

MS80.29.4*Acta Cryst.* (2005). A61, C102**14-Electron Metal Complexes Stabilized by $M \cdots \eta^3\text{-H}_2\text{C}$ Agostic Interactions**

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The coordination of inert C-H bonds to a transition metal center is of fundamental interest for stoichiometric and catalytic reactions, with particular regard to the problem of alkane functionalization via C-H bond activation. Unfortunately, information on the nature of the primary adduct is still very scarce, since saturated hydrocarbons are notoriously very poor ligands.

By use of the phosphine $\text{PR}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (R = Ph, Cy), bearing two methyl groups in the *ortho* position, rare examples of 14-electron Ru(II) and Pt(II) complexes have been isolated [1]. Solid state studies, using both X-ray and neutron diffraction techniques, reveal that non-classical $M \cdots \eta^3\text{-H}_2\text{C}$ agostic interactions take place and this result is in agreement with a structural survey on Cambridge databank, data in solution and a computational analysis. The reactivity of these complexes is reported, as well as the use of the Ru system as precursor for the preparation of highly active transfer hydrogenation catalysts.

[1] a) Baratta W., Mealli C., Herdtweck E., Ienco A., Mason S. A., Rigo P., *J. Am. Chem. Soc.*, 2004, **126**, 5549; b) Baratta W., Herdtweck E., Rigo P., *Angew. Chem. Int. Ed.*, 1999, **38**, 1629; c) Baratta W., Stoccoro S., Doppiu A., Herdtweck E., Zucca A., Rigo P., *Angew. Chem. Int. Ed.*, 2003, **42**, 105.

Keywords: agostic interactions, C-H activation, neutron structural determination

MS80.29.5*Acta Cryst.* (2005). A61, C102**Asymmetric Hydrogenation: Novel Rh(I) Catalysts & Predictive DFT Calculations**

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Recent advances in the calculation of molecular energetics based on Density Functional Theory (DFT) have raised the hope that both properties and transition state energy profiles could be predicted.¹ We have been investigating homogeneous Rhodium(I) catalysts coordinated to novel carbohydrate-phosphinite ligands and now report our attempts to predict by calculation the enantiomeric excess (ee) values for hydrogenation using variants of these ligands. We have characterized by X-ray diffraction analyses two components: "CandyPhos"(1D-3,4-(bis(O-diphenylphosphino)-1,2,5,6-tetra-O-methyl-chiro-inositol) and the active complex (CandyPhos)($\eta^4\text{-}(Z,Z)\text{-cyclo-octa-1,5-diene}$)-rhodium(I) tetrafluoroborate CHCl_3 solvate.

DFT calculations have been carried out using the Amsterdam Density Function programme suite² utilizing these diffraction coordinates and the previous in-depth analysis by Feldgus & Landis³. We will report the crystallographic details and the interim calculation results for model enamides in comparison with our in-house determined ee values. We acknowledge with gratitude the support of Professor Tom Ziegler & Dr Michael Seth of the University of Calgary, Calgary, Canada.

[1] Ziegler T., *Can. J. Chem.*, 1995, **73**, 743-761. [2] SCIENTIFIC COMPUTING & MODELLING NV, ADF Program Suite, Vrije Universiteit, Theoretical Chemistry, Amsterdam, The Netherlands. [3] Feldgus S, Landis C.R., *J. Am. Chem. Soc.*, 2000, **122**, 12714-12727.

Keywords: asymmetric synthesis, theoretical structural modelling, X-ray diffraction crystallography

MS81 TIME-RESOLVED POWDER DIFFRACTION FOR MATERIALS PRODUCTION AND PROCESSING*Chairpersons:* Eric Kisi, Paul Barnes**MS81.29.1***Acta Cryst.* (2005). A61, C102**Investigating Fast Solid State Reactions with Time-resolved Constant Wavelength Neutron Powder Diffraction at D20**

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D20 provides highest intensity in neutron powder diffraction. The incident flux on the sample reaches up to 10^8 n/s/cm² at 1.3 Å wavelength. A stationary, curved linear position sensitive detector covers continuously 153.6° in 2θ with 1536 cells in parallel. This makes D20 an ideal tool for *in-situ* diffraction studies with time constants even below a second and encourages the use of difficult sample environments. 4 vertically focusing monochromators, 15 take-off angles, and optional Soller collimators provide a large choice in Q-space, resolution, wavelength (0.8 to 2.4 Å), and flux, adapting D20 to various levels of crystallographic complexity and rapidity of an observed phenomenon. The continuous and simultaneous detection of series of complete diffraction patterns is necessary for the investigation of phase transitions during variation of a parameter like pressure or temperature (*thermodiffraction*). *One-shot* experiments study the structural evolution of solids *in situ* during a chemical reaction with single diagrams of down to 400 ms, quantifying short-living intermediate phases and elucidating subtle structural changes. High-resolution patterns can be obtained in a few minutes at high take-off angle. Faster, cyclic phenomena are observable in a stroboscopic acquisition mode. Time resolution is limited by the travel time of neutrons through sample and detection gap, ≈ 10 μs for thermal neutrons. An oscillating radial collimator with a focus aperture of 22 mm and full angular coverage suppresses background from sample environment.

Keywords: neutron powder diffraction, in-situ time-resolved powder diffraction, instrumentation

MS81.29.2*Acta Cryst.* (2005). A61, C102**Time-resolved Studies on Materials using Synchrotron Radiation at the ESRF**

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Time-resolved studies at the European Synchrotron Radiation Facility in Grenoble are becoming more and more important and span a wide range of fields of applications. The talk will outline the possibilities at the ESRF including X-ray sources, beamlines, detectors and auxiliary equipment.

The talk will be illustrated by examples of work performed on self-generated high temperature synthesis, batteries, annealing processes, phase transitions, grain growth as well very fast reactions on photo-dissociation.

Keywords: synchrotron radiation, time-resolved studies, chemical reactions

MS81.29.3*Acta Cryst.* (2005). A61, C102-C103**In-situ X-ray Diffraction Studies into Pressure Acid Leaching of Lateritic Ores**

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Nickel is the earth's 22nd most abundant element but it is not found in its native form other than in meteorites. Increasing world demand for nickel is reflected by its recent price increase. The majority of nickel is refined from sulphide ores but the oxide ores or laterites (sapolite, nontronite, limonite) represent the largest reserves

of this metal. There is increasing interest in pressure acid leaching (PAL) as a means of extracting nickel from laterites. PAL involves leaching of laterites in sulphuric acid under hydrothermal conditions, typically 250°C and 45 atmospheres pressure.

The saprolitic component of the ore is known to undergo rapid changes upon cooling following PAL thus making it difficult to examine using traditional post-mortem techniques. Time resolved, *in-situ*, X-ray diffraction (XRD) studies have been carried out into the reaction mechanisms of this process. The sample environment during this study aimed to closely emulate the conditions used in industrial processing plants. The novel experimental set-up used a capillary reaction vessel, short wavelength radiation and a position sensitive detector to enable rapid, simultaneous collection of a wide range of diffraction data. Quantification of the data via the Rietveld method has allowed the derivation of reaction mechanisms and kinetics.

This paper will present the results of both laboratory and synchrotron experiments within this system and will discuss the practice and perils of *in-situ* experimentation in general.

Keywords: *in-situ* time-resolved powder diffraction, process kinetics, quantitative phase analysis

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***In-situ* Measurement of Cation Ordering in Electroceramics**

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Electroceramics are critical elements in microwave devices widely used in communications equipment and a full understanding of their crystal chemistry is fundamental to future development. High temperature processing is crucial to the performance of these oxide materials in applications, due to the resulting control over both atomic scale structure and domain size over which the ordered structures persist.

We have developed high resolution neutron and synchrotron powder diffraction methods to study the structural development of commercially-used ceramics such as Ba₃ZnTa₂O₉ (BZT) and Ba₃CoNb₂O₉ (BCN) under industrial processing conditions[1] at temperatures of up to 1500 °C on timescales of minutes and in some cases seconds. The studies provide insight to domain growth during processing and quantitative information on order-disorder temperatures and thermodynamic processes affecting B-site cation ordering in the perovskite structures.

[1] Moussa S.M., Ibberson R.M., Bieringer, M., Fitch, A.N., Rosseinsky, M.J. *Chem. Mater.*, 2003, **15**, 2527.

Keywords: *in-situ* powder diffraction, order-disorder structure, dielectric ceramics

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Phase Transitions in Metal Hydrides by *in-situ* Synchrotron Powder Diffraction with High Time-resolution

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In-situ powder diffraction studies of hydrogen absorption/desorption in intermetallic compounds can offer valuable information about their real behaviour. The availability of the microstrip detector at the Materials Science Beamline at the Swiss Light Source, able to collect one full high resolution powder pattern in a very short time (~ 5 seconds), has allowed to follow hydrogen absorption/desorption in a sample in one shot.

A reaction tight cell rated up to 25 bar hydrogen pressure has been especially designed and built. Examples of *in-situ* studies on hydrogen absorbing intermetallic compounds like LaNi₅ will be shown. Analysis of the collected diffraction patterns has allowed obtaining the nature and amount of the phases involved during the hydrogen

absorption/desorption, the evolution of the lattice parameters, and the anisotropic character of the diffraction line broadening. From these data, the out-of-equilibrium phases have been observed.

Temperature and/or hydrogen desorption induced phase transitions in selected light metal hydrides like NaAlH₄, LiBH₄ were studied in high-temperature chamber Stoe. High angular resolution of the experimental set-up has allowed characterization of lattice defects involved in the phase transitions.

Examples of hydride structure solution by direct space method (program FOX) will be shown too.

Keywords: metal hydride, time resolved study, powder diffraction

MS82 X-RAY CHARACTERIZATION OF NANOSTRUCTURES

Chairpersons: Ugo Valbusa, Tilo Baumbach

MS82.29.1

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Quantitative Morphological Characterization of Nanostructure Arrays by scanning Probe Microscopy

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Due to the imaging principle in Scanning Probe Microscopies as Scanning Tunneling Microscopy and Atomic-Force Microscopy (AFM), the recorded image represents a topographical information $z(x,y)$ of the surface under investigation. Provided a well calibrated scanner and a sufficiently sharp probe, the three-dimensional shape and size of nanostructures can be determined with high precision. Besides analysis of individual structures, ensembles of nanostructures can be analyzed with respect to size and separation distributions applying power spectral density analysis of the recorded images. For epitaxial nanostructures with well defined facets, integral information on preferential facet orientations can be obtained by calculating histograms of local surface normals from $z(x,y)$. These procedures will be demonstrated for quantitative analysis of self-organized nanostructure arrays in semiconductor homo- and heteroepitaxy [1,2] as well as for ion-bombardment induced pattern formation [2,3].

[1] Teichert C., *Phys. Rep.*, 2002, **365**, 335. [2] Teichert C., *Appl. Phys.*, 2003, **A 76**, 653. [3] Bobek T., et al., *Phys. Rev.*, 2003, **B 68**, 085324.

Keywords: nanostructures, atomic-force microscopy, self-organization

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Ripple Structure of Ion Beam Induced Si Wafers

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Ion beam induced ripple formation in Si wafers was studied by atomic force microscopy (AFM) and non-destructive depth-resolved x-ray grazing incidence diffraction (GID). The formation of a ripple structure at high doses (7×10^{17} ions/cm²), starting from initiation at low ion beam doses (1×10^{17} ions/cm²) is evident from AFM, while that in the buried crystalline region below a partially crystalline top layer is evident from GID. GID reveals that these periodically modulated wave-like buried crystalline features become highly regular and strongly correlated as one increases the Ar ion beam energy from 60 keV to 100 keV. The vertical density profile obtained from the analysis of Vineyard profiles shows that the density in the upper top part of the ripples is decreased to about 25% to 35% of the crystalline density. The partially crystalline top layer found at low doses transforms to a completely amorphous layer for high doses. The top morphology was found to be conformal with the underlying crystalline ripple structure. The inspection of the amorphous scattering shows that the amorphous form factor of the damaged top layer is strongly textured in azimuth and scales with the ion dose.