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Study on Nickel Oxide-Silica-Alumina Catalysts for Ethylene Polymerization. IV. The Structure of the Catalysts Studied by the Oxidation of Carbon Monoxide and by Magnetic Measurements

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The oxidation of carbon monoxide and magnetic susceptibility measurements have been carried out with a series of nickel oxide-silica-alumina catalysts, all of which are the same in aluminum content but which are different in nickel content. The kinetic data of the oxidation followed an Elovich rate equation, and the initial activity per unit of surface area of the catalyst increased as the nickel content increased from 0 to 8.0 atom%. The apparent activation energy was found to be 8±2 kcal/mol. The magnetic susceptibility *vs.* temperature curves followed the Curie-Weiss relationship in the temperature range between 240 and 723°K, and the effective Bohr magneton number increased to an approximately constant value of 3.7 Bohr magnetons as the nickel content decreased. The structure of the nickel oxide-silica-alumina catalysts has been discussed on the basis of the results obtained, and the Thomas model of the nickel acid site previously proposed for the active site of the ethylene polymerization (H. Uchida and H. Imai, *Bull. Chem. Soc. Japan*, **35**, 995 (1962)) has been confirmed.

The activity of a series of nickel oxide-silica-alumina catalysts in ethylene polymerization and the selectivity in the formation of butene isomers have previously been studied,[1-3] and a Thomas model of the nickel acid site has been proposed for the active site of the ethylene polymerization.[2] In a series of catalysts, which were the same in aluminum content but different in nickel content,

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1) H. Uchida and H. Imai, This Bulletin, **35**, 989 (1962).

2) H. Uchida and H. Imai, *ibid.*, **35**, 995 (1962).

3) H. Imai and H. Uchida, *ibid.*, **38**, 925 (1965).

the specific activity showed a maximum at 3 atom% nickel and the activity was proportional to the extent of the nickel acid site on the catalysts.[3]

In the present paper, catalysts identical with those used in the preceding paper[3] are employed, and another reaction, one which is catalyzed by the supported nickel oxide, is carried out to see whether any anomaly in the activity appears or not. The oxidation of carbon monoxide was chosen because it has been extensively studied.[4] Magnetic measurements are also made, and the structure of the catalysts is discussed on the basis of the results obtained.

Experimental

Materials. The catalysts used in this paper are identical with those reported in a preceding paper[3]; they had been prepared by mixing a solution of sodium silicate with a solution of aluminum and nickel nitrates and then forming the resulting precipitate into granules 1—2 mm in size. The aluminum content of the catalyst, expressed as the Al/(Al+Si) atomic ratio, was fixed at 0.05, while the nickel content, expressed as atom % nickel (defined by $100\times Ni/(Ni+Al+Si)$), was varied over the range from 0 to 8.0.

Carbon monoxide was prepared by the decomposition of formic acid and purified through ice water, sodium hydroxide, and a liquid nitrogen trap. Cylinder oxygen was purified by passing it through palladium asbestos (at 200°C), sodium hydroxide, and a dry-ice trap.

Oxidation of Carbon Monoxide. The kinetic measurements were carried out in an all-glass circulatory flow system of a constant volume (*ca.* 550 m*l*). Gold foils were placed before and after the catalyst tube to trap any mercury vapor which might pass in. The catalyst was pretreated *in situ* by letting dried air flow in for 16 hr at 500°C and then evacuated (10^{-4} mmHg) for 3 hr at the same temperature. After the temperature of the catalyst had been lowered to a reaction temperature (120—170°C), the CO–O_2 stoichiometric mixture ($CO : O_2 = 2 : 1$) was admitted to the system to be circulated through the catalyst, and the pressure of the system was followed by a mercury manometer. The carbon dioxide formed was allowed to remain in the reaction mixture during the course of the reaction.

Magnetic Measurements. The magnetic susceptibility was measured by the Faraday method with a horizontal suspension balance similar in construction to that used by Knappwost *et al.*[5] The apparatus was calibrated with Mohr's salt.[6]

The catalysts were ground to 100—200 mesh, and about 0.1 g of the ground catalyst was pretreated by letting dried air flow in for 16 hr at 500°C; the catalyst was then evacuated (10^{-4} mmHg) at the same temperature, and sealed in a glass ampoule under the vacuum. The susceptibility of these samples was measured over the temperature range between 240 and 723°K at the field strength of 6500 gauss, and corrected for the diamagnetism of the silica-alumina support by using the measured value of -0.37×10^{-6} per gram of SiO_2-Al_2O_3. No paramagnetic impurity other than nickel was found in the susceptibility measurements.*2 The susceptibility per gram atom nickel was computed by using the chemically-analyzed nickel content.

X-Ray Analysis. Powder X-ray diffraction patterns of the catalyst samples which had been pretreated by letting dried air flow in for 16 hr at 500°C were recorded on an X-ray diffractometer (Rigaku Denki Co., Ltd.).

Results

Oxidation of Carbon Monoxide. The oxidation of carbon monoxide was carried out in the temperature range between 120 and 170°C with a 1.5 m*l* catalyst. Figure 1 shows the results

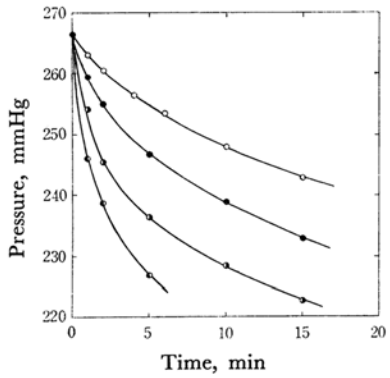

Fig. 1. Oxidation of carbon monoxide at 150°C over a series of the nickel oxide-silica-alumina catalysts.
○: 1.5 atom% Ni, 0.734 g
●: 3.0 atom% Ni, 0.796 g
◑: 6.0 atom% Ni, 0.883 g
◐: 8.0 atom% Ni, 0.888 g

obtained with a series of fresh catalysts at 150°C. The initial pressure of the CO–O_2 stoichiometric mixture was kept constant at 265 mmHg in all the experiments. The catalyst activity for the oxidation increases with an increase in the nickel content.

When the activity was measured again after regeneration, *i. e.*, by treatment by letting dried air flow in for 16 hr at 500°C, followed by evacuation (10^{-4} mmHg) for 3 hr at the same temperature, the activity decreased by some 20%. In this paper, the activity of the fresh catalyst is used for the sake of comparison.

Magnetic Measurements. In Fig. 2, the reciprocal of susceptibility per gram atom nickel,

4) E. R. S. Winter, "Advances in Catalysis," Vol. 10, ed. by D. D. Eley *et al.*, Academic Press, New York and London (1958), p. 196.
5) A. Knappwost and G. E. Bockstiegel, *Z. Elektrochem.*, **57**, 700 (1953).
6) P. W. Selwood, "Magnetochemistry," 2nd ed., Interscience Publishers, New York (1956).

*2 Fe and Mg were detected by an emission spectroanalysis of the catalysts, but the amounts of these impurities were smaller than that of Ni by the factor of 10^2.

χ^{-1}, is plotted as a function of the temperature for a series of catalysts. The χ^{-1}-T curves follow the Curie-Weiss relationship,

$$\chi = C/(T + \Delta)$$

with a negative Weiss constant, Δ, in the temperature range studied.

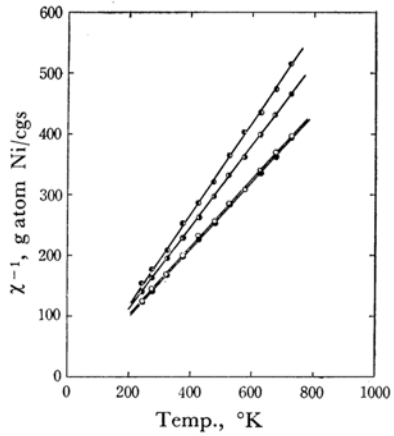

Fig. 2. Reciprocal of susceptibility per gram atom nickel (χ^{-1}) as a function of temperature.
○: 1.5 atom% Ni, ●: 3.0 atom% Ni
◑: 6.0 atom% Ni, ◐: 8.0 atom% Ni

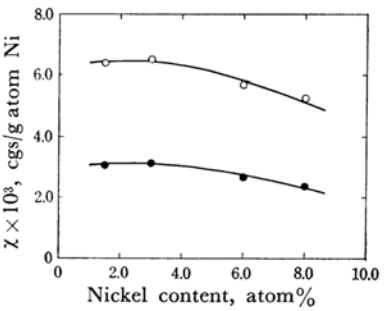

Fig. 3. Susceptibility per gram atom nickel plotted against nickel content.
Susceptibilities at 300°K (○) and at 600°K (●).

The susceptibility per gram atom nickel remains almost constant in the catalysts of 1.5 and 3.0 atom% nickel, but it decreases with a further increase in the nickel content in the temperature range studied. This is illustrated in Fig. 3.

The effective Bohr magneton number, μ_{eff} is calculated from the relationship,

$$\mu_{eff} = 2.84\sqrt{C}$$

where C is the Curie constant; this number is plotted against the nickel content, together with the Weiss constant, in Fig. 4. The effective Bohr magneton number increases to an approximately constant value of 3.7 Bohr magnetons with a decrease in the nickel content, and the absolute value of the Weiss constant decreases with a decrease in the nickel content.

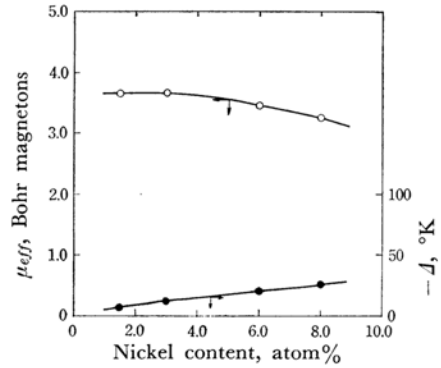

Fig. 4. Effective Bohr magneton number (μ_{eff}) and Weiss constant (Δ) plotted against nickel content.

X-Ray Analysis. No crystalline peak except a broad amorphous peak was observed in any of the catalysts.

Discussion

Oxidation of Carbon Monoxide. Several rate equations have been proposed for the oxidation of carbon monoxide over nickel oxide catalysts,[7-13] and the proposed mechanisms are not in agreement. These discrepancies can, however, be understood by considering the evidence that, setting aside the nature of nickel oxide, the inhibiting effect of carbon dioxide greatly disturbs the mechanism of the reaction.[14]

The present kinetic data were examined with all the rate equations ever proposed, and it was concluded that they followed the Elovich rate equation[7,8,12]:

$$-\frac{dP}{dt} = k_g w P_0 \exp\left[-\frac{(P_0-P)}{P_0}\frac{\alpha}{RT}\right]$$

where P_0 (mmHg) is the initial pressure of the stoichiometric mixture; P (mmHg), the pressure at time t (min); w (g), the weight of the catalyst; R, the gas constant; T (°K), the reaction temperature; and k_g and α, the constants. The conclusion is consistent with that obtained with impregnated

7) S. Z. Roginsky and T. S. Tselinskaya, *Zhur. Fiz. Khim.*, **22**, 1360 (1948).
8) G. Parravano, *J. Am. Chem. Soc.*, **75**, 1448 (1953); *ibid.*, **75**, 1452 (1953).
9) M-G. Schwab and J. Block, *Z. Physik. Chem. (Frankfurt)*, **1**, 42 (1954).
10) E. R. S. Winter, *J. Chem. Soc.*, **1955**, 2726.
11) N. P. Keir, S. Z. Roginsky and I. S. Sozonova, *Doklady Akade. Nauk S. S. S. R.*, **106**, 859 (1956).
12) A. Bielanski, J. Deren, J. Haber and J. Sloczynski, *Z. Physik. Chem. (Frankfurt)*, **24**, 345 (1960).
13) P. Rue and S. J. Teichner, *Bull. Soc. Chim. France*, **1964**, 2797.
14) J. Coue, P. C. Gravelle, R. E. Ranc, P. Rue and S. J. Teichner, "Proc. 3rd International Congress on Catalysis," Vol 1, North-Holland Publishing Co., Amsterdam (1965), p. 748.

nickel oxide-silica catalysts.[15] The fit of the kinetic data to the integrated form of the equation:

$$\frac{(P_0-P)}{P_0} = \frac{2.30RT}{\alpha} \log \frac{(t+t_0)}{t_0}$$

$$t_0 \equiv RT/\alpha k_g w$$

is demonstrated in Fig. 5.

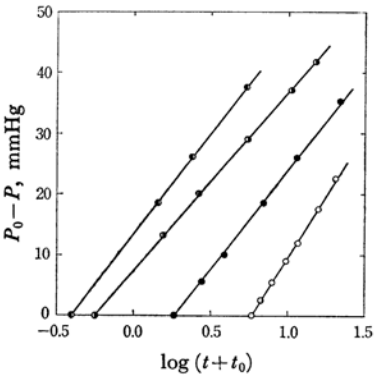

Fig. 5. Elovich plots.
○: 1.5 atom% Ni, 0.734 g
●: 3.0 atom% Ni, 0.796 g
◑: 6.0 atom% Ni, 0.883 g
◐: 8.0 atom% Ni, 0.888 g

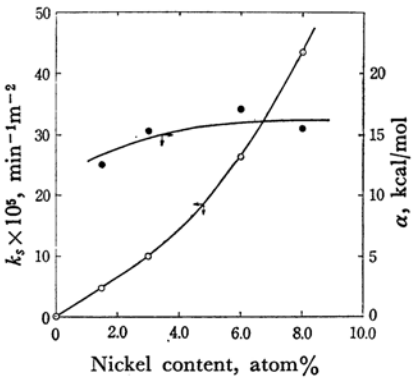

Fig. 6. Specific activity (k_s) and α value in the Elovich equation plotted against nickel content.

The specific activity, k_s, *i. e.*, the initial activity per unit of the surface area of the catalyst, is obtained by dividing k_g by the specific surface area of the catalyst[3]; it is plotted against the nickel content, together with the α value, in Fig. 6. The specific activity increases with an increase in the nickel content. Although k_s is not proportional to the nickel content, it does not show a maximum at 3 atom% nickel as is the case for the specific activity of the ethylene polymerization.[3] The α value remains roughly constant with an increase in the nickel content.

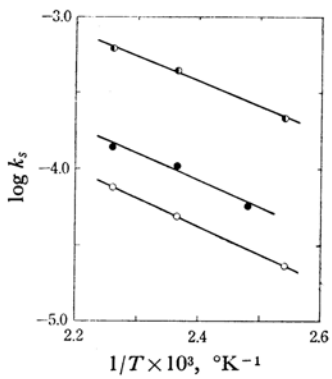

Fig. 7. Arrhenius plots.
○: 1.5 atom% Ni, ●: 3.0 atom% Ni
◑: 8.0 atom% Ni

Figure 7 shows the Arrhenius plots of the specific activity. The apparent activation energy remains at an almost constant value of 8±2 kcal/mol with an increase in the nickel content from 1.5 to 8.0 atom%. These values of the apparent activation energy are a little smaller than those, 13—20 kcal/mol, obtained with the impregnated nickel oxide-silica catalysts,[15] but they fall within the range of the literature values, 5.5—15 kcal/mol, obtained with unsupported nickel oxide catalysts.[8-10,12]

In the present paper, no attempt was made to study the mechanism of the oxidation of carbon monoxide, but, rather, an attempt was made to study the change in the surface area of the supported nickel oxide which is brought about when the nickel content is increased. Clearly, if the nature of the supported nickel oxide does not change with an increase in the nickel content, the observed k_s values can be used as a relative measure of the surface area of the supported nickel oxide.[16] Both the facts, that the α value in the Elovich equation and the apparent activation energy remain almost constant with an increase in the nickel content, suggest that the nature of the supported nickel oxide is almost the same in all these catalysts. Thus, it may be concluded that the surface concentration of the nickel is increased as the nickel content increases up to 8.0 atom%, although no quantitative relationship can be obtained. In the preceding paper,[3] it was demonstrated that the acidity due to nickel, or the number of the nickel acid sites, showed a maximum at a nickel content of 3 atom%. This fact may be explained by assuming that, in the catalysts with a higher nickel content, the supported nickel agglomerates on the silica surface to form islands of nickel oxide, the formation of

15) G. T. Rymer, J. M. Bridges and J. R. Tomlinson, *J. Phys. Chem.*, **65**, 2152 (1961).

16) P. H. Emmett, "Catalysis," Vol. 1, ed. by P. H. Emmett, Reinhold Publishing Corporation, New York (1954), p. 67.

which reduces the formation of the nickel acid sites by preventing the orientation of the nickel into the silica lattice.

Magnetic Measurements. Nickel oxide is antiferromagnetic and has a Néel temperature of about 520°K[17]; the effect of the grain size on the magnetic properties of unsupported nickel oxide has previously been studied.[17-23] In nickel oxide samples larger than 1000 Å (in diameter) the susceptibilities are typical of antiferromagnetics, but in samples smaller than 100 Å the susceptibilities increase with a decrease in the temperature, even below the Néel point, showing no maximum in the temperature range above 100°K. The susceptibility also increases as the grain size decreases. These facts have been well interpreted by the theory developed by Néel.[18] The magnetic properties of the nickel oxide supported on alumina or silica have also been studied by several authors.[6,15,24-26]

In the present catalysts, the susceptibilities increase with a decrease in the temperature and no maximum is observed in the susceptibility *vs.* temperature curves. This may reasonably be understood by the fact that the grain size of the supported nickel oxide is too small to be detected by X-ray analysis (at least smaller than 20 Å). As is shown in Fig. 3, the susceptibility increases as the nickel content decreases, reaching a constant value at a nickel content smaller than 6 atom%. This increase observed in the larger nickel content range may be ascribed at least in part to the decrease in the grain size of the supported nickel oxide; this is consistent with the conclusion obtained in the oxidation of carbon monoxide. As the observed Curie constants and the effective Bohr magneton numbers are larger than those of a free Ni^{2+} ion, the fine-grained nickel oxide alone is not responsible for the values of the susceptibility of the present catalysts; the interaction between the Ni^{2+} ion and the catalyst support must also be considered.

The facts[3] that both the activity for the ethylene polymerization and the acidity due to nickel show a maximum at the nickel content of 3 atom% clearly suggest that there is an interaction between the nickel and the catalyst support which produces the active sites for the ethylene polymerization.[27] The μ_{eff} value of the present catalyst increases to a constant value of 3.7 Bohr magnetons with a decrease in the nickel content. The oxidation state of the nickel in a present catalyst containing 3 atom% of nickel was determined to be 2.0 by quantitative reduction in hydrogen.[2] Therefore, the increase in the μ_{eff} over the spin-only value of the Ni^{2+} ion (2.8 Bohr magnetons) cannot be ascribed to the presence of nickel ions of a higher valency. As the Weiss constant corresponding to the μ_{eff} value of 3.7 is small, this increase in the μ_{eff} value can, on the other hand, be ascribed to the orientation of Ni^{2+} ions in the silica lattice.

The value of μ_{eff} cannot be explained by assuming that Ni^{2+} ions simply exchange with the protons of the silica-alumina surface, as it is larger than the values of both free Ni^{2+} ions and simple nickel salts.[28] There is a possibility of the presence of nickel silicate (Ni_2SiO_4), as has been suggested by Ozaki,[29] but the presence of the nickel silicate may be excluded by comparing the values of μ_{eff}. The nickel silicate has an olivine structure[30] in which each Ni^{2+} ion is octahedrally surrounded by the oxygen anions. The μ_{eff} value for the Ni^{2+} ion in the octahedral environment was estimated to be 3.4,[31] while the experimental value for the nickel silicate was found to be 3.04.[32] Both are different from the presently observed value.

In the Thomas model of the nickel acid site proposed for the active site of the ethylene polymerization,[2] the nickel is tetrahedrally surrounded by oxygen anions. The μ_{eff} value for the Ni^{2+} ions in the tetrahedral environment was estimated to be 3.5—4.1 by the crystal field theory[31]; this value is consistent with the present value of 3.7. The tetrahedral group [NiO_4] with a μ_{eff} value of 3.9 has been reported to be present in a silicate

17) J. T. Richardson and W. O. Milligan, *Phys. Rev.*, **102**, 1289 (1956).
18) L. Néel, *Compt. Rend.*, **252**, 4075 (1961); *J. Phys. Soc. Japan*, **17**, Suppl. **B-1**, 676 (1962).
19) K. G. Strivastava, *Compt. Rend.*, **253**, 2887 (1961).
20) J. Cohen, K. M. Creer, R. Pauthenet and K. G. Srivastava, *J. Phys. Soc. Japan*, **17**, Suppl. **B-1**, 685 (1962).
21) T. Takeda and N. Kawai, *ibid.*, **17**, Suppl. **B-1**, 691 (1962).
22) J. Cohen, R. Pauthenet and K. G. Srivastava, *J. Phys. Radium*, **23**, 471 (1962).
23) W. J. Schuele and V. D. Deetscreek, *J. Appl. Phys.*, **33**, 1136 (1962).
24) F. N. Hill and P. W. Selwood, *J. Am. Chem. Soc.*, **71**, 2522 (1949).
25) W. O. Milligan and J. T. Richardson, *J. Phys. Chem.*, **59**, 831 (1955).
26) J. T. Richardson and W. O. Milligan, *ibid.*, **60**, 1223 (1956).

27) Holm *et al.* concluded that the activity for the ethylene polymerization was dependent on well-dispersed nickel ions rather than isolated crystals of nickel oxide on the silica-alumina support; V. C. F. Holm, G. C. Bailey and A. Clark, *Ind. Eng. Chem.*, **49**, 250 (1957).
28) The values are around 3.2; *cf.*, for example, Ref. 6.
29) A. Ozaki, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 1 (1954).
30) "Landolt-Börnstein Zahlenwerte u. Funktionen aus Physik, Chemie, Astronomie, Geophysik u. Technik," 6 Auflage, Hrsg. von A. Eucken, Bd. 1, Teil 4, Springer-Verlag, Berlin, Göttingen u. Heidelberg (1955), p. 74.
31) For example, B. N. Figgis, *Nature*, **182**, 1568 (1958).
32) H. Kondo and S. Miyahara, *J. Phys. Soc. Japan*, **18**, 305 (1963).

glass.[33]

In the consequence of the above discussion, the following conclusion has been obtained concerning the structure of the present catalysts: In the catalysts with a lower nickel content, most Ni^{2+} ions are in the tetrahedral environment of the silica lattice. The presence of these tetrahedrally-surrounded Ni^{2+} ions is consistent with the Thomas model of the nickel acid site[2]; they may be the active sites for the ethylene polymerization. As the μ_{eff} value does not change in the catalysts with 1.5 and 3.0 atom% nickel, the number of these Ni^{2+} ions may be said to increase with an increase in the nickel content from 0 to 3 atom%; consequently, a maximum is produced in the activity of the ethylene polymerization. The further increase in the nickel content results in an increase of the grain size of the supported nickel oxide, an increase of which is observed by means of the decrease in the μ_{eff} and in the susceptibility values, and also by means of the sharp increase in the activity for the oxidation of carbon monoxide.

33) R. S. Nyholm, "International Series of Monographs on Inorganic Chemistry, Vol. 1, Chemistry of the Co-ordinate Compounds, A Symposium," ed. by H. Taube and A. G. Maddock, Pergamon Press, New York (1958), p. 401.

The authors are indebted to Dr. Yoshisada Ogino for his design of the apparatus of magnetic susceptibility measurements, and also to Dr. Eiichi Asada for his X-ray analyses.