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Raney Ni Catalysts Derived from Different Alloy Precursors (I) Morphology and Characterization

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Abstract−Ni-Al alloys containing 41.3, 49.2 and 59.9 wt% Ni were leached by reaction with 20 wt% aqueous NaOH solution under different temperature and time. The reactivities of alloys and morphologies of resultant catalysts were investigated. A large difference in reactivities of alloys toward alkali solution was revealed according to the composition of the alloy. As Al content in precursor alloy increased, the reactivity of alloy toward alkali solution increased. It was shown that, during leaching, reaction in Ni 41.3 wt% alloy is restricted to reaction interface, whereas that in Ni 49.9 wt% alloy occurs throughout the product layer. Surface area and pore size distribution were seen to be strongly dependent upon leaching conditions and relatively independent of the composition of precursor alloy.

Key words: Raney Ni, Ni-Al Alloy, Leaching, Morphology, Characterization

INTRODUCTION

Since their discovery, Raney catalysts have attracted much attention both in academic and industrial fields because of their curious properties and high catalytic activity in several organic reactions [Kühn et al., 1997]. Raney nickel, for example, has long been known as an efficient catalyst in the hydrogenation process and extensively employed both in industry and laboratory for hydrogenation of organic compounds [Conde et al., 2003].

Raney nickel catalyst is usually obtained from Ni-Al alloy, the Al of which is eliminated by alkaline dissolution. The Ni-Al alloys, from which Raney nickel can be produced, usually contain 40 to 60 wt% nickel and are not homogeneous. These alloys have several nickel aluminide phases, and the content of each phase can be changed according to the composition of alloy and the preparation method of alloy. It is also known that the reactivity of nickel aluminide towards an alkaline solution is different from each other [Sane et al., 1984; Hu et al., 2003].

The present investigation was undertaken to study the leaching behavior of three Ni-Al alloys having different compositions, and to characterize the morphology of the materials leached under different conditions.

EXPERIMENTAL

The precursor Ni-Al alloys were obtained from the Davison Chemical Division, W. R. Grace Co. (Baltimore, Maryland, USA). Catalysts were prepared from 300-500 μm alloy particles obtained by crushing and screening the alloy pieces. Leaching of Al was carried out by reaction of 5 g alloy powder with 250 g of 20 wt% aqueous NaOH solution. No means for stirring was provided. After complete reaction had taken place, the catalyst was thoroughly washed with distilled water to pH 7. The samples were stored under dearеated water in a stopped vessel prior to use. The compositions of precursor alloys and leached catalysts were determined by atomic absorption spectroscopy analysis on nitric aid digested samples.

In preparation of metallographic samples, alloy pieces were reacted with a very large amount of 20 wt% aqueous NaOH solution. Different reaction temperatures were used for three alloys. Individual alloy pieces were removed from leaching solution at various time intervals and washed in distilled water. These partially leached alloy pieces were mounted in cold setting resin under vacuum, cross-sectioned and polished. The reaction-affected rim of the alloy piece was visible under optical microscope, and leach depth was measured with a graduated eyepiece.

The composition of material in reaction-affected rim was also identified by electron probe microanalysis (Cameca Camebax). The point count intensities were corrected for background radiation, atomic

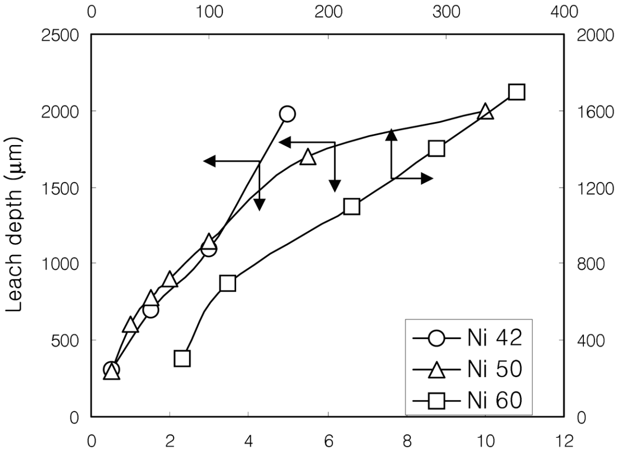

Fig. 1. Change of leach depth with extraction time (Leaching temperature: Ni 42; 50 °C, Ni 50; 50 °C, Ni 60; 107 °C).

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weight, absorbance and fluorescence effects.

The X-ray diffraction patterns of powdered precursor alloys and resultant catalysts were obtained by using a Cu-kα source (Phillips expert system). Because freshly prepared catalyst was pyrophoric, it was coated with collodion before X-ray analysis. Crystallite size was determined from X-ray line broadening corrected for instrumental factors using KCl standard.

The adsorption of nitrogen at −195 °C was measured with a Micromeritics ASAP 2000. The Raney catalysts were transferred to adsorption vessel under water, which was removed by evacuation. The samples were evacuated for 4 h at room temperature and then at 130 °C for additional 5 h. Samples were weighed by difference in adsorption vessel on the completion of each experiment. A nitrogen adsorption-desorption isotherm was measured for each sample.

Table 1. Nickel content of Raney Ni catalysts and their precursor alloys

Sample no.	Ni in alloy (wt%)	Ni in catalyst (wt%)	Leaching temperature (°C)	Leaching time (h)
1	41.3	77.7	50	4
2	49.2	75.3	50	10
3	59.9	84.6	107	125
4	41.3	93.1	107	125
5	49.2	89.8	107	125

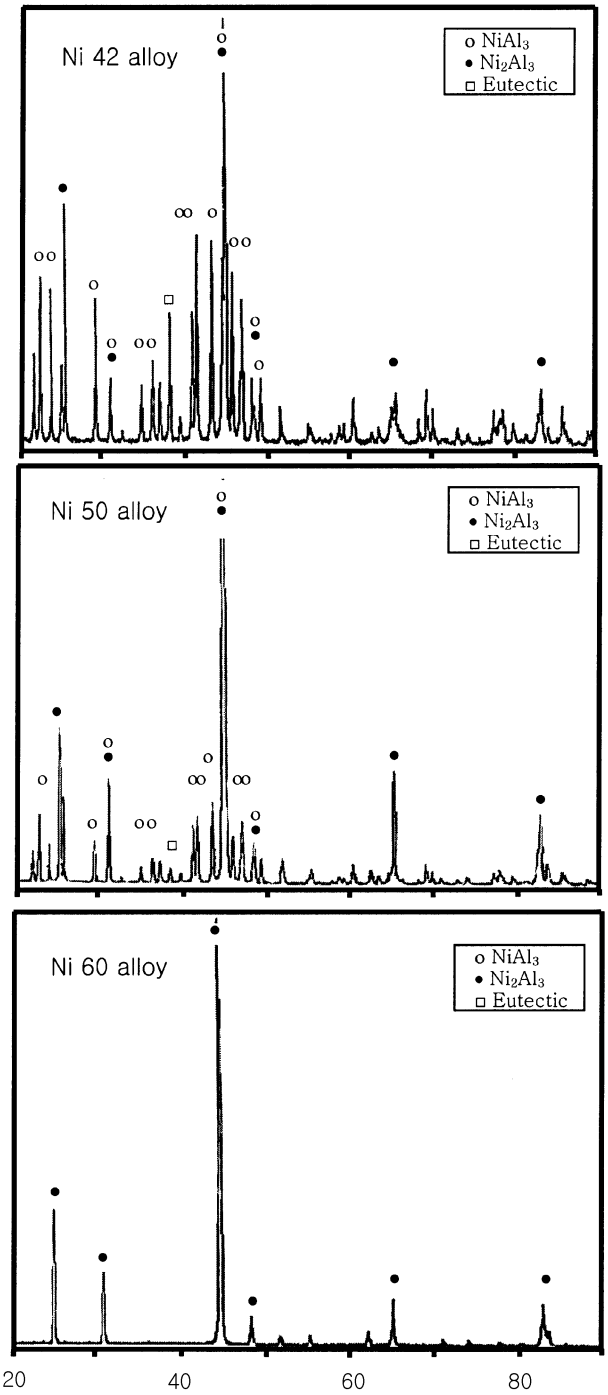

Fig. 2. X-ray diffraction patterns of Ni-Al alloys.

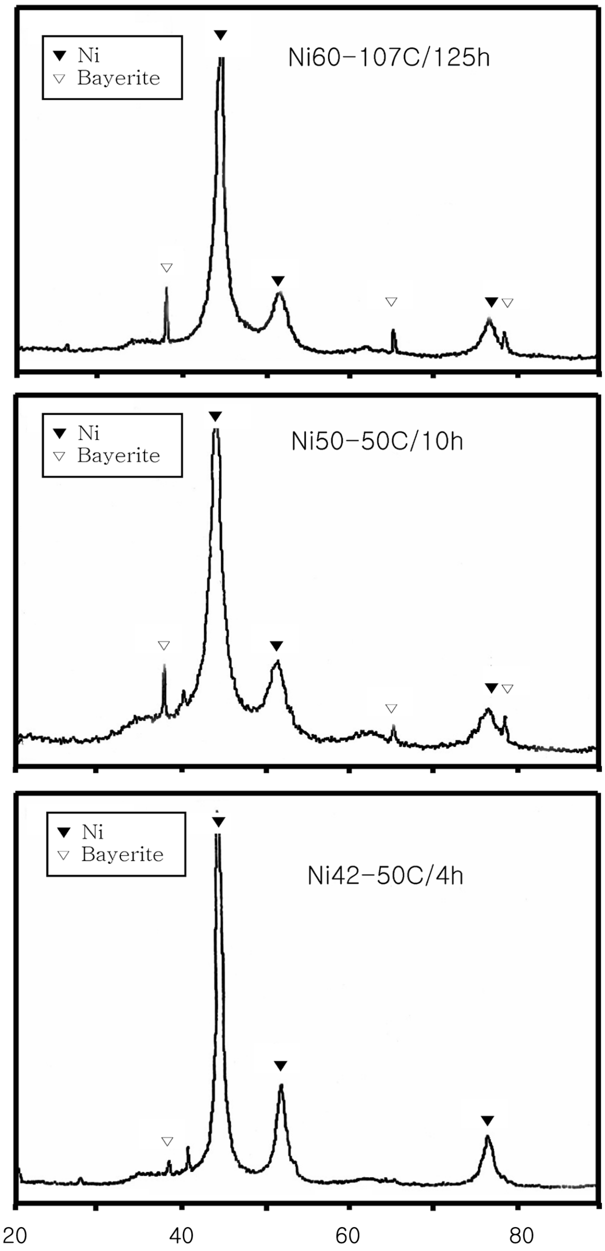

Fig. 3. X-ray diffraction patterns of Raney Ni catalysts.

RESULTS

Chemical analysis by atomic absorption showed that the three precursor alloys contained 41.3, 49.2 and 59.9 wt% Ni.

The increase in leach depth with extraction time for three alloys is shown in Fig. 1. In the case of Ni 41.3 wt% alloy (designated as Ni 42 alloy), reaction-affected rim tended to disintegrate after some extent of reaction. Hence the recession of alloy surface is presented, and the reaction kinetics was seen to be approximately linear at 50 °C. Ni 49.2 wt% alloy (designated as Ni 50 alloy), however, showed a diminution in rate with increasing extent of reaction at 50 °C. Ni 59.9 wt% alloy (designated as Ni 60 alloy) showed no leaching at lower temperature, and even at higher temperature it revealed slow leaching kinetics.

The observed X-ray diffraction patterns of precursor alloy powder before leaching are shown in Fig. 2. Ni 42 and Ni 50 alloys were found to be composed of three phases, $NiAl_3$, Ni_2Al_3 and eutectic Al, and it appeared that Ni 50 alloy contained more Ni_2Al_3 and less $NiAl_3$ than Ni 42 alloy. Ni 60 alloy was seen to contain only Ni_2Al_3.

Table 1 shows Ni content of the materials leached under standard conditions of this work. Ni 60 alloy showed lowest reactivity to alkaline solution; hence it needed to be treated under more severe conditions.

The X-ray diffraction patterns of Raney nickel catalysts prepared from three alloys by using standard conditions (designated as Ni42-50C/4 h, Ni50-50C/10 h and Ni60-107/125 h) are shown in Fig. 3. The diffractograms of all three leached samples show lines of Ni at 2θ=44.5, 51.5 and 76.1° [Liu et al., 2002]. The comparison of X-ray diffraction patterns of Raney Ni catalysts derived from same alloy (Ni 42 or Ni 50 alloy) but leached under different conditions reveals that the catalysts leached under severe conditions, 107 °C and 125 h (designated as Ni42-107C/125 h and Ni50-107C/125 h) show sharper Ni peaks than those under mild conditions, 50 °C and 4-10 h, as shown in Fig. 4. Reflections for alumina trihydrate, Bayerite, were also found at 2θ=38, 65 and 78° in some of samples.

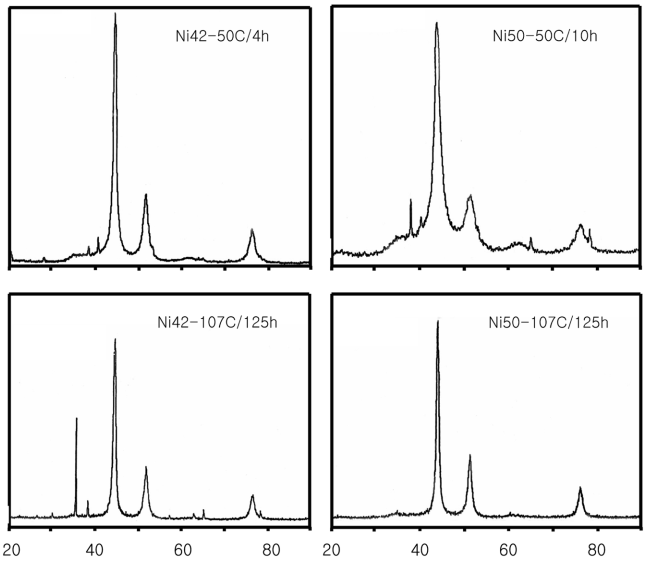

Fig. 4. Comparison of X-ray diffraction patterns of Raney Ni catalysts derived under different leaching conditions.

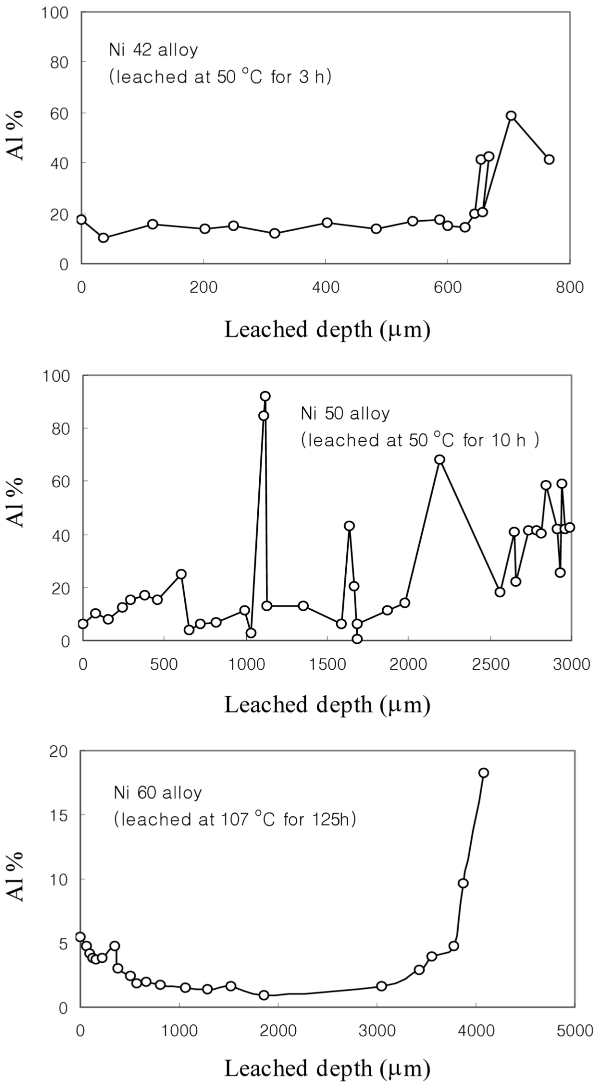

Fig. 5. Electron probe microanalysis of product rim.

Electron probe microanalyses of cross-sections of partially leached alloy pieces are reported in Fig. 5. The leaching of alloys leads to the formation of interface between reaction-affected rim and unreacted alloy core.

Nitrogen isotherms for Raney Ni catalysts prepared by using various leaching conditions are presented in Fig. 6. The catalysts derived from Ni 42 and Ni 50 alloys using mild conditions, Ni42-50C/4 h and Ni50-50C/10 h, showed low pore volume type isotherms, which are characteristics of catalyst fully extracted at 50 °C [Freel et al., 1969], whereas these isotherms changed to high pore volume type when leached under severe conditions. The catalyst derived from Ni 60 alloy using severe conditions, Ni60-107/125 h, revealed typical isotherm for high pore volume catalyst.

Surface area, average pore diameter and pore volume derived from physical adsorption isotherm are given in Table 2. The surface area was calculated by BET equation and pore volume was estimated from the amount adsorbed at a relative pressure of 0.99. An average pore diameter was calculated by the equation, d=4V/A, where d is the average pore diameter, V the pore volume, and A surface area. Higher extraction temperature favors larger pore diam-

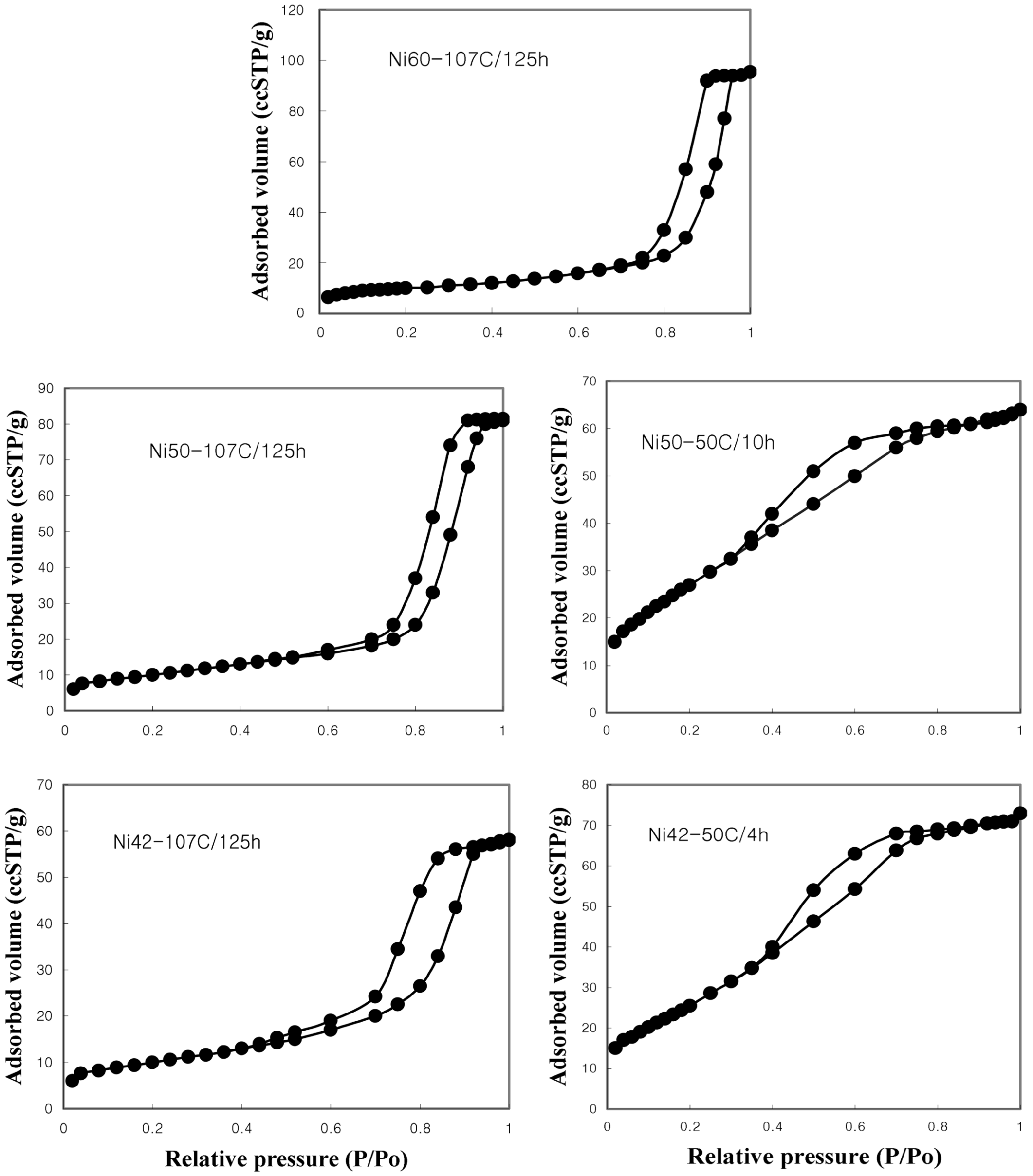

Fig. 6. Nitrogen adsorption-desorption isotherms for Raney catalysts.

eter and lower surface area.

Table 3 indicates the change of surface area and pore volume in Ni 50 alloy with leaching time. Pore volume increased with leaching time. However, surface area increased at initial stage of reaction and then decreased.

The pore size distributions for Raney catalysts prepared by using standard leaching conditions are plotted in Fig. 7. All catalysts gave a singular maximum in pore size distribution. Ni42-50C/4 h, Ni50-50C/10 h and Ni60-107/125 h catalysts showed maxima at pore diameter of 36, 29 and 146 Å, respectively. Fig. 8 shows change in pore size distribution according to leaching conditions. The pore size distribution appears to be strongly dependent on the leaching con-

Table 2. Surface properties of Raney Ni catalysts

Sample designation	Surface area (m^2/g)	Pore volume (ml/g)	Average pore diameter (Å)
Ni42-50C/4 h	102	0.110	44
Ni50-50C/10 h	101	0.097	38
Ni60-107C/125 h	36	0.146	163
Ni42-107C/125 h	36	0.090	99
Ni50-107C/125 h	35	0.127	145

Table 3. Surface area and pore volume of partially leached Ni 50 catalysts*

Sample designation	Extraction time (h)	Surface area (m^2/g)	Pore volume (ml/g)	Average pore diameter (Å)
1	2	102	0.069	44
2	5	135	0.084	25
3	10	101	0.097	38

*Leaching temperature: 50 °C

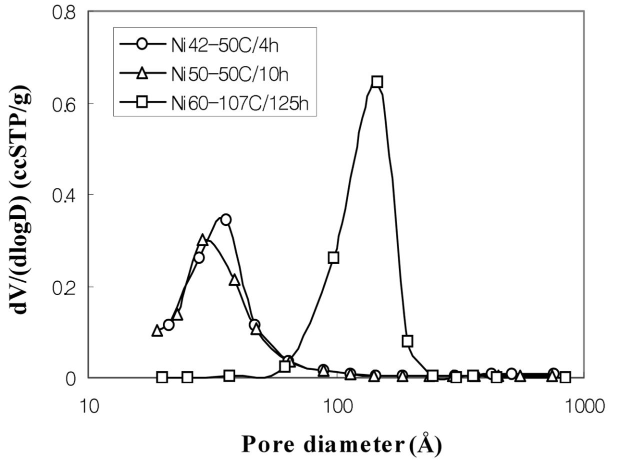

Fig. 7. Pore size distributions for Raney Ni catalysts.

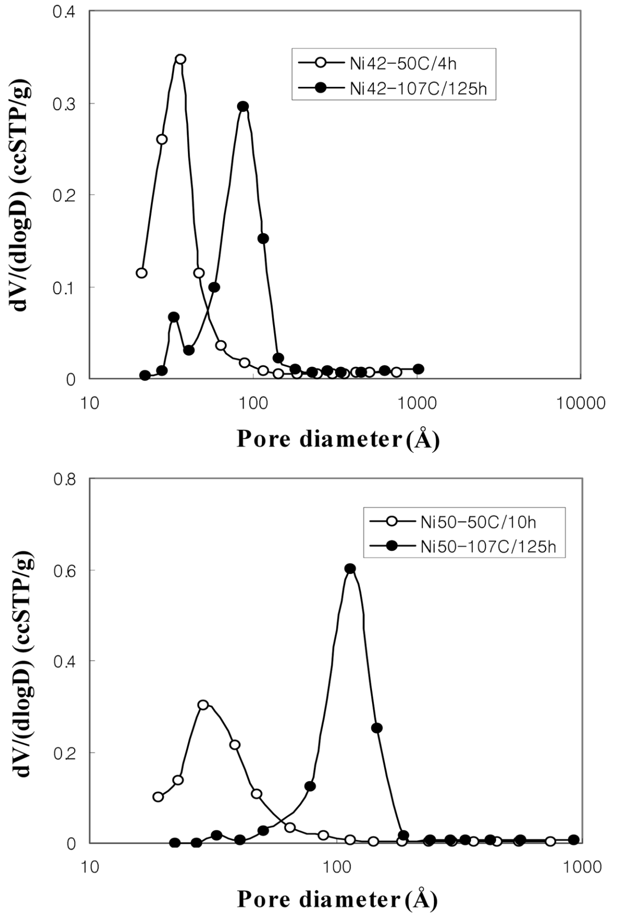

Fig. 8. Change of pore size distribution in Raney Ni catalysts with leaching conditions.

ditions and relatively independent of the composition of precursor alloy. The severe leaching condition, namely high reaction temperature and long extraction time, favors the development of large pores.

DISCUSSION

A big difference in reactivity of three alloys towards alkali solution is evident in the present results. At 50 °C, leaching of Ni 42 alloy proceeded according to rapid linear kinetics, while in the case of Ni 50 alloy a diminution in rate with increasing extent of reaction was observed. Leaching of Ni 60 alloy seems to proceed according to slow parabolic kinetics even at 107 °C, the boiling point of alkali solution. These results presumably account for the difference in function of leached product material as a diffusion barrier. The rim formed on Ni 42 alloy was initially reasonably coherent, but tended to disintegrate after some extent of reaction. Therefore, the accumulation of reaction product cannot affect the leaching process, which proceeds at an unvarying rate. The reaction is restricted only at the external surface of unreacted alloy core at all stage of reaction, thus eliminating the pore diffusion effect on leaching process, which proceeds at an unvarying rate.

Ni 50 alloy showed decreasing rates with extraction time; hence it can be assumed that the accumulation of reaction product in Ni 50 alloy, more or less, controls diffusion. Ni 60 alloy formed strongly coherent and adherent reaction product layer, and observed parabolic kinetics could result from the reaction controlled by diffusion through the product layer.

The difference in strength of product layer in three alloys was also observed in the leaching of alloy powder. The three alloy powder before leaching had same particle size of 300-500 μm, while after leaching using standard conditions the volume percent of particles having size less than 404 μm was 99, 66 and 49% for Ni 42, Ni 50 and Ni 60 alloy, respectively, even though Ni 60 alloy powder was leached under higher temperature and for longer extraction time. This observation represents that the reaction product layer in Ni 60 alloy is more coherent than that in Ni 42 and Ni 50 alloys. One of possibilities of disintegration of product layer, especially in the case of Ni 42 alloy, may be build-up of hydrogen pressure in the pore during extraction because Al in alloy reacts with alkali to form hydrogen and higher Al contents results in higher evolution of hydrogen at reaction interface [Hu et al., 2003].

From the Ni/Al ratio in alloy, it might be expected that Ni 42 and Ni 60 alloys have single $NiAl_3$ and single Ni_2Al_3 phase, respectively. However, it is known that possible phases for Ni-Al alloy containing 40-50 wt% Ni are $NiAl_3$, Ni_2Al_3 and eutectic Al [Freel et al., 1970]. As shown in Fig. 2, Ni 60 alloy has almost pure Ni_2Al_3 phase, while Ni 42 alloy appears to contain $NiAl_3$, Ni_2Al_3 and eutectic Al. Ni 50 alloy was seen to have the same three phases and it contained less $NiAl_3$ and more Ni_2Al_3 phase than Ni 42 alloy because of its higher Ni content.

In Fig. 3, none of the reflections of precursor alloy and NiO are observed. All catalysts present the reflections corresponding to the fcc lattice of Ni. The main phases in three alloys are $NiAl_3$, Ni_2Al_3 and eutectic Al, which have lattice structures of orthorhombic, hexagonal and face centered cubic, respectively [Zhu et al., 2002]. This factor, together with low solubility of nickel in alkaline solution, may lead to conclusion that leaching mechanism is selective dissolution of aluminum and recrystallization of nickel. The lattice parameters of Ni42-50C/4 h, Ni50-50C/10 h and Ni60-107C/125 h catalysts, calculated from d-value, are 3.5463, 3.5384 and 3.5344 Å, respectively. These values are slightly larger than that for pure crystalline Ni, 3.5238 Å, and it may be due to the presence of some Al in Ni lattice [Hoffer et al., 2003]. During leaching, aluminum is removed from the alloys in the form of aluminate and this aluminate can hydrolyze to produce aluminum trihydrate. The solubility of alumina in aqueous solution increases with increasing temperature. Thus, the catalysts prepared at relatively low temperature, Ni42-50C/4 h and Ni50-50C/10 h, revealed some reflections of Bayerite 2θ=38, 65 and 78° in XRD patterns, while Ni60-107C/125 h, prepared at 107 °C, did not show any reflection of alumina trihydrate.

As shown in Fig. 4, diffraction patterns for the catalysts prepared at high temperature for long duration were sharper than that at low temperature for short duration, suggesting that crystallites of former were larger than those of the latter. These findings illustrate that crystallite development has occurred, which is more marked at high temperature and long duration.

From examination of the concentration profile for partially leached Ni 42 and Ni 50 alloys, it was seen that unleached alloy core is composed of at least two aluminides having about 42 and 60 wt% Al, which might correspond to Ni_2Al_3 and $NiAl_3$ phases, respectively. These observations are consistent with the results of XRD measurements of precursor alloys. As can be seen in Fig. 5, the reaction product layer produced on Ni 50 alloy was more complex than that on Ni 42 alloy. In the case of Ni 42 alloy, the product rim has an approximately uniform composition of about 15 wt% Al. However, Ni 50 alloy revealed comparatively discontinuous change of composition in product layer. $NiAl_3$ is known to be much more reactive toward alkali than Ni_2Al_3 [Lei et al., 2001]. It was also observed that $NiAl_3$ leached according to linear kinetics at the temperature of 274 to 323 K, while Ni_2Al_3 is almost unreactive at these temperatures and, at 343 to 380 K, it leached according to parabolic kinetics [Bakker et al., 1988]. In addition, they also reported that $NiAl_3$ converts into $NiAl_3$ plus Ni during leaching and prolonged leaching leads to reaction of remnant $NiAl_3$ material leaving only Ni. These facts and above observations may suggest that the reaction on Ni 42 alloy is restricted to reaction interface whereas that on Ni 50 alloy occurs throughout the product layer. It seems from the above results that reaction in Ni 50 alloy is controlled by diffusion through product layer, as discussed earlier. In the case of Ni 60 alloy, which was leached at high temperature for a long time, the product rim shows relatively continuous change of composition.

The pore structure of leached catalyst seems to be relatively independent of the composition of precursor alloy and strongly dependent upon the temperature of extraction, 50 or 107 °C in the present work. The Ni42-50C/4 h and Ni50-50C/10 h catalysts, prepared from different precursor alloys but activated at same temperature, 50 °C, showed somewhat similar isotherms, while Ni60-107C/125 h catalyst which is activated at 107 °C showed quite different isotherm. However, Ni42-107C/125 h and Ni50-107C/125 h, which are activated under same condition as that for Ni60-107C/125 h, revealed similar isotherm to those found for Ni60-107C/125 h. These facts suggest that higher preparation temperature favors higher pore volume structure.

The crystallite sizes of Ni in Ni42-50C/4 h, Ni50-50C/10 h and Ni60-107C/125 h, determined by X-ray line broadening, were 11, 12 and 9 nm, respectively, suggesting that the crystallite sizes of fully extracted catalysts are similar irrespective of the composition of precursor alloy and leaching conditions. However, in the case of the catalysts derived from same alloy using different leaching conditions, increased extraction time and higher temperature result in an increase in crystallite, as can be expected from Ni peak width in XRD patterns in Fig. 4, which shows that more severe extraction conditions result in sharper Ni peaks. Similar findings were reported previously [Robertson and Anderson, 1971].

It is seen in Table 2 that surface area is strongly dependent on leaching conditions, that is, the same extraction conditions result in similar surface area irrespective of the composition of precursor alloy.

Pore volume of Ni 50 catalyst increases with increasing leaching time, while surface area shows a maximum, as shown in Table 3. Similar results were observed previously by Freel et al. [1969]. They found that during the leaching of Ni-Al alloy containing 50% Ni at 50 °C, both surface area and pore volume increase with leaching time and prolonged treatment increases pore volume appreciably and decreases surface area; they ascribed this trend to the change of pore structure.

The pore size distributions for three catalysts prepared by using standard conditions, shown in Fig. 7, indicate single maximum, and porosity is formed by comparatively large pores. These results may be ascribed to severe preparation conditions, namely prolonged extraction time and high reaction temperature.

Fig. 8 shows change in pore size distribution according to leaching conditions. The pore size distribution also appears to be strongly dependent on the leaching conditions and relatively independent of the composition of precursor alloy. The severe leaching conditions favor the development of large pore. The Ni42-107C/125 h catalyst show maxima at pore diameter of 33 and 88 Å, and the Ni50-107C/125 h catalyst prepared under same condition show 33 and 114 Å. From the above result, it seems that change in pore size distribution involves an increase of large pores at the expense of small pores.

CONCLUSIONS

The reactivity of Ni-Al alloy toward alkali solution was changed with the composition of the alloy; this may be due to the difference in function of leached product material as a diffusion barrier. As Al content in precursor alloy increased, the reactivity of alloy toward alkali solution increased. It has been demonstrated that, during leaching, reaction in Ni 41.3 wt% alloy is restricted to reaction interface whereas that in Ni 49.9 wt% alloy occurs throughout product layer. The surface area and pore size distribution of resultant Raney Ni seem likely to be strongly dependent upon leaching conditions and relatively independent of the composition of precursor alloy.

REFERENCES

Bakker, M. L., Young, D. J. and Wainwright, M. S., "Selective Leaching of $NiAl_3$ and Ni_2Al_3 Intermetallics to Form Raney Nickels," *J. Mater. Sci.*, **23**, 3921 (1988).

Conde, L. D., Marún, C. and Suib, S. L., "Oligomerization of Methane via Microwave Heating using Raney Nickel Catalyst," *J. Catal.*, **218**, 201 (2003).

Freel, J., Pieters, W. J. M. and Anderson, R. B., "The Structure of Raney Nickel, I. Pore Structure," *J. Catal.*, **14**, 247 (1969).

Freel, J., Pieters, W. J. M. and Anderson, R. B., "The Structure of Raney Nickel, II. Electron Microprobes Studies," *J. Catal.*, **16**, 281 (1970).

Hoffer, B. W., Crezee, E., Devred, F., Mooijman, P. R. M., Sloof, W. G., Kooyman, P. J., van Langeveld, A. D., Kapteijn, F. and Moulijn, J. A., "The Role of the Active Phase of Raney-type Ni Catalysts in the Selective Hydrogenation of D-Glucose to D-Sorbitol," *Appl. Catal. A*, **253**(2), 437 (2003).

Hu, H., Qiao, M., Pei, Y., Fan, K., Li, H., Zong, B. and Zhang, X., "Kinetics of Hydrogen Evolution in Alkali Leaching of Rapidly Quenched Ni-Al Alloy," *Appl. Catal. A*, **252**(1), 173 (2003).

Kühn, U., Warlimont, H. and Mattern, N., "Rapidly Quenched Raney Catalyst Precursors," *Mater. Sci. Eng., A*, **226**, 900 (1997).

Lei, H., Song, Z., Tan, D., Bao, X., Mu, X., Zong, B. and Min, E., "Preparation of Novel Raney-Ni Catalysts and Characterization by XRD, SEM and XPS," *Appl. Catal., A*, **214**, 69 (2001).

Liu, Z.-W., Jun, K.-W., Roh, H.-S., Park, S.-E. and Oh, Y.-S., "Partial Oxidation of Methane over Nickel Catalysts Supported on Various Aluminas," *Korean J. Chem. Eng.*, **19**, 735 (2002).

Robertson, S. D. and Anderson, R. B., "The Structure of Raney Nickel, IV X-ray Diffraction Studies," *J. Catal.*, **23**, 286 (1971).

Sane, S., Bonnier, J. M., Damon, J. P. and Masson, J., "Raney Metal Catalysts: I. Comparative Properties of Raney Nickel Proceeding from Ni-Ai Intermetallic Phases," *Appl. Catal.*, **9**, 69 (1984).

Zhu, P., Li, J. C. M. and Liu, C. T., "Reaction Mechanism of Combustion Synthesis of NiAl," *Mater. Sci. Eng., A*, **329**, 57 (2002).