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**Keywords:** nickel, organometallic, catalysis

### MS.31.3

*Acta Cryst.* (2011) A67, C80

#### 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

*Acta Cryst.* (2011) A67, C80

#### 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.

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

### MS.31.5

*Acta Cryst.* (2011) A67, C80-C81

#### 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