The Effect of Crystallite Size of Nickel on the Enantioselectivity of Modified Nickel Catalysts

Yuriko Nitta, Fumimaro Sekine, Toshinobu Imanaka, and Shiichiro Teranishi*
Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received August 6, 1980)

Enantioselective hydrogenation of methyl acetoacetate to methyl 3-hydroxybutyrate with various unsupported nickel catalysts modified by (2*R*,3*R*)-tartaric acid was studied under mild conditions in order to elucidate the dependence of the selectivity upon the surface states of the catalysts. The catalyst with the larger crystallite size has the higher enantioselectivity, presumably because of the higher probability to obtain large ensembles of regularly-arranged nickel atoms in the catalyst surface for the modifier to adsorb strongly and regularly. The nickel boride catalyst has very low enantioselectivity, mainly due to its amorphous structure. The detrimental effect of additives (B, P, and Al in Ni–B, Ni–P, and R-Ni catalysts) was explained as the effect of their lowering the crystallinity of the catalysts.

There have been many studies on the effects of the structure of modifiers, modifying conditions, and reaction conditions on the enantioselectivities of modified nickel catalysts, mainly for the hydrogenation of methyl acetoacetate (MAA) to methyl 3-hydroxybutyrate (MHB).[1-3] On the other hand, it is well known that the enantioselectivity of modified catalysts is affected strongly by the preparation methods or the conditions of pretreatments of the metal catalysts.[4-6] However, only a few studies have established a correlation of enantioselectivity to the structure or the surface state of the modified catalysts.

We have been studying the activities and selectivities of various nickel catalysts, such as nickel boride (Ni–B), nickel phosphide (Ni–P), Raney nickel (R-Ni), Urushibara nickel(U-Ni), and the other nickel blacks, for the hydrogenation of olefins, aldehydes, and ketones by comparing with the surface states of the catalysts.[7] In the present study, we examined the enantioselective hydrogenation over various nickel catalysts in order to establish the correlation between the selectivity and the surface structure of nickel catalysts. The enantioselective hydrogenation with heterogeneous catalysts has usually been investigated by using nickel catalysts and the reaction seems very sensitive to the structure of the catalysts. (2*R*,3*R*)-Tartaric acid (TA) and MAA were selected as a modifier and a reactant in this study because most previous experiments have used them.

The Ni–B catalyst, which is known to have similar activities and selectivities to the R-Ni catalyst in many hydrogenation reactions, has a very low enantioselectivity compared to that of the R-Ni catalyst. The reason for this low enantioselectivity will be discussed later.

Experimental

Catalyst Preparation. *Nickel Boride(Ni–B)*: $Ni(CH_3COO)_2 \cdot 4H_2O$ (4.24 g) in 50 ml of distilled water was reduced with 20 ml of $NaBH_4$ (1.94 g) aqueous solution at 30 °C with vigorous stirring (P-1 method according to Brown[8]). This catalyst is called Ni–B-1 here. After 10 min, the precipitated catalyst was washed 3 times with portions of 50 ml of distilled water before modification. The catalyst was separated by centrifugation after each wash. In order to vary the surface concentration of boron in the resulting catalyst,[7f] $NiCl_2 \cdot 6H_2O$ was used instead of nickel acetate. The Ni–B-2 catalyst was prepared in 95% ethanol instead of water (P-2 method).

Nickel Phosphide(Ni–P): Nickel hydroxide, obtained by the addition of NaOH aqueous solution into 30 ml of $NiCl_2 \cdot 6H_2O$ (4.1 g) aqueous solution, was reduced with NaH_2PO_2 (5.5 g) in water at about 72 °C according to a method described by Sada.[9] This catalyst is abbreviated as Ni–P-1. For the preparation of Ni–P-2 catalyst, the reduction of nickel hydroxide was carried out in 50% ethyl alcohol instead of water.[7f] The precipitated catalyst was washed in the same way as the Ni–B catalyst was.

Raney Nickel (R-Ni): Ni–Al (42 : 58) alloy (1.43 g) was added during 10 min in small portions to 60 ml of 20% NaOH aqueous solution, usually at 70 °C, and this mixture was kept at the temperature for 20 min with gentle stirring. The leached catalyst was washed 5 times with portions of 100 ml of distilled water by decantation. The alloy was also leached at different temperatures in order to make the catalysts with different surface states.[7g]

Nickel Blacks (D-Ni and H-Ni): D-Ni catalysts were prepared by decomposing $Ni(HCOO)_2 \cdot 2H_2O$ (9.5 g) at 300 °C for 1.5—6 h (usually 3 h) followed by hydrogen flushings. NiO (3.8 g) was reduced under a hydrogen stream of 8 l/h at 350 °C for 1.5 h to prepare H-Ni catalyst. After cooled to room temperature in the hydrogen atmosphere, the nickel black was washed twice with distilled water before modification.

Modification. The modification of a catalyst was carried out at 83 °C by soaking a freshly prepared catalyst in a 1.6% aqueous solution of TA(pH=5.1) for 1.5 h with occasional shaking according to the method described by Izumi *et al.*[1,10] Several kinds of amino acids were also used as modifiers to check the enantioselectivity of modified nickel boride catalyst. After the modification, the catalyst was rinsed once with water, twice with methanol, and then once with ethyl acetate (10 ml portion of each).

Hydrogenation. 10 ml of MAA was added to the described amount of catalyst in 10 ml of ethyl acetate and hydrogenated at 60 °C in a 50 ml glass autoclave (TEM-U-50, Taiatsu Glass Industry Co., LTD.) equipped with a 200 ml gas tube and with a magnetic stirring system. The starting pressure of hydrogen was 10 kg/cm² and the pressure dropped to about 3 kg/cm² at 100% conversion. Almost all conversions were 100%. Ethyl acetate, used as a solvent, was dried and distilled before use. All the reactants were obtained from commercial sources and used without further purification.

Analysis. The reaction product was filtered off and distilled under reduced pressure. The conversion and the purity of the distilled product was measured with GLC (Shimadzu model 4APT) with a 2 m column of 20% PEG

20M on Celite 545.

The optical rotation (α_D) of the distilled product was determined with a Union PM-101 automatic digital polarimeter at room temperature (about 25 °C) in a 0.1 dm cell. The optical yield (OY) of (−)-MHB was calculated from the observed α_D value by the equation $OY = (\alpha_D/22.95) \times 100$.[11]

The X-ray diffraction pattern of the catalyst filtered after the reaction was measured with a Shimadzu VD-1 diffractometer after wetting the catalyst with ethylene glycol to avoid the oxidation of nickel metal. The mean crystallite size of nickel (D_c) was calculated from the half width of the peak from the (111) plane of nickel metal.

BET surface areas of the catalysts were measured separately by N_2 adsorption at 77 K after washing with acetone and after evacuation by a diffusion pump for 4 h at ambient temperature.

The surface compositions of some catalysts used were estimated from the analysis of X-ray photoelectron spectra (XPS) with a Hitachi 507 photoelectron spectrometer. The detailed procedures were reported elsewhere.[7f]

The amount of TA adsorbed on the modified catalyst was determined colorimetrically with Hitachi 200-20 spectrophotometer by the method reported by Christian[12] and by Harada *et al.*[13]

Results and Discussion

For the enantioselective hydrogenation of MAA with Ni–B-1 catalyst modified by TA, preliminary experiments showed that the effects of modification conditions (pH, temperature, and modifying time) and of hydrogenation conditions (temperature, H_2 pressure) on the optical yields of MHB were similar to those for the hydrogenation with modified R-Ni catalyst reported previously.[1] However, as shown in Table 1, the enantioselectivity of the modified Ni–B catalyst was very low compared to that of modified R-Ni catalyst for all the substrates and modifiers examined. The enantioselectivity of Ni–P catalyst was also very low. The negative effect of water added to the reaction mixture on the optical yield of (−)-MHB was previously reported for the enantioselective hydrogenation of MAA with modified R-Ni.[14] Therefore, the effect of the water which was contained in larger quantities within the Ni–B than within the R-Ni catalyst was examined by drying the Ni–B catalyst after modification or by adding a small amount of molecular sieve to the reaction mixture to remove the water. The result showed that the water contained within the Ni–B catalyst was not the cause of the low enantioselectivity of the catalyst. No racemization of the product on the Ni–B catalyst under the reaction conditions was observed.

Using a modified R-Ni catalyst, Harada *et al.*[5] suggested that aluminum derivatives on the catalyst surface decrease the enantioselectivity of the catalyst and that the exclusion of aluminum or related metal compounds from the catalyst surface is an essential factor for obtaining a highly enantioselective catalyst.

TABLE 1. PRODUCT OPTICAL PURITIES FOR SOME HYDROGENATIONS WITH MODIFIED NICKEL CATALYSTS

Catalyst	Modifying variables			Hydrogenation variables		Conversion	Optical activity	
	Modifier	pH	Temp/°C	Substrate[a]	Time/h	%	$[\alpha]_D^{25}$	OY/%[b]
1 H–Ni	TA	5.1	83	MAA	147	94.5	−12.90	56.2
2 D–Ni	TA	5.1	83	MAA	188	100	−9.70	42.3
3 R–Ni	TA	5.1	83	MAA	41	100	−5.87	25.7
4 Ni–B-1	TA	5.1	83	MAA	21	100	−0.69	3.0
5[c] Ni–B-1	TA	5.1	83	MAA	19	100	−0.73	3.2
6 Ni–B-2	TA	5.1	83	MAA	22	100	−1.29	5.6
7 Ni–P-1	TA	5.1	83	MAA	43	99	−0.33	1.5
8 Ni–P-2	TA	5.1	83	MAA	44	97.2	−0.43	1.9
9 Ni–B-1	TA	5.1	0	MAA	22	99.2	−0.38	1.7
10 Ni–B-1	L-Glu	5.1	0	MAA	24	98.1	−0.37	1.6
11 Ni–B-1	L-Met	6.0	0	MAA	64	99	−0.58	2.5
12 Ni–B-1	L-Phe	6.3	0	MAA	19	100	+0.87	3.8
13 Ni–B-1	L-Glu	5.1	0	DAOH	168	99	+0.90	5.4
14[c] Ni–B-1	L-Met	7.3	0	DAOH	17	100	+0.71	4.3
15 Ni–B-1	L-Phe	5.7	0	DAOH	46	100	+0.58	3.5
16[c] D–Ni	TA	5.1	83	DAOH	97	35	−2.55	15.3
17[c] R–Ni	TA	5.1	83	DAOH	17	100	−1.11	6.7
18[c] Ni–B-2	TA	5.1	83	DAOH	18	100	−0.47	2.8
19[c] Ni–B-1	TA	5.1	83	DAOH	20	100	−0.44	2.7
20[c] Ni–P-1	TA	5.1	83	DAOH	19	100	−0.29	1.7
21 Ni–B-1	L-Phe	5.8	0	APH	25	100	+0.18	0.4
22 Ni–B-1	TA	5.1	83	APH	24	100	+0.11	0.2
23 Ni–B-1	TA	5.1	83	EAA	27	100	−0.82	3.4
24 Ni–B-1	TA	5.1	83	EMK	27	99	+0.05	0.4

a) MAA: Methyl acetoacetate, DAOH: Diacetone alcohol, APH: Acetophenone, EAA: Ethyl aceto acetate, EMK: Ethyl methyl ketone. b) Optical yields (OY) were calculated using the absolute rotations $[\alpha]_D^{25}=22.95$, 16.6, 44.3, 24, and 13 for the hydrogenation products of MAA, DAOH, APH, EAA, and EMK respectively. c) Hydrogenation was carried out under the initial H_2 pressure of 90 kg/cm^2 instead of 10 kg/cm^2.

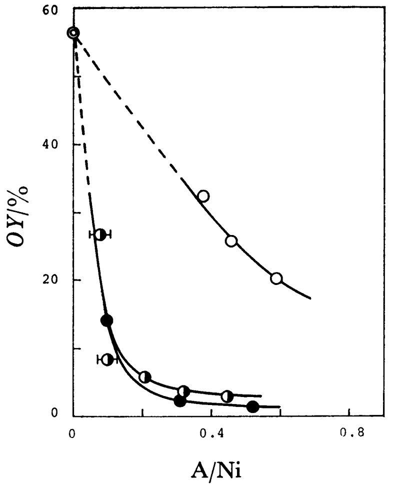

Fig. 1. Relation between optical yields and surface contents of additives in nickel catalysts. A/Ni: atomic ratio of Al, B, or P to Ni, ○: R-Ni, ◑: Ni-B, ●: Ni-P, ◎: H-Ni.

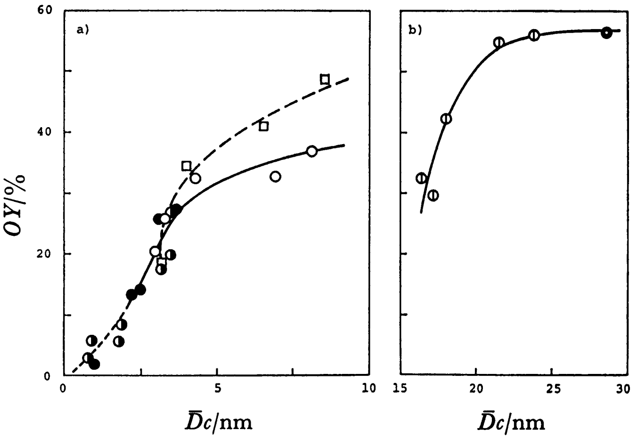

Fig. 2. Dependence of optical yields on mean crystallite sizes of nickel in various catalysts.
○: R-Ni, ◑: Ni-B, ●: Ni-P, ⦶: D-Ni, ◎: H-Ni, —: R-Ni by Gross and Rys.[4]

Therefore, the relations between the enantioselectivity of R-Ni, Ni-B, and Ni-P catalysts and the surface contents of Al, B and P in each catalyst were investigated here. Since catalytic activities and selectivities should be compared with the states on the surface (not in the bulk) of the catalysts, we measured the surface contents of additives in various nickel catalysts by XPS.

It can be seen from Fig. 1 that the enantioselectivity of the Ni-B or Ni-P catalyst increases with decrease of the surface content of B or P in each catalyst similarly to the case of the R-Ni catalyst. The enantioselectivities of the catalysts refluxed in 20% NaOH aqueous solution for 2—6 h in order to remove the additives approach the selectivity of H-Ni catalyst, which has essentially no additives on the catalyst surface. However, the extents of the decrease in the selectivity of the Ni-B and Ni-P catalysts with the increase of additives are so large compared with that of the R-Ni catalysts that the low enantioselectivities of those catalysts are not directly attributable to the amount of additives.

On the other hand, the Ni-B and Ni-P catalysts have been reported to have amorphous structures considerably different from the structure of the R-Ni catalyst and to have similar selectivities in hydrogenation reactions.[7d,7h]

Fish and Ollis suggested, from their results on an electrochemical technique for measuring the surface coverage of TA on nickel, that a reactant molecule adsorbed on an optically selective site requires more metal surface area than one adsorbed at an optically nonselective site.[15] Alternatively this suggestion may be stated as follows: the optically selective site must consist of an ensemble of regularly-arranged nickel atoms for reactant molecules and modifiers to adsorb strongly and regularly. Accordingly, amorphous surfaces of catalysts, such as the Ni-B catalyst, are supposed to exhibit a low enantioselectivity because of the low probability of finding such ensembles. A higher optical yield is expected for a catalyst with a larger crystallite size, by assuming that the surface structure reflects directly the bulk structure of the catalyst.

With these considerations in mind, the dependence of the enantioselectivities of various nickel catalysts modified by TA upon the crystallite sizes of nickel metal in them has been investigated.

As can be seen from Fig. 2, the enantioselectivities of the catalysts are clearly related to the mean crystallite sizes of nickel in the catalysts, although the crystallite sizes in the Ni-B and Ni-P catalysts are too small to calculate exactly by the XRD method. In addition, the removal of Al, B, or P from the R-Ni, Ni-B, or Ni-P catalyst by refluxing the catalyst in 20% NaOH aqueous solution led to the larger crystallite size of nickel and correspondingly to the higher enantioselectivity of the catalyst. Also noteworthy is that the plots for the three kinds of catalysts of different preparative methods (*i.e.*, Ni-B, Ni-P, and R-Ni) in Fig. 2a) are almost all on the same line, while the plots in Fig. 1 are on different lines for the three kinds of catalysts. Moreover, the data of *OY* of (−)-MHB reported by Gross and Rys[4] for a similar enantioselective hydrogenation over various R-Ni catalysts, under slightly different experimental conditions from ours, were found to be in good correlation to the crystallite sizes of nickel in the catalysts, as shown in Fig. 2a). The relatively low enantioselectivities of the D-Ni catalysts with the crystallite sizes under 20 nm in Fig. 2b) are probably due to the impurities from decomposed nickel(II) formate still remaining on the nickel surface after the short decomposition time of 1.5—3 h. A similar dependence of enantioselectivity on the crystallite size of nickel was observed for the hydrogenation of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone), as can be seen from Table 1 (Nos. 16—20).

These findings are in accordance with the report by Klabunovskii for the enantioselective hydrogenation of ethyl acetoacetate (EAA) on Ru/SiO_2 catalysts with the particle sizes of Ru smaller than 4.5 nm,[6c] although the enantioselectivity should be compared, not with the particle size, but with the crystallite size, because of the reason discussed above.

These results suggest that the size of ensembles of regularly-arranged nickel atoms on the catalyst surface is a more important factor for a catalyst to be enantioselective than the surface content of additives is. The detrimental effect of additives (B, P, and Al) shown in Fig. 1 can be attributed to the effect of their lowering the crystallinity of the catalysts. The difference between the influence of Al and that of B or P is explained by the fact that the aluminum in R-Ni segregates in the catalyst as Al_2O_3[7g)] and that it does not lower the crystallinity of the catalyst so much as B or P in the Ni–B or Ni–P catalyst.

TABLE 2. THE AMOUNTS OF ADSORBED (2*R*,3*R*)-TARTARIC ACID ON VARIOUS NICKEL CATALYSTS

Catalyst	*Sa*[a)]	Amount of adsorbed acid[b)]		*OY*[c)]
	m^2 g-Ni^{-1}	10^{-2} mmol × g-Ni^{-1}	10^{-3} mmol × m^{-2}	%
Ni–B-1	21.8	10.7	4.91	3.0
Ni–B-1[d)]	21.8	4.65	2.13	0.7
Ni–B-2	38.2	7.03	1.84	5.6
Ni–B-2[e)]	62.7	3.16	0.50	26.7
R-Ni	100.4	5.71	0.57	25.7
D-Ni	10.5	1.06	1.01	42.2
H-Ni	3.4	0.35	1.03	56.2

a) BET surface area. b) Modifying conditions: pH=5.1, 83 °C, 1.5 h. c) The optical yield of (−)-MHB. d) The catalyst was washed 6 times with water after modification instead of 2 times. e) The catalyst was refluxed for 6 h in 20% NaOH aq solution before modification.

In Table 2, the amounts of adsorbed TA on various nickel catalysts measured after modification are shown, together with the surface areas and the enantioselectivities of the catalysts. The amount of adsorbed TA on unit surface area of nickel in the Ni–B catalyst is rather more than the amount on the R-Ni or the other catalysts. When the Ni–B-1 catalyst was washed much more than usual after modification, it lost more than half of the adsorbed acid and there was a drastic decrease of the enantioselectivity of the catalyst. The remaining amount of the adsorbed acid was, however, still much more than that on the R-Ni catalyst. These facts suggest that the adsorption strength of the acid on Ni metal in the surface of the Ni–B catalyst is rather weak and that the adsorbed acid remaining after the heavy washing may be bound to the boron in the catalyst by esterification, contributing nothing to the enantioselectivity of the catalyst. On the other hand, the Ni–B-2 catalyst freed of the boron by refluxing in alkaline solution before modification had a much higher enantioselectivity than the untreated catalyst, in spite of the much smaller amount of the adsorbed acid on the treated catalyst. As for the catalysts in Table 2 other than the Ni–B, the increase of the adsorbed modifier results in the increase of the enantioselectivity.

These facts show that the total amount of the adsorbed modifier is not a direct factor affecting the enantioselectivity of modified catalysts, but the amount of the modifier adsorbed strongly and regularly on the surface of a large crystallite is important for the enantioselectivity. Thus, the poor enantioselectivities of modified Ni–B and Ni–P catalysts can be explained mainly by the exceedingly low crystallinity of these catalysts.

A binary boride catalyst, Co–Ni–B (Co : Ni=6 : 4), had only a negligible degree of enantioselectivity (OY=0.8%). This is also attributable to the more amorphous structure of the binary boride catalyst than that of Ni–B catalyst, as reported before.[16)] The much lower enantioselectivity of Raney-Cu-Ru catalyst (Ru= 0.01—0.5%) than those of Raney-Cu and Raney-Ru catalysts reported by Klabunovskii[17)] may also be explained in terms of the crystallite size of the catalyst.

From the discussion above, it can be concluded that the catalyst with the larger crystallite size has the higher enantioselectivity, presumably because of the higher probability to find ensembles of regularly-arranged nickel atoms (*i.e.*, optically selective sites) on the catalyst surface.

Recently, Klabunovskii[18)] proposed a model of the active sites for enantioselective hydrogenation located not on the plane but on the edge in the catalyst surface. In order to make clear the more detailed structure of optically selective sites in the catalyst surface, further studies will be required.

As for the reaction rate, the catalyst of the higher enantioselectivity has the lower hydrogenation activity, as can be deduced from the data in Table 1. This is easily understandable from the fact that the catalyst with the larger crystallite size generally has the smaller specific surface area. In order to obtain a highly enantioselective catalyst with a high hydrogenation activity, it seems a good idea to use supported nickel catalysts. Moreover, the supported catalysts are very useful in order to elucidate the relation between the surface states and the enantioselectivities of the catalysts, since it is possible to vary the surface states or the size distribution of metal particles of the supported catalysts by employing various preparation methods. With these expectations in mind, further studies on the effect of preparation methods upon the enantioselectivity of supported nickel catalysts are now in progress.

The authors wish to thank Professors Yoshiharu Izumi and Akira Tai, Osaka University, for their helpful suggestions, and Dr. Yasuaki Okamoto of our laboratory for his valuable advice.

References

1) Y. Izumi and A. Tai, "Stereo-differentiating Reactions," Kodansha, Tokyo, and Academic Press, New York (1971), Sec. 5.1.1, and references cited therein.

2) Y. Orito, S. Niwa, and S. Imai, *Yuki Gosei Kagaku Kyokai Shi*, **34**, 236 and 672 (1976); **35**, 753 (1977).

3) G. V. Smith and M. Musoiu, *J. Catal.*, **60**, 184 (1979).

4) L. H. Gross and P. Rys, *J. Org. Chem.*, **39**, 2429 (1974).

5) T. Harada, S. Onaka, A. Tai, and Y. Izumi, *Chem. Lett.*, **1977**, 1131.

6) a) E. I. Klabunovskii, V. I. Neupokoev, and Yu. I. Petrov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1971**, 2067; b) E. I. Klabunovskii, A. A. Vedenyapin, N. D. Zubareva, N. P. Sokolova, and Yu. M. Talanov, *React. Kinet. Catal. Lett.*, **2**, 291 (1975); c) A. A. Vedenyapin, E. I. Klabunovskii, Yu. M. Talanov, and G. Kh. Areshidze, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 2628.

7) a) Y. Murakami, S. Kishida, T. Imanaka, and S. Teranishi, *Nippon Kagaku Zasshi*, **89**, 263 (1968); b) Y. Nitta, T. Imanaka, and S. Teranishi, *Kogyo Kagaku Zasshi*, **74**, 777 (1971); c) T. Imanaka, Y. Nitta, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **46**, 1134 (1973); d) Y. Nitta, T. Imanaka, and S. Teranishi, *Nippon Kagaku Kaishi*, **1976**, 1362; e) Y. Nitta, Y. Okamoto, T. Imanaka, and S. Teranishi, *ibid.*, **1978**, 634; f) Y. Okamoto, Y. Nitta, T. Imanaka, and S. Teranishi, *J. Chem. Soc., Faraday Trans.* **1**, **75**, 2027 (1979); g) Y. Okamato, Y. Nitta, T. Imanaka, and S. Teranishi, *ibid.*, **76**, 998 (1980); h) Y. Okamoto, Y. Nitta, T. Imanaka, and S. Teranishi, *J. Catal.*, **64**, 397 (1980).

8) C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 1003 and 1005 (1963).

9) S. Sada, *Kogyo Kagaku Zasshi*, **71**, 957 (1968).

10) Y. Izumi, T. Harada, T. Tanabe, and K. Okuda, *Bull. Chem. Soc. Jpn.*, **44**, 1418 (1971).

11) T. Harada and Y. Izumi, *Chem. Lett.*, **1978**, 1195.

12) G. D. Christian, *Talanta*, **16**, 255 (1969).

13) T. Harada, A. Tai, M. Yamamoto, H. Ozaki, and Y. Izumi, *Proc. 7th Int. Congr. Catal., Tokyo*, **1980**, A24.

14) T. Ninomiya, *Bull. Chem. Soc. Jpn.*, **45**, 2545 (1972).

15) M. J. Fish and D. F. Ollis, *J. Catal.*, **50**, 353 (1977).

16) Y. Nitta, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **53**, 3154 (1980).

17) E. I. Klabunovskii, A. A. Vedenyapin, and G. Kh. Areshidze, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1975**, 2311.

18) E. I. Klabunovskii, A. A. Vedenyapin, E. I. Karpeiskaya, and V. A. Pavlov, *Proc. 7th Int. Congr. Catal., Tokyo*, **1980**, A26; E. I. Klabunovskii and A. A. Vedenyapin, *Zh. Fiz. Khim.*, **51**, 3005 (1977).