

STRUCTURE AND PHASE TRANSITION OF AN ULTRAFINE IRON OXIDE CATALYST

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I. Abstract

The structure and phase transitions of an iron oxide catalyst with average particle diameter of 30Å have been examined by means of X-ray absorption fine structure (XAFS) spectroscopy, thermal gravimetric analysis (TGA), Mossbauer spectroscopy, and transmission electron microscopy (TEM). The structure is found to be an FeOOH with surface iron ions at coordination unsaturated (CUS) sites or Lewis acid sites. At annealing temperatures of 250 to 350°C, the sample only partly converts to larger α -Fe₂O₃ particles. The conversion rate is greatly accelerated if the sample is exposed in air for several days. The results indicate that the 30Å particles become linked by water molecules adsorbed at the CUS sites after air exposure. At elevated temperature, these water molecules are evolved from between the particles, facilitating both agglomeration of the particles and phase transition to α -Fe₂O₃.

II. INTRODUCTION

In recent years, significant efforts have been made to produce highly dispersed iron catalysts for direct coal liquefaction (DCL), in order to increase surface area and minimize catalyst loading. Improved dispersion and conversion rate have been obtained by modifying the surface structure by adding small amount of sulfur and other elements to the catalyst [1]. Studies have shown that, at the sulfated iron oxide (Fe₂O₃/SO₄) surface, coordination unsaturated (CUS) sites or Lewis acid sites are formed [2]. It has been suggested that a sulfated surface may prevent agglomeration of small catalyst particles during reaction [1]. The activity is also found to be sensitive to the surface conditions as determined by the moisture content of the catalysts [1,3]. These observation indicate that the surface structure and surface conditions are crucial for catalyst performance, although the exact mechanisms are still unclear.

III. EXPERIMENTAL

The catalyst sample (NANOCAT™) is manufactured by Mach I, Inc. In addition to the as-received sample, several samples were prepared by annealing the as-received sample in air for 24 hrs at temperatures from 250 to 500°C. To observe the effect of moisture, part of the as-received sample was first exposed in air for five days at room temperature, and subsequently annealed at 250°C in air for 24 hrs.

X-ray absorption spectra were collected at the National Synchrotron Light Source (NSLS) on beam line X-19A at Brookhaven National Laboratory. All spectra were collected in the transmission mode and at liquid-nitrogen temperature.

Transmission electron micrographs and micro-diffraction patterns were obtained with a Hitachi H800 NA microscope. The operating voltage was set at 200kV for all samples.

Mössbauer spectra were recorded with a constant acceleration spectrometer. The

radioactive source consists of ~50 mCi of ^{57}Co in Pd matrix. Spectra were recorded at 10 K with an Air Products displax cryogenic system.

Thermogravimetric analysis (TGA) were performed with a Seiko 320 TGA/DSC system.

III. RESULTS

Structure of the 30Å Catalyst

The EXAFS radial structure functions (RSF) of the 30Å catalyst and several iron oxides and oxyhydroxides are shown in Figure 1. The position of the first Fe shell is close to that for oxyhydroxides. Least squares fitting for the 30Å catalyst gives first Fe coordination shell at 3.01 Å. By comparing with the first Fe shell distances of iron oxides (2.92-2.95 Å) and iron oxyhydroxides (3.01-3.05 Å), we conclude that the structure of the 30Å catalyst is oxyhydroxide (FeOOH) like. The x-ray absorption near edge structure (XANES) for the 30Å catalyst is also similar to that for the oxyhydroxides.

Although both EXAFS and XANES for the 30Å catalyst indicates an FeOOH structure in which iron ions are coordinated by total six oxygens or hydroxyl groups, the intensity of pre-edge structure (Figure 2) of the catalyst is 1.7 times that for those octahedral oxides and oxyhydroxides, indicating that part of the iron ions have coordination less than six [4]. After an extended period of exposure of the sample to air, the average coordination number is increased as indicated by the decrease of the pre-edge peak. Therefore, these low coordination sites are likely to be at the particle surface. These sites, created by dehydroxylation on the oxide surface, are also known as CUS (coordination unsaturated) sites or Lewis acid sites. More details of the structure analysis are given in Ref. 5.

Effect of Annealing

The TGA curve for the fresh 30Å catalyst is compared to that of $\alpha\text{-FeOOH}$ in Figure 3. At temperatures < 300°C, $\alpha\text{-FeOOH}$ converts to $\alpha\text{-Fe}_2\text{O}_3$ by releasing H_2O , resulting in 11% weight loss. For $\alpha\text{-FeOOH}$, the phase transition occurs between 200 to 270°C, as shown in the figure. For the 30Å catalyst, although a ~12% weight loss at $T > 700^\circ\text{C}$ suggests that the above reaction does occur, no clear phase change was observed from room temperature up to 900°C.

TEM micrograph of the sample after 250°C annealing for 24 hrs indicates the coexistence of two phases (Figure 4a); the small particle 30Å FeOOH phase and a larger particle ($d \approx 150\text{Å}$) $\alpha\text{-Fe}_2\text{O}_3$ phase. The volume fraction and average particle size of the larger $\alpha\text{-Fe}_2\text{O}_3$ particles increases with annealing temperature. However, a considerable percentage of the 30Å particles appears to be unchanged even after 24 hrs annealing at temperatures up to 350°C which would completely convert $\alpha\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$. At annealing temperatures of 400°C and higher, larger particles dominates and the particle size becomes uniform. The phase transition rate is greatly accelerated if the 30Å catalyst is exposed to moist air before annealing. After annealing at 250°C in air for 24 hrs, the moisture exposed sample mainly consists of larger particles with diameters of ~150Å, as shown in TEM micrographs (Figure 4b).

The percentages of the two iron phases in the annealed samples are determined by Mossbauer spectroscopy [6]. After annealing at identical conditions, the as-received sample consists of 65% 30Å FeOOH phase and 34% $\alpha\text{-Fe}_2\text{O}_3$ phase, whereas the air-exposed sample consists of 26% 30Å FeOOH phase and 73% $\alpha\text{-Fe}_2\text{O}_3$ phase.

IV. DISCUSSION

The difference of phase transition rates between the as-received and air exposed 30Å

FeOOH catalysts at elevated temperature is attributed to their surface conditions. A surface layer with CUS sites can effectively prevent not only the agglomeration of the small 30Å FeOOH particles, but also dehydroxylation in the sample bulk, thereby slowing down the phase transition. However, after moisture exposure, the small 30Å particles become linked by adsorbed H₂O molecules on the surface. At elevated temperature, these water molecules are evolved from the particle joints, leading to agglomeration and phase transition to α -Fe₂O₃. A diagram of this process is shown in Figure 5. It appears that the phase transition to α -Fe₂O₃ occurs immediately after the agglomeration takes place, as indicated by the TEM and Mössbauer results, which show no trace of larger FeOOH particles. At annealing temperatures below 350°C, the rate of phase transition is determined mainly by the coverage of the water molecules adsorbed on the particle surface. Agglomeration and phase transition take place mainly in those particles linked by water molecules. At T > 350°C, the transition to α -Fe₂O₃ is due to the dehydroxylation inside of the 30Å catalyst particle. It should be noted that only those H₂O molecules adsorbed on the CUS sites may remain on the particle surface at T > 250°C or higher. Physisorbed H₂O molecules, since their bonding to the particle surface is much weak, will be detached from the particle surface at temperature well below 250°C.

Acknowledgement

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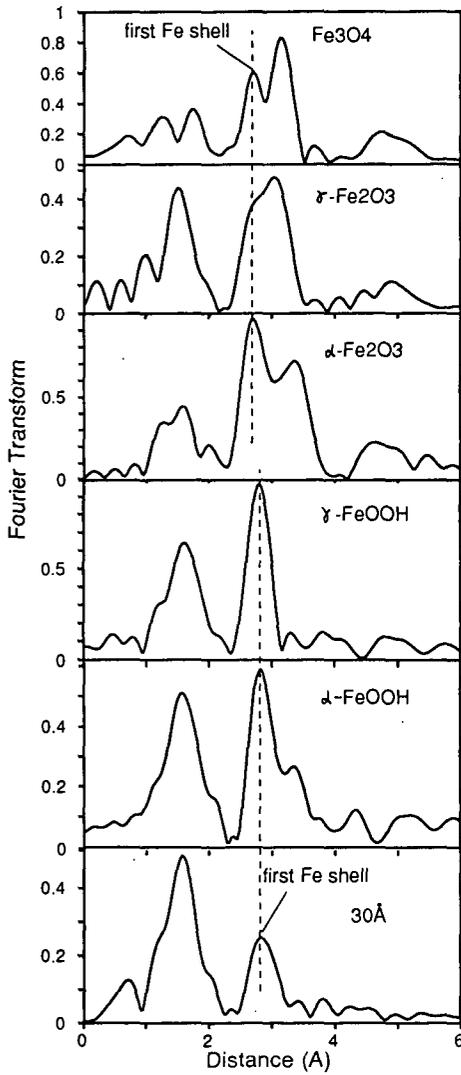


Figure 1. EXAFS RSF's for the 30Å catalyst and model compounds.

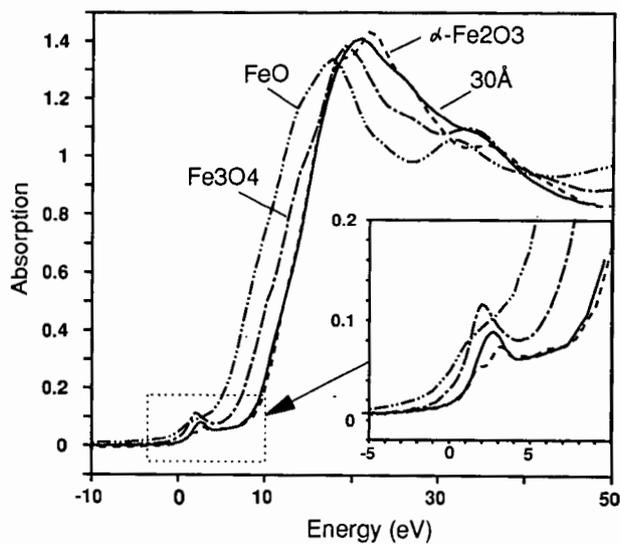


Figure 2. XANES pre-edge structures of the 30Å catalyst and model compounds.

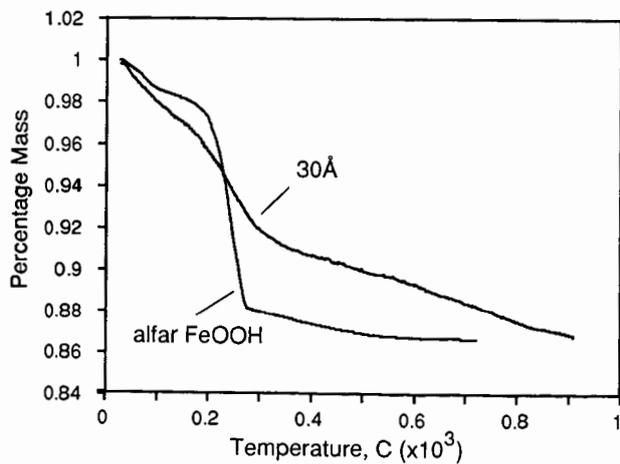


Figure 3. Thermogravimetric analysis for α-FeOOH and the 30Å catalyst.

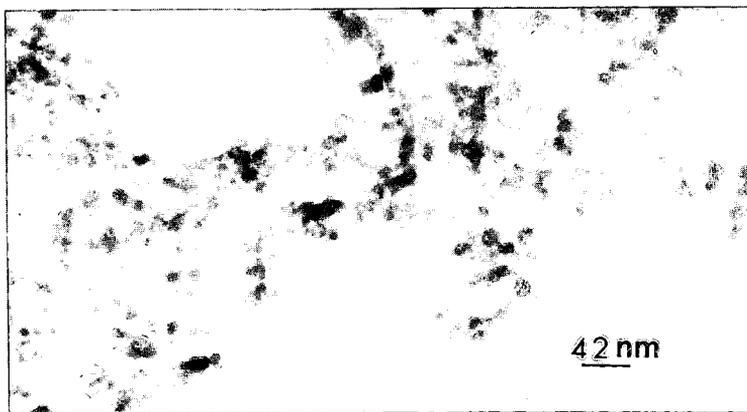
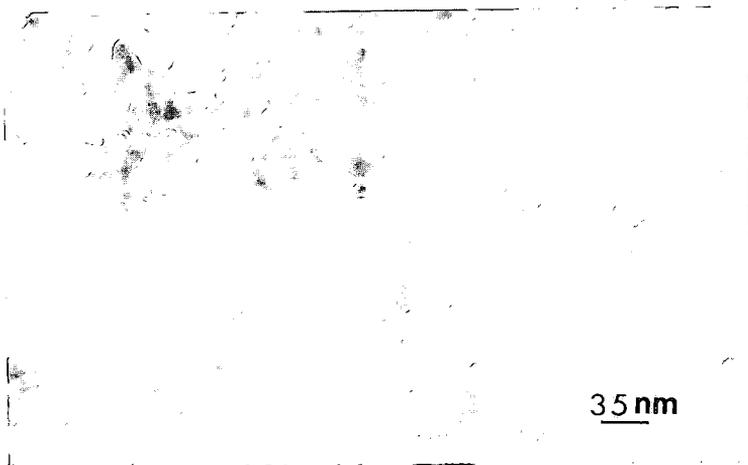


Figure 4. TEM micrographs of the as-received 30Å catalyst (top) and moist air exposed 30Å catalysts (bottom), after annealed at 250C for 24hrs.

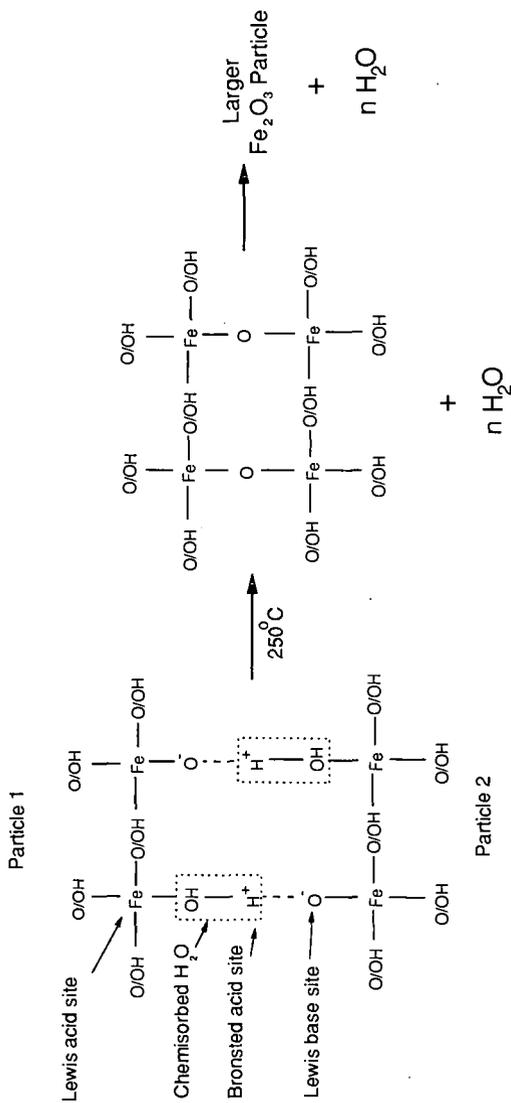


Figure 5. Proposed scheme of agglomeration and phase transition of the 30Å catalyst.