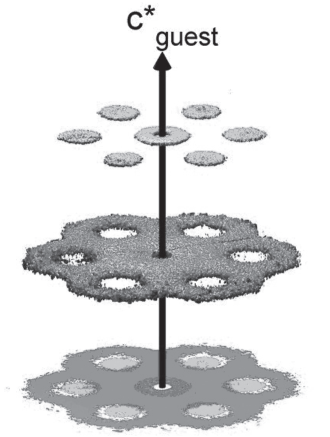

Diffuse scattering iso-surfaces in dodecane-urea host-guest compound in slabs perpendicular to the channel axis and close to multiple values of the guest reciprocal parameter. (down: projected image).

[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

Johan A. Martens, Steven Heyle, Christine E. A. Kirschhock, *Centre for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, Kasteelpark Arenberg 23, 3001 Leuven, (Belgium).* E-mail: johan.martens@biw.kuleuven.be.

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$_x$ trapping from automotive exhaust gas in lean-rich cycles. In the lean phase, NO$_x$ 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$_x$ molecules. Ru^{3+} cations are preferentially located in hexagonal prisms of the zeolite structure. Switching to rich conditions leads to the reduction of these Ru^{3+} cations to Ru^0 and disturbs the charge balance of framework and cations. It entails a migration of Na$^+$ ions from the water nets back to framework sites causing abrupt release of the trapped NO$_x$. Under lean conditions, the NO$_x$ adsorption sites are restored by oxidation and re-positioning 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 asssist 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

Clara S. B. Gomes, Leonel C. Silva, Sandra I. Costa, M. Teresa Duarte, Pedro T. Gomes, *Centro de Química Estrutural, Torre Sul, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa (Portugal).* E-mail: clara.gomes@ist.utl.pt

Indenyl complexes, which have the ability to undergo a facile ring slippage of the indenyl ligand from η^5 to a η^3 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^3-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$_3$)X] and cationic [(η-R-Ind)Ni(EPh$_3$)$_2$]BF$_4$ and [(η-R-Ind)Ni(COD)]BF$_4$ indenyl nickel complexes, containing neutral AsPh$_3$, SbPh$_3$ 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$_3$). Comparative X-ray characterisation of the neutral compounds with [(η-Ind)Ni(PPh$_3$)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*, $\Delta_{M\text{-}C}$, 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$_4$ 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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