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Abstract:

Through attempts to correlate the structure of solid catalysts with catalytic activity it has become increasingly clear that the structure of a catalyst under reaction conditions may differ from that measured under conditions which are optimized for spectroscopy (e.g. vacuum or low temperature). This has led to a great effort to build in-situ cells, and to develop in-situ spectroscopic techniques for the characterization of catalysts in reactant atmosphere and at elevated temperature (323 - 800 K). XAS has become an important tool to help us understand how solid catalysts function. For such studies time-resolution, as well as gas phase analysis, and temperature control, as available at ID24, are essential. The following are two examples of the use of time resolved XAS in the study of catalysts.

MoO₃, when heated in propene and oxygen, becomes an active catalyst for the partial oxidation of propene to produce acrolein. It has been suggested that oxygen from the molybdenum oxide bulk may participate in the partial oxidation reaction. To gain an understanding of the processes occurring during the oxidation and reduction of Mo oxides the kinetics of the oxidation of MoO₂ and of the reduction of MoO₃ in oxygen and propene, respectively, were studied using time-resolved Mo K-edge XAS. Additionally, in-situ XAS measurements during temperature-programmed reaction in propene and oxygen have revealed structural changes occurring at the onset of activity [1,2].

The synthesis of ZrO₂ based catalysts involves the calcination (heating in air) of zirconium hydroxide in which a rapid release of chemical energy produces a spike in the sample temperature (glow) Fig 1a. We have measured the Zr K-edge EXAFS during the glow with a time-resolution of about one second (possible only at an energy dispersive beamline such as ID24), and the radial distribution function calculated from the measured spectra are presented in Fig. 1b. These results show that a local structure similar to that of hydrous zirconia remains relatively unchanged until the onset of the glow, and refutes claims that the release of heat is due to the coalescence of small single crystals into larger particles [3].

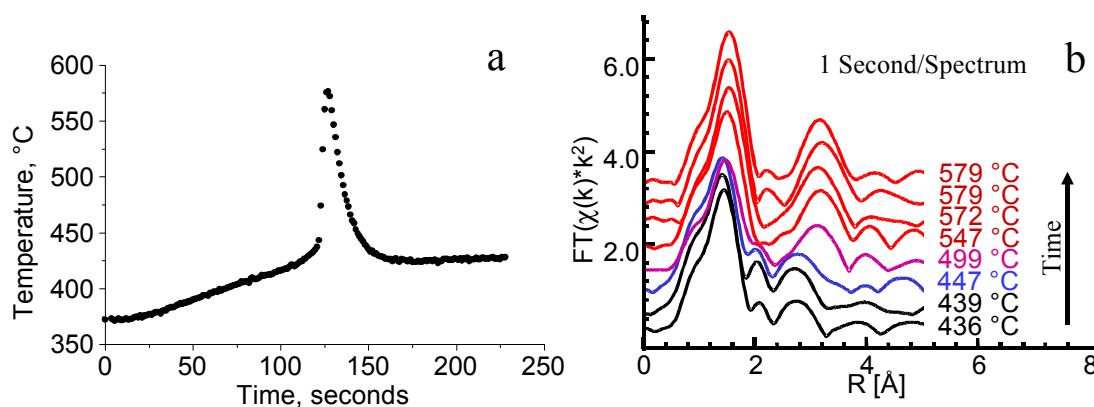


Figure 1: a) Temperature spike measured during in-situ calcination of Zr(OH)₄ to form ZrO₂, b) the radial distribution function for Zr K-edge spectra measured at the time of the temperature spike in the calcination.



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ESRF 2003

In-situ XAS Characterization of Catalysts



References:

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