MS31.P06

Acta Cryst. (2011) A**67,** C426

Advances in transmission electron microscopy for catalysis

Alfons M. Molenbroek, Stig Helveg, *Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby (Denmark).* E-mail: am@topsoe.dk.

Improvements in the understanding of catalysts and catalytic reactions strongly correlate with new developments in characterization techniques. Especially, the advancement in high-gas-pressure- and high-temperature- *in situ* probes to obtain structural and chemical information down to the atomic scale has contributed to new insights in the dynamic nanostructure of heterogeneous catalysts under operating conditions [1]. Here, the application of two recent advances in transmission electron microscopy (TEM) for heterogeneous catalysis will be discussed.

The first advancement is concerned with high-resolution TEM (HRTEM) imaging of the shape and crystal structure of industrial-style prepared graphite-supported MoS_2 nanocatalysts for hydrotreating reactions [2]. Previously, it was difficult to obtain atomic-resolved TEM images of the MoS_2 nanocatalysts due to insufficient image contrast or resolution. However, the introduction of aberration-corrected HRTEM has now made it possible to obtain atomically resolved images with a sensitivity at the single-atom level (see figure).

The second advancement is the introduction of MEMS (microelectromechanical systems) nanoreactors for *in situ* HRTEM of nanostructured materials during exposure to reactive gases at ambient pressure and high temperature. The pressure exceeds that of existing HRTEM systems by a factor of hundred and is at a level of relevance for catalyst testing. The reactor integrates a micro-meter sized gas-flow channel with a microheater and with an array of electron-transparent windows of silicon nitride. The nanoreactor performance is demonstrated on a methanol-synthesis catalyst by the observation of the formation of Cu particles on ZnO support with atomic-scale resolution [3,4].

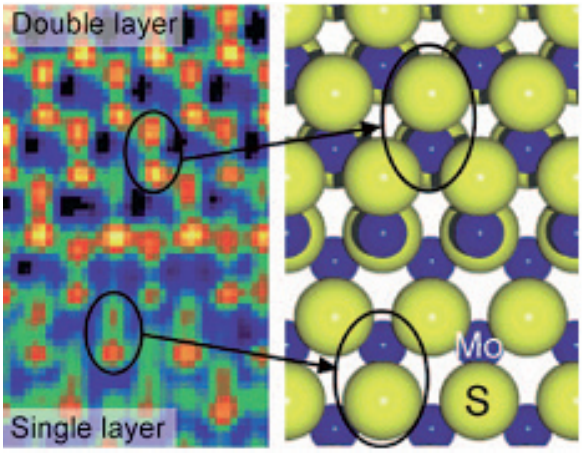


Figure: Atomic arrangement of industrial-style MoS_2 catalysts observed by single-atom-sensitive TEM.

[1] A. Stierle,A.M. Molenbroek, *Guest editors, MRS Bulletin* **2007**, *32-12*, 1001. [2] C. Kisielowski, Q.M. Ramasse, L.P. Hansen, M. Brorson, A.Carlsson, A.M. Molenbroek, H. Topsøe, S. Helveg, *Angewandte Chemie, published on line* **2010**, *15*. [3] J.F. Creemer, S. Helveg, G.H. Hoveling, S. Ullmann, A.M. Molenbroek, P.M. Sarro, H.W. Zandbergen, *Ultramicroscopy* **2008,** *108*, 993-998. [4] J.F. Creemer, S. Helveg, P.J. Kooyman, A.M. Molenbroek, H.W. Zandbergen, P.M. Sarro, *Journal of Microelectromechanical Systems, IEEE Early Access, Issue* **2010,** *99*, 1-11.

Keywords: catalysis, tem, nanocrystal

MS31.P07

Acta Cryst. (2011) A**67,** C426

Cooling rate- and temperature-dependence of the conformation of a mobile flap at the active site of urease

Matthew A. Warkentin,[a] P. Andrew Karplus,[b] Robert E. Thorne,[a] [a]*Departament of Physics, Cornell University, Ithaca, NY, (USA).* [b]*Department of Biochemistry and Biophysics, Oregon State University, Corvallis, OR, (USA).* E-mail: maw64@cornell.edu

Urease from Klebsiella aerogenes is an 86 kDa nickel-containing enzyme with four domains, one of which is a TIM-barrel and contains the active site. The unit cell is cubic $I2_13$ with a~178 Å [1]. Comparison of structures at room temperature and at T=100 K shows a dramatic change in the ~20 amino acid "flap" covering the active site. At room temperature the flap is relatively close to the active site ("closed" conformation), and is more disordered than the rest of the molecule. At T=100 K the flap is further from the active site ("open" conformation), but most of it is so disordered (B-factor ~ 80 $Å^2$) that it can scarcely be modeled.

We have examined how these changes develop on cooling by solving the structure at 13 temperatures between T=340 K and 100 K. The "closed" to "open" transition occurs between 270 and 240 K. In analogy to protein stability, the temperature of maximum stability for the folded state appears to be 340 K or higher. As the temperature is lowered, protein-protein interactions are lost in favor of hydration of protein surfaces, strengthening the analogy to protein folding.

Rapid cooling at ~10,000 K/s [2] causes the flap to be trapped in the "closed" conformation, indicating that the timescale for equilibration of the flap is on the order of milliseconds.

These findings demonstrate that information about the dynamics and energetics can be obtained from crystallographic studies if temperature and cooling rate are under experimental control.

We argue that the the driving force for closing the flap upon urea binding can be explained by the release of marginally bound waters from the active site, as opposed to any particularly strong interactions between the subtrate/transition-state and active site.

[1] E. Jabri, M.B. Carr, R.P. Hausinger, P.A. Karplus, *Science* **1995**. *268*, 998-1004. [2] P.A. Karplus, M.A. Pearson, R.P. Hausinger, *Accounts of Chemical Research* **1997,** *30*, 330-337. [3] M. Warkentin, V. Berejnov, N.S. Husseini, R.E. Thorne, *J. Appl. Cryst.* **2006**, *39*, 805-811.

Keywords: protein, temperature, dynamics

MS31.P08

Acta Cryst. (2011) A**67,** C426-C427

Alternative mechanisms for translesion DNA synthesis

Wei Yang,[a] Christian Biertuempfel,[a] Ye Zhao,[a] Feng Wang,[a] Fumio Hanaoka,[b] [a]*Laboratory of Molecular Biology, NIDDK, NIH, Bethesda, MD 20892 (USA).* [b]*Gakushiun University, Tokyo (Japan).* E-mail: wei.yang@nih.gov

DNA lesions due to loss of bases or chemical modifications prevent normal Watson-Crick (WC) pairing and stall normal DNA polymerases. Specialized polymerases are required to bypass such road block during DNA replication. DNA polymerases are divided into six families, A, B, C, D, X and Y based on sequence conservation. High-fidelity replication is normally carried out by the A, B or C-family polymerases. Most specialized translesion polymerases belong to the Y family and are distinct from replicative polymerases in sequence and structure. For example, among the four Y-family DNA polymerases found in humans, DNA pol η is encoded by XPV gene and its deficiency causes disease and skin cancer (1). Interestingly

among the B-family DNA polymerases, which include all eukaryotic replicative DNA polymerases, *E. coli* DNA pol II and eukaryotic pol ζ are exceptional and specialized for translesion and mutagenic DNA synthesis (2). In this presentation, different mechanisms of translesion synthesis by a B-family member and the Y-family human DNA pol η will be discussed. The key to the specificity of DNA polymerases, whether in high-fidelity replication or translesion synthesis, appears to be two Mg2+ ions essential for the catalysis.

Keywords: Metal ion, catalysis, nucleic acid enzymes

[1] C. Biertuempfel, Y. Zhao, et al., W. Yang, *Nature*, **2010** *465*, 1044-1048. [2] F. Wang, W. Yang, *Cell* **2009**, *139*, 1279-1389.

MS31.P09

Acta Cryst. (2011) A**67,** C427

Effects of local structure on electrocatalytic behavior of doped RuO

2Valery Petrykin,[a] Maki Okube,[b] Katerina Macounova,[a] Petr Krtil,[a] [a]*J. Heyrovsky Institute of Physical Chemistry, ASCR, Prague (Czech Republic).* [b]*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama (Japan).* E-mail: valery.petrykin@jh-inst.cas.cz

Recent theoretical works [1,2] on electrocatalytic O_2 and Cl_2 evolution on rutile-type oxides link the activity and selectivity in those processes to the cation stacking along the direction of c-axis. This order can be effectively altered by substitution of Ru in RuO_2 host by 3d metals such as Fe, Co, Ni or Zn. In particular, $Ru_{1-x}Ni_xO_2$ and $Ru_{1-x}Zn_xO_2$ materials exhibit opposite trends in terms of selectivity of chlorine and oxygen production, presenting interesting examples of local and electronic structures effects on catalytic performance of the materials. At the same time, the nature of "active sites" in both materials for both gas evolution processes is poorly understood due to the lack of structural information for these doped RuO_2 based oxides.

In this work local structure of $Ru_{1-x}M_xO_2$ (M=Ni and Zn; x=0.0-0.3) materials was examined by X-ray absorption spectroscopy (XAS) using the data collected on Ru-K, Ni-K and Zn-K edges at NW-10A and BL-12C beam lines of Photon Factory (KEK, Japan) and X18B line of National Synchrotron Light Source (BNL, USA). Visual comparison of the EXAFS functions revealed that the local structure around Ru core atoms undergoes only little change with increase of a dopant concentration. At the same time, the variation of Ni and Zn content results in rather dramatic evolution of Ni- and Zn- EXAFS functions and appearance of new features in the spectra that cannot be interpreted in terms of atomic arrangement in conventional rutile structure.

Full-profile refinement of EXAFS spectra revealed that for low Ni concentration the materials structure can be described in terms of Ni substitution into Ru site of RuO_2, which conforms to rutile structure. Ni tends to occupy metals sites along the diagonal of rutile unit cell, and the deviation of site occupancy from the statistically expected values indicates possible tendency of Ni towards clustering. For $Ru_{1-x}Ni_xO_2$ materials with x>0.1 Ni concentration, local structure around Ni cannot be explained in terms of substitution only, and one should assume formation of defects with rock salt motif in the vicinity of Ni. Such defects formation may be explained in terms of shear planes, which are common for the oxygen deficient rutile. The materials with Zn doping were found to be metastable with respect to the decomposition and at high zinc concentration they tend to realize another type of Zn-rich defect regions, which conform to the ilmenite structure within RuO_2 host. The revealed differences in the architecture around doped cations helped to explain the differences in the selectivity of those materials in the parallel electrochemical evolution of chlorine and oxygen that is connected with the formation of different type of intermediate oxo- and peroxo-species on the active surface of doped RuO_2.

[1] J. Rossmeisl, Z.W. Qu, H. Zhu, G.J. Kroes, J.K. Norskov, *J. Electroanal. Chem.* **2007**, *607*, 83-89. [2] H.A. Hansen, I.C. Man, F. Studt, F. Abild-Pedersen, T. Bligaard, J. Rossmeisl, *J. Phys. Chem. Chem. Phys.* **2010**, *12*, 283-290.

Keywords: catalyst, electrochemistry, EXAFS

MS31.P10

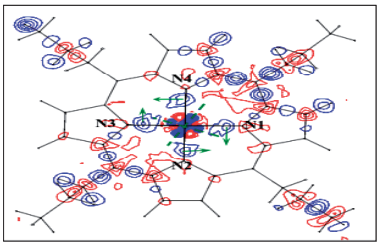
Acta Cryst. (2011) A**67,** C427-C428

Implication to the catalytic process of hemeproteins

Yoshiki Ohgo,[a,b,c] Daisuke Hashizume,[d] Kazuyuki Takahashi,[e] Hatsumi Mori,[e] Shinya Hayami,[f] Motoyasu Fujiwara,[g] Saburo Neya,[h] Yukiko Namatame[i] and Mikio Nakamura,[a,c] [a]*Department of Chemistry, School of Medicine, Toho University, Tokyo, (Japan).* [b]*Toho University Advanced Medical Research Center.* [c]*Division of Chemistry, Graduate School of Science, Toho University, Funabashi.* [d]*Molecular Characterization Team, RIKEN, Wako, (Japan).* [e]*Institute for Solid State Physics, The University of Tokyo.* [f]*Department of Chemistry, Graduate School of Science and Technology, Kumamoto University.* [g]*Institute for Molecular Science.* [h]*Department of Physical Chemistry, Faculty of Pharmaceutical Sciences, Chiba University* [i]*RIGAKU.* E-mail: yohgo@med.toho-u.ac.jp

Investigations to clarify the orbital interactions or the nature of the chemical bonds between metals and ligands in the metalloproteins are quite important not only for understanding their functional activation mechanisms, but also for the development of the related catalysts or functional materials. For example, in the case of hemeproteins, the catalytic activation mechanisms are closely connected with the electronic structures of central heme. Thus, the dπ-pπ interactions among iron(III) d-orbitals, frontier orbitals of porphyrin ring and axial ligands should be the essential manipulators in the functional activation mechanisms of the hemeproteins.

In the course of the study, we and others clarified that the non-planarity of the heme, which is induced by the protein environment, is one of the key-factors to control the functions in these catalytic cycles, because the non-planarity of the heme largely changes their electronic structure. Since it is generally quite difficult to examine the systematic studies on the subject such as correlation between the non-planarity and the electronic structures in bio-system, the model complexes studies are necessary in most cases. A number of the spectroscopic studies together with the quantum chemical calculations have been reported so far, but there are little studies that actually see chemical bonds in valence electron level experimentally. Although this is mainly because of the deficiency in the power of the X-ray source in the past, recent 3rd generation synchrotron X-ray light source make us possible to carry out the charge density study by single crystal X-ray method. Here we report the experimental electronic structure observation in the model of the nonplanar heme, which can be considered as the models for the various heme proteins, by means of the single crystal synchrotron X-ray structure analysis at the valence electron level. We also describes the "Spin-crossover Triangle" system, which are closely connected with the catalytic process of the hemeproteins, that respond to the external stimuli.[1-4]



[1] T. Ikeue, Y. Ohgo, T. Yamaguchi, M. Takahashi, M. Takeda, M. Nakamura, *Angew. Chem. Int. Ed.*, **2001**, *40*, 2617. [2] Y. Ohgo. T. Ikeue, M. Nakamura, *Inorg. Chem.*, **2002**, *41*, 1698. [3] Y. Ohgo, Y. Chiba, D. Hashizume, H. Uekusa,