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Neutron Powder Diffraction Study of Sulfated Zirconia Catalysts

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Abstract

In situ neutron powder diffraction method was used to investigate the crystal structures, phase abundance and thermal stability of sulfated zirconia catalysts prepared by impregnation of hydrous zirconium oxide gels with 0.5 M H_2SO_4 solutions. The sample studied was precipitated at pH = 10 and dried for 5 h at 493 K, and then calcined at 853 K for 3 h. Diffraction data were collected in the temperature range 295-1273 K in an Ar atmosphere and analyzed using the Rietveld method. Only the metastable tetragonal phase was observed below 673 K. Above this temperature, the sample consisted of a mixture of tetragonal (T) and monoclinic (M) phases in the proportions (T:M wt%) 85:15 (1073 K) and 61:39 (1273 K). Surface modification by sulfation was found to retard the onset of the tetragonal-to-monoclinic transformation relative to pure zirconia. The decrease in peak-broadening at the higher temperatures reflects both an increase in crystallite size and a decrease in microstrain.

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Keywords: sulfated zirconia, metastable zirconia, catalysts, phase transformation.

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1. Introduction

Sulfated zirconia catalysts have high acidity (Hammett acidity function $H_0 \leq -16$) and are known to catalyze n-butane isomerization at room temperature. Therefore, these materials have attracted considerable attention as potential solid acid catalysts in cracking, isomerization, alkylation, acylation, esterification, and oligomerization. In addition, use of zirconia catalysts could eliminate the problem of separating liquid catalysts (such as HF and H_2SO_4) from the product stream and meet the increasing need for environmentally benign processes.[1] Of particular interest is the effect of the degree of crystallinity, the crystallographic symmetry of sulfated zirconia phases, the sulfation procedures and thermal stability on catalytic activity and surface chemisorption. In this study, the crystal structure of sulfated zirconia was investigated at temperatures up to 1273 K using neutron-powder-diffraction. The objective of these experiments was to determine the combined effects of sulfation and temperature on the stability of the tetragonal and monoclinic phases of zirconia.

2. Experimental

Zirconium hydroxide was prepared by hydrolysis of 0.2M zirconium oxychloride ($ZrOCl_2 \bullet 8H_2O$, Fluka) by dropwise addition of an ammonia hydroxide solution (28wt%) until a pH of 10.0 was reached. During this process, the stirring rate, dropping speed of ammonia hydroxide and pH were controlled by a Mettler-Toledo DL 12 Titrator (Mettler-Toledo Inc.). The precipitate was washed with deionized water, filtered, and then dispersed in deionized water. This sequence was repeated until no Cl^- was detected in the filtrate. The sample was then dried in air for 5 h at 493 K. After drying, the gel was impregnated with 0.5 M H_2SO_4 (~15 ml/g gel), dried in air for 5 h at 493 K and calcined at 853 K for 4 h. Neutron diffraction experiments were carried out on the GPPD diffractometer at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. Data were collected *in situ* at 295, 373, 673, 1073 and 1273 K under a flowing Ar atmosphere (50 ml/min) using a furnace.

3. Results and discussion

Rietveld refinements of the data sets yielded R-factors (R_W) and goodness-of-fit (χ^2) values ranging from 0.0210 to 0.0711 and from 2.239 to 2.560, respectively. The refinement profiles for the sulfated zirconia at 673 and 1073 K are shown in Fig. 1. Below 673 K, only the tetragonal phase was observed. Despite numerous investigations, the stabilization of the metastable tetragonal modification at relatively low temperatures is poorly understood. One explanation is that the formation of inorganic chelating bidentate sulfated complexes on the surface of zirconia either induces surface interactions, which obstruct the formation and growth of monoclinic domains, or lowers the surface energy of zirconia resulting in stabilization of the tetragonal phase below 673 K. At the higher temperatures (1073 and 1273 K), Bragg peaks become sharper and both tetragonal and monoclinic phases are present (Fig. 1). The phase abundance as a function of temperature is shown in Fig. 2 for pure and sulfated zirconia. Apparently, surface modification by sulfation significantly affects the relative amounts of the tetragonal and monoclinic phases at higher temperatures. Based on these experiments and heat treatments carried out during synthesis, the tetragonal-to-monoclinic phase transformation in sulfated zirconia occurs in the temperature range 853-1073 K. The phase transformation may be related, in part, to the decomposition of the surface complexes. By analogy to the decomposition of sulfated Fe_2O_3[2], the decomposition reaction can be written as:

$$\text{sulfated zirconia} \xrightarrow{>873K} ZrO_2 + SO_2 + 0.5O_2.$$

Results obtained from refinement of peak-shape parameters indicate that the decrease in peak broadening at the higher temperatures reflects both an increase in crystallite size and a decrease in microstrain. Grain-size theory predicts that the tetragonal phase of pure zirconia should be unstable for a crystallite size above ~300 Å.[3] The crystallite size of the tetragonal phase of sulfated zirconia below 673 K is ~150 Å. At temperatures above the tetragonal-to-monoclinic phase transformation, this value increases from ~400 Å at 1027 K to ~1900 Å at 1273 K.

Acknowlegement

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Figure captions

Fig. 1. Rietveld profile fits for sulfated zirconia at 673 K (a) and 1073 K (b). The symbols (+) are the observed, background subtracted intensities. The solid line represents the calculated intensities. Tick marks below the profile indicate the positions of all allowed reflections for each of the phases: tetragonal (a); and alumina (from furnace), monoclinic and tetragonal zirconia from top to bottom (b).

Fig. 2. Phase abundance plotted as a function of temperature for pure [4] and sulfated zirconia (this study). The data point at 853 K (solid square) is obtained from an X-ray diffraction analysis of the calcined sample after cooling.

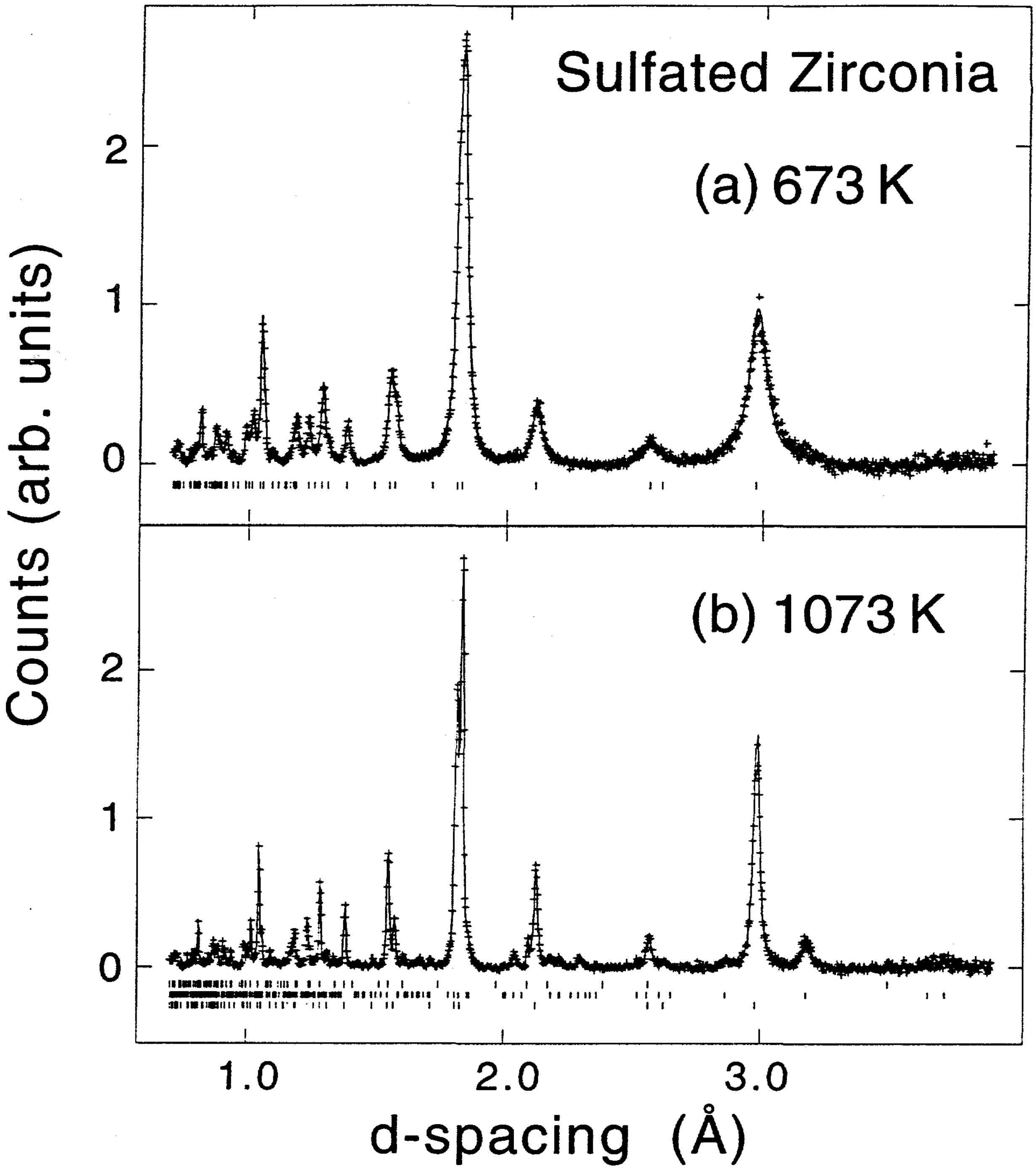

Figure 1, "Neutron Powder Diffraction ..." by Li et al.

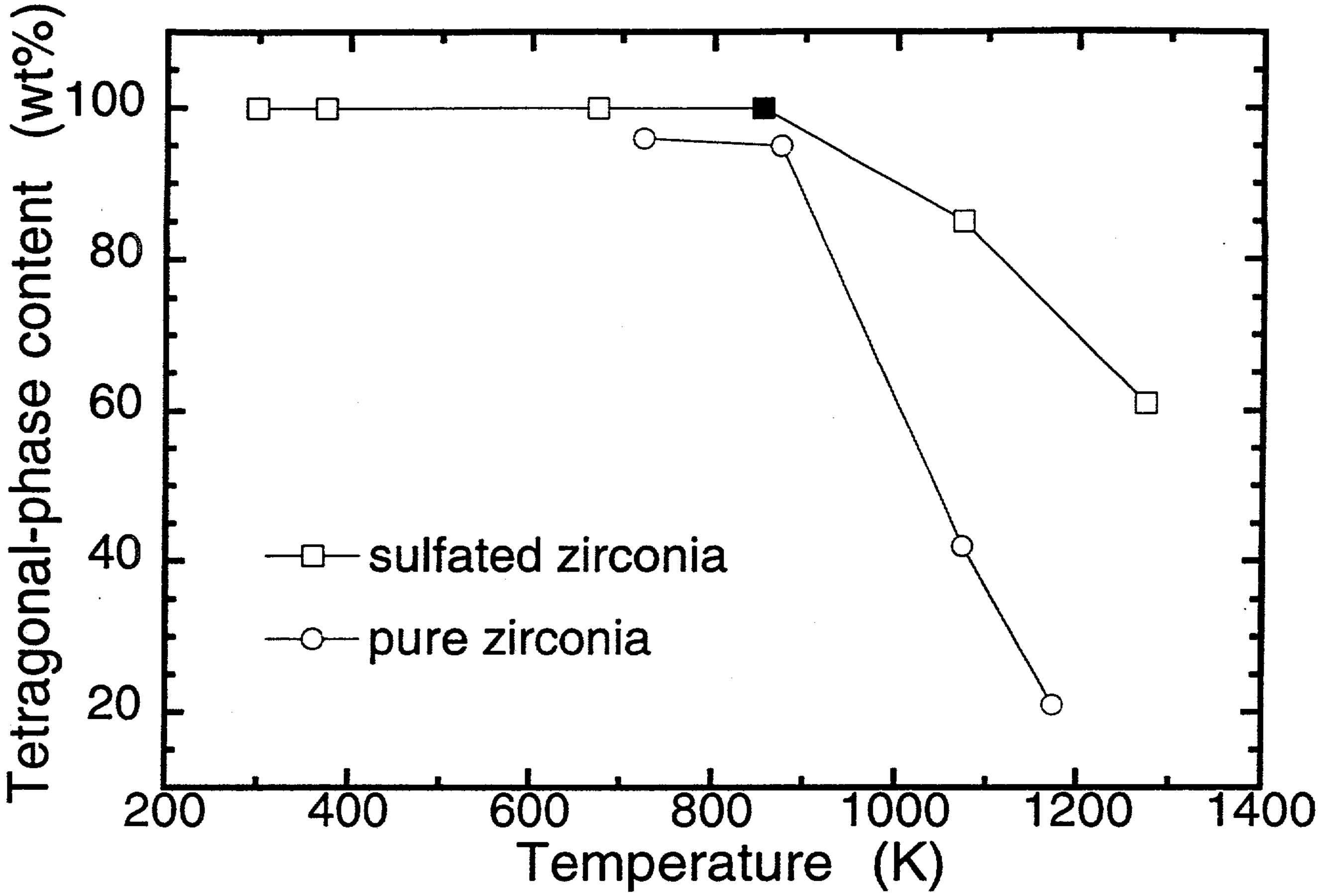

Figure 2, "Neutron Powder Diffraction..." by Li et al.

Estimation of the length of this paper

a) Title, authors, affiliation and 155-word abstract	355 words
b) Additional two affiliations listed	100 words
c) Three figures, fitting a single column	300 words
d) Manuscript text	664 words
e) References (4)	60 words
Total:	1479 words

For two printed pages: 1600 words