LETTERS TO THE EDITORS

A Mössbauer Study on the Ammonia Synthetic Iron Catalyst

Many different approaches have been made to elucidate the structure of the ammonia synthetic iron oxide catalysts containing aluminum oxide and potassium oxide. Among these are X-ray, electron microscopic, thermomagnetic, and electric methods. The results so far obtained indicate that the oxide catalyst has a magnetite structure, alumina goes into solid solution with magnetite, and the ferric iron can be easily replaced by others, such as Al^{3+} ions, without altering the structure. Very little has been known of the role and location of potassium oxide over the magnetite phase. However, it is known that the potassium oxide exerts the most effective influence on the catalytic activity (1, 2, 3).

The present report aims to elucidate the role and location of promoters in fused iron catalysts in the oxide state using Mössbauer spectroscopy, for the direct determination of the cation distribution in several kinds of ferrites (4).

The catalysts used were ammonia synthetic fused iron catalysts which were prepared in the usual method at Government Chemical Industrial Research Institute, Tokyo. The analytical data of the catalysts are listed in Table 1.

The sample used for Mössbauer effect study was prepared as follows: about 25 mg of finely powdered catalyst was well dispersed throughout 70 mg of α-Al_2O_3 in order to prevent the irrelevant electronic absorption of 14.4-keV γ-rays, and thus the prepared sample was pressed into a thin disk of 14-mm diameter. This sample was placed in the cell and was evacuated. Then it was subjected to Mössbauer study.

All spectra were obtained at room temperature using a time mode type Mössbauer spectrometer.

The catalysts in the oxide state showed the same spectra as pure magnetite; also the intensity ratios of A sites and B sites in the catalysts are different from that in pure magnetite, as shown in Fig. 1. All spectra are produced to represent a Lorentzian function fitted by computer to the experimental data.

As is well known, magnetite is a prototype ferromagnetic oxide with the cubic inverse spinel structure. In a unit cell, eight ferric ions occupy tetrahedral sites (A sites), each surrounded by four oxygen ions; and eight ferric ions and ferrous ions occupy the octahedral sites (B sites), each surrounded by six oxygen ions. Therefore, the ratio of the absorption intensities for the two sites will be 2 to 1, corresponding to an actual ratio of ions on each site (5, 6).

Turning now to the spectra obtained with the promoted iron catalysts, shown in Fig. 1, we can see that one Zeeman splitting pattern consists of six lines at 1a, 2a, 3a, and 4, 5, 6, which belong to A sites and the second Zeeman splitting pattern consists of six lines at 1b, 2b, 3b, 4, 5, 6, which belong to B sites, and the intensity ratio of A sites and B sites is changed with the content of K_2O in the catalysts. In order to determine the content of Fe^{3+} and Fe^{2+} ions, the intensity of the resonance line was determined quantitatively by the area method (7) using background correction (8). The magnitude of the spectra was measured by numerical integration with an accuracy of $\pm0.5\%$. Thus results ob-

<div align="center">

TABLE 1

COMPARISON BETWEEN MÖSSBAUER ANALYSIS AND CHEMICAL ANALYSIS

</div>

Sample	Al_2O_3 %	K_2O %	A-site %	B-site %	Fe^{3+} C[a] %	Fe^{3+} M[b] %	Fe^{3+} Δ[c] %	Fe^{2+} C[a] %	Fe^{2+} M[b] %
1	2.69	0	44.9	55.1	66.6	72.5	5.9	33.4	27.5
2	2.55	0.33	46.1	53.9	71.4	73.1	1.7	29.6	26.9
3	2.33	0.58	44.3	55.6	70.8	72.1	1.3	29.2	27.9
4	2.39	1.54	49.4	50.6	76.5	74.7	-1.8	23.5	25.3

[a] Chemical analysis.

[b] Mössbauer spectrum analysis.

[c] M-C, this value is smaller, as the structure of the sample approaches to that of magnetite.

tained are also shown in Table 1 along with the results obtained from the chemical analysis.

Figure 2 shows the spectra in the neighborhood of lines 3 and 4 at very low velocity drive. The resonance pattern between lines 3 and 4 can be seen in catalyst No. 1 but not in No. 4 and magnetite. This pattern is due to the paramagnetic properties and disappeared when K_2O was added to the singly promoted catalyst containing only Al_2O_3.

The internal fields of the iron on A and B sites of the catalysts were 495 ± 5 kOe and 470 ± 5 kOe, respectively; both are identical to those of magnetite.

The ratio of the absorption intensities of the two sites was 1 to 1, which differed from the theoretical value of 2 to 1 in the magnetite. If the equal intensity of two sites is due to the iron defects at the B site, the concentration of the defects must exceed 25%. But it is too large to compare with the value of 4% calculated from chemical analysis. Therefore, the equal intensity is not attributable to the iron defect. The lattice constant a_0 was 8.380 Å by X-ray diffraction for the samples 1 to 4, which is intermediate between magnetite
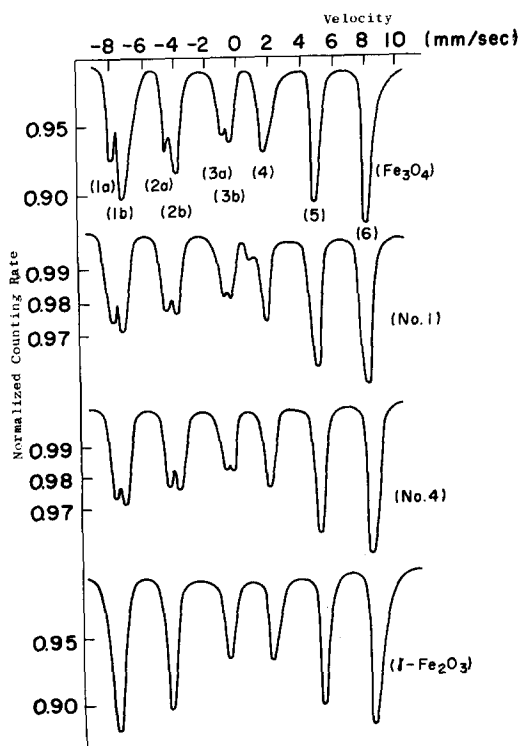

FIG. 1. Mössbauer spectra of singly and doubly promoted iron catalysts, magnetite, and γ-Fe_2O_3.
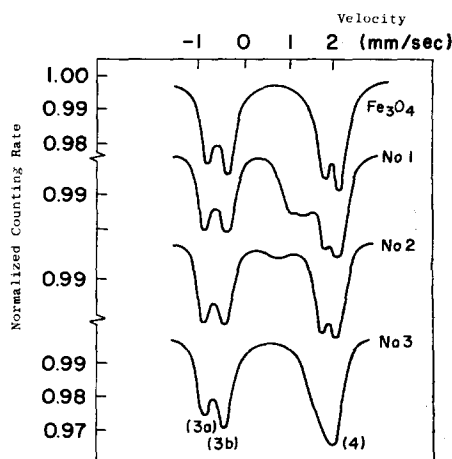

FIG. 2. Mössbauer spectra of singly and doubly promoted iron catalysts and magnetite at very low velocity drive.

(8.396 Å) (ASTM Card No. 11-614) and γ-Fe_2O_3(8.342 Å)(ASTM Card No. 10-425). Assuming the ferric oxide in the sample is γ-Fe_2O_3, the ratio of magnetite to γ-Fe_2O_3 was determined using Vegard's law as 70.4% to 29.6%. Consequently, we can estimate 76% as Fe^{3+} ion and 24% as Fe^{2+} ion, which agrees with the values shown in Table 1. Further, the reported value of the internal field of γ-Fe_2O_3 is 496 kOe (9) which is identical to that of the A site in magnetite.

In view of the above facts the most reasonable conclusions to be drawn from available data are as follows:

(i) In a singly promoted catalyst (without K_2O), the Al_2O_3 promoter goes into a solid solution with Fe_3O_4, and the Fe^{3+} ions on B sites can be replaced by Al^{3+} ions.

(ii) If K_2O is added to the singly promoted catalysts, the formation of such a solid solution will be prevented in some degree.

(iii) Equal intensities of A and B sites of the catalysts suggests the existence of γ-Fe_2O_3-like ferric oxide, which has the same magnitude as the internal field of the A site of magnetite.

Further work is in progress on doubly promoted iron catalysts in the reduced state and the adsorption of several gases in hopes of finding the action of promoters in the ammonia synthetic catalysts.

REFERENCES

1. FRANKENBURG, W. G., "Catalysis" (P. H. Emmett, ed.) Vol. 3, p. 171. Reinhold, New York, 1955.
2. BOKHOVEN, C., VAN HEERDEN, G., WESTRIK, R., AND ZWIETERING, P., "Catalysis" (P. H. Emmett, ed.), Vol. 3, p. 265. Reinhold, New York, 1955.
3. NIELSEN, A., "An Investigation of Promoted Iron Catalysts for Synthesis of Ammonia," 3rd ed. Jul. Gjellerups Forlag, Copenhagen, 1968.
4. YAGNIK, C. M., AND MATHUR, H. B., J. Phys. C. (Proc. Phys. Soc.), 1, 469 (1968).
5. VERWEY, E. J. W., Proc. 11th Intern. Congr. Pure Appl. Chem. 1, 285 (1950).
6. ITO, A., OHNO, K., AND ISHIKAWA, Y., J. Phys. Soc. Japan 18, 1465 (1963).
7. LANG, G., Nucl. Instr. Methods 27, 29 (1964).
8. YOSHIOKA, T., GOHSHI, Y., AND KOHNO, H., Annal. Chem. 40, 603 (1968).
9. KELLY, W. H., FOLEN, V. J., HASS, M., SCHREINER, W. N., AND BEARD, G. B., Phys. Rev. 124, 80 (1961).

T. YOSHIOKA*
J. KOEZUKA*
I. TOYOSHIMA†

Received December 30, 1968

* Toshiba Central Research Laboratory
Kawasaki-Shi, Japan
and
† Research Institute For Catalysis
Hokkaido University
Sapporo, Japan