

Effect of Pore Diffusion in Liquid-Phase Enantioselective Hydrogenation with Ni-SiO₂ Catalysts

Yuriko NITTA* and Toshinobu IMANAKA

Department of Chemical Engineering, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka 560

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Synopsis. A series of Ni-SiO₂ catalysts, having a constant Ni loading and different Ni crystallite sizes, were prepared by using series of silica supports with controlled wide-pore structure. The crystallite size effect in enantioselective hydrogenation was found to hold also for the reactions controlled by the pore diffusion.

Since Izumi et al.¹⁾ developed the modified Raney-Ni catalysts for the enantioselective hydrogenation of methyl acetoacetate (MAA) to optically active methyl 3-hydroxybutyrate (MHB), much effort has been devoted to the understanding of the reactions on metal catalysts.^{2–5)} The reaction is known to be highly sensitive to the catalyst-surface structure and modifying conditions. As to unsupported Ni catalysts modified under fixed conditions, we reported that amorphous catalysts have only low enantioselectivity and that the selectivity increased with increasing crystallite size of Ni up to around 10 nm.⁶⁾ Harada et al.⁷⁾ also suggested that amorphous and crystalline parts of H₂-reduced catalysts obtained from NiO provides nonselective and selective sites, respectively. With SiO₂-supported Ni catalysts, the observation that higher Ni loadings result in higher enantioselectivities was also explained by the crystallite size effect similarly to the case of unsupported catalysts.^{8,9)}

On the other hand, Sachtler interpreted the effect of Ni loading in terms of pore diffusion during catalyst modification.⁵⁾ He suggested that, to verify the crystallite size effect, one should change the size of Ni crystallites while keeping the Ni loading of the catalyst constant. Woerde et al.¹⁰⁾ reported that the liquid-phase hydrogenation is also a pore-diffusion process. Therefore, in order to establish the crystallite size effect, we should clarify the effect of pore diffusion on the apparent enantioselectivity, although we have already confirmed the crystallite size effect with Ni-SiO₂ catalysts having constant Ni loading.^{9,11,12)} For this purpose, the use of a series of wide-pore silica with controlled pore structure looks promising. The preparation of Rh catalysts using these silica supports provided series of Rh-SiO₂ catalysts with desired metal particle size.¹³⁾

In this work, we prepared a series of Ni-SiO₂ catalysts, which have a constant Ni loading and different Ni crystallite sizes, by using a series of silica supports with controlled pore structure and examined the enantioselective hydrogenation of MAA with these catalysts under different reaction conditions.

Experimental

The Ni-SiO₂ catalysts were prepared by the pore-filling procedure with aqueous solution of nickel nitrate and a series of silica (Super Micro Bead Silica Gel, Fuji-Davison Chemical Ltd.) having different pore diameters. The Ni loading was kept constant at 7.5 wt% unless otherwise stated. The samples were dried in air at 383 K for 16 h. Two grams of a sample were reduced in flowing hydrogen at 673 K for 3 h and then modified with aqueous (2*R*,3*R*)-tartaric acid solution (pH=5.1). The enantioselective hydrogenation of MAA was carried out for 17 h either with a glass autoclave (No. 1) (TEM-U-50, Taiatsu Glass Industry Co.) equipped with a vigorous-stirring system under an initial H₂ pressure of 10 kg cm⁻² at 333 K, or with a stainless-steel autoclave (No. 2) (TVS-2, Taiatsu Glass Industry Co.) attached to a shaking apparatus of 100 times per minute under an H₂ pressure of ca. 100 kg cm⁻² at 350 K. The detailed procedures of the catalyst modification and the hydrogenation reaction were described elsewhere.⁸⁾

The hydrogenation activity of the catalyst was determined from the pressure decrease during the initial 15 min of the reaction. The optical yield (OY) of (–)-MHB determined from the optical rotation of the distilled product was used as a measure of the enantioselectivity of the catalyst. The mean crystallite size of Ni (*D_c*) in the catalyst was obtained from the half-width of the peak on (111) plane of Ni metal in the X-ray diffraction pattern of the catalyst.

Results and Discussion

The physical properties of the silica supports employed here are listed in Table 1. These wide-pore supports were found to provide a series of suitable catalysts for studying the effects of pore diffusion and the Ni crystallite size.

The silica support (Silica Gel No. 1, Nakarai Chemicals, Ltd.) having been employed in our previous works^{8,11,14)} had only micropores with a

Table 1. Physical Properties of Silica Supports^{a)}

Support	Mean pore diameter	Pore volume	Surface area
	nm	cm ³ g ⁻¹	m ² g ⁻¹
S-1	16.3	1.28	212
S-2	27.8	1.06	135
S-3	52.8	0.96	65
S-4	72.8	1.11	50

a) Data were furnished by Fuji-Davison Chemical Ltd.

Table 2. Catalytic Properties of 7.5wt% Ni-SiO₂ Catalysts

Support	$D_c^a)$	$r_0^b)$	OY ^{c)}
	nm	mmol·min ⁻¹ g Ni ⁻¹	%
S-1	7.2	1.56	18.9
S-2	8.9	1.30	16.8
S-3	11.3	0.98	13.8
S-4	13.5	1.02	8.7

a) Mean crystallite size of Ni determined from the XRD measurement. b) Initial hydrogenation rate. c) Optical yield of (–)-MHB.

mean diameter of 3 nm,⁹⁾ and the supported catalysts were prepared by the precipitation method. Under these conditions, the contribution of Ni in pores to the overall reaction was negligible.⁹⁾ In such a case, the hydrogenation reactions carried out under vigorous stirring (i.e., in autoclave No. 1) were controlled by the surface reaction, whereas the diffusion process was not neglected in the reactions carried out under mild stirring (i.e., in autoclave No. 2).¹⁴⁾

With the catalysts prepared here by the pore-filling method using the wide-pore supports, Ni particles are regarded to exist mainly in the pores, based on the models proposed by Dorling et al.^{15,16)} and Dafler.¹⁷⁾ When the Ni loading was kept constant, the mean crystallite size of Ni increased with an increase in the pore diameter of the silica support as shown in Table 2. This tendency is the same as that observed in the preparation of Rh-SiO₂ catalysts with desired metal-particle size.¹³⁾

The apparent enantioselectivity of these Ni-SiO₂ catalysts observed in the reactions carried out in the autoclave No. 1 decreased with an increase in the pore diameter of silica support in spite of an increase in the mean crystallite size of Ni in these catalysts. On the other hand, when hydrogenations were carried out by using another autoclave (No. 2) with a mild shaking system, the enantioselectivity of the catalysts increased with an increase in the mean crystallite size of Ni just as with the catalysts reported previously (Fig. 1). In this case, the reactions are regarded to be diffusion controlled as already pointed out,^{10,14)} probably because of the slow mass transfer from gas-liquid interface to the catalyst surface under a low stirring intensity. Accordingly, the higher selectivity of the catalyst with the larger Ni crystallites reflects the increase in the fraction of selective sites in the catalyst surface.

As shown in Fig. 1, the catalysts with different Ni loadings (4.1 to 11.3 wt%), prepared by using S-4 silica with the widest pore (72.8 nm) as the support, exhibited an increased enantioselectivity with an increase in the mean crystallite size of Ni even in the case using the autoclave No. 1. Therefore, the results shown in Table 1 suggest that the reaction on the catalysts with narrower pores is retarded by the pore diffusion. Since the surface reaction rate on nonselective sites is higher than that on selective sites under our reaction conditions,¹⁴⁾ the reaction on nonselective sites becomes more limited when the concentration of reactants in pores is lowered by the slow diffusion, which leads to a higher enantioselectivity of the catalyst with narrower pores.

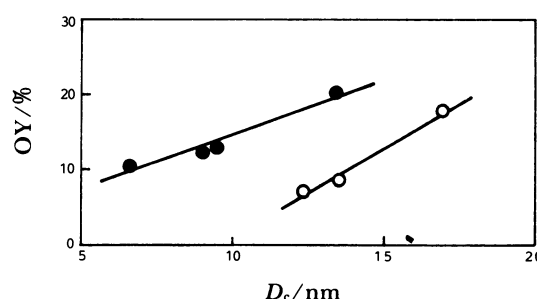


Fig. 1. Enantioselectivity of modified Ni-SiO₂ catalysts as a function of the mean crystallite size of Ni. Reactions were carried out either with the catalysts having different Ni loadings in autoclave No. 1 (O) (surface reaction controlled), or with 7.5 wt% Ni-SiO₂ catalysts in autoclave No. 2 (●) (pore diffusion controlled).

tivity of the catalyst with narrower pores.

In the liquid-phase reaction carried out by using autoclave No. 1 with a vigorous-stirring system, the rate of mass transfer of H₂ from gas phase to the pellet surface is fast enough and the concentration ratio MAA/H₂ is in the order of 10². Under these conditions the modulus Φ can be estimated as follows:¹⁸⁾

$$\Phi = \eta\phi^2 = R_p^2 \frac{r_{\text{obs}}}{D_{\text{eff}} C_{\text{H}_2}}$$

where η is the effectiveness factor, ϕ is the Thiele modulus, R_p is the radius of the spherical catalyst pellet (5 μm), and D_{eff} is the effective diffusion coefficient of H₂. With $D_{\text{eff}} = 3.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and $C_{\text{H}_2} = 3.6 \times 10^{-5} \text{ mol cm}^{-3}$ at 333 K in ethyl acetate, Φ was calculated from the observed highest rate and found to be in the order of 10⁻⁴. Since Φ is so small, the effectiveness factor for mass transfer inside the catalyst particle is essentially unity and so the reaction is essentially intrinsic. However, D_{eff} in liquid phase is difficult to estimate especially in narrower pores with relatively large Ni particles in them and might be much smaller than the value assumed above. Even values in the order of 10⁻¹⁰ to 10⁻¹⁴ have been reported for D_{eff} in Zeolites.¹⁸⁾ Therefore, the possibility that the pore diffusion interferes with the reactions on the catalysts with narrower pores cannot be denied.

These findings and discussion strongly suggest that the crystallite size effect holds for the reactions controlled by either the surface reaction or the pore diffusion. However, we should be careful in estimating the surface properties of supported

catalysts from the apparent enantioselectivities when the rate determining step varies with the catalysts.

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