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Surface Characteristics and Activities of Plate-Type Raney Nickel Catalyst

TOMIO YOSHINO,* TUNEYO ABE,* SATOSHI ABE,† AND ICHIRO NAKABAYASHI‡,[1]

**Department of Radiopharmaceuticals, Faculty of Pharmaceutical Science, Tokushima Bunri University, Yamashiro, Tokushima 770, Japan; †Nikki Chemical Company, Ltd., Ohtemachi, Chiyoda, Tokyo 100, Japan; and ‡Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, Minamijosanjima, Tokushima 770, Japan*

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Analytic and morphological studies using SEM, EPMA, and XPS were made on plate-type Raney nickel catalyst with varying contents of aluminum. The surface characteristics and hydrogenation and adsorption behavior of Raney nickel catalysts are discussed. Although the amount of residual aluminum in the catalyst (mainly $Al_2O_{3n}H_2O$) remains almost constant on its outermost surface, regardless of the leaching time, it decreases in the interior phases up to a depth of 600 Å with leaching times over 9 min. The activities of catalysts with average content of aluminum relative to nickel, i.e., 11.6 and 6.8 wt%, in their surface layers (ca. 0.4 μm thick) were 2.7 and 2.1 mmol/h BET m^2 for the hydrogenation rates of allyl alcohol and 3.6×10^{-3} and 2.4×10^{-3} mmol/BET m^2 for the adsorption amounts of I^- ion, respectively. These results suggest that the activities for hydrogenation and adsorption were enhanced when the content of the residual aluminum in the catalyst was increased, and that the role of the residual aluminum in catalytic reactions can be classified into two types: to provide an increase in active sites due to formation of interstitial lattice defects, and to make a negligible contribution to the formation of active sites because of deposition of $Al_2O_{3n}H_2O$ on the Raney nickel catalyst. © 1989 Academic Press, Inc.

INTRODUCTION

Much work (*1–7*) has been done on the effects of the aluminum content in Raney nickel catalyst on its activity or selectivity, and those of the residual aluminum on the fine structure of the catalyst. The highest hydrogenation activity is obtained when the content is in a specific range which varies with the type of the reactive compounds to be catalyzed (*3*). The active site involving aluminum compounds in Raney nickel lowers the optical yield for asymmetric synthesis in the presence of the modified catalyst because it acts as a nonenantioface-differentiating hydrogenation site (*5, 6*). In studying the fine structure of Raney nickel and the distribution and chemical forms (*8–11*) of the aluminum over or within its surface layer, it is found that the residual aluminum in the catalyst is responsible for increasing hydrogenation activity. Although a variety of methods for determining the distribution of aluminum has been used so far, XPS methods for clarifying the content, chemical forms, and distribution state of aluminum have been little reported. This is probably because the usual finely pulverized form of the catalyst is unsuitable for these methods. However, a plate type of the catalyst, originally developed by us (*12*), makes it easy to use XPS methods.

The purposes of the present work are: first, to examine the applicability of XPS techniques for determining chemical forms and distribution of aluminum by using plate-type Raney nickel; and second, to obtain information about the effects on the catalytic activities of hydrogenation and adsorption of the aluminum on the surface and in the outermost layer of the catalyst.

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[1] To whom correspondence should be addressed.

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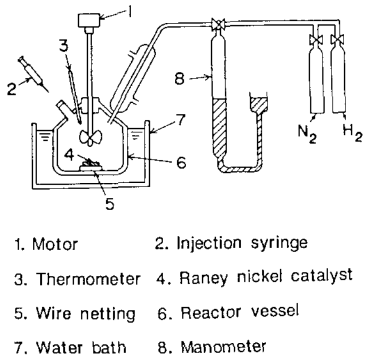

FIG. 1. System for the measurement of hydrogenation.

EXPERIMENTAL

Materials

Nickel plate (99.96%, 0.05 mm thick) and aluminum plate (99.99%, 0.10 mm thick) were used. The surfaces of these plates were polished and cleaned; then the nickel plate was sandwiched between the two aluminum plates. This sandwiched plate was placed in a quartz tube furnace, heated at 630°C for 1 to 2 min in nitrogen stream, and then quickly hot-rolled with a dental roller consisting of a pair of rollers 80 mm wide and 50 mm in diameter (Yoshida Tekko-sho Co., Ltd.).

The plate-type Raney nickel catalysts were activated by leaching the Al–Ni–Al plates in a 20 wt% solution of sodium hydroxide of 50 times the aluminum content in molar ratio at 60°C (*12*). The final aluminum content of the catalyst was controlled by varying the leaching time. BET surface areas of the catalysts were measured by N_2 physisorption.

Procedures

The activities of the catalysts were measured using liquid-phase hydrogenation of allyl alcohol, acetone, and 2-butanone under 1 atm. The apparatus used in the hydrogenation tests is shown in Fig. 1. The total geometrical surface area of the catalyst (apparent surface area) was adjusted to 5 cm^2 before it was leached. The apparatus, having a capacity of about 120 ml, was filled with nitrogen under 1 atm and cooled to 0°C before measurement. Sample pieces with allyl alcohol, acetone, and 2-butanone were quickly placed while wet in a 50-ml glass vessel as a part of the apparatus. After the nitrogen was replaced by hydrogen, the whole system was dipped into a hot bath thermostated at 70°C and 3 ml of the organic compounds described above were injected into the glass vessel by syringe. A decrease in the volume of hydrogen gas was measured as the conversions to *n*-propyl alcohol, 2-propanol, and 2-butanol took place. The resulting products were confirmed by a gas chromatograph (Yanagimoto Model G 180) to be exclusively *n*-propyl alcohol, 2-propanol, and 2-butanol without by-products.

An adsorption experiment was carried out by shaking the catalyst (apparent surface area 5 cm^2) at 30°C for 1 h in a 100-ml aqueous solution of KI (initial concentration of 5×10^{-2} mmol/dm^3) under an atmosphere of nitrogen. Adsorbed amounts of iodide ion were determined by potentiometric measurement with a microprocessor ionanalyzer (Orion Research, Model 901) (*13*).

The surface morphology and texture of the catalyst were examined by a scanning electron microscope (Hitachi, Model S-600). The content and distribution of residual aluminum on the surface layer of the catalyst particles were determined with an energy-dispersive X-ray microanalyzer (Horiba, Model EMAX-8700, 15 KV, diffraction angle 30°). For this we used a calibration curve based on specimens of the oxide prepared from a solution of nickel nitrate and aluminum nitrate mixed at a constant ratio.

X-ray microanalysis showed a surface layer of catalyst particles of ca. 0.4 μm thick, the penetration depth of the primary electrons being ca. 0.4 μm (*14*). Elements, their distribution within the catalyst, and their chemical forms were determined by

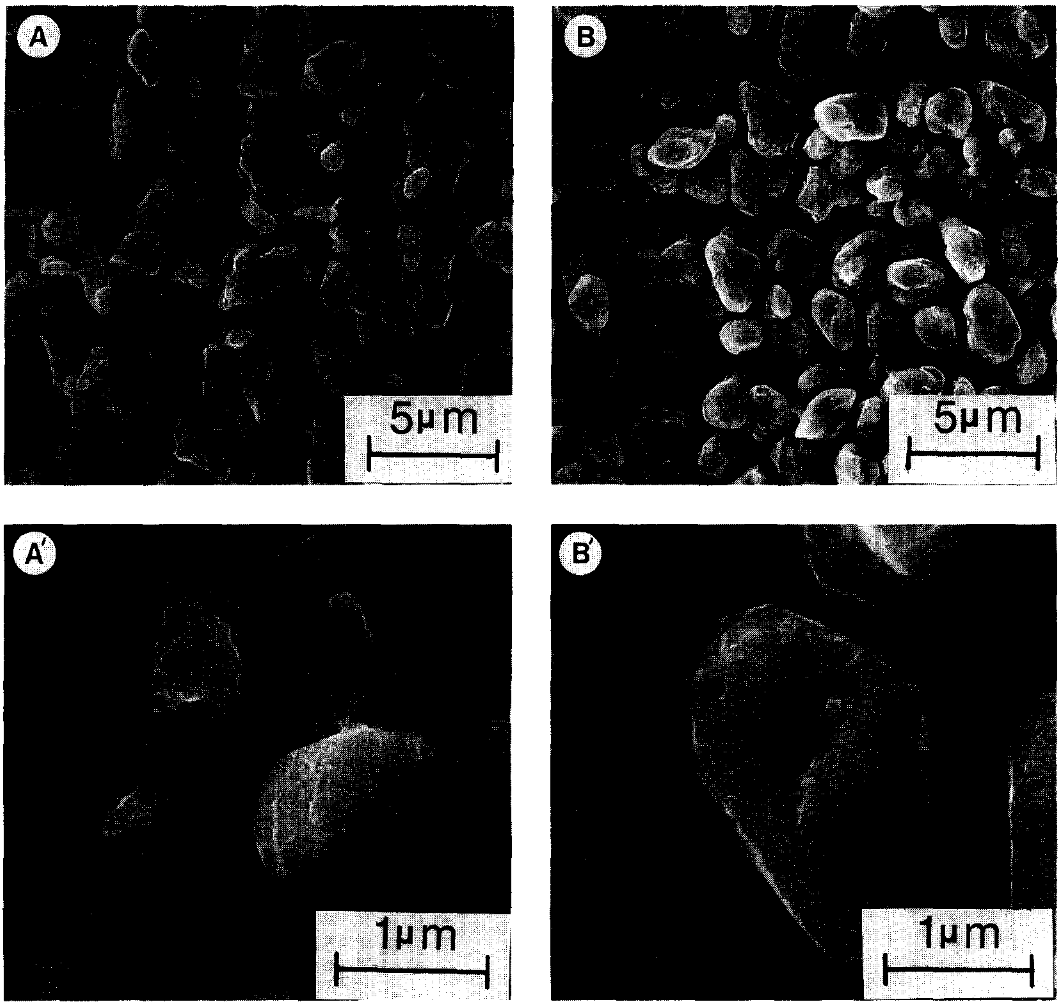

FIG. 2. Scanning electron micrographs of the catalyst particles. (A, A′) leaching for 9 min at 60°C; (B, B′) leaching for 90 min.

XPS methods (V. G. Scientific Ltd., ESCA-LAB 5, Mg X-ray target, 11 KV, 20 mÅ) by argon-ion etching with a potential of 5 KV for an etching rate of ca. 100 Å/min.

The samples used for morphological study and quantitative analysis of the catalyst surface were cut into small pieces (10 × 10 mm). They were mounted on a sample holder under acetone to preclude air oxidation and then introduced into the measuring instrument under vacuum.

RESULTS AND DISCUSSION

Nature of the Catalyst Surface

Figure 2 shows the texture of the Raney nickel catalyst surfaces after Al–Ni–Al plates were leached in aqueous alkali solution for various periods. Dissolution of aluminum look place on the surface layer after a leaching time of about 8.5 min, and then at the boundary of the Ni–Al alloy layer as a result of rapid leaching of aluminum locally in the alloy. Particles of Raney nickel

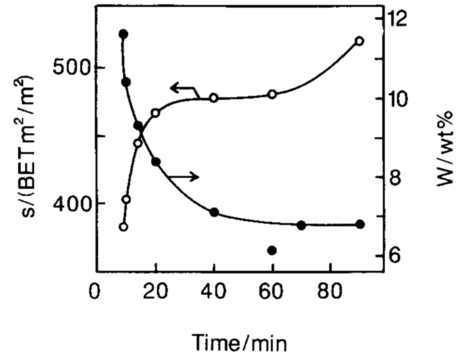

FIG. 3. Time dependencies of leaching of surface area (○) of the catalyst and content (●) of the residual aluminum relative to nickel on the catalyst surface layer (ca. 0.4 μm thick).

several μm in diameter remained. After a leaching time of 9 min, the catalyst particles showed irregular folds in their scute surfaces, whereas after a leaching time of 90 min, the particles showed many micropits in their rounded-off surfaces (Fig. 2). Correspondingly, the specific surface areas were found to be 383, 468, and 520 BET m^2/m^2 (apparent surface area) after leaching times of 9, 20, and 90 min, respectively (Fig. 3).

It has been shown that the alloy layer formed at the boundary of the nickel and aluminum plates is composed of $NiAl_3$, Ni_2Al_3, and the eutectic phase (*12, 15*). Alkaline leaching of the ordinary alloy of Raney nickel initially causes eluting out of aluminum in the eutectic phase and $NiAl_3$, followed slowly by eluting out of aluminum in Ni_2Al_3. The leaching processes give rise to the formation of micropores and microcracks in the particles, which are then reformed and modified into microcrystals. They are responsible for the large BET surface areas and, partially, for the large particles formed by loose agglomeration of small crystals up to several hundred micrometers in size in the Raney nickel catalyst (*16–18*). The present results agree well with this description, except for the uniformity of the catalyst particles due to arrested agglomeration (Fig. 2).

Composition of the Surface Layer of the Catalyst

Figure 3 shows the effect of leaching time on the average content of aluminum relative to nickel on the surface layer (ca. 0.4 μm thick) of the catalyst. Aluminum content was found to be 11.6, 8.4, and 6.8 wt% after leaching times of 9, 20, and 90 min, respectively. Aluminum leached up to 20 min contributes to increase the BET surface area, as shown in Fig. 3.

Figure 4 indicates that the catalyst after 15 min of leaching is composed of nickel, aluminum, and oxygen, with little evidence of other elements except carbon from the acetone adsorbed on the catalyst surface. In Fig. 5, the Ni 2*p* peaks of the spectra of the catalyst surface appear at the binding energies of 852.5 and 856.2 eV, and are attributed to Ni, Ni_2O_3 (855.8 eV), and/or $Ni(OH)_2$ (856.6 eV) (in the latter two substances the binding energies of O 1*s* are both 531.7 eV). A small peak probably caused by NiO (Ni 2*p*, 854.5 eV: O 1*s*, 529.9 eV) is detected on the shoulder of the broader peak (*19, 20*). Peaks of the Al 2*p*

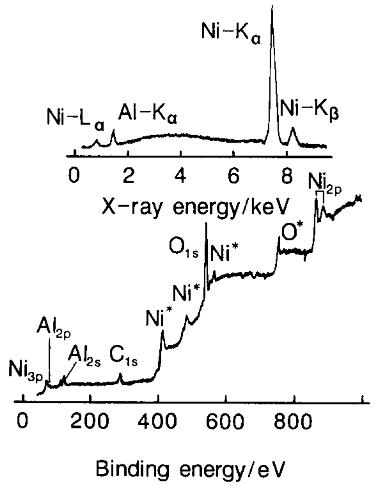

FIG. 4. EPMA (above) and XPS (below) spectra of the catalyst leached for 15 min. Above, spectrum of surface layer (about 0.4 μm thick); below, details of the spectrum of the catalyst surface. * indicates Auger spectra of Ni and O.

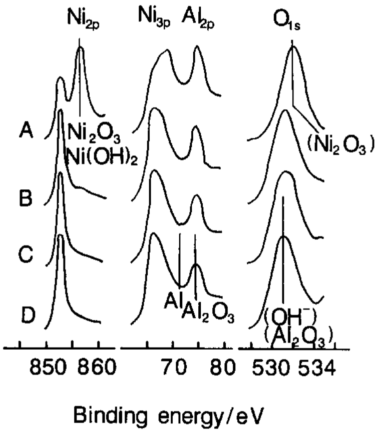

FIG. 5. XPS spectra of surface (A), at 100 Å (B), at 200 Å (C), and at 600 Å (D) of the catalyst used in Fig. 4.

spectra of the catalyst surface appear at 74.3 and 71.4 eV, and are attributed to $Al_2O_{3n}H_2O$ and/or Al_2O_3 (their binding energies of O 1*s* are both 531.0 eV) and to small amounts of elemental aluminum, whereas the interior phase (up to 600 Å in depth) of the catalyst is mainly composed of alumina hydrate and metallic nickel. XPS spectra of the catalyst deactivated by air oxidation show that NiO and Ni_2O_3 or $Ni(OH)_2$ are formed deep within the catalyst, whereas Al_2O_3 or $Al_2O_{3n}H_2O$ are distributed evenly in the vertical direction. Therefore, the existence of Ni_2O_3 and/or $Ni(OH)_2$ on the catalyst surface, as shown in Fig. 5, suggests the possibility that nickel atoms on the surface are affected by the action of air and adsorbed water during preparation of the sample.

Distribution of Aluminum in the Catalyst

Figure 6 shows the values of aluminum and oxygen relative to nickel as a function of distance from the catalyst surface; these values were obtained from areas for the peaks due to Ni, Al, and O atoms on the XPS spectrum. The aluminum contents remain almost constant on the surface of the catalyst, regardless of leaching time. They decrease distinctly in the outmost layer within a depth of 100 Å after leaching times of over 9 min. However, in the more interior phase of the catalyst (up to a depth of 600 Å), the decrease in the aluminum content becomes less as the depth increases. A value of about 1 : 2.5 for the Al : O atomic ratio in such phase can be given from their relative values, as described above. A depth-dependable decrease is also observed for oxygen content in the catalysts. On the basis of the above results, the chemical forms of aluminum are mainly $Al_2O_{3n}H_2O$ ($n = 3$, based on a value of about 1 : 2.5 for the Al : O atomic ratio) and Al_2O_3 at the layer from the surface of the catalyst to a depth of 600 Å within the catalyst. The amount of atomic aluminum seems to be very small in such a range. In contrast with nickel compounds, aluminum oxide and alumina hydrate in the catalyst must have been formed when the catalyst was prepared (Figs. 5 and 6).

Moreover, the Ni : Al ratio in the catalyst, determined by spot analysis with the EPMA, reveals large variations at different locations on a particle of catalyst, although the average values of the figures per particle were almost the same as the value given by surface analysis of the catalyst (Fig. 4). Assuming from the above results that the aluminum content of the catalyst surface is almost the same as the average aluminum content (11.6 wt%) in the ca. 0.4-μm-thick

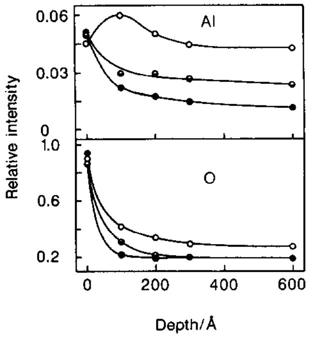

FIG. 6. Changes in the contents of Al and O in the catalysts as functions of distance from the surface. Leaching time: 9 min (◒), 15 min (○), and 90 min (●).

surface layer of the catalyst after 9 min of leaching, the Ni : Al ratio at the surface is estimated to be 88 : 12 in weight ratio or 78 : 22 in atomic ratio.

It has been reported that the catalyst surface of Raney nickel is covered with alumina trihydrate which can subsequently be dehydrated to form alumina (*11*). Results based on the electron diffraction method suggest a value of 15–45% (depending on the preparation conditions) for the surface coverage of the trihydrate. The present results indicate the value of the surface coverage by aluminum compounds to be double or more compared with that of atomic aluminum, provided that a value of 78 : 22 for the Ni : Al atomic ratio of catalyst surface is taken into account.

The amount of aluminum in the approximately 0.4-μm-thick layer of the catalyst surface is found to vary among locations where spot analysis is conducted, which reveals an irregularity of distribution of aluminum in this layer. As shown in Fig. 6, the conspicuous decrease in the outermost layer of the aluminum content of catalysts after leaching times of more than 9 min suggests eluting out of aluminum in the more interior phase through micropores and microcracks in the outermost layer. Depositing of alumina and its hydrate may occur in or near the minute structures in the outermost layer of the catalyst particles, and result in an increase in the aluminum content at or near the catalyst surface (*11, 18*).

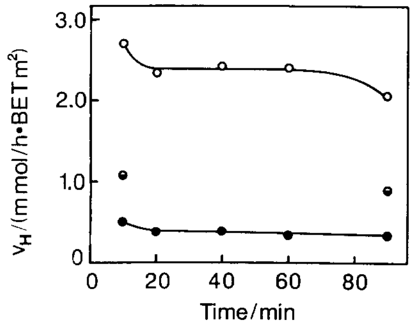

FIG. 7. Catalytic activity for hydrogenation of allyl alcohol (○), acetone (◒), and 2-butanone (●) in relation to leaching time.

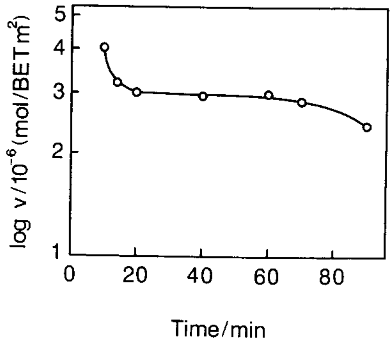

FIG. 8. I^- ion adsorptivity of the catalyst as a function of leaching time.

Hydrogenation and Adsorption Activities of the Catalyst

Figure 7 shows the effect of the leaching time on the catalyst's hydrogenation activity of allyl alcohol, acetone, and 2-butanone. Evidently, when leaching time increases the activity expressed as the rate of hydrogenation of these compounds more or less decreases. Rate values for catalysts after 9- and 90-min leaching are 2.7 and 2.1 mmol/h· BET m^2 for allyl alcohol and 0.50 and 0.34 mmol/h· BET m^2 for 2-butanone, respectively. The hydrogenation rate of the double bond in allyl alcohol is five times higher than that of the carbonyl group in 2-butanone.

Figure 8 shows the effect of leaching time on the adsorbed amount of I^- ions on the catalyst surface. Similar to the case of hydrogenation activity, an increase in leaching time of the catalyst decreases the adsorbed amount from 3.6×10^{-3} mmol/BET m^2 after 9-min leaching to 2.4×10^{-3} mmol/BET m^2 for 90-min leaching.

As shown in Figs. 7 and 8, when the content of residual aluminum in the catalyst was higher, i.e., 11.6 wt% of the catalyst after 9-min leaching compared with 6.8 wt% of the catalyst after 90-min leaching, the activity was greater by 29% for hydrogenation of allyl alcohol, 47% for 2-butanone, and 50% for adsorption of I^- ions. The active site of Raney nickel catalysts has been shown by X-ray diffraction to lie in the moiety of lattice defects, microstrains, and stacking faults on the catalyst surface (*21*). We have found that hydrogenation activity of the plate-type catalyst used in these experiments also lowers at a temperature range for disappearance of lattice defects when it is annealed (*22*). The activity of such an annealed catalyst, when it is irradiated by neutrons, is partially recovered due to lattice defects caused in the catalyst (*23*). The lattice defects in Raney nickel catalyst also arise from residual aluminum occurring as an impurity near the catalyst surface (*24*). For example, the Al-involving active site in asymmetrically modified Raney nickel catalyst acts as a nonenantioface-differentiating hydrogenation site (*5*, *6*). Disappearance of the site by eluting out of residual aluminum by pretreatment with tartaric acid or adsorption of NaBr on the site of the catalyst surface increases the optical yield in asymmetric synthesis (*5*, *6*).

Our results show that the role of the residual aluminum at the surface and in the outermost layer of the catalyst in catalytic reaction can be classified into two types: the first is to enhance the formation of active sites by increasing the interstitial lattice defects in the particles of Raney nickel; the second is to locate aluminum near the micropores and microcracks of the catalyst. The located aluminum contributes negligibly to the catalytic activity. Although the differences of catalytic activity among atomic aluminum, alumina, or alumina hydrate in Raney nickel are not fully understood, the ratio of the aluminum having these different properties is considered to depend on the preparation conditions of the catalyst.

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