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X-Ray Photoelectron Spectroscopic Studies of Iron Oxide Catalysts Prepared from the Calcination of Iron Sulfates at High Temperature

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Surfaces of iron sulfates calcined at various temperatures ranging from 500 to 900°C were examined by X-ray photoelectron spectroscopy and X-ray diffraction. The sulfates when calcined in air at 700°C, showed the highest catalytic activity for the Friedel–Crafts benzylation, benzoylation, and isopropylation of toluene, and were found to have the following surface properties: (1) the iron sulfate completely decomposes to form α-Fe_2O_3 at temperatures from 675 to 700°C. At higher temperatures, the crystalization proceeds rapidly, but any change in the chemical state of iron and oxygen ions on the surface due to the decomposition process can not be deteted. (2) A small amount of sulfur (0.15 wt%) remains as SO_4^{2-} on the surface at temperatures greater than 700°C after decomposition. The conclusion was confirmed by the benzylation with the differently sulfur-treated ferric oxide catalysts.

INTRODUCTION

In the previous paper (*1*, *2*), the Friedel–Crafts reactions catalyzed by heat-treated iron sulfates were reported. Ferrous and ferric sulfates prepared by calcining their hydrates in air showed exceedingly high catalytic activity and selectivity compared with those of other solid acids such as SiO_2–Al_2O_3, Al_2O_3, and also other calcined metal sulfates. Both iron sulfates when calcined in air at 700°C showed the highest activity for benzylation (*1*, *2*), benzoylation (*2*), and isopropylation (*3*) of toluene. The activity was independent of specific surface areas and acidity of catalyst, and the catalyst heat-treated at 700°C was shown to be a form of α-Fe_2O_3 (*2*). However, ferric oxides prepared by calcining Fe_2O_3 and $Fe(OH)_3$ at 700°C were almost inactive.

In order to investigate the surface properties of the present catalysts, the X-ray photoelectron spectroscopy (XPS or ESCA) studies were carried out. Such XPS measurements give information as to the chemical composition and valence state of atoms on the vicinity of the surface layer of solids from the observed binding energy, relative intensity, and satellite structure for core electron lines (*4*).

EXPERIMENTAL

Catalysts were prepared by calcining iron sulfates, $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot xH_2O$ (guaranteed reagents of Kanto Chemicals Company) in glass or quartz tubes at various temperatures ranging from 500 to 900°C for 3 hr in air.

Photoelectron spectra were observed by a AEI-Kokusai-ES-200 photoelectron spec-

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trometer with AlKα radiation (1486.6 eV). The sample, in powder form, was pressed into a copper mesh grid to make a thin platelet with about 0.5 m/m in thickness. During the operation of the spectrometer, pressure was ca. 5×10^{-7} Torr (1 Torr = 133.33 N m^{-2}). The observed binding energies were corrected to 83.8 eV of the Au $4f_{\frac{7}{2}}$ line from the very thin layer of gold evaporated on the surface of the specimen (*5*).

X-Ray powder diffraction spectra were obtained with a X-ray diffractometer (Rigaku 3063) by using iron filtered CoKα radiation.

RESULTS AND DISCUSSION

Photoelectron spectra were observed at 200°C because water physically adsorbed on the surface was removed at that temperature and high resolution was obtained together with a decrease of charging shift. Table 1 lists binding energies obtained for several electron levels of $FeSO_4$ and $Fe_2(SO_4)_3$ calcined at 500, 700, and 900°C, together with Fe_2O_3 for comparison. The binding energies of the Fe $2p_{\frac{3}{2}}$ level for both sulfates calcined at the temperatures greater than or equal to 700°C were within experimental error of those of α-Fe_2O_3. This fact is in accord with the results of X-ray diffraction and Mössbauer experiments, where iron sulfates were observed to be completely in the form of α-Fe_2O_3 after calcination at temperatures of 700°C and above (*2*).

Binding energy of S $2p_{\frac{3}{2}}$ for iron sulfates calcinated at 500 and 700°C was 168.5 eV, which was similar to that for $FeSO_4 \cdot 7H_2O$. It is known that there is the simple correlation between the binding energy of S $2p$ and the atomic charge (or the chemical state) of sulfur (*6*). Thus, it is concluded that the sulfur atom of $FeSO_4$ (500°C) and $FeSO_4$ (700°C), where the figure in parenthesis shows the calcination temperature, is in the state of SO_4^{2-}.

TABLE 1

Binding Energy of O 1*s*, Fe $2p_{\frac{3}{2}}$, Fe 3*s*, and S $2p_{\frac{3}{2}}$ in XPS spectra measured at 200°C

Compound (calcin. temp., °C)	O 1*s*	Fe $2p_{\frac{3}{2}}$	Fe 3*s*	S $2p_{\frac{3}{2}}$
$FeSO_4$ (500)	531.6	711.8		168.5
$FeSO_4$ (650)	531.5			
$FeSO_4$ (700)[a]	529.9 532.1			168.5
$FeSO_4$ (700)	529.9 531.9	710.8	55.4	
$FeSO_4$ (750)	530.0 531.8			
$FeSO_4$ (900)	529 8 532.1	710.7	55.5	
$Fe_2(SO_4)_3$(500)	531.5	712.1		168.3
$Fe_2(SO_4)_3$(700)[a]	529.9 531.8			168.4
$Fe_2(SO_4)_3$(700)	529.9 531.9	711.2	55.6	
α-Fe_2O_3 I[b]	529.9 531.9	711.2	55.6	
α-Fe_2O_3 II[c]	529.9 532.1	711.0		

[a] Determined at room temperature.

[b] α-Fe_2O_3 (chemical reagent) was heat-treated at 700°C for 3 hr.

[c] Prepared by calcining $Fe(OH)_3$ at 700°C for 3 hr.

Figure 1 shows the Fe $2p_{\frac{1}{2}}$ and Fe $2p_{\frac{3}{2}}$ spectra of ferrous sulfates at several temperatures together with those of Fe_2O_3's prepared by calcining $Fe(OH)_3$ and commercially available Fe_2O_3 at 700°C. A shoulder on the lower energy side of Fe $2p_{\frac{3}{2}}$ spectrum of $FeSO_4$ (500°C) is due to iron oxide which was formed by decomposition of iron sulfate. The shoulder is larger with increase of calcination temperature. The spectra of $FeSO_4$ (700°C) are similar to those of $FeSO_4$ (900°C) and α-Fe_2O_3 I and II. Therefore, in consideration of much higher activity of $FeSO_4$ (700°C) than those of Fe_2O_3 I and II for the Friedel–Crafts reactions, the catalytic activity is not attributed to the state of the iron ion itself.

Figure 2 shows the O 1*s* spectra of iron sulfates calcined at several temperatures and of α-Fe_2O_3 I and II. A large dif-

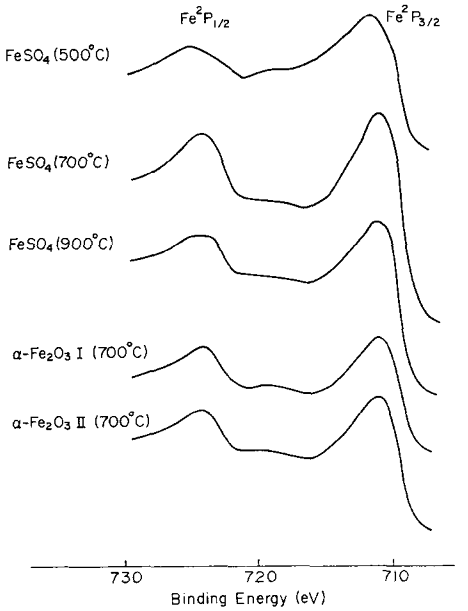

FIG. 1. XPS Fe $2p_{\frac{1}{2}}$ and Fe $2p_{\frac{3}{2}}$ spectra of ferrous sulfates calcined at various temperatures and of α-Fe_2O_3.

ference in spectra can be seen between $FeSO_4$ (650°C) and $FeSO_4$ (700°C), but the spectra of $FeSO_4$ (700°C) and $FeSO_4$ (900°C) are quite similar. The single peak at 531.6 eV for $FeSO_4$ (500°C), $FeSO_4$ (650°C), and $Fe_2(SO_4)_3$ (500°C) is attributed to the sulfate oxygen, and $FeSO_4 \cdot 7H_2O$ also shows a peak at 531.9 eV. In comparison with the spectra of Fe_2O_3, the main peak appeared at 529.9 eV for $FeSO_4$ (700, 750, and 900°C) and $Fe_2(SO_4)_3$ (700°C) is assigned to be the oxide oxygen. The samples, both sulfates calcined at the temperatures above 700°C and Fe_2O_3's also show a shoulder peak around 532 eV, the intensity being rather strong in the case of the sulfates heat-treated at 700 and 750°C. This peak is considered to be due to the hydroxyl (*7*) or sulfate oxygen. In the previous studies (*2*), it was found that iron sulfates heat-treated at 700°C contained 0.15 wt% of sulfur, but no sulfur was found after calcination at 900°C. This was confirmed by XPS. The absence of sulfur in $FeSO_4$ (900°C) was also observed by XPS. Therefore, the shoulder peak observed on both Fe_2O_3's and $FeSO_4$ (900°C) is assigned to the hydroxyl oxygen. This O 1*s* shoulder peak of α-Fe_2O_3 was observed with almost the same relative intensity up to 800°C of measurement under 5×10^{-7} Torr but disappeared at this temperature with generation of heat and also with evolution of gas. This fact indicates that some exothermic reaction occured. α-Fe_2O_3 probably changed to Fe_3O_4 at these experimental conditions (*8*). Since the hydroxyl oxygen did not disappear up to the high evacuation temperature of 800°C, it seems likely that the hydroxyl group is not adsorbed but

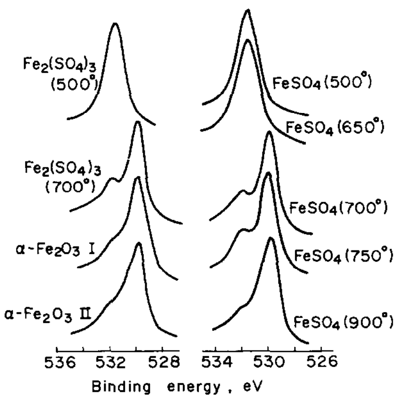

FIG. 2. XPS O 1*s* spectra of iron sulfates calcined at various temperatures and of α-Fe_2O_3.

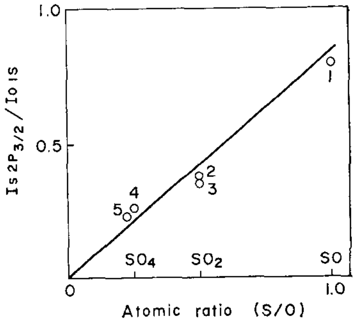

FIG. 3. XPS intensity ratio of S $2p_{\frac{3}{2}}$ to O 1*s* ($I_{S_{2p\frac{3}{2}}}/I_{O_{1S}}$) and atomic ratio of sulfur to oxygen. (1) C_7H_5NOS, (2) $C_6H_5SO_2CH_3$, (3) $CH_3SO_2CH_3$, (4) $FeSO_4$ (determined at 350°C), (5) $FeSO_4$ (calcined at 500°C).

structural species itself. In the case of $FeSO_4$ (700 and 750°C) and $Fe_2(SO_4)_3$ (700°C), the shoulder peak is considered to consist of both the sulfate and hydroxyl oxygens because of the existence of the SO_4^{2-} species, as already mentioned.

The relative sensitivity in XPS is approximately characteristic of elements and is not so much influenced by the chemical state of atoms or the presence of other elements (*9*). Thus, the intensity ratio of S 2*p* to O 1*s* could be proportional to the atomic ratio of sulfur to oxygen in a sample. This relation is confirmed by several materials containing oxygen and sulfur in the different ratio, as shown by Fig. 3. The inclination of the line gives the sensitivity ratio of sulfur to oxygen of 0.88, which agrees with Wagner's result (*9*). By use of this value, the expected intensities of O 1*s* based on the sulfate oxygen in $FeSO_4$ (700°C) and $FeSO_4$ (750°C) were estimated from their intensities of S $2p_{\frac{3}{2}}$ to be 15 and 12% of the main peaks, respectively. These values were almost equal to the differences between the shoulder intensities of $FeSO_4$ (700 and 750°C) and $FeSO_4$ (900°C). Thus, $FeSO_4$ (700 and 750°C) and $FeSO_4$ (900°C) contain almost the same amount of OH group and then the shoulder of O 1*s* of $FeSO_4$ (700 and 750°C) could be mainly due to the sulfate oxygen.

Contents of the sulfur and the α-Fe_2O_3 in iron sulfates with the calcination temperature are shown in Fig. 4. It is seen that the formation of α-Fe_2O_3 followed by decomposition of the sulfate proceeds rapidly at the temperature from 650 to 700°C. The atomic ratio of sulfur to oxygen in $FeSO_4$ (700°C) is estimated to be 0.005, which is much smaller than the value of 0.035 which was calculated from the intensity ratio of S 2*p* to O 1*s* in XPS. This fact indicates that majority of sulfur remains on the surface as SO_4^{2-} by the calcination at 700°C.

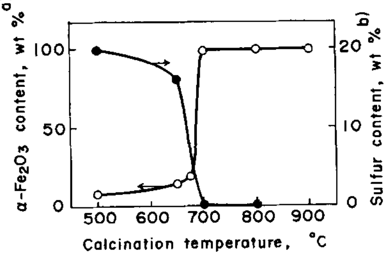

FIG. 4. α-Fe_2O_3 constituent and sulfur content in ferrous sulfates calcined at various temperatures, (a) determined by X-ray diffraction, (b) determined by chemical analysis.

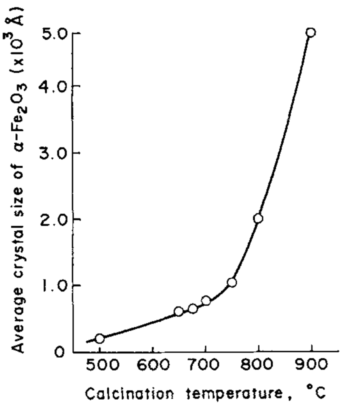

FIG. 5. Average crystal size of ferrous sulfate calcined at various temperatures.

Figure 5 shows the relation between calcination temperature and the average crystal size of α-Fe_2O_3, which was obtained by use of Scherrer's method (*10*); the figure shows that crystalization proceeds quite rapidly at the calcination temperature above 700°C.

On the basis of the results obtained, we may conclude that ferrous and ferric sulfates heat-treated at 700°C, which showed the highest activity for benzylation, benzoylation, and isopropylation of toluene, have the following surface properties: (1) The slight amount of sulfur remaining after the decomposition of the sulfate salts exists mainly as SO_4^{2-} on the surface, and (2) the sulfates completely decompose to form α-Fe_2O_3 at 675 to 700°C, and afterwards the recrystallization proceeds rapidly, but any change in the chemical state of iron and oxygen ions on the surface due to the decomposition process was not detected. This conclusion was confirmed by the benzylation of toluene with benzyl chloride[1]; that is, Fe_2O_3 II was inactive at all catalyst, whereas the benzylation was 100% complete in 1 hr over the sulfur-treated Fe_2O_3 II catalyst, which was prepared by drying ferric hydroxide at 100°C for 24 hr, followed by immersing it in 1 *N* H_2SO_4 solution, filtering, drying, and calcining at 700°C in air for 3 hr. The XPS spectra of the latter catalyst were completely consistent with those of ferrous and ferric sulfates calcined at 700°C as shown in Figs. 1 and 2.

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[1] Benzylation was carried out with 50 ml of 0.5 *M* benzyl chloride in toluene and 0.2 g of the catalyst at 80°C.

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