids, washing in distilled water and acetone, and final drying at room temperature. Secondary anodization was carried out potentiostatically at a voltage of 20 V and time $t_A = 15-360$ min. The calcination temperature varied from 200 to 600°C; the calcination time was 1 hour. The photocatalytic activity of the samples was measured in a flow reactor, and reactants were identified on a FTIR spectrometer. The study was performed using LEDs with a maximum wavelength of 365 and 450 nm. The other reaction condition were as follows: T = 40°C, relative humidity 20%, acetone concentration 800 ppm, and flow rate 60 mL/min; TiO₂ Degussa P25 was used as a benchmark.

Fig. 1a shows typical SEM images of the surface of the synthesized sample. It has been shown that in the visible spectrum (ca. 490 nm) there is a broad dip of diffuse reflection, which is related to nonstoichiometry of amorphous titanium dioxide. Atomic defects represented by vacancies in the amorphous network lead to the formation of energy levels in the band gap of titanium dioxide, which in its turn results in the absorption of visible light

with a wavelength of ca. 490 nm. This exerts a pronounced effect on the catalytic activity of the film in the visible region.

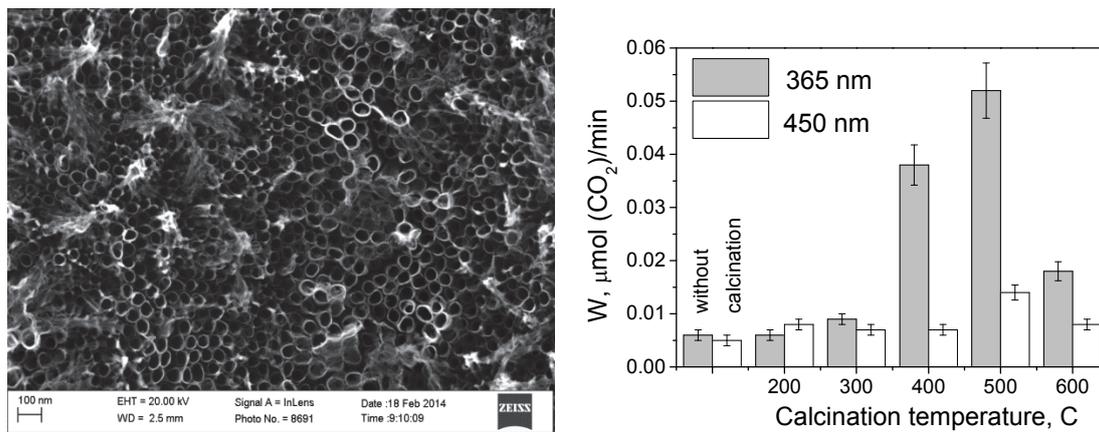


Fig. 1. SEM images of the sample anodized for 120 min (left); the activities of the synthesized nanotubes in the acetone oxidation under UV- and visible light (right).

In the preliminary experiments it has been shown that the best anodization time is 120 min; then the calcination temperature varied from 200 to 600°C. Fig. 1b shows the activity of the synthesized samples under UV- and visible light irradiation.

One can see (Fig 1b) that under UV-light the oxidation rate grows with the calcination temperature until 500°C and then drastically falls for the sample with the calcination temperature 600°C. Under visible light the highest activity is achieved by the sample calcined at 500°C too. Calcination at temperatures 200-500°C likely leads to the formation of anatase that can increase the photocatalytic activity. At higher temperatures non-active rutile phase is formed resulting in the decrease in the acetone degradation rate. Note that under visible light the highest activity for nanotubes was 14 nmol min⁻¹ g⁻¹ whereas for Degussa P25 this value was equal to 1.6 nmol min⁻¹ g⁻¹; under UV irradiation the catalytic activities were equal 52 and 64 nmol min⁻¹ g⁻¹ for nanotubes and Degussa P25, respectively. Therefore, nanotubular titanium dioxide films can be considered as an active photocatalysts for the oxidation under visible light.

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Photocatalytic Oxidation of VOC's over Uranyl Modified Catalysts under UV and Visible Light

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Methods of photocatalytic purification of water and air widely are developed over last decades [1]. Titanium dioxide is well-known photocatalyst because it is the most active metal oxide semiconductor among heterogeneous photocatalysts; it is inexpensive, chemically and photochemically stable and could provide photooxidation of almost any organic species. Unfortunately, titanium dioxide is active only under UV irradiation ($\lambda < 380$ nm) which occupies only about 4% of the solar light spectrum [2]. At the same time visible light ($\lambda > 400$ nm) occupies about 43% of the Sun irradiation. This is the reason why many researchers are trying to develop visible-light-driven photocatalysts.

It is well known that uranyl ions could be sensitized by visible light and after excitation the oxidizing potential of uranyl ions becomes as high as 2,6-2,7 V [3]. At the same time the gas phase photocatalytic oxidation of organic species with uranyl-modified photocatalysts are weakly investigated. Spectral characteristics as well as uranyl quantity, nature of the support and electronic structure are not studied. These questions were the subject of current research.

Photocatalyst samples were synthesized by incipient wetness impregnation method with the use of TiO₂ (anatase), CeO₂, γ -Al₂O₃ and SiO₂ as support. The UO₂(NO₃)₂ content was varied from 0.2 to 10 wt.%. The activity of catalysts was measured in the reaction of acetone and ethanol vapour photocatalytic oxidation in the static and flow reactors at room temperature. The high pressure Xe-lamp, the 450 and 365 LEDs were used as the light source. The visible regions of the Xe-lamp irradiation spectrum was controlled with the cutoff optical glass filters. Ethanol, acetaldehyde and CO₂ gas concentration were measured with the FTIR spectrometer equipped with the long-path gas cell. UV-VIS spectroscopy with the diffuse reflectance attachment, XPS spectroscopy and fluorescence methods were used for additional photocatalysts characterization.

Results and discussion

All the synthesized photocatalysts were active in the reactions of ethanol and acetone vapour photocatalytic oxidation under visible light up to 500 nm wavelength. In the gas phase acetaldehyde was registered as the intermediate of ethanol photocatalytic oxidation. CO₂ was registered as the final products of both acetone and ethanol photocatalytic oxidation (Fig. 1, **a**). Acetic acid and acetaldehyde were observed as surface intermediates.

Although pure unmodified TiO₂ was not active under visible light ($\lambda > 420$ nm) it was found to be the best support for uranyl nitrate and the UO₂(NO₃)₂/TiO₂ sample demonstrated highest photooxidation rate up to 500 nm incident light wavelength (Fig. 1, **b**) [4].

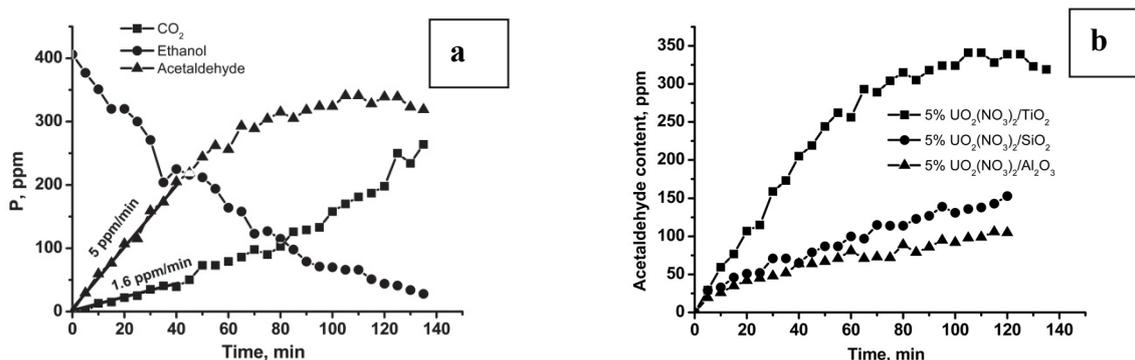


Fig. 1. (a) Kinetic curves of the ethanol vapor removal and CO₂ and acetaldehyde accumulation during the PCO of ethanol vapor in the static reactor under visible light; (b) Kinetic curves of the acetaldehyde accumulation during the ethanol PCO on the UO₂(NO₃)₂/TiO₂, UO₂(NO₃)₂/SiO₂ and UO₂(NO₃)₂/Al₂O₃ samples under visible light ($\lambda > 420$ nm)

Silica, alumina and titania samples with deposited uranyl nitrate were examined by the luminescence spectroscopy. It was found that UO₂(NO₃)₂/TiO₂ sample does not luminesce when excited with UV light (320 nm) and only slightly luminesce if excited with visible light (430 nm) unlike the uranyl modified silica and alumina which luminesce strongly in both cases.

Suggestion was made that uranium species becomes more labile if deposited on the surface of TiO₂ and less labile if deposited on the SiO₂ or Al₂O₃ surfaces and uranyl liability correlates with photocatalytic activity.

The subsequent experiments by the XPS in situ method demonstrated that indeed on the surface of titania samples U⁶⁺ is easily reduced to U⁴⁺ under UV illumination and its backward reoxidation under O₂ exposure is quick. At the same time on the surface of silica and alumina samples U⁶⁺ is hard to be reduced to U⁵⁺ under UV illumination and backward reoxidation is negligible.

Possible explanation of the increase of uranyl photocatalytic activity when it is deposited onto the TiO₂ surface is its photophysical interaction with the TiO₂ energy states.

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***Ab Initio* Modelling of Defects in the Bulk and at Surfaces of Oxide Semiconductors at Realistic Temperature, Pressure, and Doping Conditions**

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An important parameter influencing defect concentration and defect charge states is doping. It is useful to distinguish local and global effects of doping [1,2]. The local effects occur due to a direct chemical-bonding interaction and lattice relaxation around the dopant. The global effect is controlled by the presence of charge-carriers (electron chemical potential) and charge separation on meso- to macroscopic length scales.

Using *ab initio* atomistic thermodynamics [3,4], we show [5] that (and how) the global effect of doping influences the transition levels and formation energies of defects at interface significantly. In our approach, the energy density of the electric field is considered as part of the free energy of the system. Charged defects at surfaces are modelled using a variant of virtual crystal approximation [6]. Two main contributions to the defect formation energy are identified: (i) the interaction of a charged defect with the compensating charge and (ii) the shift in the Fermi level due to the space-charge formation. Both contributions are present in periodic model calculations, but must be corrected for realistic defect concentrations.

We also discuss the interplay between defect site coordination and charge-carrier trapping at oxide surfaces, and the prospects and pitfalls of tuning the fraction of the exact exchange in hybrid functionals to improve the description of defect formation.

Our results for doped MgO clearly show that the global effect of doping on interface chemical properties can be significant, so that doping (intentional or not) must be considered as a thermodynamic variable along with temperature and pressure.

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Insights into O₂ Activation on Nanoporous Gold from a DFT Study

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About a decade ago, it was demonstrated that nanoporous gold (np-Au), prepared by dealloying silver from a gold-silver alloy, can promote CO oxidation with O₂ and a range of other oxidation reactions [1-4]. It has been debated whether the remarkable catalytic properties of np-Au are mainly due to its structural features or whether the residual silver remaining in the material after dealloying is decisive for the reactivity, especially for the activation of O₂ [1,5]. It has been suggested [1] and supported by theoretical studies [5-7] that Ag impurities can facilitate the adsorption and dissociation of O₂ on np-Au.

While XPS and TPD study of active np-Au foams [8] indicated that the chemically active form of oxygen on np-Au is atomic surface O produced via O₂ dissociation, theoretical studies [5-7] predict quite a high activation barrier for O₂ dissociation on bimetallic Au-Ag catalysts. Even though Ag impurities can sizably increase the adsorption energy of O₂, calculations suggested that relatively large local Ag ensembles are needed to significantly change the O₂ dissociation barrier [5,6]. And even then the calculated activation energy seems to be too high, > 0.65 eV.

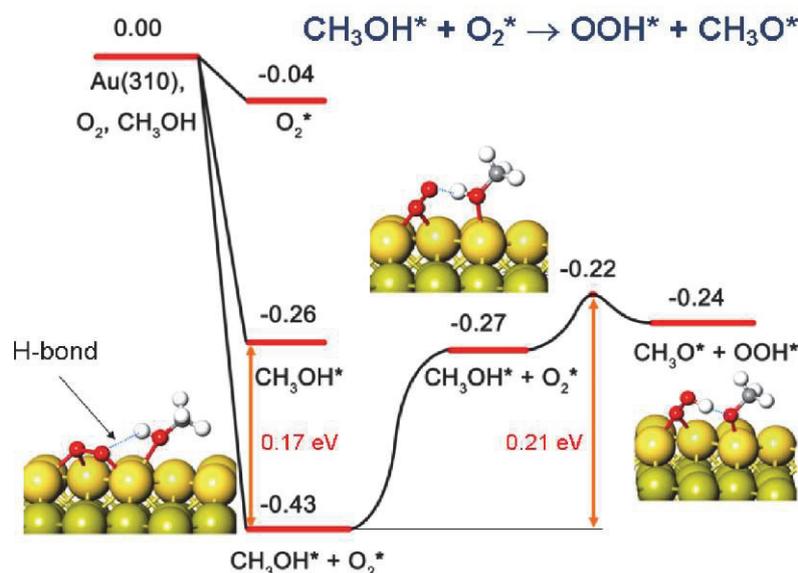


Fig. 1. Reaction energy profile (eV) and atomic geometries of the reactants, products and intermediates for the direct reaction between co-adsorbed CH₃OH and O₂ on the Au(310) surface. Color coding: Au, yellow (upper terrace) and pea green (lower terrace); C, gray; O, red; H, white.

In this work we present alternative routes for O₂ activation via its direct reaction with CO, H₂O, or CH₃OH on nanoporous gold modeled by stepped Au(321) and Au(310) surfaces with Ag impurities. The DFT calculations were carried out with a plane-wave based method using the gradient-corrected PBE exchange-correlation functional. For details see Refs. [5,6]. In all

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of the reactions considered, surface atomic O is ultimately generated via a sequence of elementary steps with calculated low-lying transition states of <0.40 eV with respect to co-

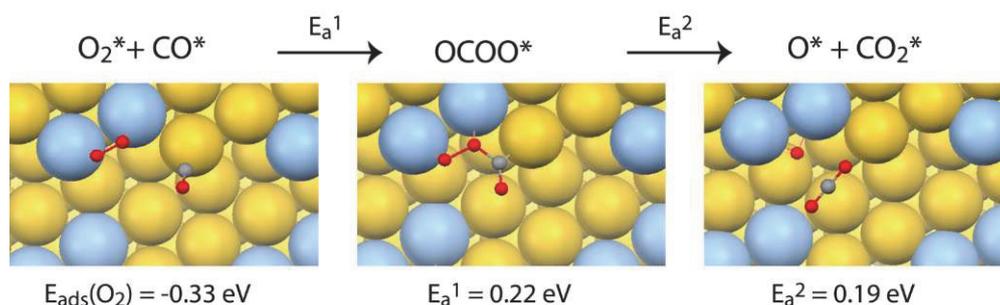


Fig. 2. Atomic geometries of the reactants, products, and surface OCOO* intermediate for the direct reaction between co-adsorbed CO and O₂ on the Au(321) surface with Ag impurities. Color coding: Au, yellow; Ag, blue; C, gray; O, red.

adsorbed reactants, see Figs. 1 and 2. Ag impurities are shown to increase the adsorption energy of O₂ and hence the probability of a surface-mediated reaction.

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Strong Metal Support Interaction as a Key Factor for Au Activation in CO Oxidation

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Due to its inert nature, gold has traditionally been ignored as a catalyst. However, ever since Haruta et al.'s discovery that gold nanoparticles (Au NPs) supported on metal oxides are catalytically active [1], the nature of the active sites on gold is still a matter of active debate in the literature [2]. Here we report on our recent studies of the catalytic properties of Au NPs on different supports during CO oxidation.

All measurements were performed in the near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) endstation at the ISSS beamline at HZB/BESSY II (Berlin, Germany). Au containing samples were characterized using *in-situ* XPS and *ex-situ* EELS, SEM and TEM. CO and O₂/O₃ were introduced to the chamber at different ratios while keeping a constant pressure of 0.3 mbar at 100°C. The catalytic performance of the catalysts was further tested in a CO-reactor under ambient pressure.

Our *in-situ* measurements show Au NPs on oxygen-free supports (HOPG, functionalized CNTs, Au foil) do not show any catalytic activity irrespective of the NPs' size, the type of support, and the method of synthesis [3]. In contrast, Au NPs on oxygen containing supports show high catalytic activity, which depends on the method of preparation and can be associated with the formation of an ionic Au species. Only samples prepared by deposition-precipitation showed significant CO conversion at low temperature, despite the large size of the Au NPs (~20 nm). XPS reveals the presence of two Au species (metallic and ionic Au) on the surface of the active Au/TiO₂ and Au/Fe₂O₃ samples. The binding energy shift of the ionic Au depends on the support and is 0.6 eV and 0.9 eV higher than metallic gold for Au/TiO₂ and Au/Fe₂O₃, respectively. TEM images indicate the formation of an overlayer on Au particles after CO oxidation. EELS spectra confirm such overlayers have the composition of the transition metal oxide support [4]. DFT calculations performed on the Au/TiO₂ show that oxidized TiO₂ and Au interact weakly, with calculated work of adhesion (W_{∞}) < 0.1 J/m², whereas reduced and defective TiO₂ supports show a strong metal-support interaction, increasing W_{∞} to ≥ 1.0 J/m². DFT predicts the Au 4f shifts of the ionic Au mirror these changes in adhesion and are 0.0 eV, 0.2 eV, and 0.7 eV for oxidized, reduced, and defected TiO₂, respectively.

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Quasi In-Situ Catalytic Studies Using a TEM Grid Microreactor

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Conventionally, catalysts are analyzed in the transmission electron microscope (TEM) under static conditions in the vacuum. However, catalysts surfaces dynamically response to the reaction conditions. In addition, comparing TEM images before and after the catalytic reaction may give conclusions that are difficult to verify, because of the inhomogeneous conditions along the catalyst in normal fixed bed reactors [1]. For obtaining relevant information it is advisable to study the material under catalytic relevant conditions (gas composition, pressure, temperature) which also includes the monitoring of conversion. Therefore, in-situ TEM approaches, such as environmental TEM (ETEM) or microelectromechanical systems (MEMS)-based gas cell TEM holders, were developed. They allow the direct observation of the dynamic changes of a catalyst during the prevailing time of a reaction [2]. However, drawbacks regarding the reaction pressure and fast dynamics give rise to pressure gaps and may limit the resolution, respectively.

To overcome these limitations we have developed a TEM grid microreactor that allows a decoupling of the catalytic reaction and the imaging process. This quasi in-situ method combines relevant and well-controlled conditions for all catalyst particles at ambient pressure with high resolution imaging of exactly the same particles. In order to avoid the exposure to ambient air, a secure transfer of the catalyst to and from the TEM can be guaranteed via the glovebox and vacuum transfer holders. Furthermore, the catalytic conversion can be followed by using an ultra-sensitive proton-transfer reaction mass spectrometer (PTR-MS).

Here, we present the utilization of this microreactor in the CO oxidation over metal catalysts. For instance, identical location imaging of active Pt nanoparticles (proven by PTR-MS measurements) reveals structural changes, which are induced by the catalytic process.

In conclusion, the microreactor complements the state of the art in-situ imaging, where one can study the structural dynamics, by delivering catalytic relevant kinetic information, which can be coupled to changes on the atomic scale.

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Structure and Catalytic Properties of $\text{MnO}_x/\text{Al}_2\text{O}_3$ in the Reaction of CO Oxidation

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Manganese oxides are of interest to industry, since they are considered as promising catalysts for total oxidation. For the alumina-manganese system, the effect of thermal activation has been observed. It appeared that the specific catalytic activity in the model oxidation reactions increases after calcination at high ($900 \div 1000$ °C) temperatures. The phenomenon of thermal activation is accounted for by phase changes in the system $\text{MnO}_x/\text{Al}_2\text{O}_3$ due to interaction between initial oxides accompanied by the transition in the oxidation state of manganese cations. By varying of the calcination temperature and treatment media one can get purposely specific changes in the phase composition, microstructure and catalytic properties of the catalysts.

The catalysts were prepared by co-precipitation and then the product was calcined in Ar or air at temperatures of $700 \div 1200$ °C. It was found that increase in the calcination temperature to $950 \div 1000$ °C lead to the growth of catalytic activity for both series, especially for catalysts calcined in air. An increase in the catalytic activity of the catalysts calcined in Ar was related to the formation of $\text{Mn}_{3-x}\text{Al}_x\text{O}_4$ cubic spinel which was stable during specimen cooling in inert atmosphere. It was found that active component in the air-calcined catalysts was formed via decomposition of the high-temperature precursor (cubic spinel $\text{Mn}_{3-x}\text{Al}_x\text{O}_4$) followed by the appearance of aggregates consisting of imperfect $\text{Mn}_3\text{O}_{4+\delta}$ oxide and amorphous Mn-Al-O phase. The decomposition was accompanied by the formation of weakly bound oxygen which appears to be active in oxidation reactions. The structure of the active component was directly related to the composition of the high-temperature precursor - the higher the concentration of manganese cations are in the $\text{Mn}_{3-x}\text{Al}_x\text{O}_4$ cubic spinel, the more Mn_3O_4 and weakly bound oxygen appear in the decomposition product.

The $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalysts were prepared by a mixing method with the introduction of mechanically activated components into a paste of aluminum hydroxide followed by calcination in air at 950°C. The catalysts contained a mixture of the phases of $\beta\text{-Mn}_3\text{O}_4$ (Mn_2O_3), $\alpha\text{-Al}_2\text{O}_3$, and $\delta\text{-Al}_2\text{O}_3$. The presence of low-temperature $\delta\text{-Al}_2\text{O}_3$ suggested the incomplete interaction of manganese and aluminum oxides. It was found that the catalytic activity of $\text{MnO}_x/\text{Al}_2\text{O}_3$ depends on the degree of interaction of the initial reactants, and its value is correlated with the amount of $\beta\text{-Mn}_3\text{O}_4$ in the active constituent. The increase in interaction between the aluminum- and manganese-containing components is provided by variation of mechanical activation parameters: reducing the size of balls, optimization of time, the activation of both components simultaneously.

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Mechanism of Carboxylic Acids Formation under Oxidation of Functional Hydrocarbons over Vanadia-Titania Catalyst

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Carboxylic acids are very common and an important class of organic compounds. Some of them are consumed in a pure form as foods (acetic, butyric acid etc.) or as pharmaceuticals (nicotinic, succinic, and ascorbic acid). In a large scale, carboxylic acids are used in the manufacture of plastics, polymers, artificial fibers, aromatic substances, and insecticides, and in the light, food and pharmaceutical industries. Conventional liquid-phase syntheses of carboxylic acids are complicated multistage processes. In recent years, there is a clear trend towards heterogenisation of such processes.

In order to establish the regularities of catalysts selection, a detailed study of the reaction mechanism is necessary. In this work, we investigated the oxidation of formaldehyde to formic acid, ethanol oxidation to acetic acid, and isomeric picolines (2-, 3-, 4-methylpyridine) oxidation to corresponding carboxylic acids over vanadium-titanium oxide catalysts by in situ infrared spectroscopy. The vanadium-titanium oxide catalysts used are highly selective in all reactions under study. The oxidation of formaldehyde was studied at 70-200 °C, the oxidation of ethanol was investigated at 100-300 °C, the oxidation of picolines was carried out at 120-300 °C. The transformation of surface intermediates was investigated both in the presence of oxygen in the reaction medium, and in the oxygen-free atmosphere (He).

The mechanism of carboxylic acid formation includes the following steps:

- the generation of surface species molecularly bound through interaction of an atom of the original molecule with a high electron density (O in the case of aldehyde and alcohol reagents and N atom of pyridine ring in the case of picolines) with the highly charged electronegative cation of active center (V^{5+});
- the heterolytic dissociation of C-H bond of CHO-group of aldehyde, CH_2O -group of alcohol or CH_3 -group of picoline isomers;
- the oxidation of hydrocarbon moiety accompanied by the reduction of the active center, and the interaction of the oxidized reactant moiety with the catalyst oxygen;
- the formation of carboxyl surface complex (formate, acetate, nicotinate, picolinate, and isonicotinate) stabilized at reduced active sites;
- carboxylate decomposition and acid desorption;
- the reoxidation of the catalyst in a separate step according to redox mechanism (in the case of 4-picoline oxidation) or in the joint stage of oxygen adsorption and acid desorption in accordance with an associative mechanism in the other cases.

Carboxylate complexes are surface salts; their carbon skeleton has a structure of anionic part of corresponding acid.

The oxygen is involved in the reactions under study in two forms: lattice oxygen participates in the formation of surface complexes, whereas the oxygen of gas phase participates in the reoxidation of the cations of the active center and in the oxygen vacancies filling.

The condition of the selective reaction is the presence of strongly bound oxygen (at least 60 kcal/mol according to G.K. Boreskov [1]) and the high mobility of bulk oxygen. These characteristics are realized on vanadium-titanium oxide catalysts [2].

The rate of acids release under reaction conditions (the presence of oxygen in the gas phase) significantly exceeds the rate of carboxylate decomposition in the absence of oxygen. Thus, the reoxidation of the catalyst and the acid release proceeds in the joint stage. This is what we call the modified redox mechanism of Mars-van Krevelen.

The water plays a special role in the selective oxidation of hydrocarbons to acids. Its role is manifold:

- the adsorption of water generates strong Brønsted acid centers, which are additional sites of adsorption and activation of the oxidizing reagents of the basic character;
- the acid sites are also protons donors in the formation of carboxylic acid from conjugate bases (carboxylate);
- water accelerates the desorption of the acid hydrolysing the surface and thereby displace the carboxylate from the active center.

We affirm that, despite the different structure of the oxidized groups (CH_3 , CHO , or CH_2O) and the chemical nature of the oxidized reagents, the mechanism of the acids formation is common. The key steps in the mechanism are the formation of carboxylate (direct precursor of the carboxylic acid) and the decomposition of the surface complex in the joint stage with the catalyst reoxidation. According to DFT calculations [3], the catalyst reoxidation results in the weakening of carboxylate-vanadium bond leading to easy acid desorption.

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Preparation of Model Catalysts by Atomic Layer Deposition

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Nanomaterials based on supported V_2O_5 has been previously shown to exhibit high activity in the selective oxidation of formaldehyde to formic acid [1], methanol to methyl formate and dimethoxymethane [2], and the selective oxidation of ethanol to acetaldehyde and acetic acid [3]. The most activity in the selective oxidation of methanol to methyl formate and dimethoxymethane was demonstrated the monolayer VO_2/TiO_2 catalyst. To clarify the structure of the active sites of vanadium-titanium oxide catalyst the model catalyst was investigated. To prepare the model monolayer VO_x/TiO_2 catalyst we have used the atomic layer deposition (ALD) method. The $TiO_2(110)$ single crystal was used as a support, before ALD process the crystal was cleaned via multiple cycles of Ar^+ sputtering and annealing in UHV at $730^\circ C$. The surface cleanness and smoothness of $TiO_2(110)$ were controlled by XPS, HREELS, and LEED. Vanadium (V) oxytriisopropoxide (VTIP) was used as a precursor. The deposition cycle consisted of exposition of the sample in the VTIP vapour at $190^\circ C$ to form a layer of adsorbed precursor molecules and subsequent treatment in oxygen at $350^\circ C$ to remove the carbon-containing ligands from the surface.

The process of growth of vanadium oxide films was studied by LEED, XPS, and HREELS. The formation of epitaxial layer of vanadium oxide film on the surface of $TiO_2(110)$ crystal was evidenced by blurring reflections on the LEED-image of the single crystal surface. XPS study revealed that after the VTIP deposition vanadium presents in the fully oxidized state (V^{5+}) and partially reduced V^{4+} and V^{3+} states. The further treatment in oxygen results in the full oxidation of vanadium to V^{5+} . According to our estimation, 0.25 monolayer of VO_x forms on the crystal surface during one deposition cycle. It was shown that the monolayer $VO_x/TiO_2(110)$ catalyst is thermally stable up to $350^\circ C$ in the oxygen atmosphere. Adsorption of methanol on the model catalyst was studied by XPS, LEED, HREELS and PM IRAS. It was shown that methanol dissociates to form methoxy and hydroxyl groups starting with room temperature. Thus, deposited VO_x film could be used as a model catalyst to study selective oxidation of methanol.

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Single Site Vanadium Oxides on Tailored Multi-walled Carbon Nanotubes by Atomic Layer Deposition

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The oxidative dehydrogenation (ODH) of ethylbenzene is an industrial relevant process for the production of polystyrenes. The catalytic reaction is enhanced by carbonyl surface groups of carbon materials and even more by the presence of vanadium oxide.[1]

Multi-walled carbon nanotubes (MWCNT) exhibit beneficial properties like high thermal stability and high surface area for the application in catalysis.[2] The modification of the MWCNT can be realized by acidic and gaseous treatment resulting in distinct ratios of different functional groups and structural defects. The created functional groups serve as anchoring sites for the reaction with vanadium precursor in an atomic layer deposition (ALD) process to form covalent bonds between MWCNT and vanadium oxide in contrast to rather structural defect stabilized cluster formation by simple impregnation techniques.[3] The activity of the different surface functional groups for the ODH process or the reaction with the vanadium precursor varies due to their chemical potential. A detailed analysis of the type of generated functional groups and their reactivity with the vanadium precursor is required to gain a fundamental understanding between these correlations. The well-established thermo-gravimetric mass spectrometry (TG-MS) method was modified with a non-linear temperature program to separate the decomposition of functional groups and therefore enable the precise determination (Figure 1). The ALD process is self-limiting due to the reaction of the precursor with distinct functional groups and enables therefore the formation of single-site vanadium oxides (Figure 2). The specific formation of single-site metal oxides is bridging the gap between model and real catalysis.

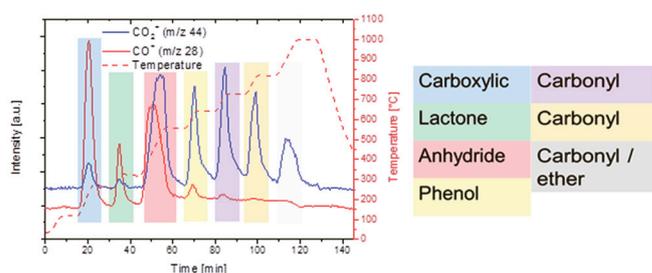


Figure 1: Non-linear thermogravimetric mass spectrometry enables the determination of different functional groups.

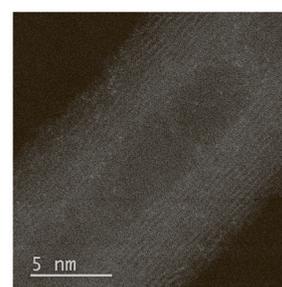


Figure 2: TEM image of single site vanadium oxides on MWCNT.

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Supercritical Fluids in Catalysis: Crossing a Fine Line between Homogeneous and Heterogeneous Catalysis

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A large number of industrial important heterogeneous catalytic processes are realized at elevated temperatures and pressures. Quite often it means that some chemical processes *de facto* take place in the environment being at sub- or supercritical conditions [1,2]. Therefore the detailed study of the physical and chemical peculiarities of the processes that occur at the atomic and molecular level in supercritical fluids (SCF) is the important step for the development of efficient catalytic processes requiring high temperatures and pressures.

The efficient and qualified application of supercritical fluids in catalysis demands the clear understanding of the peculiarities and influence of the SC media on the heterogeneous catalysts and the reaction mechanism in this environment. Carrying out the chemical processes at sub- and supercritical conditions it is necessary to concern not only about the temperature, pressure, reactant concentrations, but also about the local density as well as the local concentrations of the chemical agents taking part in the catalytic process since its variation can lead to significant changes in the rate constants of elementary reactions that ultimately affects the selectivity of the overall process [3]. Despite the huge amount of accumulated experimental data concerning the properties of the SCF, unfortunately it should be noted that the understanding of the mechanisms of heterogeneous catalytic reactions in supercritical media has a fairly weak predictive power.

Here we report the data concerning the phenomena associated with the increase of the local concentration of ions in sub- and supercritical fluids that precedes the cluster formation process followed by solid particles formation under certain conditions [4,5]. On the other hand by the example of silicon-based systems in supercritical methanol it was shown that the local concentration phenomenon could strongly influence (or even destroy) the heterogeneous systems leading to the formation of homogenous catalysts that could affect the mechanism of the reactions in SCF and increase the selectivity of the process [6,7]. The insight to the interrelation of homogeneous and heterogeneous systems in SCF allows us also to suggest an advanced approach for the synthesis of multicomponent catalysts [8].

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Pd-M Heterometallic Complexes as the Effective Catalyst Precursors for Highly Selective Liquid-Phase Hydrogenation of -C≡C- Bonds

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The selective hydrogenation of triple C≡C bonds is of significant importance for both the industrial chemistry and the fine organic synthesis. Pd-supported catalysts are the most common systems for the hydrogenation of alkynes giving a favourable activity but insufficient selectivity especially at high (> 80-90%) alkyne conversion. One of the most effective approaches for improving catalyst selectivity is modification of palladium by alloying with other metal but the serious problem is to obtain homogeneous Pd-M particles in a final catalyst and to avoid formation of bimetallic Pd cluster. To solve this problem the heterometallic Pd-M acetate complexes can be used as precursors. The complex structure allows retaining intimate contact between Pd and the second metal during all stages of catalyst preparation preceding bimetallic particle formation. This enables to avoid formation of monometallic Pd species, and hydrogenation proceeds over highly homogeneous Pd-M nanoparticles with high selectivity [1-3].

Our research is focused on the detail studying the performance of Pd-M supported catalysts in liquid-phase hydrogenation of terminal and internal alkynes. Commercial Lindlar catalyst was taken as a reference.

For all synthesized bimetallic catalysts we observe improvement of selectivity in the formation of olefinic compounds even at high alkyne conversions. Similar catalytic characteristics were demonstrated in comparison to those of commercial Lindlar catalyst. It should be mentioned that favourable activity/selectivity parameters are achieved at substantially lower palladium content and in the absence of toxic lead additive.

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Novel Catalysts with Improved Stability for Hydrotreatment of Biomass Pyrolysis Liquids into Valuable Products

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In the past decades the pronounced depletion of mineral resources have boosted the research interests towards intensive involvement of renewable resources into the energy market. Much attention is paid to the technologies allowing the production of biofuels and valuable products from lignocellulosic feedstocks. Crucial role in this research area is assigned to thermochemical processing of lignocellulosic biomass into liquid product also known as pyrolysis oil (PO) or bio-oil [1]. Among different types of PO application its co-processing with conventional oil refinery products on FCC units should be outlined. Since PO is a product of thermal degradation of main lignocellulosic polymers it has very complex chemical composition. Due to such complexity it becomes essential to improve operational properties of PO prior its integration into conventional oil refinery. The polarity and viscosity of the feed need to be reduced, and thermal stability should be increased. Catalytic hydrotreatment (HDO) is a potential way towards achievement of these goals.

Earlier studies have shown that the most promising approach to the bio-oil upgrading is a two-stage hydrotreatment at high pressures of hydrogen (10-20 MPa) [2]. In this case, the first stage at 150-250 °C ("stabilization stage") consists in the partial deoxygenation of bio-oil components and hydrogenation of highly reactive groups. It allows one to increase thermal stability of products thus obtained for their deeper deoxygenation at higher temperatures 350-400 °C corresponding to the second stage. Final products can be used as additives to fossil crude-oil in the standard oil-refining. The catalysts for PO hydrotreatment should meet a number of requirements, such as high activity in hydrogenation/hydrodeoxygenation reactions and high stability in aggressive feed. The development of catalysts presents an obstacle and is still in progress.

Recent studies have shown that catalysts with high Ni content (about 50 wt%) prepared by sol-gel technique are quite promising for pyrolysis oil upgrading [3-5]. This choice was associated with well-known activity of Ni in hydrogenation reactions. Besides the driving force was the necessity to provide high specific surface area of catalyst after its modification, as modifying agents mostly do not show self-activity in target reactions. Subsequent works have shown that introduction of P-/Mo-containing modifiers into Ni-based systems by wet impregnation significantly improves those mechanical strength, resistance to corrosion, and enables lowering of coke deposits [6]. In the present study the first stage of PO hydrotreatment ("stabilization") was performed both in batch and continuous modes. The catalysts modified by P and Mo directly at the sol-gel preparation stage were used in the process. The effect from variation of modifying agents content was investigated and systems

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with optimized composition (in terms of activity and stability) were found. A number of physicochemical techniques (XRD, HRTEM, CO chemisorption, etc.) were used to characterize the catalysts before and after the reaction to provide understanding of nano-scale transformations taking place. In addition the kinetics of catalysts leaching in model acidic solution (1M acetic acid) was studied. A remarkable result was obtained when the samples were characterized after acidic treatment. First of all it turned out that the catalysts are subjected to reoxidation when contacting with boiling acid. Secondly it was noted that their active surface area became developed after such treatment. This result can be profitable in terms of catalyst activation prior to the reaction or even *in situ* during hydrotreatment process. Finally, pilot testing (BTG, The Netherlands) of catalysts was performed and showed significantly prolonged operation (>1100 hours) in the case of modified Ni-based systems in contrast to those non-modified (150-200 hours of operation).

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Synergetic Effect of Metal and Acid Sites of Supported Ni₂P Catalysts in Methyl Palmitate Hydrodeoxygenation to Hydrocarbons

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The transition metal phosphides are known to be a promising alternative to sulfide or noble-metal-based catalysts for the hydrodeoxygenation (HDO) of oxygen-containing compounds from renewables. Among them the silica-supported Ni₂P system attracts the attention of researches due to the high HDO activity and stable behavior. Hydrodeoxygenation of fatty acids esters, model compounds of triglyceride-based feedstocks, was stated to proceed through a complicated reaction network including the several metal- and acid-catalyzed reactions (dehydrogenation, hydrogenolysis of C-O and C-C bonds, hydrolysis and dehydration). It was shown earlier that aliphatic ester transformation is the rate-limiting stage of the overall HDO reaction over silica-supported Ni₂P catalysts [1]. Taking in mind the different possible routes of methyl palmitate hydroconversion (metal-catalyzed hydrogenolysis or acid-catalyzed hydrolysis) we speculated that enhancement of acidity of Ni₂P catalytic system could lead to acceleration of methyl palmitate (MP) hydroconversion. To verify the above hypothesis several catalytic systems with different acidity were compared in HDO of methyl palmitate: Ni₂P/SiO₂; physical mixture of Ni₂P/SiO₂ and alumina; alumina-supported Ni₂P. Besides, the acidity of Ni₂P/SiO₂ was changed by adjusting the preparation method.

Nickel acetate and diammonium hydrogen phosphate (phosphate precursor, *A*-samples) or nickel hydroxide and phosphorous acid (phosphite precursor, *I*-samples) have been used for the catalyst preparation by incipient wetness impregnation of SiO₂ and Al₂O₃ (grains of 0.25-0.50 mm) with an aqueous solution of the precursors, followed by temperature-programmed reduction in hydrogen flow. Before the catalytic experiments, the samples were reduced *in situ* in H₂ flow at 450-650°C, then their catalytic properties were evaluated in trickle-bed reactor (3.0 MPa, H₂/feed - 600 Nm³/m³, 250-330 °C) on the bases of GC analysis of liquid and gas phases. Chemical analysis (ICP-AES), H₂-TPR, NH₃-TPD, ³¹P MAS NMR, XRD, and TEM have been employed for the characterization of the catalysts.

Ni₂P/SiO₂ catalysts. The optimal conditions for preparation of *I*-Ni₂P/SiO₂ and *A*-Ni₂P/SiO₂ catalysts were found by comparison of catalytic activity of samples reduced *in situ* at different temperatures in the range of 450-650°C. The negligible amounts of oxygen-containing intermediates observed in the experiment indicated that conversion of MP was the rate limiting stage of overall HDO reaction over silica-supported Ni₂P catalysts. The optimal

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reduction temperature of *A*-Ni₂P/SiO₂ precursors was found to be 600°C, while the *I*-Ni₂P/SiO₂ catalyst showed higher activity after reduction at 450°C. The coinciding of temperature dependence was found for the catalytic activity and the quantity of acid P-OH groups in the samples (defined by NMR) confirming the hypothesis about the important role of acid sites in the HDO of aliphatic ethers. The H₂-TPR revealed different reduction mechanisms of *I*-Ni₂P/SiO₂ and *A*-Ni₂P-/SiO₂ formation: precursors of *I*-Ni₂P/SiO₂ can be reduced at the lower temperatures due to the intermediate formation of highly reactive PH₃. The results of XRD and TEM data revealed the formation of smaller Ni₂P particles in case of *I*-Ni₂P/SiO₂, that could along with the higher content of phosphorus explain its higher activity.

Physical mixture of *A*-Ni₂P/SiO₂ and γ -Al₂O₃. The noticeable synergetic effect of *A*-Ni₂P/SiO₂ and γ -Al₂O₃ was observed when the catalytic properties of *A*-Ni₂P/SiO₂ catalyst mixed with the inert SiC or γ -Al₂O₃ were compared. Conversion of MP and overall O-containing compounds was increased with the temperature growth for both catalytic systems, but the activity of Ni₂P/SiO₂- γ -Al₂O₃ system in MP conversion was much higher in comparison with Ni₂P/SiO₂-SiC one. The second feature of Ni₂P/SiO₂- γ -Al₂O₃ system was the noticeable difference in conversions of MP and overall O-containing compounds, pointing out that the HDO of intermediate O-containing compounds became the rate limiting step. The analysis of obtained results led us to assumption that Lewis acid centers of γ -Al₂O₃ provided additional route for MP transformation through the acid-catalyzed reaction of MP hydrolysis with the formation of palmitic acid and methanol. The tentative reaction scheme and hypothesized mechanism of MP hydrodeoxygenation with the participation of metal and acid sites have been proposed after studying the transformation of O-containing intermediates.

Ni₂P/ γ -Al₂O₃ catalysts. It was shown that the formation of nickel phosphide phase on alumina took place after the catalyst precursor reduction at temperature of 650°C and higher. AlPO₄ phase was detected along with Ni₁₂P₅ phase in *A*-Ni₂P/ γ -Al₂O₃ sample and formation of Ni₂P phase was observed in *I*-Ni₂P/ γ -Al₂O₃ catalyst. *I*-Ni₂P/ γ -Al₂O₃ catalyst contained smaller phosphide particles and demonstrated the higher catalytic activity in comparison with the *A*-Ni₂P/ γ -Al₂O₃ sample, but the reasons of such difference are under investigation.

Our result allowed us to conclude, that increasing of quantity of acid centres promotes the catalytic activity of Ni₂P/SiO₂ catalysts. The synergetic effect of metal and acid sites of supported Ni₂P catalysts most likely could be explained by the acceleration of MP conversion through acid-catalyzed hydrolysis.

Acknowledgements. This work was partially supported by the Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V. 45.3.2).

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Highly Efficient Combined [RedOx + Zeolite] Catalysts for Selective Catalytic Reduction of NO_x by NH₃

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NH₃-SCR is one of the most efficient aftertreatment technologies for removal of NO_x from engines exhaust [1]. Zeolites promoted with transition metals (Fe, Cu) have found commercial success in SCR application due to their good activity, high hydrothermal stability and sulphur tolerance. However, in order to meet stringent restrictions imposed by environmental legislations on NO_x emission from mobile sources low-temperature (T_{react.} < 200°C) performance of zeolites, especially Fe-exchanged, is needed to be improved. Our recent studies [2,3] indicated that the effective solution can be provided by the application of combined catalysts comprising zeolite (possessing high activity in Fast SCR) and RedOx (having high activity in NO oxidation) components. It was observed that strong synergistic effect between components significantly enhances SCR performance at low temperature and makes it possible to reduce the amount of zeolite in the aftertreatment system without sacrificing activity.

Detailed study of a possible mechanism of the observed synergistic effects suggests that the improvement of SCR activity can be attributed to “bifunctional” pathway comprising NO oxidation over RedOx component (1) followed by Fast SCR on zeolite (2).



On the other hand, comparison of NO oxidation activity of RedOx component and the observed synergistic effect revealed inconsistency between these two parameters. The observed synergistic effect obviously surpasses the improvement expected on the basis of Fast SCR stoichiometry and NO to NO₂ conversion over RedOx component. This observation allows us to conclude that except NO₂ RedOx component may generate other species (*e.g.* nitrate or nitrite), which may be the key intermediates in SCR process over combined catalysts.

Acknowledgements. This work was partially supported by the Russian Foundation for Basic Research (Research project No. 15-03-07802 A).

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Formation of “Core-Shell” Nanocomposites during Methane Catalytic Decomposition

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The paper proposes a method to produce "core-shell" structures by the methane catalytic decomposition on the metal-carbon composites with particles of transition metals (Co, Fe, Ni) uniformly distributed in the amorphous carbon matrix. These composites were obtained by previously developed low-temperature method of carbon materials synthesis based on chemical and thermal dehydrochlorination of chlorine polymers. Chemical dehydrochlorination of polyvinyl chloride and chlorinated polyvinyl chloride led to the formation of conjugated polymers, which were converted into carbon structures by heat treatment at 200-400 °C [1].

Using amines as the dehydrochlorination agent allowed us to obtain nitrogen-metal-carbon composites with up to 10 % metal content [2]. This process is carried out through coordination of the metal with nitrogen during the introduction of metal salts (Co(NO₃)₂, Fe(NO₃)₂, Ni(NO₃)₂) into the initial reaction mixture.

Resulting metal-carbon composites after metal recovery in a hydrogen atmosphere were studied as catalysts for the methane decomposition. Chromatographic analysis showed the hydrogen evolution at 620-850 °C, which indicates the decomposition of the methane on particles of a transition metal.

TEM studies of metal-carbon composites after methane treatment showed that deposited carbon forms a shell of close-packed graphene layers around the metal particles (Fig. 1).

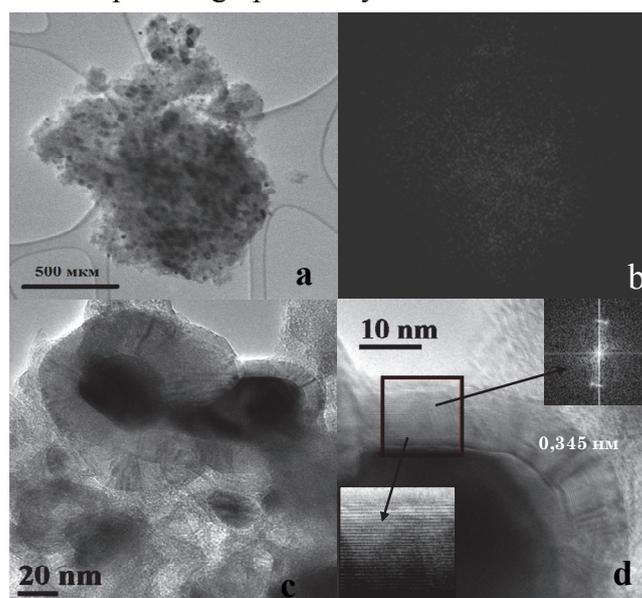


Fig.1 TEM image of Co-containing carbon material (a) and corresponding TEM-EDX mapping image of Co (b), core-shell“ structures (c), detailed structure and electron diffraction of graphene layers (d).

It is important to note that no nanotubes or nanofibers known to be formed during methane decomposition on transition metals were detected in this case.

Resulting “core-shell” structures have from 10 to 30 graphene layers with an interlayer distance 0,34-0,35 nm, close to the values characteristic of graphite.

Such "core-shell" particles with metal part surrounded by an inert shell and thereby protected from external influences can be widely used in nanoelectronics, magnetic devices, and other applications.

Acknowledgements. The research was supported by RSF (project No. 14-33-00018) and carried out on facilities of the Omsk Regional Shared Equipment Center SB RAS, Omsk.

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NAP XPS Investigation of Methane Oxidation over Bimetallic Pt-Pd/Al₂O₃ Catalysts

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Lean burn gas engines currently become more attractive due its ability to use various gases as natural gas, biogas and synthetic methane [1]. However, well known problem is release of a small amount of unburned methane into the exhaust. For the combustion of the residual methane from the exhaust of gas engines the Pd/Al₂O₃ catalysts usually used [2-4]. Nevertheless one of the main problems for these catalysts is a low stability in a reaction conditions. Most of researches suggest that the reason is a deactivation of active sites/component by the water steam, which is a reaction product as well as exhaust component [2-4]. Adding Pt prevents the deactivation of catalysts under wet conditions and improves catalytic activity [1, 5-6]. However the reasons of synergetic effects exhibiting in Pt-Pd bimetallic catalysts still under discussion. The systematic investigation of the total methane oxidation over bimetallic Pt-Pd/Al₂O₃ catalysts using the NAP XPS technique could help to get more reliable data concerning surface structure and chemical composition of active metals depending on different treatments.

The aim of this work was combined NAP XPS and MS techniques for investigation of electronic and catalytic properties of bimetallic Pt-Pd nanoparticles supported on Al₂O₃ under methane oxidation reaction.

It has been shown that the bimetallic catalysts demonstrate the higher catalytic activity compared to monometallic catalysts (Pt/Al₂O₃ and Pd/Al₂O₃). Moreover the bimetallic catalysts with a lower Pt amount have been more active in a reaction compared to the samples with a higher Pt concentration.

The chemical states of the palladium and platinum depending on the reaction conditions as well as on Pt/Pd ratio has been investigated using NAP XPS. It has been shown that both the metallic and oxidized Pd and Pt species coexist at the catalyst surface during the methane oxidation reaction. The formation of active sites on the surface in a reaction mixture flow under room temperature has been suggested.

Acknowledgements. This work was supported by the Russian Science Foundation (project no. 14-23-00146).

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Novel Research Platforms ISISS and EMIL at BESSY II: In Situ Surface Characterisation of Catalysts by Synchrotron Based Near Ambient Pressure X-ray Electron Spectroscopy

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The surface of functional materials like catalysts responds to the ambient conditions. X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (XAS) are one of the most versatile methods for the investigation of surfaces on the atomic scale providing quantitative information about the elemental composition and chemical specificity. Surface sensitive *in situ* spectroscopy, i.e. in the presence of a reactive environment allows studying the formation of the interface (gas/solid or liquid/solid) of a catalyst with time and thus adds a dynamic dimension to the spectroscopic characterization. The ISISS facility (Innovative Station for *In Situ* Spectroscopy) operated by the Fritz Haber Institute (FHI) at the synchrotron radiation source BESSY II of the Helmholtz-Zentrum Berlin (HZB) is dedicated to this kind of *in situ* studies by near ambient pressure XPS (NAP-XPS) and variable pressure soft-XAS (vP-XAS). Examples for the dynamic formation of the electronic surface structure by interaction with the ambient gas under equilibrium will be presented.

As one example, Figure 1 below displays the variation in vanadium oxidation state and abundance at the surface of a complex mixed oxide catalyst (M1 phase (ICSD 55097) of MoVTenb oxide [1-3]) under selective propane oxidation conditions to acrylic acid and its variation with and without steam added to the feed.

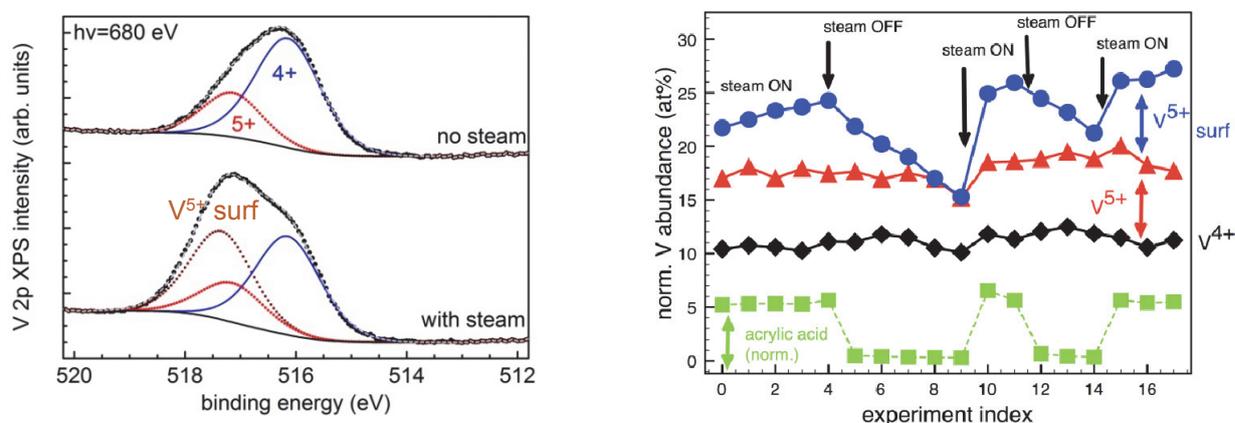


Figure 1: Deconvolution of V2p_{3/2} XP core level spectra under reaction conditions with and without steam added to the feed, respectively (left panel). The panel on the right shows the abundance of V species in the course of the experiment compared to the simultaneously determined abundance of the selective reaction product acrylic acid.

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The full power of *in situ* spectroscopy becomes obvious when comparing the variation of vanadium species with the simultaneously determined selective reaction product acrylic acid (right panel). A refined analysis of vanadium 2p_{3/2} XP core level spectra becomes feasible (left panel). This allows distinguishing 4+ and 5+ vanadium species that are assigned to the matrix of the oxide while an additional V⁵⁺ appears at the outermost surface in the course of the reaction when adding steam to the feed. The former vanadium species represent the rather stable M1 oxide phase that facilitates the formation of an active species that goes along with the abundance of the reaction product acrylic acid, i.e. the catalytic performance of the material. This study demonstrates the power and versatility of near ambient pressure electron spectroscopy methodologies to determine details of the electronic surface structure and its dynamic evolution on a molecular level in the presence of reactive gases at elevated temperature.

Finally, an outlook on future activities at HZB/BESSY to develop further synchrotron based ambient pressure characterisation methodologies will be given. Recently, the advent of reaction cells based on electron transparent membranes at low kinetic energy (i.e. high surface sensitivity) has found much interest [4]. First results of the application of this type of cells allowing performing XPS studies at 1000mbar gas pressure and in liquids will be presented [5, 6]. Currently, HZB and FHI are establishing EMIL, The Energy Materials In-Situ Laboratory Berlin at BESSY II. This novel facility includes a new laboratory building hosting beamlines providing an unusual broad photon energy range from 80eV – 8000eV in one spot and (among others) a NAP-high kinetic energy XPS endstation capable to operate at kinetic energy of photoelectrons up to 7000eV that allows studying buried layers and liquid/solid interfaces [7]. Prospects of this new facility for catalyst research will be discussed.

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On the Way to Bridging the Gaps in Catalysis: Atmospheric Pressure X-ray Photoelectron Spectroscopy

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The discrepancy between higher operating pressures applied in catalytic processes and lower measurement pressures accessible during surface characterization is known in the community as the “pressure gap” [1]. To bridge this gap, new experimental and instrumental methods have been developed such as Ambient Pressure XPS (AP-XPS), which allows the collection of photoelectrons at pressures in the millibar range [2]. The wealth of information provided by these experimental setups is of prime importance to the understanding of complex systems. However, the study of solid-gas interfaces with partial pressures beyond a few tens of millibars remains a major challenge. Recently, this technique was

extended to higher kinetic energy (HAXPES). Notably, this approach combined with a small aperture nozzle increases the operation pressure up to 100 millibars [3]. Here we introduce an atmospheric pressure XP spectroscopy cell based on an array of micro holes coated with graphene that solves the

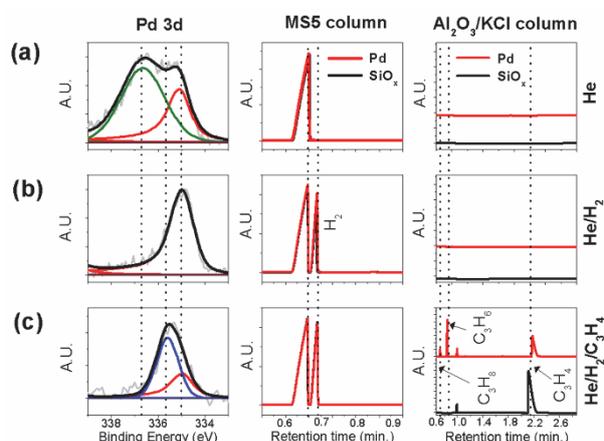
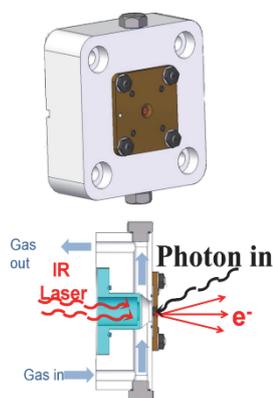


Figure 1: a) Pd 3d XP spectra and gas chromatography traces (VARIAN μ GC 4900) using a mol sieve MS5 column (VARIAN CP740148) and $\text{Al}_2\text{O}_3/\text{KCl}$ column (AGILENT 494001440) : a) He, b) He/ H_2 , and c) He/ H_2 / C_3H_4 gas mixtures.

mechanical stability problem of free standing graphene covering large open areas and still provides high transmission for low kinetic energy electrons (higher than 400 eV) combined with a high rate of fabrication reproducibility. We will illustrate the operation of this setup with different examples in liquid and gas phase such as the selective hydrogenation of alkynes into alkenes/alkanes (see Figure 1) [4] and in the characterization of electrochemical process on electrified interfaces under aqueous conditions [5].

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Modeling of Ceria-supported Silver Species

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Deposition of transition metals (TM) on various oxides is known to enhance their catalytic activity. For example, ceria supported silver particles exposes reactivity in low temperature oxidation reactions. The active form of adsorbed silver on oxide surfaces is under question. Various studies report metallic nanoislands, metal clusters, isolated ions and dispersed Ag₂O species as catalytically active surface species. To quantify between various adsorbed silver species we considered localization of monomer, trimer and tetramer silver species on a model Ce₂₁O₄₂ cluster which mimicks nanostructured ceria surface [1]. This cluster model suggests small (111) and (100) facets as well as edges at their intersection.

All calculations were carried out with the VASP code [2]. The effect of core electrons on the valence density has been taken into account by means of the projector augmented wave (PAW) method [3]. The GGA+U scheme [4] with the PW91 parametrization of the exchange-correlation functional and explicit inclusion of a Hubbard type on site correction U-term of 4 eV for Ce 4f states.

Our calculation shows that silver species are more strongly bound to (100) facet, via interaction with two-coordinated O atoms. The adsorption energies of Ag, Ag₃ and Ag₄ clusters are calculated to 2.2, 2.9 and 3.0 eV, respectively. Silver atom is localized in a hole position and interacts with four O atoms (the so-called O₄-pocket [5]). Adsorbed silver trimer is in upright position. The most stable ceria-supported tetrameric silver cluster features tetrahedral structure. The isomer with parallel to (100) facet silver rhombus is ~0.7 eV less stable.

Adsorption of Ag_n species on the (111) facet results in less stable complexes with binding energies of ~1.2, 1.7–2.5 and 1.6–2.0 eV for Ag, Ag₃ and Ag₄ clusters, respectively. Single silver atom is localized in a hollow position between one two-coordinated O and two three-coordinated O atoms. Analogously to Ag₃ species at (100) facet, silver trimer on (111) facet is in upright position. Binding energies for Ag₄ species located on (111) facet are calculated to 2.0 and 1.6 eV for tetrahedral and rhombus conformation, respectively.

On interaction with ceria surface Ag_n moieties are oxidized. Each Ag and Ag₃ adsorbates donate to the substrate particle one electron. Ag₄ clusters in rhombus and tetrahedron configurations donate one and two electrons, respectively. Each donated electron is localized on just one cerium center, reducing it from Ce(IV) to Ce(III). Somewhat more stable structures are formed when donated electrons are localized on the six-coordinated Ce atoms.

It was found that silver species on the (111) facet is readily interact with oxygen molecule forming superoxo-like species.

The structure, electronic state and binding energy of silver species at ceria support will be compared with those calculated for similar clusters on MgO and SiO₂ surfaces.

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Bimetallic Catalysts for Direct Conversion of Ethylene to Propylene: From the Idea to the Real Catalyst

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There is an increasing worldwide demand for propylene due to a higher demand for polypropylene than polyethylene. Direct conversion of ethylene to propylene without any addition of other hydrocarbons is the most desirable route, but no single catalyst with high ethylene conversion and propylene selectivity has been found so far. In our previous reports NiO-Re₂O₇/B₂O₃-Al₂O₃, PdO-Re₂O₇/B₂O₃-Al₂O₃ catalysts were considered as catalysts for direct synthesis of propylene from ethylene claiming high propylene selectivity [1, 2]. The design of these catalyst systems is based on ethylene transformation into propylene via ethylene dimerization over Ni or Pd-containing active sites and subsequent metathesis of 2-butene and ethylene over Re-containing active sites.

The aim of our studies is preparation a new PdO-Re₂O₇ catalyst, based on SO₄²⁻/ZrO₂ and SO₄²⁻/ZrO₂-Al₂O₃ for the direct conversion of ethylene to propylene at an equilibrium conditions. A special attention is paid to the influence of the supported metal oxide (PdO, Re₂O₇) content, to the support nature of PdO-Re₂O₇/SO₄²⁻/ZrO₂ and PdO-Re₂O₇/SO₄²⁻/ZrO₂-Al₂O₃ catalysts and their catalytic stability at the reaction condition.

A series of PdO-Re₂O₇/SO₄²⁻/ZrO₂ catalysts showed high propylene yield (42.4-55.2 wt. % at 40°C and 49.8-62.1 wt. % at 80°C) but after 1 h the initial activity of PdO-Re₂O₇/SO₄²⁻/ZrO₂ catalysts is rapidly decreases to 10.0-15.8 wt. %.

The addition of Al₂O₃ in the support of catalyst PdO-Re₂O₇/SO₄²⁻/ZrO₂ in an amount of 20-40 wt. % leads to the formation of active and stable rhenium centers. In this way, modification of PdO-Re₂O₇/SO₄²⁻/ZrO₂ catalyst with Al₂O₃ is extending the catalyst stability from 1 to 150 hours without significant changes in the catalytic activity (33.4-55.2 wt. % of propylene yield at 40°C).

Acknowledgements. We would like to thank Omsk Collaborative Center SB RAS for measurements.

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Design of Pt/MgAl(M)O_x Dehydrogenation Catalysts with the Use of Layered Structure Supports

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Catalysts platinum supported on aluminum–magnesium oxide materials are promising in base-catalyzed reactions and in the conversion of hydrocarbons. The formation of the properties of the catalysts may depend considerably on the structure and composition of the platinum precursor and the precursor of oxide support, namely, layered double hydroxides (LDHs). LDHs have the composition $(M^{2+}_{1-x}M^{3+}_x(OH)_2)^{x+}(A^{n-})_{x/n}nH_2O$, where M^{2+} and M^{3+} are bi- and trivalent metal cations, and comprise positively charged hydroxide layers and anions A^{n-} located in the interlayer space. It is important that variation of the nature of interlayer anion, the composition and charge of hydroxide layers makes it possible to control not only acid-base properties of the support, but also the amount of anchored platinum precursor, its location in the support structure, the strength and nature of precursor–support interaction, the extent of modifying effect of the support. The interaction of Pt (0), Pt(II) and Pt(IV) anionic complexes with the LDHs that comprise Mg^{2+} , Zn^{2+} , Al^{3+} and Ga^{3+} cations and differ in the nature of interlayer anions (CO_3^{2-} or OH^-) at M^{2+}/M^{3+} ratio ranging from 2 to 4 was studied. These parameters were found to affect both the support properties (structure, texture, acid-base and ion-exchange properties) and the dispersion, morphology and electronic state of supported platinum. Reactions of propane and n-decane dehydrogenation were employed for testing the catalysts.

LDHs with carbonate counter ions ($M^{2+}M^{3+}-CO_3$) and with $M^{2+}/M^{3+}= 2-4$ were synthesized by coprecipitation of appropriate hydroxides from solutions of nitrates of metals at their interaction with solutions containing carbonate and hydroxide ions. To obtain a sample containing mainly the interlayer OH^- anions ($M^{2+}M^{3+}-OH$), the initial support was calcined at 550 °C and hydrated again. Anchoring of platinum was carried out with the use of complexes with different composition and geometry ($[PtCl_6]^{2-}$, $[PtCl_4]^{2-}$, $[Pt_3(CO)_6]_n^{2-}$). Structural features of the synthesized samples of LDH and mixed oxides were studied by XRD (D8 Advance, Bruker). Adsorption–desorption isotherms of nitrogen at 77.4 K were measured using a static volume vacuum system ASAP-2020M (Micromeritics). Elemental analysis was made by ICP-AES on Varian 710-ES spectrometer. CO and H₂ pulse chemisorption (AutoChem II 2920, Micromeritics) and transmission electron microscopy (JEM-2100, JEOL) were used to estimate the particle size of platinum. X-ray photoelectron spectroscopy was carried out on a spectrometer (SPECS, Germany). EXAFS spectra of the AuLIII absorption edge were measured at the ID26- beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) in fluorescence mode at 12 K. Differences in the anchoring mechanism of metal complexes on LDH were revealed by ¹⁹⁵Pt MAS NMR (Avance-400, Bruker). Catalytic properties of Pt/Mg(M)AlO_x were investigated under the following conditions: T = 550 °C, atmospheric pressure, WHSV 8 h⁻¹ and H₂/C₃H₈ molar ratio of 0.25 (in propane dehydrogenation); T=460 °C, pressure 0.2 MPa, WHSV 17 h⁻¹, H₂/C₁₀H₂₂ molar ratio of 7 (in n-decane dehydrogenation). Before reaction, samples were calcined at 550 °C and reduced in hydrogen at 550 °C.

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The nature of interlayer anion is an essential parameter affecting the amount of anchored platinum, the composition of surface species, and their location in the structure of layered material. A low exchange capacity of carbonate LDH species toward the double-charged anionic chloride complexes of platinum made it possible to anchor platinum selectively with participation of OH groups of the hydroxide layers and adsorption of hydrolyzed complexes on the surface. Their reduction led to the formation of isometric platinum particles of size 2-4 nm. When platinum complexes were anchored on aluminum-magnesium hydroxide with interlayer OH⁻ anions, the precursor was located mainly in the interlayer space with subsequent formation of particles having a plane morphology, length of 50 nm and thickness close to interlayer distance in the layered support (0.75 nm). No adsorption of [Pt₃(CO)₆]_n²⁻ occurred on LDH MgAl-OH owing to steric difficulties. During adsorption complexes on MgAlO_x their anchoring occurred with saving of structure of mixed oxides (solvent - acetone) as well as with recovery of LDH structure (solvent - acetone + 5 vol. % H₂O) with a decrease in the size of complexes at their contact with basic support.

Pt/MgAlO_x catalysts obtained using different platinum complexes were investigated in propane dehydrogenation. Propane conversion and propylene yield decrease with increase Mg/Al ratio for catalysts made from chloride precursors. Platinum dispersion decrease with increase Mg/Al ratio too. Herewith catalysts obtained from [PtCl₄]²⁻ were more active in comparison to the samples obtained from [PtCl₆]²⁻ due to the larger platinum dispersion. Propane conversion, platinum dispersion and stability of catalysts obtained from platinum carbonyl complexes were above respective characteristics for samples, made using chloride precursors. The introduction of zinc and gallium, which are used to modify the state of supported platinum, into hydroxide layers during LDH synthesis provides a uniform distribution of the modifying element in the support structure; the extent of modification can be adjusted continuously by varying the content of zinc and gallium. The presence of zinc was found to increase the dehydrogenation activity of supported platinum even at lower values of its dispersion. The exchange of aluminum cations for gallium cations increased the propane conversion; in addition, it provided a high (99%) selectivity of propylene formation over the entire time of experiment.

Pt/MgAlO_x catalysts afford high n-decene formation selectivity (90%) in n-decane conversion without any modifier introduced. As the magnesium content of the support is increased, the yield of decane cracking and skeletal isomerization products decreases (as a result of the decrease in the number of acid sites in the support) and diene formation is hampered. The latter effect is likely due to the dependence of the adsorption and electronic properties of supported platinum on support basicity. The best catalytic properties are shown by the samples synthesized via anchoring of Pt(IV) chloro complexes as a component of outer-sphere complexes in the interlayer space of LDH MgAl-OH.

Approaches to the design of platinum sites of Pt/Mg(Zn)Al(Ga)O_x catalysts for dehydrogenation of light and higher alkanes using specific properties of layered supports were considered. It was shown that choosing the interlayer anion with desired exchange properties and varying the ratio and nature of bi- and trivalent cations of the hydroxide layers can be used as efficient tool for the formation of supported platinum particles with specified dispersion, morphology and electronic state.

The Study of Ni Anchoring to a Nanodiamond Support

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Nanodiamond (ND) materials attract attention as the promising catalyst supports due to developed and highly defective surface area comprising several types of functional groups, nanosize of particles, superhardness and chemical stability [1]. Excellent efficiency of Ni/ND and Pd/ND catalysts was demonstrated in [2, 3]. Each primary ND unit comprises nanocrystal diamond core 4-5 nm in size coated with onion-like carbon shell covered with a number of various functional groups, depending on purification method used at ND production [4]. In [5] the participation of surface functional groups in coordination of metal precursor during metal supporting by impregnation was supposed on the base of FTIR study. The nature of Ni anchoring to ND surface in the catalysts prepared by impregnation of detonation ND with NiNO₃ water solution was investigated in this work using EXAFS, temperature-programmed reduction (TPR), IR-spectroscopy, zeta-potential and catalytic studies.

ND was obtained from "Sinta" JS Company (Belarus). The Ni K-edge EXAFS spectra were recorded at the beamline "Structural Materials Science" of the Kurchatov Center for Synchrotron Radiation and Nanotechnology (Moscow, Russia). The DR IR spectra were recorded on a Bruker Equinox 55/S Fourier transform IR spectrometer (Bruker, USA), zeta potential in water suspension was measured on Malvern ZETASIZER nano-ZS (Malvern, UK). GC-MS analysis was performed on Thermo Trace DSQ II instrument.

On the base of IR and zeta-potential measurements, the presence of various oxygen-containing groups (carboxyl, lactone, cyclic ether, ester or ketone, carbonyl groups etc.) on the ND surface was confirmed. After Ni supporting low-intensity absorption bands at 1192 and 1257 cm⁻¹ disappeared due to coordination with Ni. This observation finds confirmation in the change of zeta-potential from negative to positive value pointing on the binding of carboxyl groups with metal precursor.

TPR investigation demonstrated staged NiO reduction in NiO/ND catalytic precursor, which was explained in terms of two type of Ni bonding with ND surface, through physical sorption by van der Waals interaction (weakly bonded Ni) and through chemical interaction with surface functional groups (strongly bonded Ni). EXAFS data for Ni/ND produced by *in situ* reduction of NiO/ND with H₂ in EXAFS spectrometer cell at 150, 300 and 900°C were compared with the experimental EXAFS data for Ni, NiO, Ni(CH₃COO)₂, and NiCO₃. Indeed, both Ni_{-Ni} and Ni_{-O-C} scattering paths were found in Ni/ND catalysts using wavelet transform of EXAFS data on the base of modified Morley function [6], which gives instrument to distinguish light carbon

and oxygen atoms that have close atomic numbers. *In situ* experiment demonstrated that the ratio between two forms depends on the temperature of NiO/ND reduction with H₂. Even at 150°C the reduction of loosely bonded particles NiO to Ni(0) can proceed. At 300°C significant part but not all NiO is reduced; nickel carbide and Ni(0) are formed at higher reduction temperature (900°C). The presence of Ni-O-C scattering path in Ni/ND reduced at 150°C is indicative of the presence of Ni²⁺ strongly bonded with ND through oxygen-containing surface groups. This hypothesis was confirmed by preparation of two particular Ni/ND samples. For the first sample (Ni/ND_Ar-900) functional groups were deleted from ND surface by annealing in Ar at 900°C. The removal of carboxyl groups was confirmed by ζ – potential measurements. Therefore Ni/ND_Ar-900 contained mainly weakly bonded Ni. The other sample Ni/ND-300 was produced by calcination of the NiO/ND precursor in air at 300°C instead of 150°C and comprised mainly strongly bonded Ni. The increase of calcination temperature was supposed to favor the Ni-O bonding during Ni(NO₃)₂ decomposition. The significant enrichment of these samples with corresponding Ni forms was confirmed by TPR experiment (Fig. 1, b). These samples demonstrated drastic difference in styrene formation selectivity during hydrogenation of phenylacetylene (fixed-bed system, 50-300°C, flow-type H₂ and pulse PhA supply, GC-MS products analysis): Ni in Ni/ND_Ar-900 weakly bonded with ND gave mainly ethylbenzene; Ni/ND-300 comprising Ni strongly bonded with ND via Ni-O-C bond provided mainly styrene formation (Fig. 1, a). In-between styrene selectivity was achieved on Ni/ND containing both types of Ni active sites.

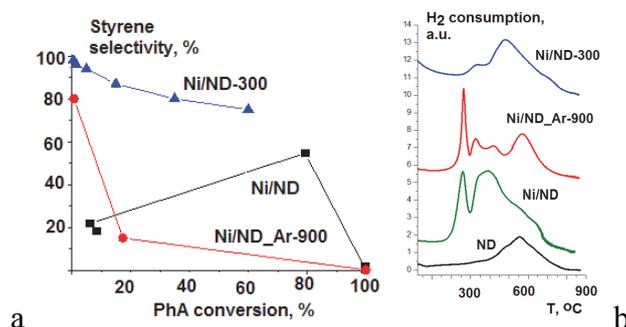


Fig. 1. Catalytic properties in PhA hydrogenation (a) and TPR data (b) for Ni/ND-300, Ni/ND_Ar-900, ND and Ni/ND (annealed at 150°C)

In conclusion, the anchoring of Ni on ND surface can proceed by physical forces and through Ni-O-C bond formation in which surface oxygen-containing functional groups take part.

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Amorphous Features of Na-Mn-W-Oxide OCM Catalyst; an *In-Situ* Raman Approach

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1. Introduction

The Mn-Na₂WO₄/SiO₂ for oxidative coupling of methane (OCM), has been extensively investigated over the last decades. The reaction temperatures applied in OCM are usually above 730°C. Under these reaction conditions, liquefaction of an active component that contains alkali and transition metal oxides should be taken into consideration. To investigate the influence of sodium (Na) on the physical and catalytic properties of supported Na-Mn-WO₄ model catalysts, we have studied the thermal behaviour of supported and unsupported mixtures of sodium carbonate and manganese tungstate applying thermal analysis, X-ray diffraction, and *in-situ* Raman spectroscopy. To make the model catalysts as simple as possible steatite which is non-porous and inert has been applied as support.

2. Results and discussion

Different phases have been formed depending on the composition of the mixtures after heat treatment at 850°C and cooling down to room temperature. TG-DSC results, shown in Figure 1, reveal a complex behaviour showing two main endothermic events. Based on results of *in-situ* Raman, two DSC endothermic events at 570°C and 650 °C are related to a first order phase transition of Na₂WO₄ from the cubic structure to the orthorhombic structure *Fddd*[1] and to the melting point of Na₂WO₄, respectively. The catalyst with the highest sodium content (80%) is characterized by the lowest activity and comparatively low selectivity. The catalytic properties of the other catalysts are dominated by the sodium content. With increasing sodium content the activity increases. At comparable conversions the highest selectivity to C₂ (Ethane + Ethene) products has been achieved with the catalyst that contains the lowest amount of sodium. Presence of sodium induce lower stability for MnWO₄, which wind up with presence of partially molten or dissolved MnWO₄ under the reaction conditions, see Figure 2. That could play a rule for superior performance of OCM catalyst.

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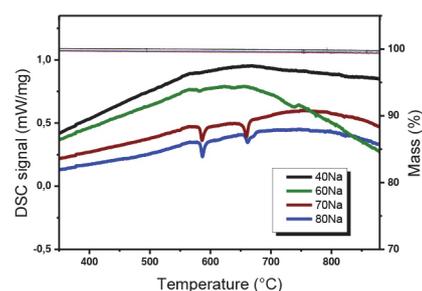


Figure 1. TG-DSC profiles of steatite-supported catalysts recorded at a heating rate of 10K/min

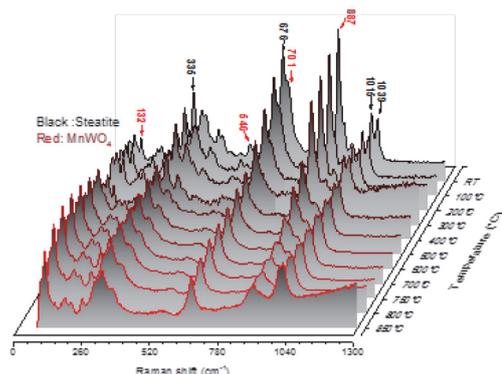


Figure 2. *In-situ* Raman of sample composed of 40%Na, while heating under the flow of OCM feed

The Synthesis of Higher Alcohols from Syngas over Co-modified Cu Catalysts

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Higher alcohol synthesis (HAS) via hydrogenation of carbon monoxide is a promising route for providing important basic chemicals, alternative fuels and additives in gasoline blends. For large-scale application catalysts based on non-noble metals such as Cu, Co and Fe are considered to be promising systems. Institute Français du Pétrole (IFP) reported on selective alkali-doped Co-modified Cu/ZnO/Al₂O₃ methanol synthesis catalysts in HAS. However, the activity was moderate and large-scale application has not yet been realized.

Our recent results indicate that these catalysts undergo severe structural changes during activation and during the first hours under reaction conditions. Therefore, only the thorough characterization of the catalyst after activation and/or after HAS provides important information to further adjust the optimum reaction conditions and catalyst compositions to enhance product selectivities and the degree of conversion.

Co-modified Cu/ZnO/Al₂O₃ methanol synthesis catalysts were prepared similar to the method described by IFP. The activated and utilized catalysts with different Na loadings were characterized by X-ray photoelectron spectroscopy (XPS), temperature-programmed techniques (TPR, TPD), reactive frontal chromatography (RFC) and X-ray diffraction (XRD). Activation and HAS were performed in a 4-fold parallel test facility, which allows the transfer of the activated and utilized catalyst under inert conditions preventing re-oxidation and contamination by air. The catalytic tests were performed at 280 °C, 60 bar and H₂/CO = 1.

Increased presence of metallic Co⁰ after reduction at 350 °C was confirmed by X-ray photoelectron spectroscopy indicating metallic Cu⁰ to act as a reduction promoter. Catalysts with low Na loadings (≤0.6 wt%) showed strong initial deactivation presumably due to coking of isolated Co⁰ surface sites favoring hydrocarbon formation. The selectivity to higher alcohols gradually increased during the first 10 h TOS indicating enhanced Cu-Co surface alloy formation considered as active sites for HAS. In contrast, with high Na loadings (≥0.8 wt%) deactivation did not occur and stable performance with constant CO conversion and product distribution was observed indicating significantly altered structural properties. High Na loadings caused the stabilizing amorphous oxide matrix to collapse resulting in strong sintering of the metallic Cu particles, and an increased carburization of metallic Co⁰ forming bulk Co₂C was observed by X-ray diffraction. Close contact between metallic Co⁰ and Co₂C, which is known to facilitate molecular CO adsorption, is assumed to generate additional active sites for HAS.

The Influence of Catalyst Bed Dilution on Methanol Production

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Introduction

Many industrial exhausts contain considerable concentration of carbon dioxide. Conversion of CO₂ to methanol by its catalytic hydrogenation is recognized as a process to mitigate atmospheric CO₂ level [1]. Methanol is produced industrially from syngas – a mixture of CO, CO₂, and H₂. The exhaust gases from the steel mill plants can also be used as a feedstock for methanol synthesis since its main components are CO₂, CO, N₂ and H₂.

Experimental methodology

Methanol synthesis is performed over a commercial Cu/ZnO/Al₂O₃ catalyst in a flow type fixed bed reactor. Effects of catalyst bed dilution are investigated in this study.

Results and discussion

Catalyst beds are often diluted with particles of inert to improve the isothermicity of the bed and to suppress bypassing. Materials such as SiO₂, α-Al₂O₃, and SiC are preferred as dilution because of their relative inertness and good heat transfer properties [2].

The first measurement is done using SiO₂ as diluent. The catalyst should reveal high stability. The experiment performed at 250°C shows the decrease in the methanol production rate in first 40 - 70 hours, after that the catalyst works stable. The results of stability tests show that the catalyst can operate in the stable way without presence of carbon monoxide in the gas feed. However, bed dilution may also negatively influence the reactant conversions. The particle size should be optimal in order to have good fluid dynamics and to avoid pressure drop in the reactor. Different particle sizes is used in catalyst test to estimate the optimal values for higher CO₂ conversion and methanol yield. It is shown that particle size has high impact on catalytic properties. Methanol production rate is in the range of 0.8 – 1.1 g/(g_{cat}*h) depending on particle size of diluent (Fig.1). Using different inert materials the catalytic activity is measured at different molar H₂:CO₂ ratios and different temperatures.

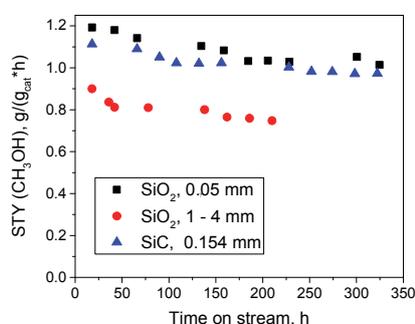


Fig. 1. Time on stream measurement at 250°C, 30 bars using different diluent material

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The Weight of Methanol Synthesis: Combined Thermogravimetric and Reactivity Study

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The current works aims to illustrate the potential of the thermogravimetric technique combined with activity measurements in quantitative assessment of the adsorbates accumulated during methanol synthesis under industrial conditions on Cu based catalyst. *In-situ* high pressure thermogravimetry coupled with mass-spectrometry was used to examine the catalyst surface coverage with adsorbed species in different feeds. The reactivity measurements in steady and transient state in combination with surface titration experiments were performed for the analysis of stable surface spectators and exploring the nature of the active catalytic site with respect to the specific catalyst. The Cu/ZnO/Al₂O₃ catalyst exhibits a dramatically different behavior in the presence or absence of CO₂ in the feed gas. The performance of the system deteriorates in CO/H₂ but reversibly gain the immense activity upon re-addition of CO₂ into the feed [1]. Exposition to the feed gas leads to accumulation of surface species on the catalyst surface. There is 1.9% weight gain observed in CO₂-containing feed and reversible partial weight loss of 0.67% when switched to CO only (Fig. 1).

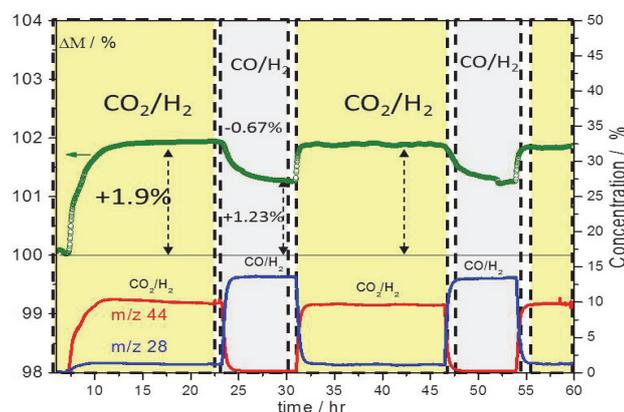


Fig 1. Cu/ZnO/Al₂O₃ *in situ*-thermogravimetry at 503 K and 30 bar in different feed gases.

Recent spectroscopic study [2] qualitatively analyzed the stable chemisorbed species on copper supported catalyst. These results are consistent with theory and previously reported data on surface adsorbates. Our attempt to quantify the stable reaction spectators under reaction conditions demonstrated that during CO₂ hydrogenation to methanol the catalyst accumulates around 1.3 wt% water and hydroxyl group and around 0.5-0.8wt% by CO hydrogenation. The amount of the carbon contained species is assessed as 0.6 wt% for CO₂ hydrogenation 0.73-0.43 wt% for CO. It is likely to be formates/methoxy in case of CO₂/H₂ and methoxy in case of CO/H₂.

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Selective Catalytic Hydrogenation of Carbonyl Compounds under Ambient Conditions

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Carbonyl compounds are abundant natural products, and their reduction to the corresponding alcohol play a significant role in modern synthetic chemistry. Nowadays the common approach to obtain target alcohols from aldehydes and ketones implies the use of stoichiometric reducing agents or homogeneous catalysis by metal complexes with such drawbacks as the necessity of product isolation and separation and problems with recyclability of the catalysts, while heterogeneous catalysts are still considered as not selective. On the other hand, today there is a great need in new “greener” and cost-effective technologies in organic synthesis to obtain basic products and diverse synthons with “atomic precision”. In this case, the design of the novel heterogeneous catalysts with high activity, selectivity, predictable features and ability to work under mild conditions (comparable with those for homogeneous catalysts) represent a big challenge for scientists ^[1].

In the present study we have synthesized a series of nano-hybrid catalysts containing Pt nanoparticles (NPs). The interesting feature of the designed catalysts is that Pt NPs supported on TiO₂, CeO₂, CeZrO₂ are able to initiate an intensive hydrogen spillover even at -50-0°C, i.e. they become the source of “active hydrogen” ^[2]. Moreover, by using the TPR-H₂ method, we can predict the temperature interval of activity of the catalysts in the hydrogenation reaction. Thus, we used this unique ability of our catalysts to donate the “active hydrogen” in the selective low-temperature hydrogenation of aliphatic, aromatic and other unsaturated carbonyl compounds to the corresponding saturated and unsaturated alcohols with yields ranging within 50-100% at temperatures from -15°C to RT under H₂ medium and the active component content 0.5-0.9% mol. The activity of the obtained catalysts exceeded that of the common commercial Pd/C by more than 3 times.

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Mechanism of Ethanol Transformation into Syngas on Complex Oxides

Promoted by Pt/Ni+Ru: *In Situ* Transient Studies

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This work presents results of studies of the mechanism of ethanol partial oxidation, steam and dry reforming into syngas for stable to coking catalysts comprised of oxides with a high oxygen mobility and reactivity (PrSmCeZrO, MnCr₂O₄, CaTiO₃, La(Pr)Ni_{0.95}Ru_{0.05}O₃/Mg-Al₂O₃) promoted by Pt or Ru+Ni [1, 2] using *in situ* FTIRS (a flow cell) and transient kinetic methods (H/D and ¹⁸O SSITKA, pulse microcalorimetry) [3, 4]. Surface species (adsorbed ethanol, ethoxy complexes, acetaldehyde, acetate, etc) were identified and their thermal stability and reactivity were estimated. Acetate species were shown to be spectators for all types of catalysts. Transformation of ethoxy species by dehydrogenation is a fast step (the value of the H-D kinetic isotope effect was equal to 1), while the rate-determining stage is the C-C bond rupture in thus formed acetaldehyde on the metal sites. Ethanol transformation in pulses fed to the steady-state surface proceeds with the rate and products selectivities close to those in mixed pulses of ethanol with an oxidant. The step of the oxides surface reoxidation by oxidants (CO₂, H₂O, O₂) is fast producing, along with CO or H₂, reactive oxygen species rapidly migrating along the surface/domain boundaries (oxygen self-diffusion coefficient up to 10⁻¹⁴ cm²/s at ~ 400 °C) to metal sites where acetaldehyde is transformed to CO_x and H₂. Hence, steady-state (ss) reactions of EtOH reforming are described by a simple redox scheme with independent stages of EtOH and oxidants activation. The strength of oxygen bonding with the ss surface corresponds to bridging M₂O forms (heat of O₂ adsorption ~ 600 kJ/mol for fluorite and perovskite-like supports, and ~400 kJ/mol for spinel). ¹⁸O SSITKA studies revealed that in ethanol selective oxidation into syngas decomposition of ethanol/acetaldehyde on Pt nanoparticles mainly yields CO while CO₂ is formed with participation of the oxide support oxygen including WGS reaction. For Ru- and Ru-Ni - supported nanoparticles ethanol/acetaldehyde are mainly transformed into CO₂ due to a higher coverage of reactive oxygen species, while CO is produced by reverse WGS reaction.

Acknowledgements. Support by FP7 BIOGO project, RFBR-CNRS projects and Russian Ministry of Education and Science is gratefully acknowledged.

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New Insights on Active Sites of Carbon-based Catalyst Monitored by Quasi *In Situ* Adsorption Microcalorimetry

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Adsorption phenomena play an important role in heterogeneous catalysis. Typically, only a minor fraction of all surface atoms form active centers, thus the determination of their number, strength, and energetic distribution requires a sensitive analytical method. We focus on quasi *in situ* adsorption microcalorimetry^{1,2}. To facilitate the correlation of microcalorimetric results with the catalytic performance, reactants are used as probe molecules and the catalyst surface is quenched in the active state. The adsorption was performed at a lower temperature than the reaction to separate the adsorption processes from the catalytic transformations.

The oxidative dehydrogenation (ODH) over carbon-based catalysts has been discovered in 1979 by Alkhozov et al.³ Surface quinone groups are believed to be the active sites. We choose the ODH of propane and ethylbenzene (EB) over oxygen functionalized multiwalled carbon nanotubes (oCNT) as the model reactions. The research project was performed in a multidisciplinary approach (microcalorimetry, XPS, kinetics, DFT).

The redox cycle of surface C=O and C-OH groups is the key process, which includes only a small fraction of surface O species and, according to DFT, favourably occurs at the zigzag-termination of sp² carbon planes. Higher activation barriers in the reduction step well correlate with the higher stability of the aliphatic C-H bond in propane over the benzylic C-H bond in EB and hence lower adsorption enthalpy for propane compare to EB.

XPS was performed in 0.5 mbar hydrocarbon (HC), HC/O₂, and pure O₂, respectively, at 423-623 K. A substantial fraction of ketones and quinones were detected on the carbon catalyst surface. The highest fraction of redox-active nucleophilic C=O groups can be detected in O₂/C₃H₈ and in pure O₂, respectively. Their intensity decreases in O₂/EB, whereas they are almost absent in pure EB vapour. This impressively illustrates the impact of chemical potential of the different hydrocarbon molecules and reaction conditions on the dynamic catalyst surface.

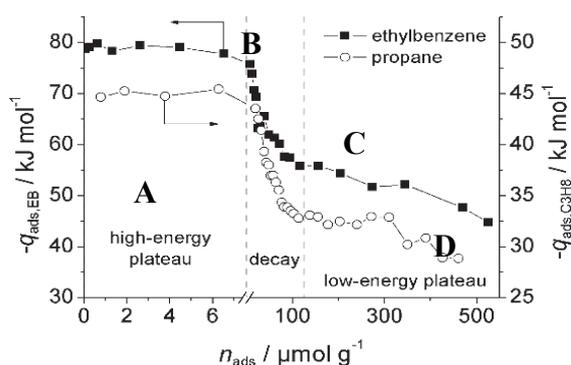


Fig. 1. Differential heats of adsorption of ethylbenzene (■) and propane (○) on the active surfaces of CNT catalysts.

Assignments [2]: **A** to ketone and quinone groups, **B** to carboxylic anhydrides, **C** to lactone/ester, phenol, and ether sites, and **D** to adsorption on the basal plane of graphitic carbon

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Fig. 1 shows the differential heat profiles of propane² and EB adsorption on the oCNT surface. The shape of the heat profiles and the extracted site classifications² are very similar. In both cases the amount of homogeneous high-energy adsorption sites (most likely the quinones) is 8 $\mu\text{mol/g}$. EB reacts stronger (80 kJ/mol) with the C=O double bonds (ketone/quinone) than propane (45 kJ/mol). From the quantitative point of view microcalorimetry reveals an astonishing analogy of active surface equilibrated in EB and propane ODH reaction.

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Reactivity Studies of Fe-based Model Catalysts for Ammonia Synthesis

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NH₃ synthesis via the Haber-Bosch-process was the first process in chemical industry conducted over heterogeneous catalysts and is still in use today as the second largest inorganic synthetic route [1]. The reaction is highly structure sensitive. Based on a bunch of investigations including the surface science approach a model of the active site is established, with C7 sites on the (111) facets of Fe being the active sites in NH₃ synthesis [1,2]. These sites are exposed on the industrial ammonia catalyst, which is produced via a very harsh fusion process and a non-topotactic reduction resulting in a special platelet structure of the so called “ammonia iron” [1]. Nevertheless, the active state of the catalyst at industrial relevant conditions is hard to characterize and this problem is still not solved today. That is why this study aims at investigations of systematic series of model catalysts for NH₃ synthesis produced via milder and more defined routes like (co-)precipitation. These preparation routes allow a variation of the preparation conditions with respect to e.g. temperature, composition, or aging time. These variations can have an influence on the structure of the reduced catalysts and, thereby, allow the elucidation of structure-activity relations.

As starting materials FeOOH-based nanosheet catalysts with varying Fe loading, support materials, and potassium promoter concentration as well as ex-layered-double-hydroxide-(LDH)-based Fe systems with varying composition were chosen. Both material classes were successfully tested in the NH₃-synthesis reaction at 90 bar in a kinetic flow set-up. Potassium promotion had a beneficial influence on the activity of the samples.

For the nanosheet-based catalysts support by Al₂O₃ was mandatory to achieve a stable catalyst productivity in contrast to unsupported or MgO supported catalysts. Additionally, it was possible to achieve active catalysts by encapsulation of the nanosheets by SiO₂. With an ex-LDH-Fe₂MgO catalysts with 2 wt% K it was even possible to achieve already more than 40 % of the productivity of a multipromoted industrial Fe-based catalyst. Therefore, this material is a promising starting material for further development and systematic studies.

For the future it is planned to complement the reactivity studies at 90 bar by studies at atmospheric pressure and a variety of characterization methods including in-situ methods to clarify the structure of the working catalyst.

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Gold-based Three-Way Catalysts: Examining the Potential of an Unusual Catalyst Component

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The Three-Way Catalyst (TWC) is a well-established technology to convert toxic and harmful compounds (unburned hydrocarbons, CO, nitrogen oxides (NO_x)) in the exhaust of gasoline driven automobiles to harmless substances [1], which targets ecological concerns and protects our natural environment. Two oxidation and one reduction reaction are catalyzed simultaneously on this catalyst. Under the severe conditions of practical application, only noble metals (Pt, Rh, Pd) have proven satisfactory activity and stability properties in TWCs. However, these metals are limited and subject to drastic price alterations. Operation of present-day catalysts is insufficient when the catalyst monolith is at low temperatures, e.g. during the cold start phase or under idling conditions [2]. This has been addressed by a number of secondary approaches (traps, close-coupled converters), but further improvements of the TWC itself are also desirable to solve these problems more directly. Including gold into TWC formulations is an interesting approach along this line. The potential of supported Au nanoparticles for low-temperature oxidation reactions originally found by M. Haruta, has attracted huge attention [3], but three-way catalysis has hardly ever been covered by these studies. We are therefore tackling the described issues by examining TWC preparations containing Au. As Au has a rather low melting point, it has to be predominately used as an alloy (e.g. Pd-Au, Pt-Au).

Different Au-based catalysts are prepared by a version of the traditional deposition-precipitation (DP) method [4]. All catalytic reactions are performed at ambient pressure in a catalytic microflow reactor of 15 mm inner diameter. The feed contains CO (1.1 %), O₂ (stoichiometric: 0.95 %), H₂O (10 % or none), NO (1000 ppm), C₃H₆ (1000 ppm), which was used to simulate unburned hydrocarbons and He (balance) and is applied with a GHSV of 60,000 h⁻¹ (183 ml/min feed on 125 mg catalyst). For comparison, CO and propene were also converted stoichiometrically with oxygen in absence of further reactants. Product analysis was performed by a combination of a calibrated mass spectrometer with a non-dispersive IR photometer. Prior to the actual TWC reaction each catalyst was pre-treated with a moist oxygen feed (2 % O₂, 2.4 % H₂O, balance He) for 1 h at 150 °C. The setup offers additionally the capability to simulate periodic fluctuations of feed composition (λ -fluctuations) typically encountered in exhaust of gasoline cars. The morphology of the Au catalysts was determined by elemental analysis, specific surface area analysis (BET), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and Transmission Electron Microscopy (TEM).

In the reaction of stoichiometric model mixtures for gasoline car exhaust (comprising, CO, propene, NO, O₂, with or without water) over supported monometallic Au catalysts, propene was observed to exert strong poisoning effects on CO oxidation. The poisoning effect depended on the nature of the support and on the water content of the gas. It was most intense in dry feed but partly alleviated in presence of moisture. The effect was most pronounced with Au on Al₂O₃, but its intensity decreased when La-Al₂O₃ and TiO₂ supports were employed, and was rather weak with Ce-ZrO₂. While exhibited promising catalytic potential of gold for oxidation of CO and propene in particular when supported on Ce-ZrO_x, NO was only partly converted in the TWC mixture. At low temperatures, NO conversion resulted in significant N₂O formation but selectivity to N₂ increased with temperature. Despite poisoning by propene, Au/Ce-ZrO_x outperformed a commercial reference catalyst in CO and propene oxidation.

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IV German-Russian Seminar on Catalysis
Bridging the Gap between Model and Real Catalysis

ABSTRACTS

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