MS31.P06

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

Advances in transmission electron microscopy for catalysis

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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].

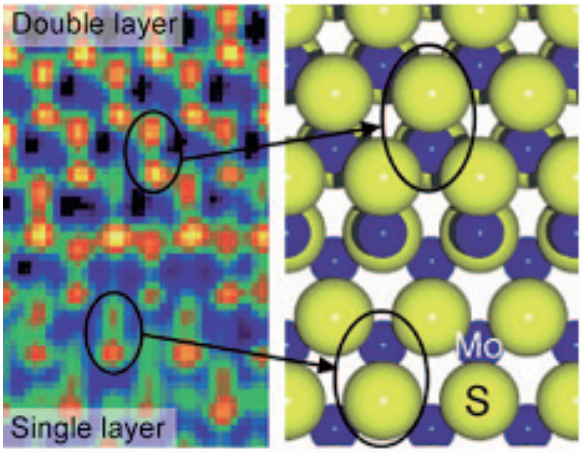

Figure: Atomic arrangement of industrial-style MoS_2 catalysts observed by single-atom-sensitive TEM.

[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

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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

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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