

## Effect of Supports on Enantioselectivity of Modified Ni Catalyst

In a previous paper (1) we have shown that  $\text{SiO}_2$  is the best support for the preparation of highly selective and active nickel catalysts for the enantioselective hydrogenation of methyl acetoacetate (MAA) to methyl 3-hydroxybutyrate (MHB). However, the effect of the physical or chemical properties of supports on the enantioselectivity of the catalysts still remains ambiguous. In this study, we examined various supported nickel catalysts prepared by using different types of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , obtained from different sources, having different pore structure or different particle sizes.

The supports employed in this work (Nos. 1-8: $\text{SiO}_2$ , Nos. 9 and 10: $\text{Al}_2\text{O}_3$ ) and the properties of Ni catalysts prepared by using these supports are listed in Table 1. Supported catalysts were prepared by the precipitation method with  $\text{Na}_2\text{CO}_3$  and were reduced at  $400^\circ\text{C}$  for 3 h unless otherwise stated. The modification of a catalyst with (*R,R*)-tartaric acid was carried out at  $83^\circ\text{C}$  for 1 h. The detailed procedures of catalyst preparation and modification are described elsewhere (1). Ten milliliters of MAA in 10 ml of ethyl acetate was hydrogenated at  $60^\circ\text{C}$  under a starting hydrogen pressure of  $10 \text{ kg/cm}^2$  by using a glass autoclave (TEM-U-50, Taiatsu Glass Industry Co.). The optical yield (OY) of (-)-MHB was calculated from the optical rotation of the distilled product and was used as a measure of the enantioselectivity of a catalyst. Pore-size distribution of a support was measured up to 30 nm (=300 Å) by the Cranston-Inkley method (2). Mean crystallite size of nickel ( $\bar{D}_c$ ) in a catalyst was calculated from the half-width of the peak from the (111) plane of nickel metal in the X-ray diffraction pattern of the catalyst.

Table 1 shows the values of OY obtained in the reactions on the catalysts (Ni:support = 1:1) prepared with the use of various supports. The values obtained for a given kind of support were dependent on the type of support used. Supports obtained from different sources may have different pore-size distributions and may contain different impurities, which may lead to different enantioselectivities of supported catalysts. In order to check this hypothesis, at first pore-size distributions of several types of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were examined (Fig. 1). Although Wakogel G and Wakogel Q-63 have quite similar distributions of pore size, the enantioselectivity of the catalyst supported on Wakogel G is much higher than that of the catalyst supported on Wakogel Q-63. Similarly, the catalysts supported on Silicagel No. 1 and Vicor glass, which also have similar pore-size distributions, had different enantioselectivities. On the other hand, in the case of Wakogel C-200 and Wakogel Q-63, which have different pore-size distributions, the selectivities of the catalysts are almost equal. The enantioselectivities of the catalysts supported on Wakogel C-300, JRC-SIO-1, and Vicor glass are also equal to each other although the pore-size distributions of these supports are different. A similar tendency was observed in the case of  $\text{Al}_2\text{O}_3$ ; the pore-size distributions of JRC-ALO-2 and JRC-ALO-5 were similar to each other, but enantioselectivities of resulting supported catalysts were different. Accordingly, the enantioselectivity of supported Ni catalysts seems to be independent of the pore-size distribution of the support, especially of that of the micropores with diameters smaller than about 10 nm; however, mesopores with diameters around 10 to 30 nm seem to have a rather

TABLE I  
Supports and Properties of Supported Ni Catalysts<sup>a</sup>

No.	Name	Source	Particle size (mesh)	$S_a^b$ ( $\text{m}^2 \text{g}^{-1}$ )	$\bar{D}_c^c$ (nm)	OY <sup>d</sup> (%)
1	Silicagel No. 1	Nakarai Chemicals, Ltd.	60–200	600	7	56.2
2	Wakogel G	Wako Pure Chemical Industries	30–50	660	11	54.6
3	Wakogel C-100	Wako Pure Chemical Industries	40–100	370	10	47.2
4	Wakogel C-200	Wako Pure Chemical Industries	100–200	370	8	43.8
5	Wakogel C-300	Wako Pure Chemical Industries	200–300	370	6	37.6
6	Wakogel Q-63	Wako Pure Chemical Industries	325	700	6	43.7
7	JRC-SIO-1	Catalysis Society of Japan	800	166	5	36.4
8	Vicor Glass (No. 7930)	Corning Glass Works	350	183	11	38.5
9	JRC-ALO-2	Catalysis Society of Japan	250	300	19	15.8
10	JRC-ALO-5	Catalysis Society of Japan	60–200	253	22	43.7

<sup>a</sup> Ni:support = 1:1 in weight.

<sup>b</sup> BET surface area of supports.

<sup>c</sup> Mean crystallite size of Ni in the catalysts reduced at 400°C for 3 h.

<sup>d</sup> Optical yield of (–)-MHB.

negative effect on the selectivity of the resulting catalyst.

In the following experiments, the effect of particle size of the support on the enantioselectivity of supported catalysts was studied. Three types of SiO<sub>2</sub> (Nos. 3 to 5 in Table 1), obtained from the same source, were used; these three types of supports differed from each other only in particle size. As can be seen in Fig. 2, the selectivity of the catalysts supported on each type of SiO<sub>2</sub> increased with increase in Ni loading in agreement with previously reported results (1). However, at the same Ni loading the values of OY were dependent on the type of SiO<sub>2</sub> used and decreased in the order Wakogel C-100 > Wakogel C-200 > Wakogel C-300. Thus particle size of support seems to be important for the preparation of enantioselective catalysts. Average particle sizes of supports can be obtained from the mesh given in Table 1. Figure 3 shows the correlation between the enantioselectivity of supported catalysts and average particle size of supports used for the preparation of the catalyst; the larger the particle size of support, the higher the

enantioselectivity. We propose the following explanation for this observation: a support with larger particle size has smaller outer surface area, which causes lower dispersion of nickel metal on the support and, consequently, increases  $\bar{D}_c$  of nickel (3). The correlation between the enantioselectivity and  $\bar{D}_c$  of nickel, shown in Fig. 4, strongly supports this idea. It is noteworthy that the plots for the catalysts, prepared by using supports with the same pore-size distribution, overlap each other independently of Ni loading. This seems to confirm our previous conclusion that the enantioselectivity of supported Ni catalysts depends primarily on the crystallite sizes of Ni, similar to the case of unsupported catalysts (1, 3).

Nickel metal in micropores (e.g., pores smaller than 5 nm) of supports can exhibit only negligible activity toward the hydrogenation of MAA because the diffusion of MAA or MHB is difficult in such small pores. Nickel metal in mesopores, around 10 to 30 nm, will already have some hydrogenation activity, but enantioselectivity will be low; under such conditions the crys-

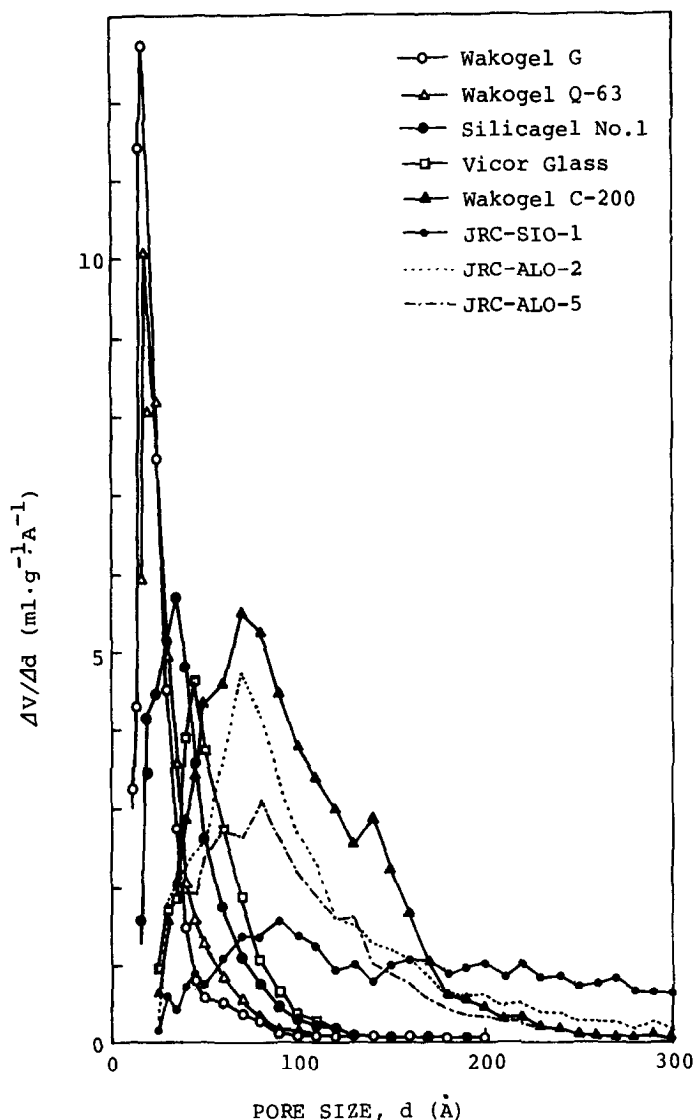


FIG. 1. Pore-size distribution of various types of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

tallite size of Ni cannot be large enough. Thus micropores of supports have no effect on the enantioselectivity of the resulting catalyst, whereas mesopores have negative effect on the selectivity. This seems to be the reason for obtaining slightly higher values of OY for supports like Wakogel Q-63 and Wakogel G (Fig. 4), which do not have mesopores (Fig. 1). In order to obtain a highly enantioselective Ni- $\text{SiO}_2$  catalyst, it seems preferable to use a support with a large particle size and a small amount of mesopores. In this sense, Wakogel G or Sil-

icagel No. 1 appears to be the best support.

Concerning catalysts supported on  $\text{Al}_2\text{O}_3$ , especially on JRC-ALO-2, the enantioselectivity depends strongly on the reduction temperature of the catalyst (Fig. 5). The selectivity of the catalyst with lower Ni loading was very low when the catalyst was reduced at  $250^\circ\text{C}$ . It increased with increasing reduction temperature up to  $400^\circ\text{C}$  but decreased with further increase in the temperature. The increase in the reduction temperature was accompanied with an increase in  $\bar{D}_c$  of nickel and in hydrogenation

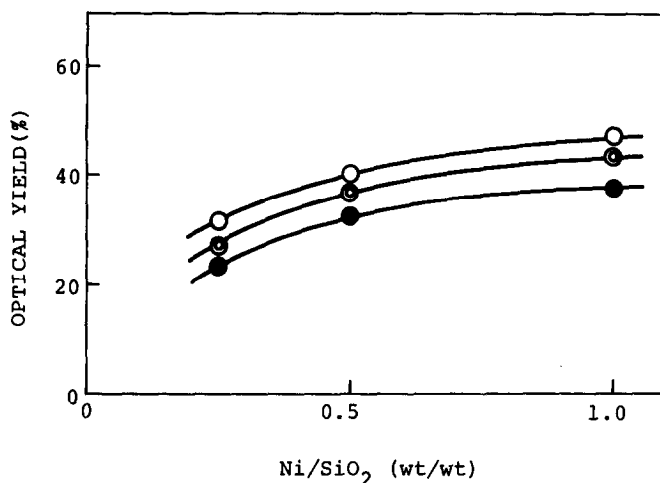


FIG. 2. Effect of nickel loading on the enantioselectivity of Ni-SiO<sub>2</sub> catalysts prepared by using supports with different particle sizes. ○: Wakogel C-100; ⊙: Wakogel C-200; ●: Wakogel C-300.

activity. On the other hand, the selectivity of the catalyst with higher Ni loading was considerably high when reduced at 250°C but, when reduction temperature increased from 250 to 300°C, the selectivity decreased in spite of accompanying increase in  $\bar{D}_c$  of nickel. In the case of SiO<sub>2</sub>-supported catalysts, we did not observe such a strong effect of reduction temperature on the enantioselectivity. These findings can be ex-

plained in terms of the different extent of interaction of nickel with support, as discussed in our previous report (1). Stronger interaction of nickel with Al<sub>2</sub>O<sub>3</sub> than with SiO<sub>2</sub> retards the reduction of small particles of nickel salt on Al<sub>2</sub>O<sub>3</sub>. After deactivation of relatively large crystallites of nickel with high enantioselectivity by sintering at high reduction temperature, small crystallites with low selectivity will become active and

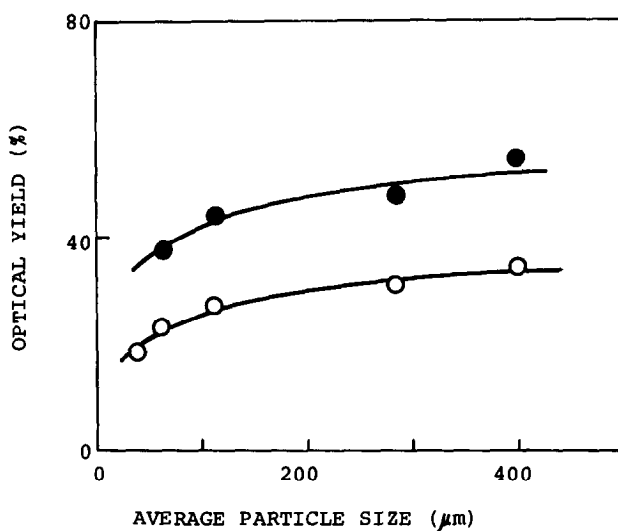


FIG. 3. Dependence of the enantioselectivity of Ni-SiO<sub>2</sub> catalysts on the average particle size of supports. ○: Ni-SiO<sub>2</sub> (1:4) catalysts; ●: Ni-SiO<sub>2</sub> (1:1) catalysts.

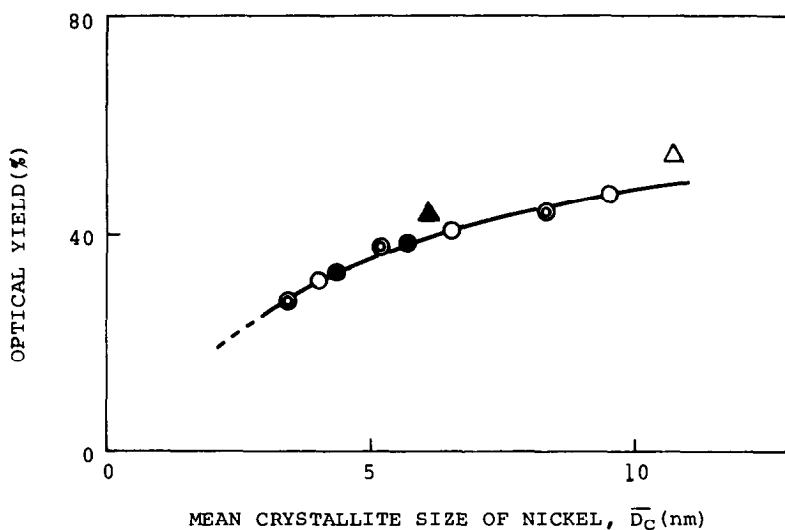


Fig. 4. Dependence of the enantioselectivity on the mean crystallite sizes of Ni in various Ni-SiO<sub>2</sub> catalysts. ○: Wakogel C-100; ⊙: Wakogel C-200; ●: Wakogel C-300; △: Wakogel G; ▲: Wakogel Q-63.

lower the selectivity of the reaction. Thus the chemical properties of supports are also very important in determining the enantioselectivity of supported nickel catalysts.

Supports having lower extent of interaction with nickel are more suitable for preparation of a highly enantioselective catalyst.

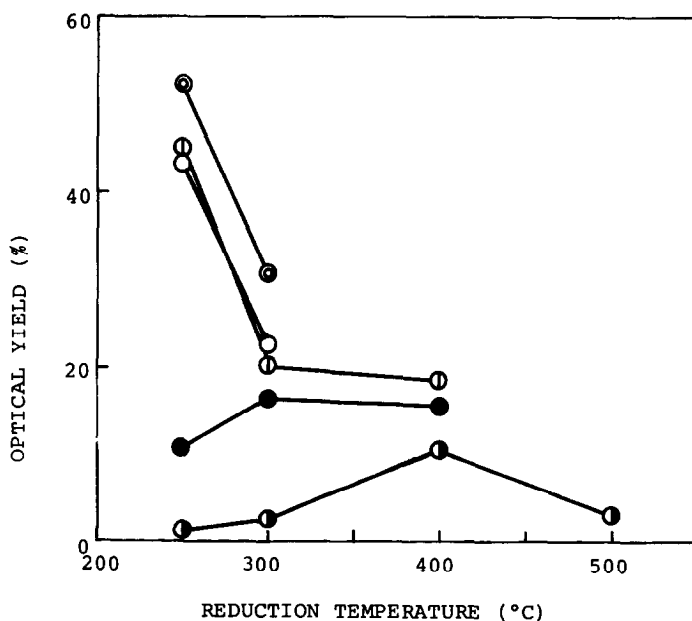


Fig. 5. Dependence of the enantioselectivity of Ni-Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-2) catalysts on the reduction temperature. The weight ratios of Ni to Al<sub>2</sub>O<sub>3</sub> are ●: 1/2; ●: 1/1; ⊙: 2/1; ○: 3/1; ⊙: 4/1.

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