

Diffuse scattering iso-surfaces in dodecane-urea host-guest compound in slabs perpendicular to the channel axis and close to multiple values of the guest reciprocal parameter. (down: projected image).

[1] J.M. Hastings et al., *Phys. Rev. Lett.* **1977**, *39*, 1484. [2] R.J. Nelmes et al., *Phys. Rev. Lett., PRL* **1999**, *83*, 4081. [3] Toudic et al., *Science* **2008**, *319*, 69. [4] T. Janssen et al., *Aperiodic Crystals: From Modulated Phases to Quasicrystals*, Oxford Univ. Press **2007**. [5] T. Weber et al., *Acta Cryst. B* **2000**, *56*, 132. [6] C. Mariette et al., "Phase ordering" phase transition leading to a modulated aperiodic composite in *n*-heptane/urea, to be submitted.

**Keywords:** phase-ordering, inclusion compounds, aperiodic

## MS.31.1

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### The impact of crystallography on design of adsorption and catalytic sites in zeolites

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In this lecture two examples will be developed illustrating the essential need to combine crystallography with other diagnostic tools for designing zeolite adsorbents and catalysts.

The synthetic FAU type zeolites known as zeolite X and Y are important industrial adsorbents. The cubic symmetry of the FAU zeolite crystals renders them particularly suitable for investigations of the organization of framework charge compensating cations and guest molecules using diffraction techniques and structure refinement. Adsorbates are known to alter cation positions and bring about important cation redistribution. While in early studies, cation redistribution upon adsorption and desorption were considered to be rather of secondary importance, the more recent insight is that cation migrations are essential and can even be triggered in order to facilitate regeneration of the adsorbent. In this lecture we present an example where the chemical reduction of an isolated ruthenium cation triggers a cascade of cation migrations leading to the elimination of the adsorption site.

This specific adsorbent is meant for NO<sub>x</sub> trapping from automotive exhaust gas in lean-rich cycles. In the lean phase, NO<sub>x</sub> is trapped while in the lean phase it needs to be desorbed and reduced to the harmless dinitrogen over a catalyst. At the typical water content of exhaust gas sodium cations and water molecules form very specific cation-water-networks extending in the channels of zeolite Y. In these networks the water ligands can reversibly be replaced by NO<sub>x</sub> molecules. Ru<sup>3+</sup> cations are preferentially located in hexagonal prisms of the zeolite structure. Switching to rich conditions leads to the reduction of these Ru<sup>3+</sup> cations to Ru<sup>0</sup> and disturbs the charge balance of framework and cations. It entails a migration of Na<sup>+</sup> ions from the water nets back to

framework sites causing abrupt release of the trapped NO<sub>x</sub>. Under lean conditions, the NO<sub>x</sub> adsorption sites are restored by oxidation and repositioning of the ruthenium cation. Knowledge of site occupancies from structure refinement of the adsorbent in saturated and regenerated state enabled the design of an optimal Ru,Ba,Na-Y zeolite adsorbent composition.

In the catalysis area the hydrocracking of *n*-decane model molecule has been used systematically in our laboratory for probing zeolite pore architectures in terms of dimensionality of the pore system and pore diameter. It is particularly useful to assist the structural characterization of complicated materials such as structural intergrowths, nanozeolites and fragile materials. In the lecture some examples will be given on how such catalytic testing and crystallography go hand in hand in answering practical catalytic questions such as the actual location of active sites.

**Keywords:** zeolites, cation positions, adsorption

## MS.31.2

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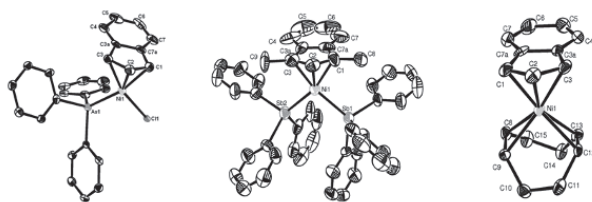
### Indenyl nickel catalysts: the effect of structure on oligomerisation reactions

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Indenyl complexes, which have the ability to undergo a facile ring slippage of the indenyl ligand from η<sup>5</sup> to a η<sup>3</sup> allyl-type coordination, have shown to be active in olefin oligo-/polymerisation [1]. On the other hand, several Ni(II) complexes containing simultaneously cyclopentadienyl and neutral arsenic or antimony donor ligands have been synthesised in the past [2]. More recently, Ni(II) complexes containing arsine and stibine donor ligands and the η<sup>3</sup>-allyl moiety have been prepared and their cationic derivatives showed to be highly active catalysts for the oligomerisation of styrene [3]. Taking this into account, we decided to study complexes containing an indenyl ligand, whose behaviour lies in between those of the allyl and cyclopentadienyl ligands.

Herein, we describe a novel methodology for the synthesis of new neutral [(η-R-Ind)Ni(EPh<sub>3</sub>)X] and cationic [(η-R-Ind)Ni(EPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> and [(η-R-Ind)Ni(COD)]BF<sub>4</sub> indenyl nickel complexes, containing neutral AsPh<sub>3</sub>, SbPh<sub>3</sub> or COD (1,5-cyclooctadiene) and/or halide (X=Cl, Br, I) ligands, which were characterised by NMR, elemental analysis and, when possible, by X-ray diffraction. In these complexes, the indenyl ligand contains methyl or silyl substituents (SiMe<sub>3</sub>). Comparative X-ray characterisation of the neutral compounds with [(η-Ind)Ni(PPh<sub>3</sub>)Cl] [4], enabled the confirmation of the dependence of the indenyl ligand distortion upon the neutral ligand donor ability. Structural parameters, such as the *slip parameter*, Δ<sub>M-C</sub>, the *hinge angle*, HA, and the *fold angle*, FA, were calculated from crystal data allowing the quantification of the indenyl slip-fold distortion. These compounds are highly active as homogeneous catalysts for the oligomerisation of styrene, at room temperature. Neutral complexes are only active when in situ halide abstraction is induced by MBF<sub>4</sub> salts (M=Ag or Tl), whereas the cationic ones are very active without the need of an aluminium co-catalyst. Their catalytic activity and the oligomer mass properties depend upon the nature of the substituents present in the indenyl ligand and of the donor ligand used.

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[1] D. Zargarian, *Coord. Chem. Rev.* **2002**, 233, 157-176. [2] For example: a) H. Yamazaki *et al.*, *J. Organomet. Chem.* **1966**, 6, 86-91; b) V.M. De Bellis *et al.*, *Inorg. Chim. Acta* **1985**, 104, L11-L12. [3] a) M. Jiménez-Tenorio *et al.*, *Chem. Commun.* **2003**, 1168-1169; b) M. Jiménez-Tenorio *et al.*, *Dalton Trans.* **2009**, 1842-1852. [4] T.A. Huber *et al.*, *Organometallics* **1995**, 14, 4997-4999.

**Keywords:** nickel, organometallic, catalysis

### MS.31.3

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#### Trapping and visualization of catalytic intermediates

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We described in the past a number of crystal structures of enzymes in which the intermediate catalytic states have been successfully trapped and visualized. In this presentation we will describe the kinetic and thermodynamic methods of trapping the intermediates and illustrate them with four examples of recently obtained structures. Two of these examples illustrate the kinetic trapping while the other two can be described as thermodynamic enrichment of the intermediate state. We will discuss the influence of external conditions on the course of the reaction as well as specific insights reached in the individual systems. Finally, we will sketch out general lessons regarding our understanding of bio-catalysis.

**Keywords:** enzyme catalysis, catalytic intermediate, stabilization of transition states

### MS.31.4

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#### Catalytic decomposition of ammonia monitored by in situ X-ray diffraction studies

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The decomposition of ammonia into nitrogen and hydrogen is one way to generate CO<sub>x</sub>-free hydrogen for fuel cell applications. Ammonia decomposition can also be applied in ammonia-fed solid oxide fuel cells. Both processes require temperatures above 400 °C. Therefore, highly active catalysts with high-temperature stability and long lifetime of the catalysts have to be developed. Supported ruthenium clusters have been shown to be the most active catalysts but high cost and limited availability force the development of alternative active catalysts. At present, metal oxides, nitrides and carbides are considered as potential catalysts. Recently, we have published the preparation and catalytic performance of core-shell structured iron oxide catalysts

[1]. Interesting materials for the catalytic ammonia decomposition are molybdenum and tungsten oxides, carbides and nitrides.

In the present contribution we present the behavior of different iron and molybdenum catalysts during catalysis. Phase transformation processes taking place under reaction conditions, as well as changes of the crystal structure and the microstructure were studied. The structural and compositional behavior of the catalysts was followed by means of in situ powder diffraction studies. The in situ experiments were conducted under reaction conditions in a XTK900 reaction chamber (Anton Paar) mounted on a X'Pert Pro diffractometer (PANalytical) in Bragg-Brentano geometry. Additionally to the diffraction experiments, all samples were characterized by gas adsorption measurements and electron microscopy studies.

For iron oxide catalysts, successive changes of the starting oxides with reaction temperature were observed. Starting from oxide species, several different oxides are formed, followed by iron nitride formation. Metallic iron phases are the crystalline phases stable at elevated temperatures. The long term catalytic stability can be related to the final particle size, which, on the other hand, is dependent on the synthesis and type of catalyst used.

Molybdenum oxide catalysts were synthesized with different molybdenum precursors and silica as dopant phase. The influence of the synthesis parameters on the products and on the catalytic properties was studied systematically. At lower temperatures changes of the crystal structure are taking place, followed by the formation of an intermediate phase and subsequent reduction of the primary oxide. The catalytic decomposition of ammonia starts at about 500°C, which is associated with the formation of molybdenum nitrides. Significant changes of the microstructure properties can be correlated to the catalytic performance of the different compounds.

Different molybdenum carbides and nitrides are further systems which were studied during the decomposition of ammonia.

[1] M. Feyen, C. Weidenthaler, R. Güttel, K. Schlichte, U. Holle, A.H. Lu, F. Schüth, *Chem. Eur. J.* **2011**, 17, 598-605.

**Keywords:** catalysis, in-situ, diffraction

### MS.31.5

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#### Mechanism of PSII oxygen evolution predicted from its 1.9 Å resolution structure

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Photosystem II (PSII) performs light-induced electron transfer and water-splitting reactions, which lead to the formation of molecular oxygen. PSII from thermophilic cyanobacteria consists of twenty subunits and many cofactors with a total molecular weight of 350 kDa for a monomer. X-ray crystal structures of PSII have been reported at 3.8-2.9 Å resolutions for *Thermosynechococcus elongatus* or *T. vulcanus*. However, the detailed structure of Mn4Ca-cluster, the catalytic center of light-induced oxygen evolution, has not been resolved. We have improved the diffraction quality of PSII crystals significantly, and succeeded in solving the crystal structure of PSII from *T. vulcanus* at a resolution of 1.9 Å [1]. Electron density distributions for the five metal ions in the Mn4Ca-cluster are clearly separated. Five oxygen atoms