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Role of Molybdenum at the Iron Oxide Surface

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The structure of Mo at the surface of Fe_2O_3/SO_4 and ferrihydrite catalysts was investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy. Molybdenum is found to be surrounded by 3–4 oxygens at 1.73–1.75 Å with no extended coordination shells beyond the nearest oxygen shell. X-ray diffraction results for the Mo/ferrihydrite catalysts after high temperature annealing demonstrate that the incorporation of Mo at the ferrihydrite surface effectively prohibits crystal growth and allows the catalyst to maintain its dispersion to higher temperatures. © 1994 Academic Press, Inc.

I. INTRODUCTION

Sulfated iron oxide catalyst, Fe_2O_3/SO_4, is known to be active for direct coal liquefaction (DCL) (1, 2). The Fe_2O_3/SO_4 catalyst has a hematite (α-Fe_2O_3) strucure with sulfate anions (SO_4^{2-}) at the surface (2). The role of the SO_4^{2-} is to induce the formation of coordination-unsaturated (CUS) sites, or Lewis acid sites, at the catalyst surface, and thereby increase the surface acidity. The presence of SO_4^{2-} at the surface also inhibits the crystal growth of the Fe_2O_3 phase. Recently, Pradhan *et al.* (3) showed that the dispersion and DCL conversion can be further improved by incorporating Mo or W in the Fe_2O_3/SO_4 catalyst.

Ferrihydrite is the initial precipitate that results from rapid hydrolysis of Fe(III) solutions. It is regarded as one of the eight major iron oxide/oxyhydroxides by geologists, although its structure remains a controversial topic (4). The material has a very small particle size of ~30 Å and a large surface area of >200 m²/g. Although the name ferrihydrite is not commonly used in catalysis, it is usually the initial iron oxide phase formed in silica- and alumina-supported Fe catalysts, normally identified as highly dispersed α-FeOOH (5). Unsupported ferrihydrite catalysts have been used for oxidative dehydrogenation of 1-butene (identified as amorphous FeOOH) (6), for enhancing the burning rate of rocket fuel (as α-Fe_2O_3) (7), and for direct coal liquefaction (as FeOOH and α-Fe_2O_3) (8, 9). The problem with the material as a catalyst, however, is that it is unable to maintain its dispersion at high temperature (6, 7, 8). At temperatures between 250 and 300°C, it quickly agglomerates and transforms to α-Fe_2O_3, which results in a significant reduction in surface area.

Recently, using X-ray absorption fine structure (XAFS) spectroscopy (10), we found that the bulk structure of ferrihydrite is similar to that of iron oxyhydroxides in which iron ions are coordinated by six oxygen/hydroxyl groups. In addition, as many as 20–30% of the iron ions are likely to be located at surface coordination-unsaturated (CUS) sites. By means of chemisorbed water molecules, these CUS sites become favorable locations for crystal growth responsible for the particle agglomeration and phase transition of ferrihydrite to α-Fe_2O_3 at low temperatures (11). However, if there are impurity anions present in the precipitation solution, the CUS sites may preferentially consist of the impurity anions instead of water molecules. Consequently, crystal growth is inhibited and the catalyst is able to maintain its dispersion to higher temperatures. A Si/ferrihydrite (Si/Fe = 0.05) catalyst has been shown to maintain its dispersion to temperatures as high as 400°C (12).

In this paper, we investigate the structures of Mo at Fe_2O_3/SO_4 and ferrihydrite catalyst surfaces and the effect of a surface Mo layer on the dispersion of the ferrihydrite catalysts. XAFS and X-ray diffraction (XRD) were used for this investigation.

II. EXPERIMENTAL

A $Mo/Fe_2O_3/SO_4$ catalyst was prepared by homogeneous coprecipitation followed by an incipient wetness impregnation with Mo (3). An $(NH_4)Fe(SO_4)_2 \cdot 12H_2O$ solution was reacted with urea at about 95°C for 2 h. After washing and drying, crystalline α-FeOOH was formed with residual sulfate anions SO_4^{2-} adsorbed at the catalyst surface. The $FeOOH/SO_4$ was then impregnated with Mo and calcined in air at 500°C. The atomic concentration ratio of Mo/Fe is 1% (3).

Mo/ferrihydrite (Mo/FHYD) catalysts were prepared by a precipitation method. Ammonium hydroxide was added to a solution of $Fe(NO_3)_3 \cdot 9H_2O$ and $(NH_4)_6$

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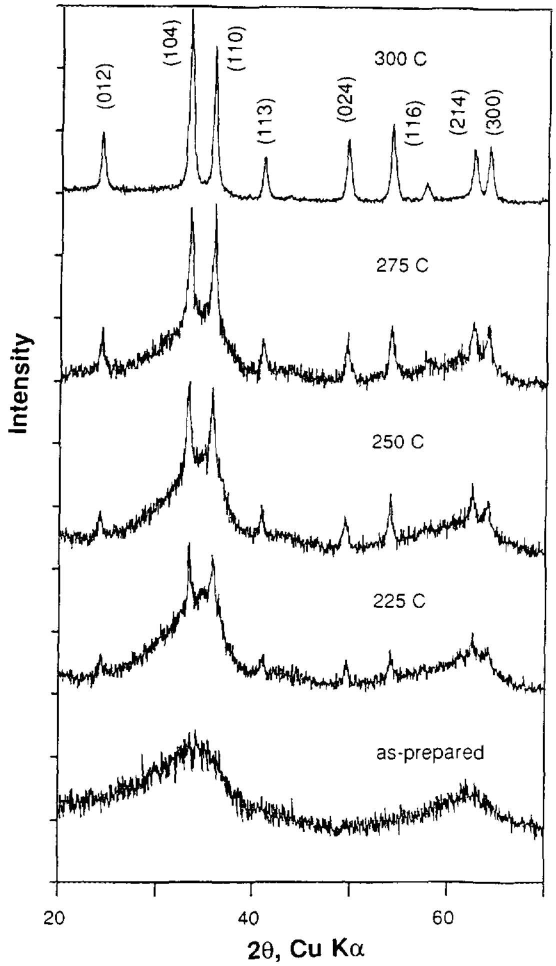

FIG. 1. XRD patterns for the pure ferrihydrite catalyst before (bottom) and after 5 h annealing at 225–300°C. Before annealing, the XRD pattern (bottom) shows two broad peaks, typical for 2-line ferrihydrite. After annealing, crystalline α-Fe_2O_3 starts to form, as indicated by the sharp diffraction peaks superimposed on the two broad peaks for 2-line ferrihydrite.

$Mo_7O_{24} \cdot 4H_2O$ to bring the pH to 10. After filtering and washing, the precipitate was dried at 50°C in air and then ground into a fine powder. Before use, it was vacuum dried at 150°C for 3 h to remove water molecules adsorbed at the surface. Two Mo/FHYD catalysts were prepared with atomic concentration ratios of Mo/Fe = 5 and 35%, respectively. The Mo loading was determined by the atomic ratio of Mo/Fe in the precipitation solutions.

Both Fe*K*-edge (7,112 eV) and Mo*K*-edge (20,000 eV) X-ray absorption fine structure spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL). The radiation was monochromatized with a Si(220) double crystal monochromator. The XAFS data were collected from samples at room temperature with a Lytle fluorescence detector. A Rigaku DMax X-ray diffractometer with Cu*Kα* emission line was used for characterization of the phases in the catalysts.

TABLE 1

List of the Position, (*hkl*) Index, *d*-spacing, and Relative Intensity of the Diffraction Peaks of the α-Fe_2O_3 Phase Shown in Fig. 1

2θ	(*hkl*)	*d*-spacing, Å	Intensity, % (relative)
24.2	012	3.67	35
33.2	104	2.70	100
35.7	110	2.51	85
40.9	113	2.20	26
49.7	024	1.84	33
54.2	116	1.69	43
62.6	214	1.48	30
64.1	300	1.45	31

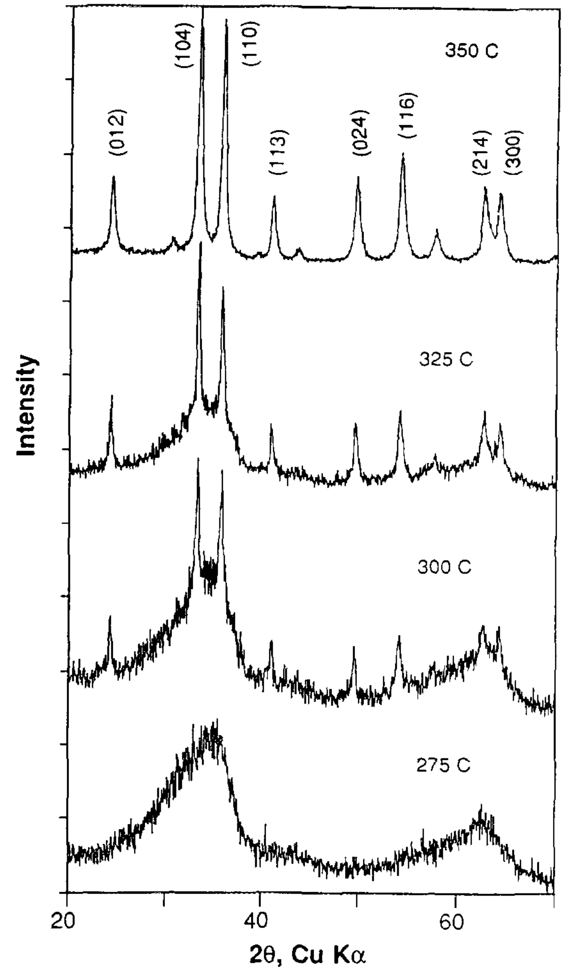

FIG. 2. XRD patterns for $Mo_{0.05}$/FHYD after 5 h annealing at 275–350°C. On comparing these XRD data with those in Fig. 1 for pure ferrihydrite, the appearance of α-Fe_2O_3 occurs at considerable higher temperature.

III. RESULTS AND DISCUSSION

The structure of the Fe_2O_3/SO_4 catalyst had been previously identified by XRD and Mössbauer spectroscopy as α-Fe_2O_3, with average particle size ~200 Å (2, 9). The XRD pattern for an as-prepared pure ferrihydrite catalyst (provided by Mach I, Inc. (7)) shows two broad diffraction peaks (Fig. 1), typical for 2-line ferrihydrite (4). After annealing at 225°C for 5 h, crystalline α-Fe_2O_3 begins to form, as indicated by the sharp diffraction peaks superimposed on the ferrihydrite peaks (Fig. 1). The percentage of the α-Fe_2O_3 phase increases with annealing temperature and at 300°C, only α-Fe_2O_3 is seen (Table 1). For $Mo_{0.05}$/FHYD, similar behavior is observed, except that the formation of α-Fe_2O_3 begins at 300°C and the phase transformation is not completed until 350°C (Fig. 2). The XRD pattern for $Mo_{0.35}$/FHYD before annealing shows a large shoulder at $2\theta < 35°$, but otherwise it is similar to that for the pure ferrihydrite catalyst shown in Fig. 1. For this sample, new phases start to form at 500°C (Fig. 3): the positions of the diffraction peaks at $2\theta = 23.0°$ (d-spacing = 3.87 Å), 25.3° (3.52 Å), and 27.6° (3.23 Å) agree with those for bulk MoO_3 with d-spacings = 3.81, 3.46, and 3.26 Å, and the position and shape of the diffraction peaks at $2\theta > 35°$ are similar to those for 6-line ferrihydrite, a better ordered ferrihydrite phase (4). However, no α-Fe_2O_3 is seen in the XRD pattern for the 500°C annealed sample. The results demonstrate that incorporating Mo in ferrihydrite effectively prevents particle agglomeration, allowing the catalysts to maintain their dispersion to higher temperatures.

Figure 4 shows the Fourier transforms of the FeK-edge EXAFS spectra for the two Mo/FHYD catalysts. The spectra are similar to that reported for pure ferrihydrite (10). Two major peaks are observed at ~1.6 Å and ~2.9 Å, which correspond to an O/OH shell at 2.01 Å and Fe shells at 3.01–3.15 Å, respectively (10).

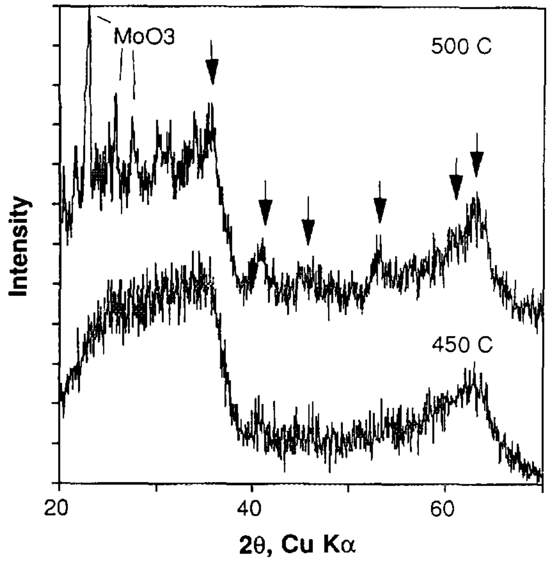

FIG. 3. XRD patterns for $Mo_{0.35}$/FHYD after 5 h annealing at 450 and 500°C. Arrows indicate the diffraction peaks for 6-line ferrihydrite.

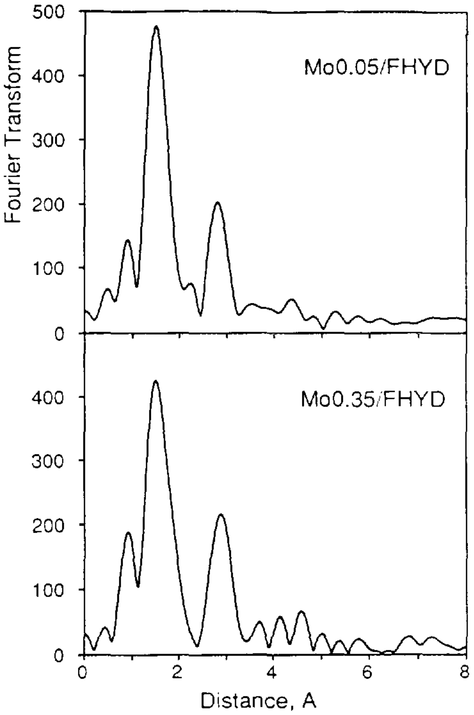

FIG. 4. Fourier transforms of the FeK-edge EXAFS for the Mo/FHYD catalysts.

MoK-edge XAFS spectroscopy provides evidence that the Mo species are at the surface rather than in the interior of the $Mo/Fe_2O_3/SO_4$ and catalysts. The Fourier transforms of the Mo/FHYD EXAFS spectra for the three samples show a dominant peak at 1.3 Å (Fig. 5). To obtain structural parameters, the phase shift and scattering amplitude functions for a Mo–O pair were first extracted from the MoK-edge XAFS spectrum of MoO_2 with known values of coordination number (N) and interatomic distance (R), and then used as constants to fit the EXAFS spectra of the catalysts to obtain N and R for Mo in the samples. The best fit values of structural parameters are listed in Table 2, in which σ is the Debye–Waller factor and $\Delta\sigma^2$ represents the difference between the value of σ^2 for MoO_2 and the value σ^2 for the samples. For all three catalysts, Mo is found to be surrounded by 3–4 oxygen atoms at 1.73–1.76 Å. Such Mo–O distances are typical for tetrahedrally coordinated MoO_4^{2-} anions and close to the shorter Mo–O distances for octahedrally coordinated MoO_3 in which Mo has four oxygen neighbors at 1.67–1.94 Å and two oxygen neighbors at 2.25 and 2.34 Å (Table 2). Similar Mo EXAFS spectra have been reported for Co–Mo/Al_2O_3 catalysts (oxide phase) (13, 14) and a Mo-attached Al_2O_3 catalyst (15). No distinguishable

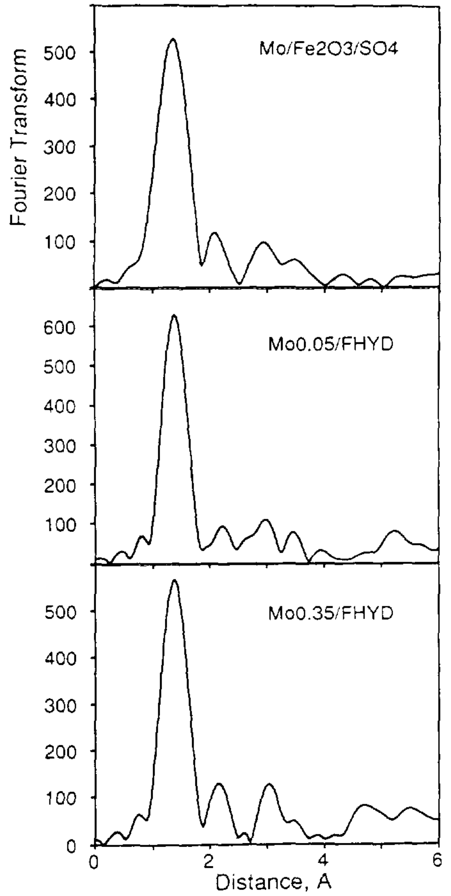

FIG. 5. Fourier transforms of the Mo*K*-edge EXAFS for the Mo/Fe_2O_3/SO_4 and the Mo/FHYD catalysts.

TABLE 2

Interatomic Distance (*R*) and Coordination Number (*N*) Comparison for the Mo Oxide Phases

Sample	N_{oxygen}	R(Mo–O), Å	$\Delta\sigma^2$
$Mo_{0.01}/Fe_2O_3/SO_4$	4.2	1.73	0.0015
$Mo_{0.05}$/FHYD	3.2	1.75	−0.0009
$Mo_{0.35}$/FHYD	3.2	1.76	−0.0015
MoO_2	6	1.98–2.07 (average = 2.01)	
MoO_3[13]	4	1.67–1.94	
	2	2.25, 2.34	
K_2MoO_4[13]	4	1.76	
$Na_2MoO_4 \cdot 2H_2O$[13]	4	1.72	
Co-Mo/γ-Al_2O_3[13] (oxide)	3–4	1.73	

EXAFS features are observed beyond 2 Å (Fig. 5), indicating that the Mo species are probably isolated at the surface with no extensive coordination shells beyond the nearest oxygen shell.

In conclusion, our results indicate that Mo in the Mo/Fe_2O_3/SO_4 and Mo/FHYD catalysts is at the surface, most probably as tetrahedral MoO_4^{2-}. According to the surface structural models for the Fe_2O_3/SO_4 and ferrihydrite catalysts (2, 10, 11, 12), these Mo species are likely to be chemisorbed at the surface CUS sites. As we have shown, such chemisorbed Mo inhibits crystal growth, prevents the formation of larger Fe_2O_3 particles, and allows the catalyst to maintain its dispersion to higher temperatures, thereby enhancing catalytic activity (3).

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