JOURNAL OF CATALYSIS 16, 264–271 (1970)

NOTES

Mössbauer Spectral Observation on the Supported Iron Catalyst

Catalyst properties are significantly influenced by supports, as studied by many workers from various viewpoints (*1–5*). Some Mössbauer spectroscopic studies have been carried out on the subject (*6–11*). Their investigations, however, have not resulted in sufficient information being given about the effects of catalyst variables, such as the supports and iron concentration. In the present paper, the results of further investigations on supported iron catalysts are presented with special references to the effects of kinds of supports and iron concentration, using Mössbauer spectroscopy.

A series of catalyst samples containing various amounts of iron contents were prepared by impregnating the supports with ferric nitrate solution in different concentration. The supported iron samples were dried at 110°C for 2 hr, and then calcined in air at 500°C for 16 hr for alumina samples and at 250°C for silica gel samples. About 100 mg of the prepared sample (oxidized) was set on a thin aluminum foil and it was then subjected to the measurement of Mössbauer spectroscopy in air at room temperature. The obtained results are shown in Table 1. The obtained spectra were classified by three typical patterns as shown in the third column of Table 1. Type A is the spectrum of superparamagnetic fine α-Fe_2O_3 particles with a quadrupole split two lines. Type C is an

TABLE 1
RESULTS OF MOSSBAUER EFFECT

Support	Iron content (Wt %)	Type of Mossbauer spectrum	Mossbauer parameter[a]		
			δ(mm/sec)	ϵ(mm/sec)	H(kOe)
Silica gel	0.8	A	+0.62	0.84	—
	7.0	B	+0.63	0.73	—
	21.0	C	—	—	500
α-Alumina	0.9	A	+0.58	0.71	—
	2.2	B	+0.63	0.72	—
	16.0	C	—	—	510
η-Alumina	2.2	A	+0.58	0.95	—
	18.0	B	+0.64	0.82	—
	23.0	B	—	—	—
γ-Alumina	2.2	A	+0.59	0.99	—
	20.0	B	+0.60	0.87	—
Bulk Fe_2O_3	70.0	C	—	—	515

[a] Key: δ = isomer shift, referring to sodium nitroprusside; ϵ = quadrupole splitting; and H_{int} = internal field.

antiferromagnetic spectrum with six lines due to magnetic hyperfine splitting. Type B is comprised of Type A and Type C.

The values for the isomer shift and quadrupole splitting of the iron oxide on the various supports in Table 1 are varied from 0.58 to 0.63 mm/sec, and 0.71 to 0.99 mm/sec, respectively. The differences in their isomer shift are not significant and are of the same order as experimental error. These values are essentially identical with the typical values of trivalent iron salt (*12*). Quadrupole splitting depended on the particle size of α-Fe_2O_3 (*13*). The variation from 0.71 to 0.99 mm/sec may be attributable to the variation of particle size from 130 to 40 Å. That is, supports have no influence on the oxidation state of iron but on the degree of dispersion of iron oxide.

The transition from superparamagnetic Type A to antiferromagnetic Type C, depending on increasing iron concentration, can be attributed to the increase in the particle size. According to the results of Kundig *et al.* (*8*), the Mössbauer spectrum of Type A is for a small particle where size is less than 130 Å, and Type C for particles whose radius is larger than 130 Å (*8*). Therefore, it must be noted that transition concentartion W_t, at which the spectrum changes from Type A to Type B, can be a good scale to determine whether the particle size is about 130 Å or not. If particles with a diameter of 130 Å could occupy the surface site without mutual interactions (as if in Langmuir adsorption), the weight of such particles sufficient to cover the surface, W_{max}, might be given by

$$W_{max} = \frac{4}{3}\pi r^3 \rho \cdot \frac{S}{\pi r^2} = \frac{4}{3} r \cdot S \cdot \rho, \quad (1)$$

where r is the particle diameter, S is the surface area of the supports, ρ is the density of the iron oxide, and the particle is assumed to be in the form of a sphere. The ratio $\theta (= W_t/W_{max})$ may become a good measure to characterize the surface properties of supports. The value of θ is given by Table 2.

The surface area after acid treatment

TABLE 2
DEGREE OF IRON DISPERSION[a]

Sample	S(m²/g)	θ	S'(m²/g)	θ'
Iron–silica gel	420	0.006_3	380	0.007_0
Iron–α-alumina	5	0.09_0	—	—
Iron–η-alumina	350	0.02_6	280	0.03_3
Iron–γ-alumina	340	0.03_0	—	—

[a] Key: S, surface area of support; S', surface area of support after acid treatment; and $\theta' = \frac{4}{3} r S' \rho$.

S' was measured, because the supports were attacked differently by acid when the sample was prepared. According to the results of Table 2, both θ and θ' for the η-alumina sample are larger than those for the silica gel sample. The difference of θ for two supports must be due to the difference in the dispersion state.

In order to investigate the state of the iron dispersion on the supports, the surface area and the pore volume of the two supports were measured with respect to the iron concentration. The results are shown in Fig. 1.

In a silica gel sample, both surface area and pore volume are increased when the iron concentration is increased. In the η-alumina sample, on the contrary, both quantities are decreased. These facts sug-

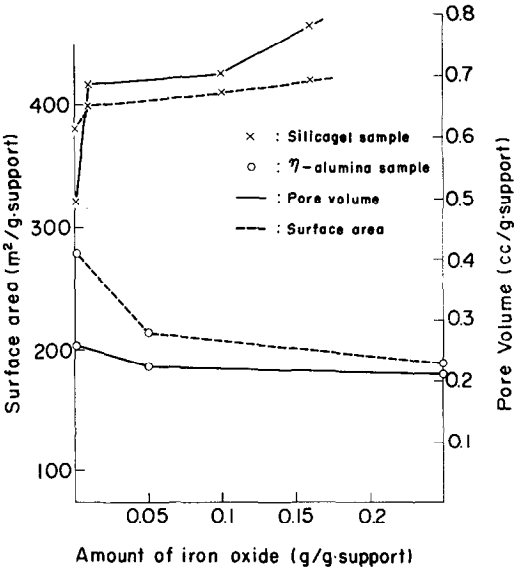

FIG. 1. Variation of the surface area and pore volume with respect to the iron concentration.

gest that some of the pores in η-alumina are filled up by supported iron, while, in the silica gel, new pores are yielded by the supported iron oxide. Thus it is considered that the iron dispersion is not only affected by the surface area of the support, but also by the pore structure of the support.

Summarizing, θ is very small for the silica gel sample, which is highly porous, it has the highest value for α-alumina, which is nonporous, and is a medium value for the η-, and γ-alumina.

The interaction between the catalyst metal oxide and the support appears to an important effect on the catalytic properties of the supported catalysts. It is said that the reducibility is a useful means for detecting the interaction (*14*). In the Mössbauer experiments, the reducibility was defined as the fraction of yielded metallic iron when the superparamagnetic sample (showing Type A spectrum) was reduced in hydrogen at 450°C for 8 hr. The reducibility of the ferromagnetic iron oxide (showing Type C spectrum) on any support was 100%. This result is quite reasonable, because the antiferromagnetic iron oxide is expected to have similar properties to bulk iron oxide.

In the course of the study, another parameter, degree of sintering by heat treatment, was found to describe the interaction between the catalyst and support. The iron–alumina samples were heated at 780°C for 16 hr in air and then Mössbauer measurement was carried out at room temperature. The degree of sintering was defined as the decrease in the superparamagnetic fraction (or increase in the antiferromagnetic fraction) of the sample by the heat treatment, because superparamagnetic fine particles changed into ferromagnetic large particle by sintering. The results are given in Fig. 2, along with the results of reduction.

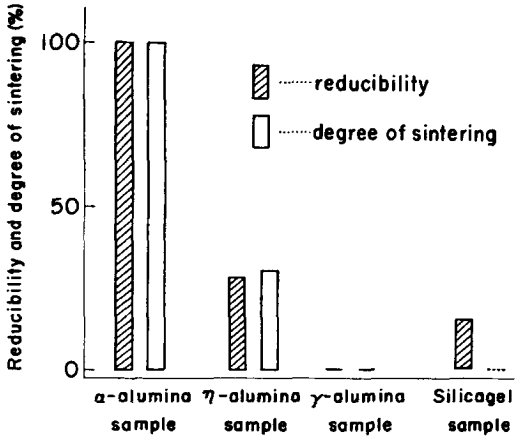

FIG. 2. Correlation between the reducibility and the degree of sintering.

As shown in Fig. 2, there is a good correlation between the reducibility and the degree of sintering. Using these parameters, we can obtain the order of decreasing extent of interaction, γ-$Al_2O_3 > SiO_2 > \eta$-$Al_2O_3 > \alpha$-Al_2O_3. Since the nature of the interaction is not yet obvious, further investigation will be required.

The Mössbauer effect was an effective tool for studying the state of iron dispersion on a support. It was proved that the degree of sintering was a good parameter, similar to reducibility, to describe the interaction between iron oxide and the support.

ACKNOWLEDGMENTS

The authors would like to thank Dr. K. Nohga and Dr. H. Shiratori for their constant interest in the progress of this work. Sincere appreciation is expressed to Professors T. Takaishi, T. Tachibana, and Mr. Y. Gohshi for their helpful discussions. The authors gratefully acknowledge the sample preparation done by Miss T. Ohya and the measurement of BET surface area and pore volume done by Miss N. Sakai and Mr. J. Kashiwakura.

REFERENCES

1. BOND, J. C., "Catalysis by Metals," p. 40. Academic Press, New York, 1962.
2. SELWOOD, P. W., *Advan. Catalysis* **3**, 28 (1951).
3. SCHUIT, G. C. A., AND REIJEN, L. L. V., *Advan. Catalysis* **10**, 243 (1958).
4. SELWOOD, P. W., ADLER, S., AND PHILIPS, T. R., *J. Am. Chem. Soc.* **77**, 1462 (1955).
5. TAYLER, W. F., SINFELT, J. H., AND YATES, D. J. C., *J. Phys. Chem.* **69**, 3857 (1965).
6. HOBSON, M. C., AND CAMPBELL, A. D., *J. Catalysis* **8**, 294 (1967).
7. CONSTABARIS, G., LINDQUIST, R. H., AND

KUNDIG, W., *Appl. Phys. Letters* **1**, 59 (1965).
8. KUNDIG, W., BOMMEL, H., CONSTABARIS, G., AND LINDQUIST, R. H., *Phys. Rev.* **142**, 327 (1966).
9. HOBSON, M. C., AND GAGER, H. M., "Fourth International Congress on Catalysis," Preprint of 48, Moscow, 1968.
10. DUNKEN, H., AND HOBERT, H., *Z. Chem.* **6**, 276 (1966).
11. ROW, M. G., "The Solid-Gas Interface," Vol. 2, p. 947. Dekker, New York, 1967.
12. ERICKSON, N. E., "Mössbauer Effect and Its Application in Chemistry," p. 86. Am. Chem. Soc., Washington, 1967.
13. KUNDIG, W., ANDO, K. J., LINDQUIS, R. H., AND CONSTABARIS, G., *Czech. J. Phys.* **B17**, 467 (1967).
14. VERNON, C. F. H., AND CLARK, A., *J. Catalysis* **11**, 305 (1968).

T. YOSHIOKA
J. KOEZUKA
H. IKOMA

Toshiba Research and Development Center
Tokyo Shibaura Electric Co., Ltd.
Kawasaki, Japan

Received April 14, 1969; revised July 1, 1969

Catalytic and Electrocatalytic Oxidation of Acetate

Electrocatalysis refers to electrode processes, the rates of which are dependent on the nature of the electrode. It is a form of heterogeneous catalysis where an overall charge transfer across the electrode–solution interface takes place. A chemical reaction in solution, which is catalyzed by a conducting surface, is likely to involve charge transfer with the catalyst, i.e., it will take place by anodic and cathodic electrochemical processes. In this case, catalysis and electrocatalysis will be closely related since the catalytic activity of a material for such a reaction will be a combination of its electrocatalytic activities for the individual processes.

The concept of simultaneous anodic and cathodic processes is well established in the fields of corrosion and displacement reactions (*1, 2*). In the field of heterogeneous catalysis it has been applied to a few systems (*3–7*). In this communication, it is shown that the platinum catalyzed reaction between acetate and oxygen,

$$CH_3COO^- + H^+ + 2O_2 \rightarrow 2CO_2 + 2H_2O, \quad (1)$$

takes place through the electrochemical processes,

$$CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e, \quad (2)$$

and

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O. \quad (3)$$

The electro-oxidation of acetate to carbon dioxide, reaction (2), has been shown (*8*) to proceed on platinum at potentials lower than 0.7 V against a reversible hydrogen electrode and its rate is determined by the first electron transfer. The electroreduction of oxygen, reaction (3), is well documented (*9, 10*).

Electrochemical mechanisms of this type must be expected for other heterogeneously catalyzed organic oxidations in solution as well as the more obvious charge transfer reactions such as the iron(III)–iodine reaction discussed by Spiro (*7*).

The rate of an electrode process is dependent on the potential across the electrode–solution interface. When a catalytic process takes place by individual electrode processes, a steady state potential is set up which must be such that the rates of the anodic and cathodic processes are equal and opposite since there is a zero net current. If the processes occur at the same rates in the presence and absence of each other, then the catalytic activity can be predicted exactly from the electrochemical properties of the individual proc-