Interaction between ammonium sulfate–iron oxide shown by ESR and Mössbauer spectroscopy

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The ammonium sulfate–iron oxide system treated at different temperatures has been characterized by ESR, IR and Mössbauer spectroscopy. Results show that during the heat treatment some interaction between ammonium sulfate and iron oxide takes place. As a result of this interaction a surface sulfato complex of iron is formed. The complex is involved in the sites responsible for activity for acid catalytic esterification. Above 573 K, the sulfato complex will gradually decompose with a further increase in temperature. A new structure scheme of the sulfato complex is proposed.

Keywords: Ammonium sulfate; iron oxide; solid acid; ESR; Mössbauer spectroscopy; IR

1. Introduction

Some investigations have been carried out on the samples obtained by treating the ammonium sulfate–iron oxide (ASFO) system above 773 K [1,2]. Such samples belong to the solid acid compounds and are used as catalysts for various reactions [1]. But the real structure of the active sites and the mechanism of their formation are still an open question. Especially regarding the investigation of the samples obtained below 773 K, no report has been found so far. In fact, such samples also exhibit acid-catalytic activity. Investigation of such samples is a valuable supplement to the early results. This letter presents the results from the investigation of the samples obtained in an extended temperature region by ESR, IR and Mössbauer spectroscopy.

2. Experimental

Ammonium water was added to an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ to yield precipitation. The precipitate was washed repeatedly, filtered, dried at 373 K,

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and finally calcined in air at 773 K for 3 h to become iron oxide. It is identified as α-Fe_2O_3 by X-ray diffraction. The average size of particles is estimated to be 50 nm by micrographs taken on a Hitachi X-650 scanning electron microscope.

Iron oxide was immersed in a solution of ammonium sulfate, followed by evaporation to dryness to become ammonium sulfate–iron oxide. Loading of ammonium sulfate is 8% (mass fraction), based on SO_3.

The ammonium sulfate–iron oxide systems treated at different temperatures for 2 h are designated as ASFO(K), where K refers to the temperature at which the sample was prepared.

IR measurements were conducted in accordance with a method described in ref. [3].

ESR spectra were recorded on a Bruker ER 200D EPR spectrometer (X-band, modulation frequency of 100 kHz). All ESR spectra were measured at room temperature.

Mössbauer spectra were measured with an Oxford MS-500 constant acceleration spectrometer at room temperature. The source is $^{57}Co/Rh$. The velocity is calibrated with an α-Fe foil.

3. Results and discussion

In the IR spectrum of ASFO(373) two absorption bands at 1400 and 1147 cm^{-1} are observed (fig. 1). This spectrum is an overlap of the spectra of iron oxide and ammonium sulfate: the band at 1400 cm^{-1} originates from the bending vibration of NH_2 in NH_4^+ and the band at 1447 cm^{-1} is assigned to the stretching frequency of S=O in isolated sulfate ion [1]. This spectrum shows no interaction between ammonium sulfate and iron oxide in ASFO(373). This finding is supported by Mössbauer and ESR results.

As is commonly known, α-Fe_2O_3 is a mostly anti-ferromagnetic compound. Above the Morin transition temperature (263 K), α-Fe_2O_3 shows weak ferromagnetism due to the slight angle between the spins of the two magnetic sublattices. It has no paramagnetic behavior. Just such a case is the initial α-Fe_2O_3 sample used in this work, as shown by the straight line in the ESR spectrum (fig. 2). Moreover, the nuclear spins are fixed (on the Mössbauer timescale) in a mostly anti-ferromagnetic way, which results in a sextet pattern (fig. 3).

What is seen for ASFO(373) in the ESR and Mössbauer spectra is similar to what is noticed for the initial α-Fe_2O_3 sample. Therefore, the statement of absence of interaction between ammonium sulfate and iron oxide in ASFO(373) is plausible.

With an increase of the treatment temperature the band at 1147 cm^{-1} in the IR spectrum gradually becomes a broad one composed of four components: 997, 1072, 1112 and 1221 cm^{-1}. In addition, their intensity continuously increases and has a maximum at 573 K.

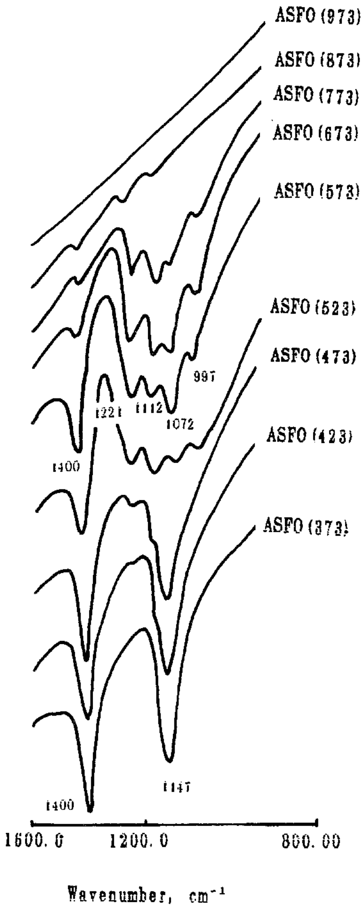
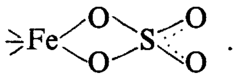


Fig. 1. Changes of IR spectra of ASFO(K) with temperature.

According to ref. [4], the change of the band at 1147 cm^{-1} into the four component broad band represents transformation of the sulfate ion from the isolated into the bidentately bound form, i.e. formation of a sort of sulfato complex of iron.

Yamaguchi and Tanabe [1] suggested a structure scheme for the sulfato complex:



It can be deduced from our IR results (fig. 1) that with increasing the treatment temperature (until 573 K) the sulfato complex of iron proposed by Yamaguchi and Tanabe is formed in the relevant ASFO samples by some interaction between the ammonium sulfate and the iron oxide.

ESR and Mössbauer results can be taken as circumstantial evidences. As shown

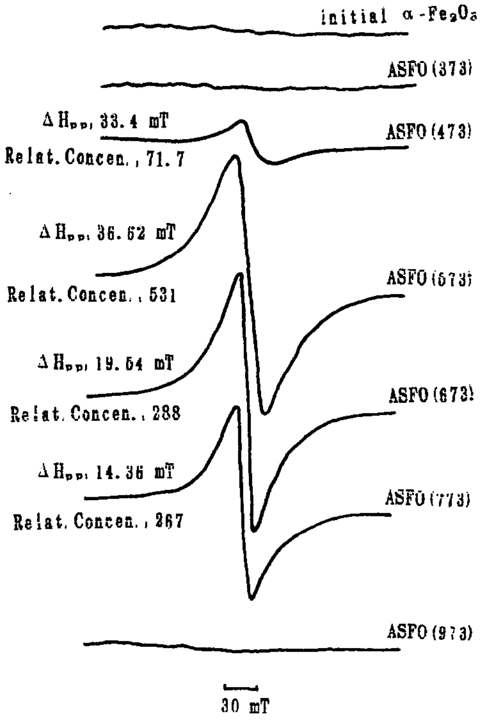


Fig. 2. ESR spectra of ASFO(*K*) treated at different temperatures. Measurements carried out at room temperature; microwave frequency, 9.77 GHz; microwave power, 2 mW; modulation intensity, 0,32 mT; center field, 348.02 mT; scan range, 300.0 mT.

in figs. 2 and 3, paramagnetic signals and singlets respectively develop in ESR and Mössbauer spectra of ASFO(473–573).

The ESR signals and the Mössbauer singlets are not caused by the change of the particle size or the crystalline structure of the samples at all, because no change in them occurs during the heat treatment, as shown by micrographs and diffractograms of the samples. Their development must originate from a paramagnetic phase formed in an appropriate temperature region.

Moreover, the temperature dependencies of their intensities are like that of the IR characteristic absorption of the sulfato complex. Therefrom it follows that the paramagnetic phase should be constituted by the surface sulfato complex of iron.

The formation of the surface sulfato complex leads to a change of the coordination field of a part of the surface Fe atoms in the α-Fe_2O_3 samples concerned, and causes the paramagnetic behavior of the samples.

The IR characteristic absorption, the Mössbauer singlet and the ESR signal all have a maximum at 573 K. Therefore the concentration of the surface sulfato complex of iron in ASFO(573) seems higher than that in any other ASFO samples.

Since a Mössbauer singlet has no quadrupole splitting, Fe^{3+} in the surface sulfato complex might be located in surroundings with higher charge distribution

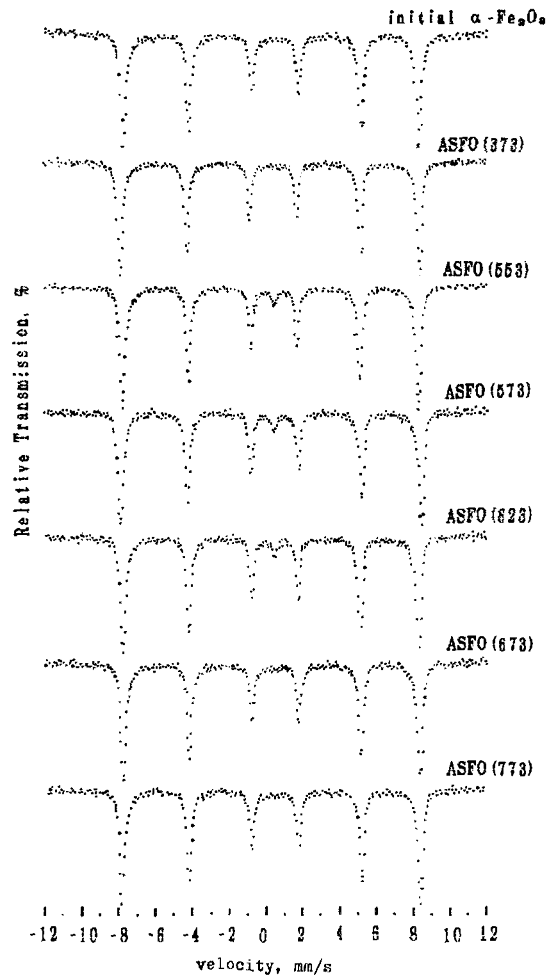
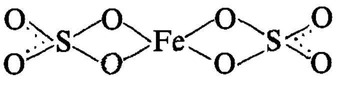


Fig. 3. Mössbauer spectra of ASFO(*K*) treated at different temperatures. IS, 0.50 mm/s (relative to α-Fe). Relative intensity of singlet: 2.653×10^{-2} for ASFO(553); 3.378×10^{-2} for ASFO(573); 3.148×10^{-2} for ASFO(623).

symmetry. In this way, the structure scheme of the sulfato complex of iron,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is probably better than that proposed by Yamaguchi and Tanabe.

Above 573 K, the intensities of the ESR signal, the Mössbauer singlet and the IR characteristic absorption related to the sulfato complex of Fe, all gradually decrease with a further decrease in temperature. This signifies that the sulfato complex of Fe will decompose at the temperatures higher than 573 K. At about 973 K, there might be little sulfato complex of Fe present in the sample, since the spectrum of ASFO(973) turns into the one, similar to that of the initial α-Fe_2O_3.

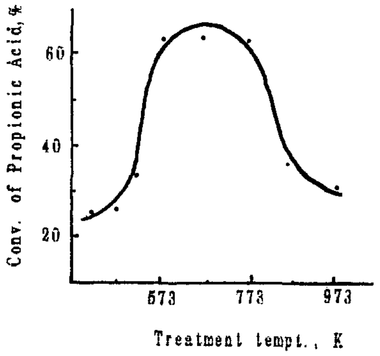

Fig. 4. Activities of ASFO(K) for esterification as a function of treatment temperature. Reaction temperature, 383 K; amount of catalyst, 0.5 g; butanol : propionic acid= 0.3 mol : 0.3 mol.

Below 573 K, the change of the activities of ASFO(K) for acid catalytic esterification has a strong correlation with the change of the intensities of the ESR signal, the Mössbauer singlet and the IR characteristic absorption of the surface sulfato complex (fig. 4). This means that the surface sulfato complex is involved in the active sites for the catalytic esterification, as proposed by Yamaguchi and Tanabe. But the real situation is probably more complicated. From the results obtained above 573 K it is seen, for example, that ASFO(773) has an activity near that of ASFO(573). However, the intensity of the IR characteristic absorption, or of the ESR signal or the Mössbauer singlet of ASFO(773), is much less than that of ASFO(573).

Perhaps in the samples obtained above 573 K there is an unknown factor which leads to the divergency between the changes of the activity and the amount of the sulfato complex. For example, the sites involving the surface sulfato complex may have greater acid strength, although their number is less.

4. Conclusion

When treated at 473–573 K, ammonium sulfate can interact with the surface of α-Fe_2O_3 to form a sort of surface sulfato complex of iron. The complex is involved in the sites responsible for catalyzed esterification. Above 573 K, the complex will gradually decompose with a further increase in temperature.

References

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