BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2180—2183 (1969)

Mössbauer Spectral Observation of α-Fe_2O_3 Supported on Silica Gel during Activation

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(Received December 28, 1968)

Mössbauer spectral studies were made of samples of α-Fe_2O_3 highly dispersed on silica gel before and after activation, which consisted of evacuated heating at 475°C. The spectra gave evidence that Fe^{2+} ions were produced from α-Fe_2O_3 during the activation process. Reduction was impossible after the activation and oxidation had been repeated three times. However, the inactivated sample came to be again reduced by activation after having been exposed to water vapor at room temperature. In order to explain these facts, a working hypothesis was advanced that the hydroxyl groups near the surface of the particles play a principal role in reacting with organic contamination from the vacuum system, as a result bringing about the partial reduction of α-Fe_2O_3.

Some metal oxide powders acquire adsorptive or catalytic activity by the activation process consisting of heating *in vacuo* at a high temperature. It is also known that some metal oxides produce non-stoichiometric oxide by the activation, thus changing their color. Very little work has, however, been done on these states of metal oxide. Blyholder and Richardson[1] reported, in their infrared spectral studies of the surface of α-Fe_2O_3, that the presence of Fe^{2+} ions near the surface might be expected as a results of a prolonged heating process at an evacuated atmosphere.

This report will describe some results of the Mössbauer spectral observation of supported α-Fe_2O_3 particles during activation.

Experimental

Two samples, A and B, of α-Fe_2O_3 supported on silica gel were prepared by impregnating silica gel with ferric nitrate solutions (enriched in Fe-57 for sample A), drying it at 120°C, and calcining it at 250°C for 16 hr in air. The Fe_2O_3 content was 2 wt% for sample A and 20 wt% for sample B. Both samples showed the spectrum[2] characteristic of α-Fe_2O_3. The average particle size was roughly estimated to be less than 130Å for sample A, and above 300Å for sample B, by comparing our spectra with the results of Shinjo *et al.*[3] and Kündig and Bömmel.[4] The broadening analysis of the X-ray diffraction patterns gave similar results.

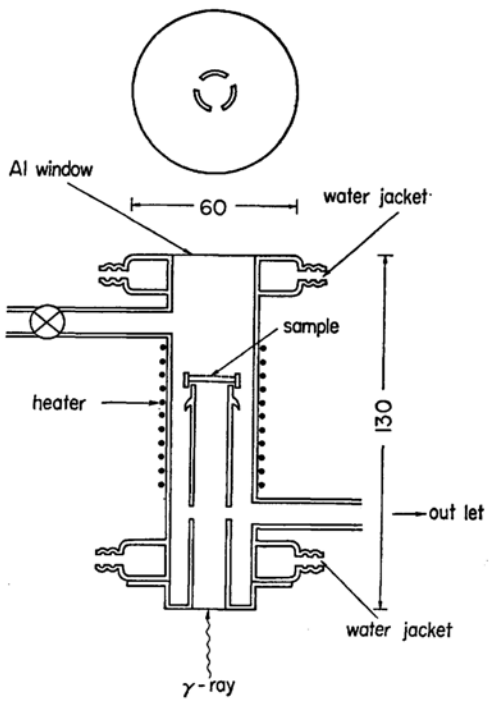

Fig. 1. A cross section of quartz-made cell.

In order to observe the effect of the activation, the sample was put into a small quartz-made supporter, which was mounted in a quartz cell equipped with windows of aluminum foil 100 μ thick as shown in Fig. 1. The activation was carried out by degassing the sample at room temperature for 3 hr, then heating it at 375°C in

1) G. Blyholder and E. A. Richardson, *J. Phys. Chem.*, **68**, 3882 (1964).

2) G. Constabaris, R. H. Rindquist and W. Kündig, *Appl. Phys. Letters*, **7**, 59 (1965).

3) T. Nakamura, T. Shinjo, Y. Endo, N. Yamamoto, M. Shiga and Y. Nakamura, *Phys. Letters*, **12**, 178 (1964).

4) W. Kündig and H. Bömmel, *Phys. Rev.*, **142**, 327 (1966).

an atmosphere of oxygen for one hour, and finally maintaining it at 475°C and under a pressure of 10^{-5} Torr for 8 hr. The spectra were measured after the sample had then been allowed to cool to room temperature. A time-mode Mössbaure spectrometer was used in this experiment.

Results

Figure 2 shows the Mössbauer spectra of sample A before and after the activation. The base lines of the spectral curves are all normalized to one. Curve (a) of the figure is the spectrum of normal sample A. It consists of only a quadrupole-split center line, indicating that the α-Fe_2O_3 is superparamagnetic. Curve (b), the spectrum of activated sample A, is a complex spectrum quite different from that of the original sample. This indicates that Fe atoms of α-Fe_2O_3 particles in the bulk as well as on the surface were changed into a state different from the original one by the activation.

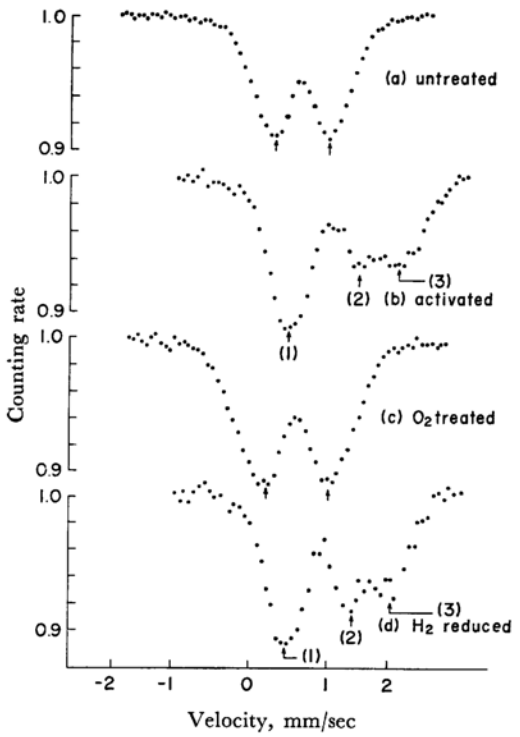

Fig. 2. Mössbauer spectra of a 2 wt% α-Fe_2O_3-on-silica gel sample undergoing several treatments.

Figure 3 shows the spectra of sample B. Before the activation, sample B gave a spectrum of six hyperfine-split line, indicating antiferromagnetic characteristics, as is seen with α-Fe_2O_3 in bulk. Only the innermost doublet of the six lines appears in curve (a) of Fig. 3. This spectrum was replaced by curve (b) of the figure after the activation. However, the change was much smaller than that in the sample A. From this result, it follows

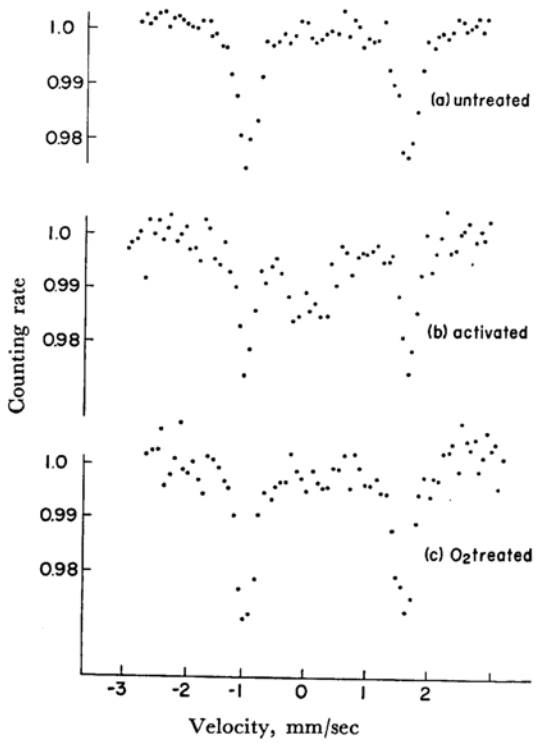

Fig. 3. Mössbauer spectra of a 20 wt%-α-Fe_2O_3-on-silica gel sample undergoing the activation and oxidation.

that, in observing the spectral change upon activation, it is more profitable to experiment with sample A. The following investigation was, therefore, completely conducted with sample A.

The spectrum was observed again after the activated α-Fe_2O_3 had been exposed to thoroughly-dried oxygen gas at 1 atm and at 200°C for about one hour. The resulting spectrum is curve (c) of Fig. 2, which is almost identical with curve (a) of the figure, though the parameters are somewhat larger than those of curve (a). This is shown in Table 1. Similar result was, though ample time is required, obtained also by the experiment at room temperature.

As the cycle of the oxygen treatment and the degassing was repeated, it was found to become

Table 1. Differential chemical shift* (δ), quadrupole splitting (Δ), and full width at half maximum (Γ) for curve (a) and (c) in Fig. 1

Curve	(a)	(c)
δ	0.60	0.63
Δ	0.75	0.88
Γ	0.63	0.80

Unite: (mm/sec) Error: $<\pm 0.02$ (mm/sec)

* Values relative to sodium nitropruside

gradually more difficult to obtain a sample which showed the activated-state spectrum. After the third cycle, the sample obtained no longer exhibited the activated-state spectrum. However, when this sample was placed in oxygen gas at 200°C and then exposed to water vapor at its saturation pressure at room temperature, it came to reproduce the activated-state spectrum (curve (b) of Fig. 2) upon evacuated heating.

Next, sample A was reduced by heating it in a hydrogen gas stream at 450°C for 8 hr. The resulting spectrum is curve (d) of Fig. 2, which is approximately the same as curve (b) of the figure, *i. e.*, the activated-state spectrum. This result gives evidence that some Fe ions of the activated sample were in a reduced state.

Discussion

The activated state spectrum (curve (b) of Fig. 2) was almost the same as the hydrogen-reduced spectrum which had previously been obtained by Hobson and Cambell.[5] The spectrum is apparently different from that of metallic iron. The spectra, (b) and (d), of Fig. 2 have three peaks, 1, 2, and 3, numbering from left to right. As with Hobson and Cambell, these spectra are resolved into two doublets, consisting of 1-3 and 1-2 peaks. The differential chemical shift, δ, and the quadrupole splitting, Δ, for the superposed doublets are given in Table 2. When we compare these data with the spectral data*1,6) of many iron compounds, it is not unreasonable to conclude that the doublet 1-3 ($\delta=+1.37$ mm/sec, $\Delta=1.77$ mm/sec) may be ascribed to a Fe^{2+} ion. The chemical shift of the 1-2 doublet ($\delta\fallingdotseq+1.05$ mm/sec, $\Delta=1.14$ mm/sec) has a value between the typical Fe^{2+} and Fe^{3+} states, with a rather large quadrupole splitting.

Table 2. Differential chemical shift* (δ) and quadrupole splitting (Δ) for curve (b) and curve (d) in Fig. 1

Curve	(b)		(d)	
peak	1-2	1-3	1-2	1-3
δ	+1.05	+1.37	+1.02	+1.36
Δ	1.14	1.77	1.01	1.65

Unite: (mm/sec) Error: $<\pm0.02$ (mm/sec)
* Values relative to sodium nitropruside

The nature of this state was not yet been elucidated, but it is evident that two electronic states of the Fe ion, one of which is a typical Fe^{2+} state, exist in the activated α-Fe_2O_3. This activated state is recovered into the original α-Fe_2O_3 when it comes in contact with oxygen gas, so it is probably an unstable and non-stoichiometric iron oxide.

It should be interesting to consider the mechanism by which the Fe^{2+} state is produced from α-Fe_2O_3 by the evacuated heating. Some articles[7,8] show that powders of such metal oxides as TiO_2, MoO_3, are partially reduced by the evacuated heating into a lower oxidized state and that the reduction results from some organic contamination from the vacuum system or from an impurity carbon in the original sample. In our experiment, it is unreasonable to take the latter into consideration, since a considerable amount of carbon must be assumed to explain the complet change in the spectrum of the sample upon activation. Since our experiment was done in a conventional vacuum system equipped with a greased stopcock and an oil-diffusion pump, doubtless our sample was also exposed to an organic contamination. Nevertheless, in this atmosphere it was impossible to activate a sample which had been subjected to repeated degassing and oxidation. This fact suggests that some change was brought about on the surface of α-Fe_2O_3 particles by the repeated activation procedures. Here it is noticeable that such an inactivated sample has its reactivity restored upon exposure to water vapor at room temperature.

Evidence[9] has been given that the chemisorbed water is present in the form of the OH group on the surface of ferric oxide and that it provides the active site for a surface chemical reaction on ferric oxide. This leads us to assume that the OH group on the Fe atom of α-Fe_2O_3 particle surface might act as active sites in reacting with an organic contamination during the activation.

The surfaces of most oxide adsorbents have been found to be composed of hydroxyl groups which are removed during the activation and again formed immediately on exposure to water vapor at room temperature.[10] It is probable that an α-Fe_2O_3 sample which has lost its surface hydroxyl groups by means of the repeated activation procedure can no longer be activated by being in contact with organic contamination. Consequenly, it seems reasonable to assume that the hydroxyl groups on the surface of α-Fe_2O_3 particles play a principal role for reacting with organic contamination and that, as a result, the partial reduction of α-Fe_2O_3 occurs.

In order to draw a decisive conclusion, however,

5) M. C. Hobson, Jr., and A. D. J. Cambell, *J. Catalysis*, **8**, 294 (1967).

*1 $1.33<\delta(Fe^{2+})<1.75$
$0.55<\delta(Fe^{3+})<0.82$

6) A. R. Champion, R. W. Vanghan and H. G. Drickamer, *J. Chem. Phys.*, **47**, 2583 (1967).

7) J. Gebhardt and K. Herrington, *J. Phys. Chem.*, **62**, 120 (1958).

8) M. Onchi and I. Kusunoki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.,)* **85**, 612 (1964).

9) G. Okamoto, R. Furuichi and N. Sato, *Electrochim. Acta*, **12**, 1287 (1967).

10) T. Morimoto, M. Nagao and F. Tokuda, This Bulletin, **41**, 1533 (1968).

much remains to be done with the Mössbauer spectral measurements. However, since the application of the Mössbauer spectroscopy to surface work is at present yet in its infancy, it seems valuable to make this report as a preliminary step.

We wish to thank Dr. Kin-ichi Nohga of the Toshiba Central Research Laboratory for his continuous encouragement during this work. We are very grateful to Professor Tetsuo Takaishi of Saint Paul's University for his helpful discussions. The expenses of this work have been supported in part by a Scientific Research Grant from the Ministry of Education.