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A New Catalyst for Ethylene Polymerization Containing Nickel Oxide

Ken-ichi Maruya and Atsumu Ozaki

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo

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A new catalyst for ethylene polymerization NiO–$NiSO_4$, was found from a study of NiO–SiO_2, and $NiCl_2$ catalysts. The Ni–$NiSO_4$ catalyst prepared from mixtures of formate and sulfate is much less active than NiO–$NiSO_4$ prepared from mixtures of hydroxide and sulfate. Poisoning behavior of carbon monoxide and water is quite similar to NiO–SiO_2 catalyst. An equimolar mixture of NiO–$NiSO_4$ gives maximum activity. The active species is postulated to be hydroxy sulfate of nickel. The structure of the active site is discussed.

Nickel oxide-silica is known to be effective for the dimerization of ethylene at room temperature.[1] As an extention of the study on its active site various nickel salts were tested for their activity in dimerization. It was found that nickel chloride could be activated for dimerization, when it was evacuated at above 230°C after a preevacuation at 140°C.[2] Both catalysts have common features. (1) Isotopic mixing in ethylene [1,3] and isomerization of *n*-butene[4,5] simultaneously take place over these catalysts. (2) They are poisoned by a small amount of CO for dimerization but not for isomerization. (3) The rate

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[1] K. Kimura, H. A–I, and A. Ozaki, *J. Catal.*, **18**, 271 (1970).

[2] K. Maruya, N. Ando, and A. Ozaki, *Nippon Kagaku Zasshi* **91**, 1125 (1970).

[3] A. Ozaki, H. A–I, and K. Kimura, Int. Congr. Catal., 4th, Moscow, paper 40 (1968).

[4] K. Maruya, N. Ando, and A. Ozaki, *Nippon Kagaku Zasshi* **92**, 699 (1971).

[5] A. Ozaki, and K. Kimura, *J. Catal.*, **3**, 395 (1964).

of dimerization decreases with the increase in carbon number of olefin.[4,6] This similarity in catalytic properties suggests that an essentially identical active site is responsible for the dimerization over nickel oxide-silica and nickel chloride.

It has been suggested that the active site for dimerization is formed by an interaction of a nickel ion of low valency with an acid site.[1] The characteristic reaction on the low valent nickel is the chemisorption of CO and the isotopic mixing in ethylene. The acid site is characterized by butene isomerization.[5] It was shown that nickel oxide alone is activated for the isotopic mixing in ethylene by evacuation above 300°C, but it is inactive for the dimerization.[3] This is possibly due to the fact that no acid site can be developed on pure nickel oxide. An acid nature of nickel oxide silica has been shown.[1,5] Other catalyst systems for dimerization could thus be obtained by incorporating low valent nickel with acid component. This view was examined by combining nickel formate or hydroxide expected to give reduced nickel or nickel oxide after decomposition, with a number of sulfates which are known to be acidic.[7] In this way a new catalyst system of $NiO-NiSO_4$ was found for the polymerization of ethylene.

Experimental

Preparation. Catalysts containing nickel formate were prepared by evaporating mixed aqueous solutions of nickel formate and sulfate. Although nickel formate was deposited during the course of evaporation, the mixture was evaporated to dryness with stirring. The product thus obtained was green powder. The catalysts contianing nickel hydroxide were prepared by evaporating mixtures of nickel sulfate solution and the nickel hydroxide freshly prepared from nickel nitrate by precipitation with aqueous ammonia.

Procedure. The rate of polymerization of ethylene was determined at 30°C with an initial pressure of 45 cmHg, measuring pressure decrease in a constant volume static system, utilizing an oil manometer for less active catalysts. Reaction products were analyzed by gas chromatography using ODPN or pola-pack column. The rate of isomerization of 1-butene was estimated by conversion within 15 min at room temperature.

Results

Nickel Formate-based Catalyst (Catalyst I). Six sulfates (Mg^{2+}, Al^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) were tested for their effectiveness as co-catalysts to nickel in the ethylene polymerization by combining each with nickel formate. It was found that only nickel sulfate was effective for the purpose.

Different mole ratios of nickel formate-nickel sulfate mixtures were evacuated at 300°C for 3 hr and tested for their activities. The rates of polymerization were so low that the pressure change was followed by an oil manometer. The pressure change with time is exemplified in Fig. 1. There is an induction period for the pressure change after a rapid initial change due to adsorption. The initial rates of ethylene consumption and the induction periods obtainable by the extrapolation shown in Fig. 1, are given in Fig. 2 as a function of catalyst composition. It can be seen that the maximum rate is obtained at around equimolar composition accompanied by minimum induction period, and that nickel sulfate itself has a small activity.

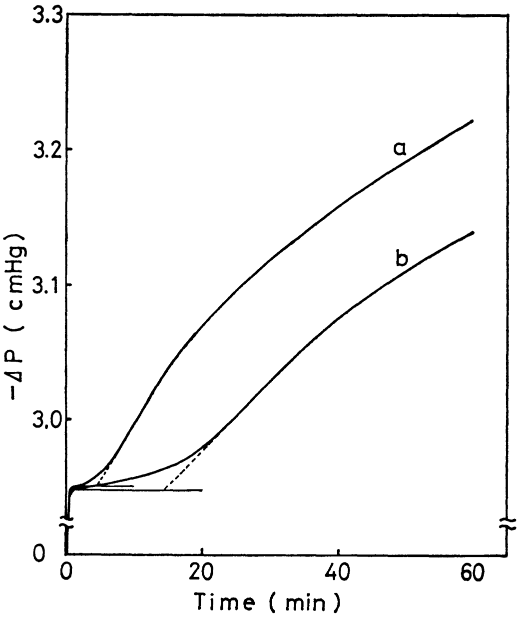

Fig. 1. Typical time course of ethylene polymerization over catalyst I.
$Ni(HCOO)_2/NiSO_4=1$ in a, 1/10 in b

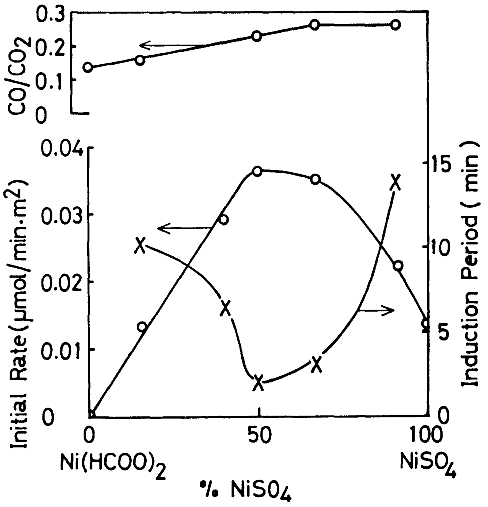

Fig. 2. Variations of induction period, initial rate of ethylene consumption and CO/CO_2 ratio in the decomposition product of $Ni(HCOO)_2-NiSO_4$ mixture with composition.

The product obtained from the gas phase was exclusively *n*-butenes.

The rate of ethylene consumption by the equimolar mixture was drastically reduced to about one seventh by 0.5 μmol/g of preadsorbed CO, or by 50 μmol/g of preadsorbed H_2O. However, in the case of pure nickel sulfate no effect of CO was observed.

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6) M. Koizumi, *J. Institute Polytechnics, Osaka City Univ.*, **4**, No. 1, Series C (1953).

7) K. Tanabe and T. Takeshita, *Advan. Catal.*, **173**, 15 (1967).

The nature of decomposition product of nickel formate was examined by the reaction of C_2H_4 and D_2 on a catalyst rich in nickel sulfate ($Ni/NiSO_4=1/10$) at 30°C for 2 hr. Neither exchange nor hydrogenation was detected, suggesting that no metallic phase of nickel exists at least on the surface. The ratio of CO/CO_2 in the gaseous decomposition product from the catalyst mixtures is shown in Fig. 2 as a function of catalyst composition. It can be seen that the ratio increases with the concentration of nickel sulfate.

The decomposition of nickel formate has been described by several authors[8,11] in terms of the following two simultaneous reactions

$$Ni(HCOO)_2 \longrightarrow \begin{cases} Ni + H_2 + 2CO_2 & \text{(a)} \\ Ni + H_2O + CO + CO_2 & \text{(b)} \end{cases}$$

although the relative importance of each reaction seems to depend on reaction condition and particle size of the sample.[12] According to Kornienko,[13] however, about 10% of nickel is transformed into NiO in the absence of H_2 and CO. It was found in the present case that 3.4 (ml S. T. P.) of hydrogen was absorbed for 3 hr at 300°C by the decomposition product from 1 g of $Ni(HCOO)_2 \cdot 2H_2O$. It was suggested that the nickel formate was partly transformed into nickel oxide instead of metallic nickel. The presence of nickel sulfate appeared to enhance the formation of nickel oxide. Thus the question arose of whether the real catalyst might not be a composite of nickel oxide and nickel sulfate. This led to the following study of $NiO–NiSO_4$ system.

Nickel Hydroxide-based Catalyst (Catalyst II). An equimolar mixture of nickel hydroxide and nickel sulfate was evacuated at 300°C for 1 hr and tested for its activity in the ethylene polymerization at 30°C. The pressure change with time is shown in Fig. 3. It is obvious that ethylene is rapidly consumed with no induction period. The rate of consumption is about 30 times that by equimolar catalyst I. Figure 3 also shows another run in which 1 μmol/g of CO was preadsorbed. It is clear that the pressure change stops after the initial rapid decrease which should be due to adsorption process. This shows that carbon monoxide effectively poisons this catalyst also.

Since the initial decrease due to adsorption is nearly over within the first one minute, it is better to estimate the initial rate of ethylene consumption after this period. Thus the initial rates are obtained from the pressure change in the period 1—3 min and plotted against the temperature of evacuation (Fig. 4). It can be seen that the activity appears above 200°C reaching a maximum at 350°C. It is remarkable that the acidity of nickel sulfate attains a maximum by the heat treatment at 350°C.[7]

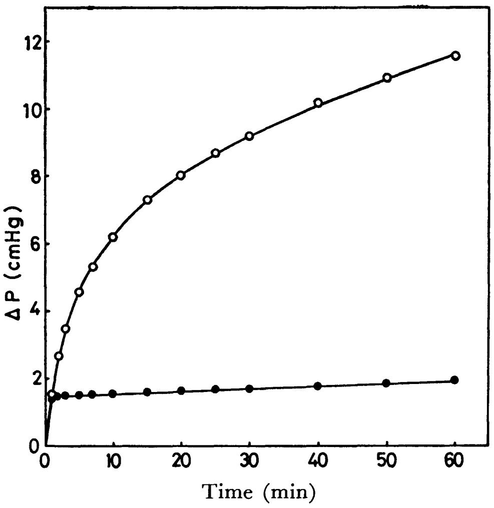

Fig. 3. Time course of ethylene polymerization at 30°C over $NiO–NiSO_4$ (1/1) catalyst evacuated at 300°C 1 hr. Solid circle shows the run with preadsorbed CO of 1 μmol/g.

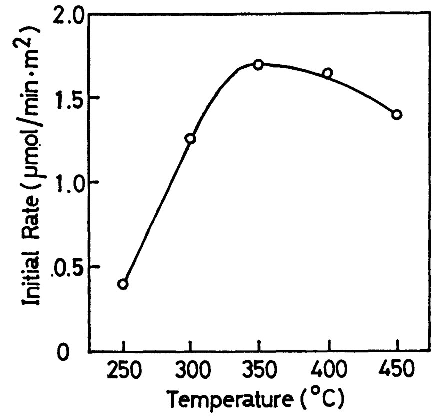

Fig. 4. Variation of initial rate with the evacuation temperature. $NiO/NiSO_4=1$.

The effect of composition on the initial rate per surface area was examined where the catalysts were evacuated at 250°C. As shown in Fig. 5, the maximum activity is obtained at equimolar composition. Another series of runs were made to study the effect of composition on isomerization of butene on this catalyst system. The result is also shown in Fig. 5. Since nickel sulfate is known to be acidic and to catalyze the isomerization of butene and since nickel oxide is known to be inactive, it can be expected that the activity of a mechanical mixture of the two components for the isomerization of butene increases with the content of nickel sulfate. In this respect the result shown in Fig. 5 is remarkable. The activity for isomerization also attains a maximum at the equimolar composition. This is not due to the change in surface area as shown in Fig. 5. The result, as well as that on the rate of polymerization, suggests that the mixture is not merely a mechanical mixture and the equimolar composition is significant as regards the active site.

The nature of the active site for isomerization was

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8) A. A. Balandin, E. S. Grigoryan, and Z. S. Yanisheva, *Acta Physicochem. USSR*, **12**, 737 (1940); *J. Gen. Chem. USSR*, **10**, 1031 (1940).

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10) T. Sasa, *Yuki Gosei Kagaku Kyokai Shi*, **11**, 463 (1953).

11) T. Yamanaka, Y. Takagi, and K. Taya, *Sci. Papers I. P. C. R.*, **5**, 78 (1959).

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13) V. P. Kornienko, *Ukrain. Khim. Zhur.*, **18**, 579 (1952).

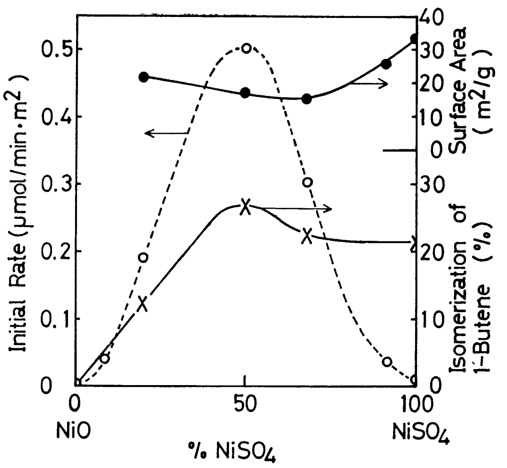


Fig. 5. Variations of initial rate of ethylene polymerization, extent of 1-butene isomerization and specific surface area with catalyst composition of $NiO-NiSO_4$ system.

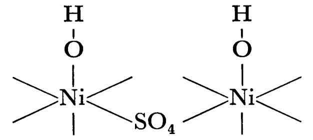
examined by the effect of preadsorbed carbon monoxide. It was found that 1 μmol/g. cat. of carbon monixide gave no effect on the extent of isomerization, although the amount of carbon monixide was enough to inhibit the polymerization. The result is reasonable when the active site for isomerization is an acid one.

Discussion

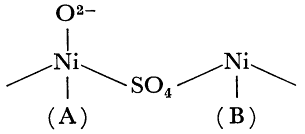
The postulate for the active site could develop a new catalyst system formed by the interaction of nickel oxide with nickel sulfate. However, the postulate should be corrected on the basis of the present results. The term "low valent nickel" originated from the fact that the $NiO-SiO_2$ catalyst was drastically poisoned by carbon monoxide, since a low-valent nickel is favorable to chemisorb carbon monoxide.[1] Catalyst I of the present study was adopted to test the idea "low valent". That catalyst I was much less active than catalyst II shows that the metallic state of nickel is inadequate to form the active site. A slight activity observed in catalyst I can be ascribed to a small amount of nickel oxide formed in the decomposition of nickel formate. It is to be noted that the $NiO-SiO_2$ catalyst is remarkably deactivated by hydrogen reduction to $Ni-SiO_2$.[14] Even in $Ni-SiO_2$ catalyst we can assume unreduced nickel, because oxide reacted with silica gel is hardly reducible.[15]

An essential feature common to $NiO-SiO_2$ and $NiO-NiSO_4$ is the fact that both catalysts are activated by dehydration from the surface, forming a carbon monoxide-sensitive site. This is also observed with nickel oxide alone, although the dehydrated nickel oxide is not active for dimerization, but active for isotopic mixing in ethylene[3] and hydrogenation of ethylene.[16] The active site for dimerization has been postulated to be formed by an interaction of the carbon monoxide sensitive site of the nickel oxide with an acid site. In fact, the expected activity was obtained by incorporating nickel sulfate which is known to provide an acid site. However, it is to be noted that none of the other sulfates known to be acidic could give activity by incorporation with nickel formate. In view of this fact, it is interesting that the acidic component in $NiO-SiO_2$ is formed by the reaction between nickel hydroxide and silica gel, as observed in the $SiO_2-Al_2O_3$ system. It seems that nickel ion is involved in the acidic component to cause an effective interaction between the carbon monoxide sensitive site and the acid component.

We found that an equimolar mixture of $Ni(OH)_2$ and $NiSO_4$ gives a maximum activity. The equimolar mixture may be regarded as a hydroxy nickel sulfate $Ni_2(OH)_2SO_4$. Although the structure of hydroxy sulfate of nickel is unknown, there can be pairs of $-Ni(OH)$ groups which are separated by sulfate ions as



When the hydroxy sulfate is subjected to heat treatment, $-Ni(OH)$ would be dehydrated forming two types of sites (A) and (B).



Since both (A) and (B) are coordinatively unsaturated, such pairs of nickel ion would disappear upon rearrangement at higher temperature. However, at intermediate temperature, pairs of (A) and (B) are likely to exist as an intermediate metastable state, being separated from each other by the sulfate ion. If this presumption is correct, site (A) may have a higher electron density than (B) owing to high electron density in the attached oxide anion. The observed poisoning by CO is reasonable on the type (A) site. It has been noted that CO poisons both the ethylene dimerization and the isotopic mixing in ethylene but not the isomerization of butene over the same catalyst.[1] This was confirmed with this catalyst system. The view is reasonably interpreted as selective occupation of type (A) site by CO, type (B) site being unoccupied. (B) is essentially an acid site and can act as a site for the butene isomerization.

The activation by heating in a vacuum followed by degradation at higher temperature is also reasonable as dehydration to form the pair of nickel ions followed by structural rearrangement. It is interesting that the activation of $NiO-NiSO_4$ reaches a maximum by heat treatment at 350°C at which the acidity of $NiSO_4$ reaches a maximum.[7] This coincidence would be reasonable if the basic structure is similar in both systems so that the maximum is determined by the temperature at which the structural rearrangment begins.

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[14] M. Koizumi, *Nippon Kagaku Kaishi*, **64**, 257 (1943).

[15] J. J. B. van Eijk van Voorthuijsen, and P. Franzen, *Rec. Trav. Chim.* **70**, 793 (1951).

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