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A Magnetic Resonance Study of the Fe_2O_3/Al_2O_3 Catalyst in a CO-N_2O Reaction

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A magnetic resonance study was performed in order to determine the phase of iron oxide supported on Al_2O_3 and to measure *in situ* the surface conditions during the reaction. The irreversible transition of α-Fe_2O_3 into Fe_3O_4 by the reduction of the supported catalyst and the reversible transition between Fe_3O_4 and γ-Fe_2O_3 were confirmed at 280 °C. The spectrum appearing at $g=2.03$ and having the line width of about 1000 gauss clearly showed ferrimagnetic behavior; it could be attributed to the ferrimagnetic resonance (FMR) of Fe_3O_4 and/or γ-Fe_2O_3. Kinetic study suggested that the CO–N_2O reaction took place in the oxidation-reduction mechanism. The concentration of γ-Fe_2O_3 was calculated from not only the kinetic equation, but also the *in situ* measurement of the FMR signal; these values were consistent. The γ-Fe_2O_3/Al_2O_3 had nearly the same activity as the α-Fe_2O_3/Al_2O_3, whereas the unsupported γ-Fe_2O_3 had a lower activity than the α-Fe_2O_3. Such a difference in catalytic activity was discussed in comparison with other oxidation reactions.

It is well known that iron and iron oxides are differentiated into ferromagnetic and paramagnetic inorganic compounds according to their chemical composition.[1] Fe metal, Fe_3O_4 (magnetite), and γ-Fe_2O_3 (maghemite) are ferromagnetic or ferrimagnetic, and they have large magnetic moments. A Magnetochemical investigation of catalysts has been already carried out by Selwood.[2] However, it seems that such magnetic measurements should be replaced by magnetic-resonance studies because the latter have a higher sensitivity and greater availability. Nevertheless, only a few reports about magnetic resonance studies of catalysis or adsorption have been published. For example, Loy and Noddings have investigated the hydrogen chemisorbed on a nickel catalyst.[3] The ferromagnetic resonance (FMR) of nickel is very simple, because nickel metal should be only ferromagnetic. On the other hand, iron compounds are fairly complex, because three different phases can be observed by the FMR, as has been described above. However, the magnetic resonance of iron oxides provides a unique phenomenon, and it is particularly suitable for the measurement of solids containing small quantities of these species.

The purpose of the present study is to demonstrate the usefulness of the FMR study of the CO–N_2O reaction on Fe_2O_3 supported by the Al_2O_3 catalyst. The FMR measurements as well as the kinetic study will be used to show the reaction mechanism and the transition of the solid phases during the CO–N_2O reaction. Furthermore, the difference in catalytic activity between α- and γ-Fe_2O_3 in this reaction will be discussed.

Experimental

Catalyst and Reagent. The Al_2O_3 (Sumitomo KHD) was calcined at 450 °C for 3 h and then dipped into a solution of $Fe(NO_3)_3\cdot 9H_2O$. After drying at 110 °C, this was calcined at 450 °C for 2 h in the stream of an O_2–N_2 (1 : 4) mixture. The final Fe_2O_3 content in the supported Fe_2O_3/Al_2O_3 catalyst was in the range between 0.15 and 13.0 wt%. Unsupported iron oxide was prepared from precipitates of $Fe(OH)_3$ obtained by the neutralization of a $Fe(NO_3)_3\cdot 9H_2O$ solution with ammonia water. The calcination was carried out at 500 °C for 5 h in the air.

The N_2O (99.8%) and CO (99.9%) were supplied from the Takachiho Chemical Co., Ltd., and were used without further purification.

Apparatus and Procedure. An *in situ* cell, made with a Pyrex glass outer tube (3 mm i.d.) and inner tube (1 mm o.d.) was placed in an ESR cavity and heated with temperature-variant equipment. A reactant gas cosisting of N_2O, CO, Ar, and He was allowed to flow into the reactor, and the products were directly analyzed by means of a gas chromatograph connected with the reactor cell. A Porapak Q column (2.8 m) for CO_2 and N_2O and Molecular Sieve 13X column (3.5 m) for Ar, N_2, and CO were used at room temperature for the separation. The ESR was measured by means of a JEOL X-band spectrometer (JEX-ME-1X).

A conventional pulse technique was performed with helium carrier gas deoxidized through a Ti-sponge bed at 700 °C.

The amount of CO adsorbed was measured gravimetrically with a quartz spring balance.

Results and Discussion

Measurement of Phases of Supported Fe_2O_3 by Magnetic Resonance and Stoichiometry. The Fe_2O_3 supported on Al_2O_3 catalysts with different loadings have been measured in the ESR cavity at room temperature up to 280 °C. Figure 1 shows the ESR spectra of the fresh Fe_2O_3/Al_2O_3 catalyst, with 6.7% by weight Fe_2O_3 loading, as an example. As is shown clearly, this spectrum can be fitted to the simulated one assuming three differenet species with Lorentz line shapes. The computation was performed with a FACOM 230-75 at Nagoya University Computation Center. Obviously, the signal showed a greater intensity at room temperature than at 280 °C, as is usually observed in the ESR measurement of paramagnetic species.

The spectrum observed here is approximately identical with the spectrum of the iron impurity in ammonium-exchanged NaY-zeolite previously reported by Derouane *et al.*[4] According to their identification, there are three distinct paramagnetic species, *i.e.*, Fe^{3+} species in the alumino-silicate framework at $g=4.3$, an exchangeable Fe^{3+} ion at $g=2.1$, and another precipitated Fe^{3+} compound with a strong spin-exchange interaction at $g=2.3$. Consequently, the observed spectrum in Fig. 1 may be composed of these identified species. The

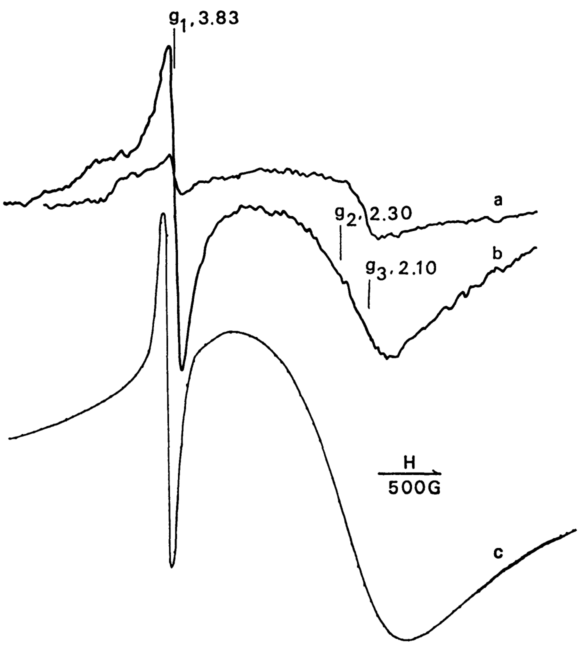

Fig. 1. Obsd ESR spectra of fresh 6.7 wt% Fe_2O_3/Al_2O_3 catalyst at 280 °C (a) and room temp (b) and simulated spectrum (c), which was obtained by the assumption of g_1, g_2, and g_3 signals whose parameters were 70, 1500, and 700 G (1 G = 10^{-4} T) as line width and 0.005, 0.933, and 0.062 as normalized coefficient of linear combination, respectively.

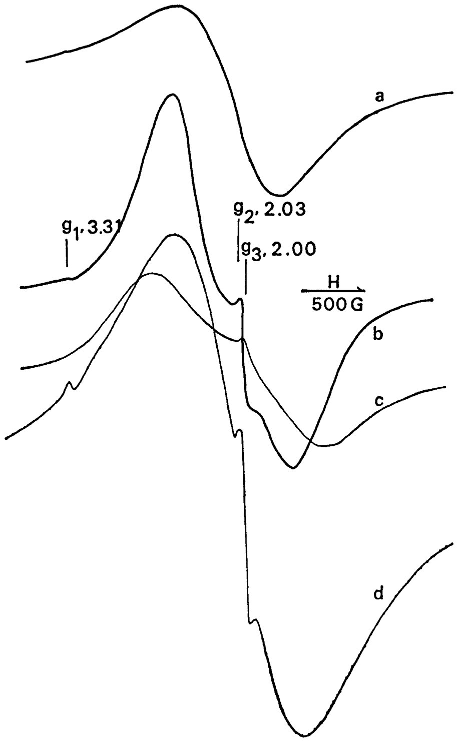

Fig. 2. Obsed ESR spectra of treated 6.7 wt% Fe_2O_3/Al_2O_3 catalyst in the reduced state at 280 °C (a) and in the oxidized state at 280 °C (b) and room temp (c). Simulated spectrum (d) was obtained by the assumption of g_1, g_2, and g_3 signals whose parameters were 50, 960, and 50 G (1 G = 10^{-4} T) as line width and 0.0002, 0.999, and 0.001 as normalized coefficient of linear combination, respectively.

substituted Fe^{3+} species may be shifted lower from $g=4.3$ to $g=3.8$ because of the difference in the support.

The sample of Fe_2O_3 was then reduced by the current of CO at 280 °C; after confirming the steady state of ESR signal, it was reoxidized by N_2O at 280 °C. Such a treatment of the catalyst drastically changed the ESR spectrum, the intensity being magnified by about 100 times (Fig. 2). The spectrum of the oxidized sample in Fig. 2-b contained three different species, while that of the reduced sample lost the sharp signal at $g=2.00$. The oxidized one showed a broader signal at room temperature than at 280 °C.

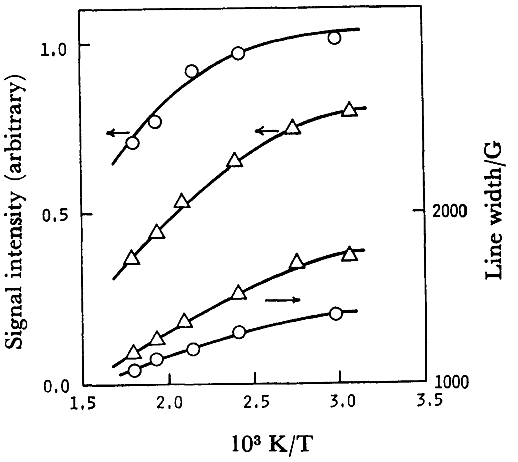

Fig. 3. Dependence of the signal intensity and the line width on the measurement temp using oxidized (○) and reduced (△) samples of the treated catalyst.

The spectra of such reduced and oxidized samples of the treated 6.7-wt% Fe_2O_3/Al_2O_3 were examined in more detail at different temperatures. After the sample had been reduced or oxidized with a $CO-N_2$ or N_2O-N_2 mixture at 280 °C respectively, it was sealed and subjected to measurement. In Fig. 3, the intensity and line-width of the g_2 signal are plotted against the reciprocal absolute temperature. Remarkably, the line width increased with a decrease in the temperature. Such a dependence does not indicate the paramagnetic property, but the ferro- (or ferri-) magnetic property of the samples. The small deviation from the linearity between the signal intensity and the reciprocal absolute temperature may also show the ferro- (or ferri-) magnetic property.

A pulse technique was then used to determine the phases of the treated Fe_2O_3/Al_2O_3. The injection of CO into the bed of reoxidized 6.7-wt% Fe_2O_3/Al_2O_3 formed CO_2 at 280 °C. Successive injections of CO reduced the catalyst by the depletion of the catalyst oxygen. The total amount of the CO_2 formed on 150 mg of the catalyst was 29.6 μmol. This was nearly in agreement with the expected value, 21 μmol, in which the iron oxide was assumed to be reduced to the magnetite; *i.e.*,

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2.$$

Consequently, the phase of the reduced catalyst may be identified as Fe_3O_4.

As has previously been indicated,[5] the unsupported

α-Fe_2O_3 was reduced by carbon monoxide to Fe_3O_4 at a low temperature such as 280 °C. However, the magnetite was not reversibly reoxidized to γ-Fe_2O_3 unless it was oxidized above 400 °C.[6] In other words, the reduction-reoxidation of the Fe_2O_3 can be described as;

$$\alpha\text{-}Fe_2O_3 \xrightarrow[\text{red}]{} Fe_3O_4 \underset{\text{red}}{\overset{\text{oxi}}{\rightleftharpoons}} \gamma\text{-}Fe_2O_3 \,.$$

The magnification of the signal by the reduction-reoxidation and its temperature dependence are, therefore, correlated with the change in the magnetic property, *i.e.*, from the paramagnetic Fe^{3+} ion to ferrimagnetic Fe_3O_4 and γ-Fe_2O_3. The sharpening of the line-width at a high temperature, as is the case of a treated catalyst, has already been indicated by Singer in the measurement of the magnetite.[7] Furthermore, it was found by the pulse method that the reoxidized catalyst could be only reduced to the level of the Fe_3O_4. Therefore, the signal at $g=2.03$ (g_2) of the treated catalyst is attributed to the ferrimagnetic-resonance (FMR) spectra of γ-Fe_2O_3 and Fe_3O_4 in the oxidized and reduced samples respectively. The g-values of γ-Fe_2O_3 and Fe_3O_4 were not distinguished from that of the pure oxide; they have been reported to be 1.96[8] and 2.13[9] respectively.

X-Ray diffraction, Mössbauer spectroscopy, or XPS has been used to distinguish the phases of iron oxide.[5,10] Infrared spectroscopy has also been recommended to identify them[11] However, these analytical methods can not be used for the supported catalysts, for the iron oxide content is too low to be detected. In fact, the X-ray diffraction of the Fe_2O_3/Al_2O_3 catalyst revealed only aluminum oxide as the support. Furthermore, it was found that the ir spectroscopy could not be used because of the intense absorption of the Al–O band. The ESR or the magnetic resonance is the most suitable for this case, for iron oxides should exhibit different resonances with high intensities depending on their magnetic properties.

On other samples of the Fe_2O_3/Al_2O_3 catalyst with a different loading of iron oxide, nearly the same spectrum as that shown in Fig. 1 was observed in the fresh condition. Although the intensities of the substituted Fe^{3+} ion at $g=3.8$ increased with the loading up to about 9 wt%, the principal signal at $g=2.3$ showed nearly the same intensity regardless of the iron-oxide content, while it turned into the FMR signal upon reduction-reoxidation treatment. The sharp signal of the treated catalyst at $g=2.00$ (g_3) which was observed in the oxidized condition became outstanding in the catalyst with a low iron content. Because this signal has a broader line-width at room temperature than at 280 °C, it might be attributed to ferromagnetic Fe metal, which may be considered to disappear upon the formation of $Fe(CO)_x$ in the reduction by CO.

In Situ *Measurement of the Reversible Transition between* γ-Fe_2O_3 *and* Fe_3O_4. By the use of an *in situ* cell, the FMR spectrum was measured *in situ* during the reduction and reoxidation of the catalyst at 280 °C. A Fe_2O_3/Al_2O_3 catalyst supported by 6.7-wt% Fe_2O_3 which had been treated by CO and N_2O was measured. The intensity of the signal at $g=2.03$ due to γ-Fe_2O_3 gradually decreased in flowing carbon monoxide (Fig. 4) and attained a steady state 15 min later. Simultaneously, the line-width also increased. As has been described above, the reduced state of the catalyst was attributed to Fe_3O_4. The reduced catalyst was then reoxidized by the flowing of N_2O. As is shown in Fig. 4, the signal intensity was increased rapidly by the reoxidation, and the resultant spectrum was in good agreement with the initial one. Consequently, it can be said that the transition between γ-Fe_2O_3 and Fe_3O_4 proceeds reversibly and that the rate of reoxidation is obviously faster than that of reduction. Furthermore, the intensity of Fe_3O_4 is evaluated to be 0.60 times that of γ-Fe_2O_3. The relative ratio of these signal intensities will be used in the next section of this paper to calculate the relative concentration of γ-F_2O_3. The relative intensity was measured over as wide a range of the spectrum as possible in order to minimize the error which would be contained in the evaluations of the intensity of the broad spectrum. *In situ* measurement afforded the advantage of the precise determination of the relative intensity, because the sample was measured under exactly the same conditions except for the oxidation state of the catalyst.

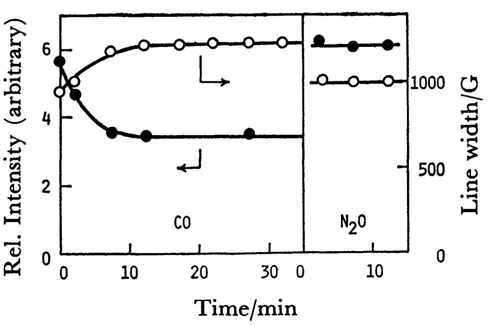

Fig. 4. Variation of signal parameters with the course of reduction by CO or oxidation by N_2O over the ferrimanetic Fe_2O_3/Al_2O_3 catalyst.

Kinetics and in Situ *Measurement of the CO–N_2O Reaction.* The reduction of dinitrogen monoxide by carbon

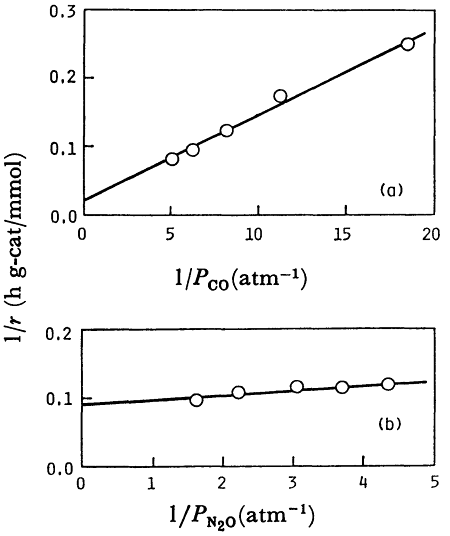

Fig. 5. Kinetics of the CO–N_2O reaction on the treated catalyst at 270 °C; Partial pressures of CO (a) or N_2O (b) were varied with other conditions kept const.

monoxide on the ferrimagnetic 6.7 wt% Fe_2O_3/Al_2O_3 catalyst was then investigated kinetically using the *in situ* cell. Simultaneously, the FMR spectrum was measured in order to monitor the condition of the catalyst.

Although the CO–N_2O reaction should form equimolar amounts of CO_2 and N_2, the CO_2 exceeded slightly the N_2 in this experiment. This was caused by the impurity of the oxygen in the cylinder of N_2O (0.16 vol%). Consequently, the rate of CO–N_2O reaction is here described by the rate of N_2 formation. Figure 5 shows the kinetics of the N_2O–CO reaction at 270 °C, in which the partial pressures of CO or N_2O are shown to vary in Fig. 5-a and Fig. 5-b respectively. The reciprocal plots between the rate of formation and the partial pressure both gave straight lines.

By taking into consideration the reversible transition between γ-Fe_2O_3 and Fe_3O_4, this reaction was assumed to proceed according to the following oxidation-reduction mechanism;

$$CO + \gamma\text{-}Fe_2O_3 \xrightarrow[k_1]{} CO_2 + Fe_3O_4 \qquad (1)$$

$$N_2O + Fe_3O_4 \xrightarrow[k_2]{} N_2 + \gamma\text{-}Fe_2O_3. \qquad (2)$$

In the stationary state, we abtain;

$$\frac{1}{r_{N_2}} = \frac{1}{k_1P_{CO}} + \frac{1}{k_2P_{N_2O}}, \qquad (3)$$

where r_{N_2} denotes the rate of N_2 formation and where P_{CO} and P_{N_2O} show the partial pressures of CO and N_2O respectively. Furthermore, the concentration of γ-Fe_2O_3 during the reaction can be described as

$$\left[\gamma\text{-}Fe_2O_3\right] = \frac{1}{1+\dfrac{k_1P_{CO}}{k_2P_{N_2O}}}. \qquad (4)$$

Based on Eq. 3, the values of k_1 and k_2 can be calculated from the slope and intercept in Fig. 5. The k_1 and k_2 calculated from Fig. 5-a were 76 and 270 (mmol/h g-cat atm) respectively. Likewise, 84 and 170 (mmol/h g-cat atm) were obtained from Fig. 5-b as the values of k_1 and k_2. Because these values of the rate constant were approximately consistent, the mechanism described above seems reasonable.

The simultaneous observation of the FMR signal showed that the reaction proceeded in a state close to the γ-Fe_2O_3, for the signal intensity decreased only a little, even when there was more CO than N_2O in the gas phase. This is in agreement with the rapid reoxidation by N_2O described above and is supported by the greater value of k_2 (reoxidation step) than k_1 (reduction step).

The relative concentration of γ-Fe_2O_3 can be estimated from the kinetic equation (4) as well as from the observed FMR signal intensity (see the previous section); the concentrations of γ-Fe_2O_3 we have obtained are compared in Fig. 6. These are consistent, though a little deviation from linearity was observed in a reduced condition.

The precise determination of the concentration of γ-Fe_2O_3 from FMR is rather difficult in this case, for the signal does not vary much. Such an *in situ* measurement of the catalyst should, however, have a potential ability to show direct evidence for help in solving a given problem. In this paper, the reaction mechanism shown above for the CO–N_2O reaction is supported by the *in situ* measurement of the FMR spectra.

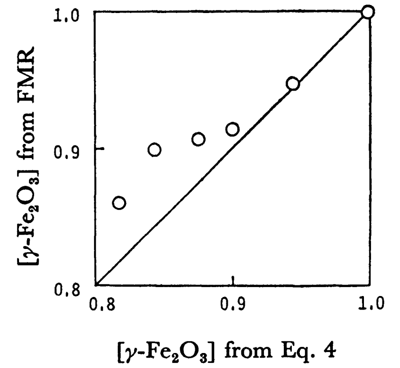

Fig. 6. Plot for the comaprison between calcd concns of γ-Fe_2O_3 based on the kinetics and the FMR signal.

Reactivity of α- and γ-Fe_2O_3. Misono *et al.* have already shown that γ-Fe_2O_3 has a higher activity for the oxidative dehydrogenation of 1-butene than does α-F_2O_3.[5] They suspected, because of its structural characteristics, that the high reactivity of γ-Fe_2O_3 probably originates from the rapid uptake and removal of oxygen. The reactivities of α- and γ-Fe_2O_3 were measured also in the CO–N_2O reaction. Figure 7 shows the activity of α- and γ-Fe_2O_3/Al_2O_3 catalysts of various loadings in the CO–N_2O reaction. The reaction was performed in the *in situ* cell, and the phase of the catalyst was confirmed by ESR. The catalytic activity increased linearly with iron-oxide content up to about 5 wt%, while it kept nearly constant in higher concentrations. As is clearly shown, no difference was observed between the activities of α- and γ-Fe_2O_3/Al_2O_3.

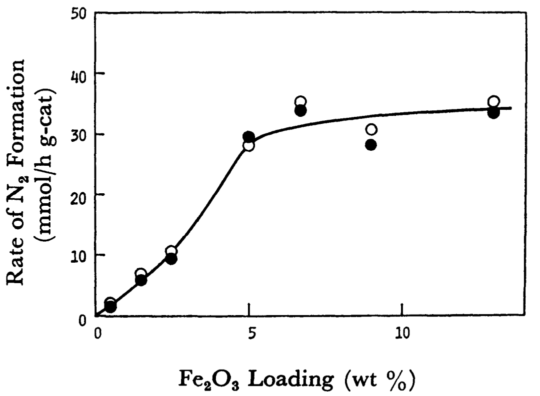

Fig. 7. Activity of α- (●) and γ- (○) Fe_2O_3/Al_2O_3 catalysts having different loadings in the CO–N_2O reaction at 280 °C in the *in situ* cell. Partial pressures of N_2O and CO were 0.23 and 0.22 atm, respectively, and 0.14 atm of Ar was contained as the internal standard for the chromatography.

In order to confirm this fact, various reactions, *i.e.*, the CO–N_2O reaction, the oxidative dehydrogenation of 1-butene, and the oxidation of hydrogen, were carried out on both supported and unsupported iron oxides by

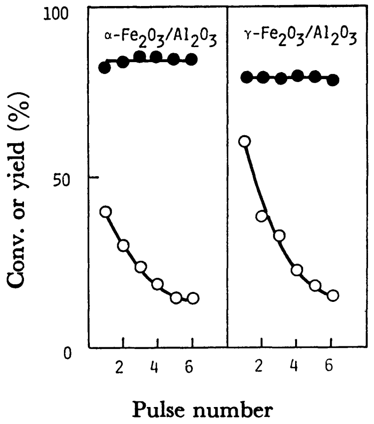

Fig. 8. Comparison of catalytic activities between α- and γ-Fe_2O_3/Al_2O_3 supported by 6.7 wt % Fe_2O_3; 0.2 ml of $CO–N_2O$ (1 : 1) (●) or 0.1 ml of 1-butene (○) was injected successively into the catalyst bed at 280 °C, and conversion into CO_2 and butadiene were plotted *vs.* number of pulse.

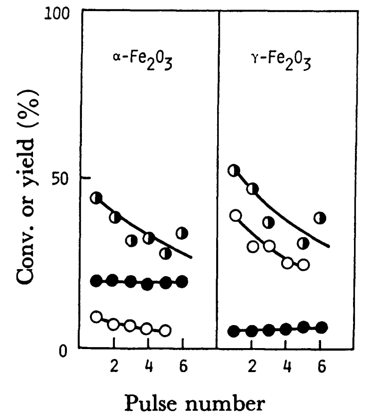

Fig. 9. Comparison of catalytic activities between α- and γ-Fe_2O_3 in the pulse reaction of $CO–N_2O$ (●), 1-butene (○) or H_2 (◑); Oxidation of hydrogen was done at 313 °C, and other were referred to in Fig. 8.

the pulse technique. Figure 8 shows the activities of α- and γ-Fe_2O_3/Al_2O_3 for the $CO–N_2O$ reaction and the oxidative dehydrogenation of 1-butene. Furthermore, Figure 9 shows the activity of unsupported oxide in these oxidation reactions. Both α- and γ-Fe_2O_3/Al_2O_3 had similar activities in the $CO–N_2O$ reaction (Fig. 8). In the case of pure iron oxide, on the other hand, α-Fe_2O_3 had a higher activity than γ-Fe_2O_3 in the $CO–N_2O$ reaction (Fig. 9). The high activity of γ-Fe_2O_3 in the oxidative dehydrogenation of 1-butene which was reported by Misono *et al.*[5] was reproducible also in this study. However, the difference between them was very small in the supported catalyst.

Not only the $CO–N_2O$ reaction, but also the oxidative dehydrogenation of 1-butene, is considered to take place in the oxidation-reduction mechanism, as has been mentioned above and described previously by Misono *et al.*[5] Furthermore, the specific surface areas of α- and γ-Fe_2O_3 were exactly the same, 18 m^2/g. Nevertheless, the catalytic activity of α- and γ-Fe_2O_3 was reversed in these reactions. Therefore, different characteristics controling these activities should be considered.

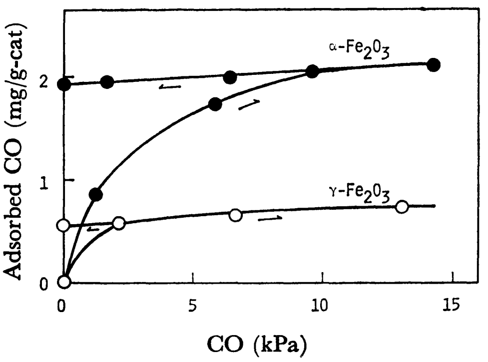

Fig. 10. Adsorption isotherms of CO on α- (●) and γ- (○) Fe_2O_3 at room temp, following the arrow in the figure.

The amount of CO adsorbed on iron oxides may be one of the reasons, because the saturated adsorbed amounts of CO on α- and γ-Fe_2O_3 at room temperature were 1.93 and 0.55 (mg/g-cat), and such a difference was analogous to the activity profile of the $CO–N_2O$ reaction. As is shown in Fig. 10, the adsorption of CO was irreversible at this temperature, and probably it was stabilized as a carbonyl complex with an exposed iron ion. In other words, the metal ions responsible for the adsorption of carbon monoxide are exposed on the surface of α-Fe_2O_3 more than on that of γ-Fe_2O_3 and seem to contribute to the high activity of the $CO–N_2O$ reaction.

As is shown in Fig. 9, γ-Fe_2O_3 had a higher activity than α-Fe_2O_3 also in the hydrogen oxidation, which can be regarded as the simplest oxidation reaction, and therefore as the reaction which is the most sensitive to the activity of surface oxygen. This adds support to the consideration by Misono *et al.* about the high activity of oxygen of γ-Fe_2O_3. On the other hand, the $CO–N_2O$ reaction may be influenced by the activation of carbon monoxide by the surface iron ion.

References

1) M. M. Scieber, "Experimental Magnetochemistry," Interscience Publ., New York (1967), p. 157.

2) P. W. Selwood, "Adsorption and Collective Paramagnetism," Academic Press, New York (1962).

3) B. R. Roy and C. R. Noddings, *J. Catal.*, **3**, 1 (1964).

4) E. G. Derouane, M. Mestdagh, and L. Vielvoye, *J. Catal.*, **33**, 169 (1974).

5) M. Misono, Y. Nozawa, and Y. Yoneda, Preprint of VIIth Intern. Congress on Catalysis, (1976), p. 386.

6) B. Klimaszewski and J. Pietrzak, *Bull. Acad. Sci. Ser. Sci. Math., Astr. Phys.*, **17**, 51 (1969).

7) L. S. Singer and D. N. Stamires, *J. Chem. Phys.*, **42**, 3299 (1965).

8) A. H. Morrish and E. P. Valstyn, *J. Phys. Soc. Jpn.*, **17** Suppl. B-1, 392 (1962); in the study of Klimaszewski *et al.*[6] also, the shift by the transition of Fe_3O_4 to γ-Fe_2O_3 was hardly observable.

9) L. R. Bickford, Jr., *Phys. Rev.*, **78**. 449 (1950).

10) D. V. Sokolskii, G. K. Alekseeva, A. S. Khlystov, V. I. Yashkevich, and G. K. Kotova, *Reac. Kinet, Catal. Lett.*, **6**, 59 (1977).

11) T. Maekawa and M. Terada, *Nippon Kinzoku Gakkaishi*, **29**, 421 (1965).