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Keywords: nickel, organometallic, catalysis

MS.31.3

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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

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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_x-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 XRK900 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

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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

forming oxo-bridges between the metal ions are identified, and four water molecules are found to be associated with the metal cluster, some of which may serve as substrates in the oxygen-evolving reaction. The most significant structural feature of the Mn4Ca-cluster is its distorted chair form. The large distortion from a symmetric cubane is principally caused by the existence of Ca and O5, the fifth oxo-bridge connecting three Mn ions and one Ca ion. The distances between the four metal ions and O5 are remarkably longer than those between the other oxygen and metal ions. This suggests that the bonds between O5 and each of the Mn and Ca ions are very weak, implying that O5 is apparently different from the other four oxygen atoms and may therefore have a higher reactivity. It may also suggest that O5 has a lower negative charge compared with a valence of -2 expected for normal oxygen atoms in oxo-bridges, which in turn suggests that O5 may exist as a hydroxide ion in the S1-state of the Kok cycle.

In order to elucidate the mechanism of PSII oxygen evolution, it is crucial to identify the two substrate-water molecules participating in the O-O bond formation. Based on the above structural features revealed, O5 may form part of the reaction site. Among the four water molecules bound to the Mn4Ca-cluster, two are located most closely to O5, with their distances to O5 around 3 Å. In addition, these two water molecules have a distance of 3.3 Å between each other. Thus, it is most probable that O-O bond formation is taken place within these two water molecules and O5. In the conference, based on the crystal structure precisely determined at the resolution of 1.9 Å, we will propose two types of oxygen evolution mechanism. One includes O5 and one of the four water molecules bound to the Mn4Ca-cluster as the substrates of oxygen evolution reaction, whereas the other one does not include O5 and assumes that the O-O bond formation is taken place within two of the four water molecules.

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Keywords: oxygen evolution, photosynthesis, photosystem II

MS.32.1

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Rietveld refinement using G-Faktor applied on early OPC hydration

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The quantitative phase analysis during early hydration (24h) of Ordinary Portland Cement (OPC) is challenging due to the presence of variable amounts of different amorphous phases and water [1]. For some phases which are crystalline like monosulphate 14-hydrate structural data are not available. Classical use of Rietveld refinement does not deal with that challenge because the calculation of fitted phases is always normalized to 100 wt.-%. The use of an internal standard is not appropriate due to the known filler effect on the hydration of the OPC. Therefore a remastered external standard method using the G-factor can be employed [2]. We made use of Silicon as an external standard material. The G-factor can be derived from equation 1:

$$\text{Eq. 1} \quad G = s_{\text{Si}} \frac{\rho_{\text{Si}} V_{\text{Si}}^2 \mu_{\text{Si}}^*}{c_{\text{Si}}} \quad \text{with:}$$

s_{Si} = Rietveld scale factor of silicon
 ρ_{Si} = Density of silicon

V_{Si} = Unit-cell volume of silicon
 c_{Si} = Silicon content(100 wt.-%)
 μ_{Si}^* = Mass attenuation coefficient (MAC) of silicon

By determination of that G-factor any single phase might now be calculated from the equation 2 [3]:

$$\text{Eq. 2} \quad c_j = s_j \frac{\rho_j V_j^2 \mu_{\text{SAMPLE}}^*}{G}$$

Data needed can be extracted from Rietveld results. Only the μ_{SAMPLE}^* has to be calculated from the chemical composition which was determined in our investigation by XRF of the dry cement and the amount of mix water. Using that technique we followed the hydration reaction of OPC during the first 24h after contact with water. The quantitative data show an enormous accuracy with errors smaller than 0.1 wt.-% within one preparation. Main advantage of the method is the independent phase determination of any phase without normalization to 100 wt.-%. These accurate phase content was compared to the heat evolution of the cement measured by isothermal calorimetry. The multiple heat flow events in the pattern could be assigned with the help of the quantitative phase evolution. In a next step heat flow (HF) patterns were calculated from the quantitative phase data using equation 3.

$$\text{Eq. 3} \quad HF = \frac{\partial \text{wt.-% phase}}{\partial t} \times \Delta HR \quad \text{with}$$

$$\frac{\partial \text{wt.-% phase}}{\partial t} = \text{Derivative of the phase content from G-factor}$$

$$\Delta H_R = \text{Enthalpy of reaction}$$

Heat flow calculated from the change of phase content during hydration time determined by G-factor analyses fit very well the measured heat flow curves.

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Materials development; novel applications of time-resolved diffraction

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For almost a decade the development of ultra-fast, high-flux diffractometers has largely exceeded the experimental requirements of most users. Fortunately, in recent years the unique capabilities of these instruments have become more widely recognised and they are being applied as a reliable means of analysis. When combined with position sensitive detectors (PSDs) capable of a wide angular range (5-160° 2θ) and very fine time-resolution (<100ms), high-flux diffractometers begin to emerge as an industrially relevant technique in the design, characterisation and certification of advanced materials. The ability to implement such detailed analysis has been significantly aided through the concurrent development of batch Rietveld data processing suites and the Quantitative Phase Analysis (QPA) technique.

This present research will outline developmental work using the D20 diffractometer (ILL, France) in the exploration of a case study; *M_{n+1}A_xN Phases*. D20 has enabled us to explore the ultra-fast reaction kinetics of a Self-propagating High-temperature Synthesis (SHS) of