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In situ cell for measuring X-ray absorption spectra of catalysts: *n*-butane isomerization on transition metal ion promoted sulfated zirconia

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Transition metal ion promoted sulfated zirconia catalysts are active for the skeletal isomerization of *n*-butane even at room temperature [1]. However, the active species in this catalyst is formed only during an induction period after the catalyst is in the feed. Therefore, we are interested in measuring changes in the transition metal promoters during this induction period to try and understand their role in the catalyst [2]. Initial attempts to measure the Mn K-edge of a 2 wt% Mn promoted sulfated zirconia catalyst during its use for the isomerization of *n*-butane were not successful. The catalyst was not active for this reaction when it was mixed with BN and pressed into a pellet. We were thus prompted to construct an in situ cell which could be used to measure fluorescence mode X-ray absorption spectra of a powder catalyst while operating in a fixed bed reactor. The design parameters for the cell were the ability to heat the sample to 723 K (necessary to activate the catalyst), a catalyst capacity of 0.5 to 1 gram, reactant gas flows of 80 ml/min, simultaneous measurement of a reference foil, a minimal beam path in the reactant gases, and accurate control of the temperature of the catalyst in the measured volume at a reaction temperature of 333 K.

The cell consists of an external body which contains an internal reactor, and is shown in Figure 1. The external body is a stainless steel cross with CF flanges. The flanges are used to attach Kapton® windows (Figure 1) for the incident beam (a), fluorescence signal (b), and to allow a portion of the beam which bypasses the catalyst bed to be used for the measurement of a reference foil (c). A bottom flange (d) has an outlet for He from the external body and a throughput for a thermocouple which measures the He temperature in the middle of the cell, near the reactor. A top flange (e) holds the reactor body in the center of the cell and has reactant gas inlet and outlet, a thermocouple, electrical supply to heat the reactor body, and a He inlet for the external body. The reactor body is

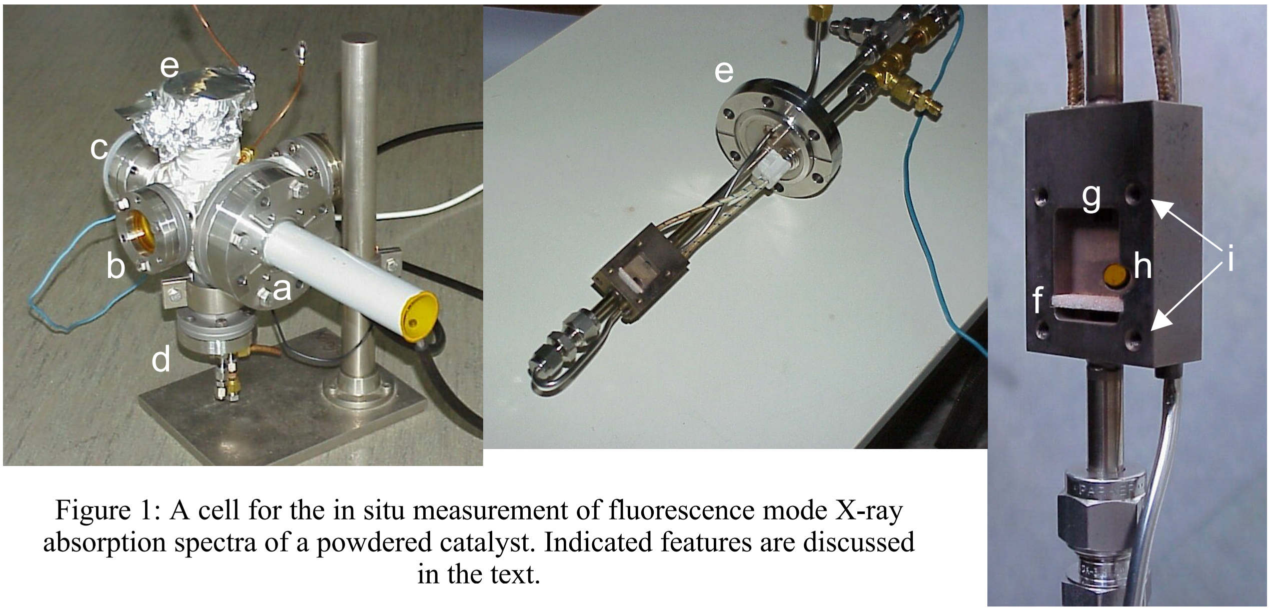

Figure 1: A cell for the in situ measurement of fluorescence mode X-ray absorption spectra of a powdered catalyst. Indicated features are discussed in the text.

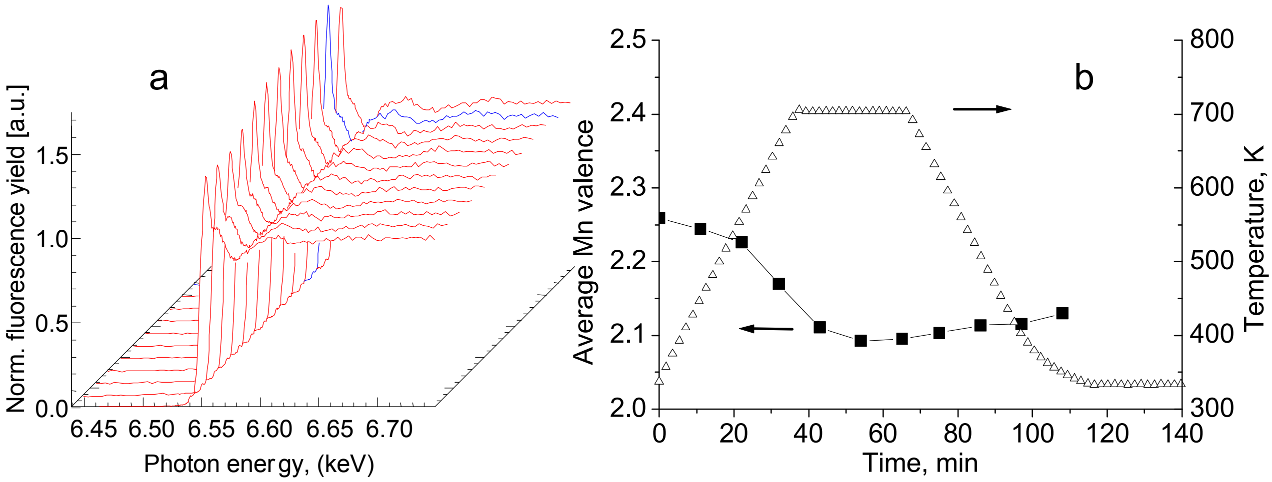

Figure 2. a) Mn K-edge X-ray absorption spectra of a 2% Mn promoted sulfated zirconia catalyst during reduction in 50% hydrogen for 30 minutes at 703 K. b) Average Mn valence during reduction calculated from data presented in 3a.

constructed of stainless steel with a glass frit (f) to support the catalyst bed, a thermocouple at the reactant gas inlet (g), and a 4.2 mm diameter hole which fits a Kapton® tube for the beam bypass (h). The reactor window is sealed with Kapton which is secured with a Cu block attached with 4 screws (i), and which has a 4 mm x 15 mm slot for transmission of the beam onto the sample. For temperatures above 373 K the reactor body is heated with two 40 watt cartridge heaters. Gas product concentrations are monitored with a mass spectrometer connected to the reactor outlet.

A series of Mn K-edge spectra taken during the reduction of a 2% Mn promoted sulfated zirconia catalyst in 50% hydrogen at 703 K is shown in Figure 2a. The Mn K-edge energy is a function of the Mn valence. With the accurate energy calibration possible when a fraction of the beam bypasses the catalyst bed and is used to measure a Mn foil spectrum, the data in Figure 2a can be used to calculate the average Mn valence in the catalyst during reduction, and these results are presented in Figure 2b.

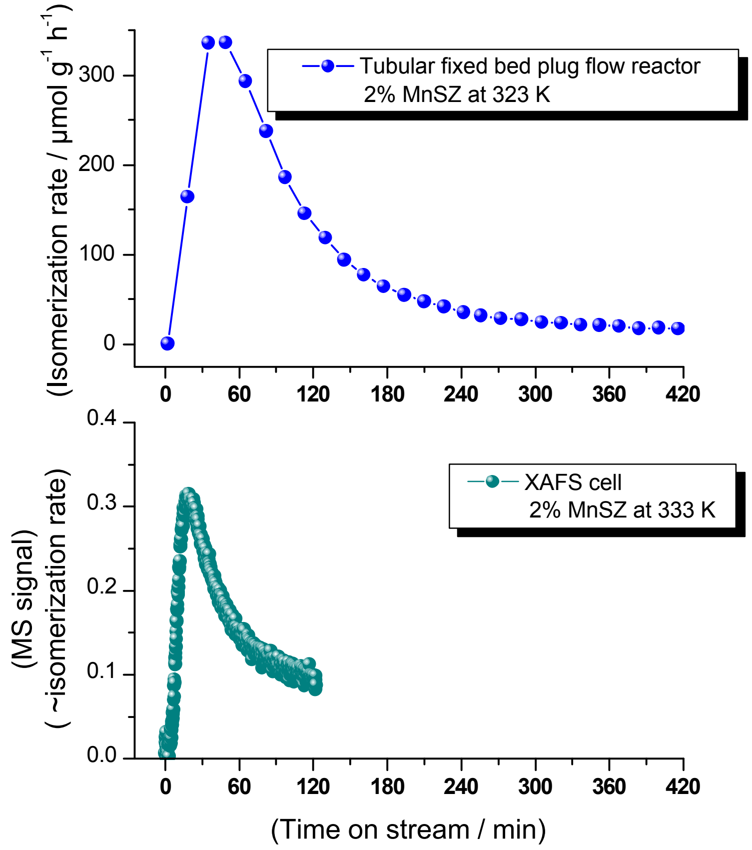

Figure 3. Time on stream profiles for 2% Mn promoted sulfated zirconia catalyst in 1% *n*-butane in a fixed bed reactor (above) and in the XAS cell (bottom).

The reaction profile for *n*-butane isomerization with promoted sulfated zirconia exhibits a period of increasing conversion followed by deactivation, and the length of these periods decreases with increasing temperature. Figure 3 shows the reaction profile of a 2% Mn promoted sulfated zirconia catalyst for the isomerization of *n*-butane to form isobutane at 323 K in a fixed bed reactor, and for the same reaction at 333 K in the in-situ cell reactor. The similar reaction profiles demonstrate that the catalyst in the in situ cell is under conditions similar to those in a fixed bed reactor.

In this new in situ cell we can measure fluorescence mode X-ray absorption spectra of catalysts while they are at work in a laboratory scale fixed bed, plug flow reactor.

References

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[2] R.E. Jentoft, A. Hahn, F.C. Jentoft, and T. Ressler, J. Sync. Rad. 8, 563 (2001).