Zr K-edge EXAFS of ordered mesoporous sulfated zirconium oxide catalysts

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Supramolecular assemblies of amphiphiles are used as structure directing agents in the formation of M41S type ordered mesoporous materials [1]. These materials are of great interest to the catalysis community as catalysts themselves, and as supports for catalysts. This technique has recently been expanded to the synthesis of similar materials using non-siliceous oxides such as TiO_2, WO_3, Fe_2O_3, and $AlPO_4$ [2]. The synthesis of ZrO_2 ordered mesoporous materials using amphiphile templating techniques has faced challenges, both in the formation of a mesostructured oxide/surfactant composite, and in stability of the oxide during the removal of the surfactant. The solution has been the addition of sulfate or phosphate during synthesis. The structure is then stable enough to undergo template removal through calcination, with the ordered mesopores and amorphous pore walls [3-7] being retained.

Sulfated ZrO_2 itself is an active catalyst for the structural isomerization of light alkanes at temperatures < 523 K [8]. One of the unresolved questions concerning this catalyst is the effect of the bulk ZrO_2 structure on the activity. Sulfate stabilizes the tetragonal phase of ZrO_2 catalysts when they are formed through calcination of zirconium hydroxide. The tetragonal phase of ZrO_2 is commonly accepted as the phase of the most active catalysts. However recent reports show that the monoclinic phase can also be active, albeit at higher reaction temperatures [9]. The ability to produce an ordered mesoporous sulfated ZrO_2 with amorphous pore walls allows us to investigate the structure and activity of a sulfated ZrO_2 catalyst that is neither tetragonal nor monoclinic.

The mesoporous sulfated zirconium dioxide was synthesized using hexadecyl-trimethyl-ammonium bromide (CTAB) as template and zirconium *n*-propoxide as the oxide precursor. The synthetic procedure is adapted from that of Ciesla et al.[5] and is described in detail elsewhere [10]. The resulting suspension was dried at 333 K overnight to give a composite of sulfate, oxide, and template. The composite was calcined at 813 K for 16 h in air to give the sulfated mesoporous zirconium dioxide. For comparison of structure and catalytic properties a commercially available catalyst from MEL Chemicals (XZO682/01) calcined at 923 K in air for 3 h was also investigated.

Catalytic tests were carried out in a once-through fix bed reactor with 200 mg of catalyst at 378 K using 1 vol% *n*-butane (30 ml/min). The catalyst was activated in flowing N_2 for 90 min. at 723 K.

X-ray absorption spectra (XAS) were taken at beamline X1. The fine structure analysis was performed using the software package WinXAS v2.1 [11]. EXAFS data analysis was carried out using theoretical backscattering phases and amplitudes calculated with FEFF7 [12]. Single scattering and multiple scattering paths were calculated up to 4.1 Å with a lower limit of 2 % in amplitude with respect to the strongest backscattering path. EXAFS fitting and simulation were performed using the standard EXAFS formula (k range from 3.6 to 15.2 $Å^{-1}$, R range 1.1 to 4.2 Å). Refinements were carried out in R space to magnitude and imaginary part of a Fourier transformed k^3-weighted experimental $\chi(k)$. Structural parameters refined were (i) E_0 shifts for Zr and O backscatterers, (ii) Debye temperatures for Zr and O backscatterers, (iii) distances of
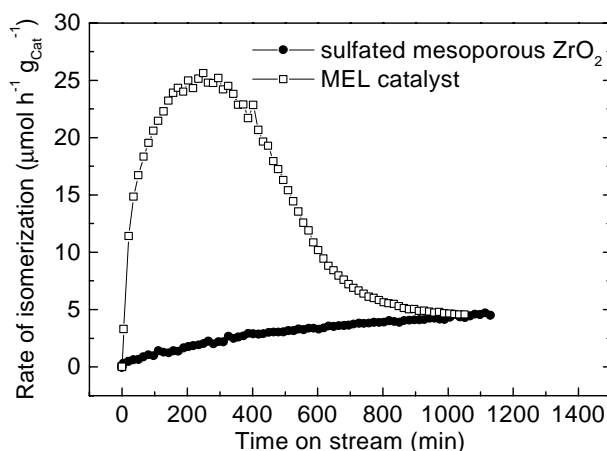

Figure 1: Reaction test results of for n-butane isomerization. See text for conditions.

single scattering shells. Backscatterers of like atom in the monoclinic ZrO$_2$ structure whose distance differed by < 0.05 Å were constrained to vary the same in the refinement. Coordination numbers and S_0^2 were kept invariant in the refinement.

Fig. 1 shows that the activity of the tetragonal MEL catalyst goes through a maximum followed by deactivation to a stable level. Ordered mesoporous sulfated ZrO$_2$ does not have the initial high activity, but does have a similar long term activity. Fig. 2 shows the FT(χ(k)) of the mesoporous sample in as-synthesized and calcined forms from measured spectra, and the FT(χ(k)) for cubic, tetragonal, and monoclinic zirconia (c-, t-, m-ZrO$_2$) obtained by calculation using model structures. Zr and O Debye temperatures obtained in EXAFS refinement of the measured data were used to modify the amplitude of the Fourier transforms of the calculated χ(k). The calcined mesoporous ZrO$_2$ could be sufficiently described by modification of a m-ZrO$_2$ structure as shown in Fig. 3. The Zr-O coordination in the first shell of the as-synthesized sample did not change significantly upon calcination, but a slight contraction of the Zr-Zr distances in the higher shells did occur. For the calcined sample, the data exclude the presence of tetragonal crystallites of a size below the XRD detection limit. Given the thinness of the walls, a large fraction of zirconium atoms are surface atoms and are expected to have a coordination that is incomplete or different from the bulk, at least in the second shell (Zr-Zr). Consistent with this picture, the data are most similar to the least symmetric reference, i.e. the monoclinic modification of ZrO$_2$.

These results help to show that the mesoporous sulfated zirconia is an active catalyst with a bulk zirconia structure which is distinctly different from that of the tetragonal MEL catalyst on both a local (< 4 Å) (XAS) and long range order (XRD) scale. The mesoporous sample also has a distinctly different pattern of activity with time on stream suggesting that the bulk structure does affect the catalytic activity.
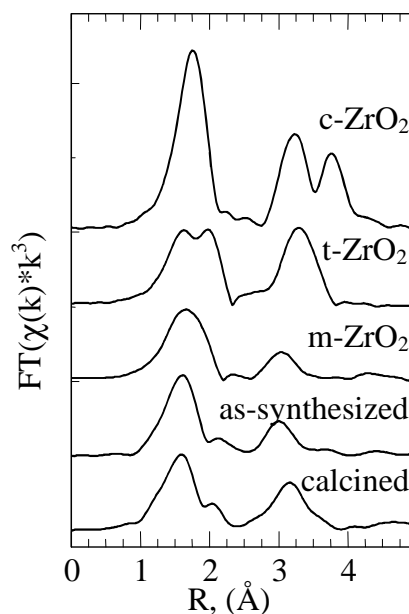
Figure 2: Radial distribution function for calcined and as-synthesized mesoporous ZrO$_2$ (measured), and cubic, tetragonal, and monoclinic ZrO$_2$ (calculated).
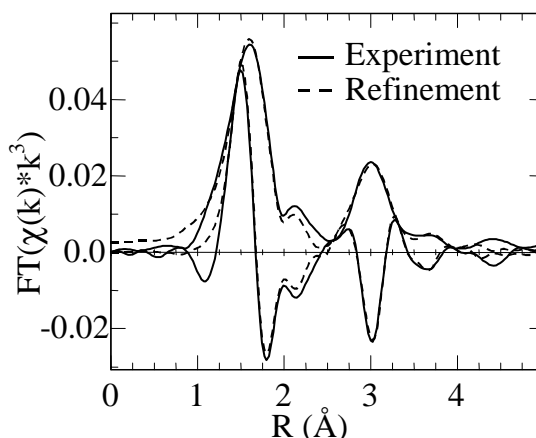
Figure 3: EXAFS refinement to spectrum of calcined ordered mesoporous sample

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