

The Structure of Raney Nickel

I. Pore Structure

J. FREEL, W. J. M. PIETERS, AND R. B. ANDERSON

*From the Department of Chemical Engineering, McMaster University,
Hamilton, Ontario, Canada*

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Raney nickel alloys were examined by metallographic methods. The alloys were extracted by aqueous sodium hydroxide in several ways and nitrogen isotherms at -195°C determined. The pore structure of the activated catalyst was relatively independent of phase composition of the original alloy. Significant differences in pore structure were observed between samples extracted at 50°C and those prepared at the boiling point of the alkali solution, 107°C . Preparations at 50°C had a surface area of $110 \pm 10 \text{ m}^2/\text{g}$ and a pore volume of $0.07 \pm 0.02 \text{ cc/g}$ compared with $80 \pm 10 \text{ m}^2/\text{g}$ and $0.12 \pm 0.02 \text{ cc/g}$ for extraction at 107°C . Both types of samples had a bimodal pore distribution with maxima for pore diameters in range 20–24 Å and 34–48 Å, but 50°C preparations contained a larger fraction of small pores than the 107°C samples. Further treatment of the 50°C preparation with fresh aqueous alkali changed the pore structure to that typical of high-temperature extraction. Data are given for partly extracted catalysts and preparations made with less than the stoichiometric amount of alkali.

INTRODUCTION

Much of the terminology associated with Raney nickel (e.g., sponge nickel, skeletal catalyst), results from the concept that the unusual method of preparation leads to a porous material. Since the pore geometry of commercial catalysts is of technological significance, it seemed worthwhile to investigate the pore structure of Raney nickel in some detail.

Variations in the properties of Raney nickels prepared by different methods have been demonstrated (1, 2), similar diversity being reported (3, 4) with variation in the nature of the starting nickel-aluminum alloy. It might be anticipated that the pore geometry of the catalyst would be subject to such changes. We have therefore investigated several methods of catalyst preparation as applied to Raney alloys of significantly different phase composition.

Several workers have studied the phys-

ical adsorption of nitrogen on Raney nickel at -195°C , and the variation of BET area with thermal treatment (1, 5, 6), storage (7), and duration of extraction (8) have been examined.

Complete nitrogen isotherms have also been reported (9, 10) and useful information has been derived from studies of the adsorption of organic acids from the liquid phase (11). However, variations in the pore geometry of Raney nickel as a function of the method of preparation have not previously been described.

EXPERIMENTAL

Metallographic examination of starting raney alloys. Three nickel-aluminum alloys of diverse structure were selected from several commercial samples. Alloy A, nominally 50 wt % nickel, and alloy B, nominally 42 wt % nickel, were received as small pieces some $\frac{1}{4}$ cc in volume and alloy C, 42 wt % nickel, as a larger, single

TABLE 1
CHEMICAL AND PHASE COMPOSITION OF STARTING ALLOYS

Alloy designation	Nominal comp. (wt % nickel)	Nickel analysis (wt % nickel)	Metallographic analysis		
			Ni ₂ Al ₃ (av vol %)	NiAl ₃ (av vol %)	Eutectic (av vol %)
A	50	50.8 ± 0.1	59	40	~1
B	42	40.5 ± 0.1	45	32	23
C	42	42.2 ± 0.1	15	83	~2

ingot of about 120 cc volume. Each alloy was crushed mechanically, sieved, and the 30–50 mesh fraction used throughout.

The alloys were analyzed for nickel by the gravimetric dimethylglyoxime method. Phase content was investigated by optical microscopy, and the assignment of phases by optical contrast, reported by previous workers (12) was confirmed by the use of an Acton electron probe microanalyzer. No NiAl was detected in any of these alloys, although small amounts of this compound may occur (12) in 50 wt % nickel alloys. Concentrations of the three phases present in each alloy were estimated by standard metallographic procedures (13) applied to about 60 pieces of each material.

The results of these studies are given in Table 1. The microstructures of alloys A and B thus determined would be predicted for quenched alloys from the phase diagram (14). The phase composition of alloy C is consistent with an annealed specimen. Typical optical micrographs of the three alloys are given in Fig. 1.

Catalyst preparation. Catalysts were

prepared by the reaction of 30–50 mesh Raney alloy with aqueous sodium hydroxide in a 1-liter round-bottomed flask immersed in a thermostated water bath. Gas-tight seals to the four necks of this flask contained a stirring device, a thermometer, a burette for adding alkali, and a reflux condenser connected to a wet test meter, which was used to measure evolved hydrogen. The contents of the flask were stirred vigorously during the extraction and washing procedures.

Four methods of alkali treatment were used.

Method I: 30 g of alloy was added stepwise to 300 ml of 20% aqueous sodium hydroxide. The large solution/alloy ratio led to relatively facile temperature control and solution temperature was maintained at $50^{\circ} \pm 5^{\circ}\text{C}$ by adding alloy in five equal increments at 5-min intervals. This general type of catalyst activation in which alloy is added to concentrated sodium hydroxide at moderate temperature has been widely employed, e.g., by Adkins *et al.* (2, 15) in

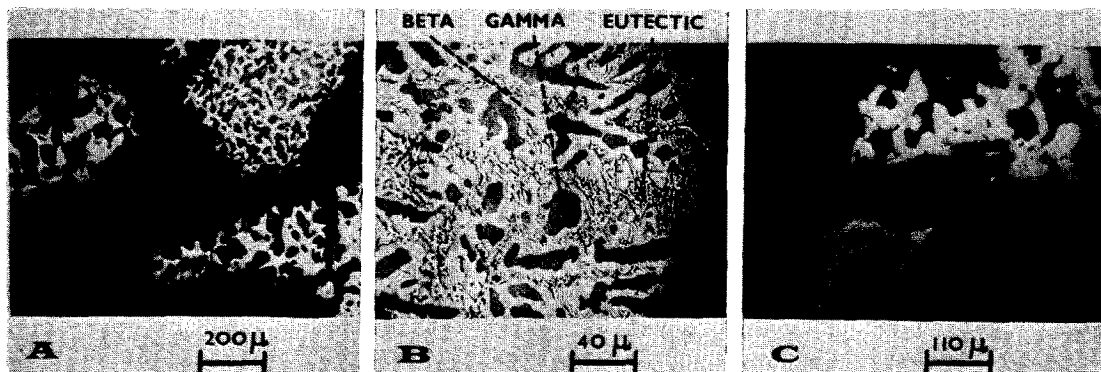


FIG. 1. Optical micrographs of starting alloys: (a) Alloy A showing dark Ni₂Al₃ grains in a matrix of the light-colored NiAl₃. (b) Alloy B showing Ni₂Al₃ (gamma), NiAl₃ (beta) and eutectic phases. (c) Alloy C, primarily NiAl₃.

the W4-W6 series of catalysts and by Dominguez *et al.* (16) for the T-1 catalyst.

Method II: This procedure was derived from an alternative low-temperature technique advocated by Nishimura and Urishibara (17) among others, and involved the stepwise addition of 150 ml of 40% aqueous NaOH to a suspension of 30 g of alloy in 150 ml of distilled water. Reaction was initiated by 5 ml alkali. Similar volumes were added at 2-min intervals for the first 10 min after which 50-ml additions were made at 5-min intervals. This procedure again resulted in fairly constant solution temperature of $50^{\circ} \pm 5^{\circ}\text{C}$. The major part of the hydrogen evolution therefore occurred in dilute alkali, the final part in concentrated NaOH.

Method III: 30 g of alloy were added to 300 ml of boiling 25% NaOH in a single batch. The maximum temperature obtained was about 107°C .

Method IV: To obtain a catalyst with high alumina content, the procedure used by Dirksen and Linden (18) was employed. Thirty milliliters of 20% NaOH was added to 40 g of alloy in 300 ml of distilled water at 80°C . Substantially less alkali than that required to convert the aluminum content of the alloy to sodium aluminate is therefore used, and Dirksen and Linden have shown that the resultant catalyst may contain as much as 60 wt % alumina.

Various times of reaction were used in each method and will be referred to when appropriate. All extracted catalysts were washed with distilled water, at 25°C first by decantation and finally by water flow in a stirred vessel for $1\frac{1}{2}$ hr. Unless otherwise stated, samples were finally washed in ethanol, transferred to stoppered test tubes, and stored under ethanol at 0°C . Measurements were made within 24 hr of catalyst preparation.

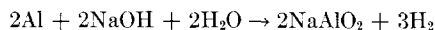
Two activated commercial catalysts, furnished by the Davison Chemical Company were also examined.

Adsorption studies. The adsorption of nitrogen at -195°C was studied in a conventional glass volumetric system. Samples were transferred to the adsorption vessel

under the storage liquid, which was pumped off and frozen out in a cold trap. The samples were evacuated for 8 hr at room temperature to remove the storage liquid and heated slowly to the desired degassing temperature, normally $130^{\circ} \pm 2^{\circ}\text{C}$, which was maintained until a vacuum of 10^{-5} torr or less was obtained. Rapid heating to 130°C was avoided since some catalysts evolved gas explosively during such heating, presumably due to the reactions described by Mars, Scholten, and Zweitering (6). Samples were weighed by difference in the adsorption vessel on completion of the experiment. All subsequent data were based on the weight of the degassed samples.

RESULTS

Low pore volume preparations. Method II, the most readily reproduced, was used to prepare catalysts from alloys A, B, and C. Each sample was extracted for 90 min, at which time the evolved hydrogen indicated about 90% aluminum oxidation based on the reaction (18)



Preliminary studies showed that neither the temperature of evacuation between ambient and 130°C , nor the 24-hr storage in ethanol or water had significant effect on the nitrogen isotherms obtained. Duplicate preparations gave essentially the same isotherms.

These catalysts yielded closely similar nitrogen isotherms typified by that of a IIB catalyst given in Fig. 2. This general type of sample will be called the "low pore volume" or LPV type. Surface areas for these samples, calculated by the simple BET equation (N_2 cross-sectional area of 16.2 \AA^2), pore volumes expressed as cc of nitrogen as normal liquid, and mean pore diameters assuming nonintersecting cylindrical pores are given in Table 2. The pore volume (V_s) was calculated from the volume (cc STP) of gaseous nitrogen sorbed at a relative pressure of 0.99. The mean pore diameter may then be expressed as

$$d = 4V_s/A$$

TABLE 2
SUMMARY OF ADSORPTION DATA FOR VARIOUS RANEY NICKELS

Sample notation	Extraction conditions		% Hydrogen evolved ($\pm 4\%$)	Storage medium	Storage temp. ($^{\circ}\text{C}$)	Storage time (hr)	Adsorption data			Chemical analysis	
	Time (min)	Temp. ($^{\circ}\text{C}$)					BET area (m^2/g)	Pore volume (cc/g)	Mean pore diameter (\AA)	Nickel (wt %)	Aluminum (wt %)
IIA	90	50	90	Ethanol	0°	24	99	0.062	25		
IIB	90	50	90	Water	25°	24	100	0.064	26		
IIC	90	50	94	Ethanol	0°	24	115	0.082	29	84	4.1
IA ₁	90	50	95	Ethanol	0°	24	117	0.090	31		11.9
IA ₂	90	50	85	Ethanol	0°	24	96	0.059	25		
IA ₃	150	50	90	Ethanol	0°	24	95	0.055	23		
Com. I	10	50	50	Ethanol	0°	24	16	0.010	25		
Com. I	—	—	—	Water	25°	Weeks	82	0.125	61	91–96 ^a	3–8 ^a
Com. II	—	—	—	Water	25°	Months	82	0.125	61		$\sim 1^a$
IIIA ₁	45	107	92	Ethanol	0°	24	86	0.125	58	89	3.9
IIIA ₂	120	107	92	Ethanol	0°	24	61	0.145	96		7.1
IIIA ₂ -B	120	107	92	5% NaOH	25°	120	57	0.136	96		
IVA	120	80	80	Ethanol	0°	24	62	0.048	31	49.2	7.6
IIA-W ₁	90	50	90	Water	70°	16	73	0.070	39		
IIA-W ₂	90	50	90	Water	100°	60	60	0.071	48		
IIA-B ₁	90	50	90	2% NaOH	50°	3	118	0.098	33		
IIA-B ₂	90	50	90	5% NaOH	50°	5	119	0.098	33		
IIA-B ₃	90	50	90	2% NaOH	50°	60	86	0.130	61		
IIB-B ₁	90	50	94	10% NaOH	70°	3	59	0.141	96		
IIB-B ₂	90	50	94	10% NaOH	70°	3	98	0.126	52		

^a Data of Kokes and Emmett (1) and Lippman and Dew-Hughes (27).

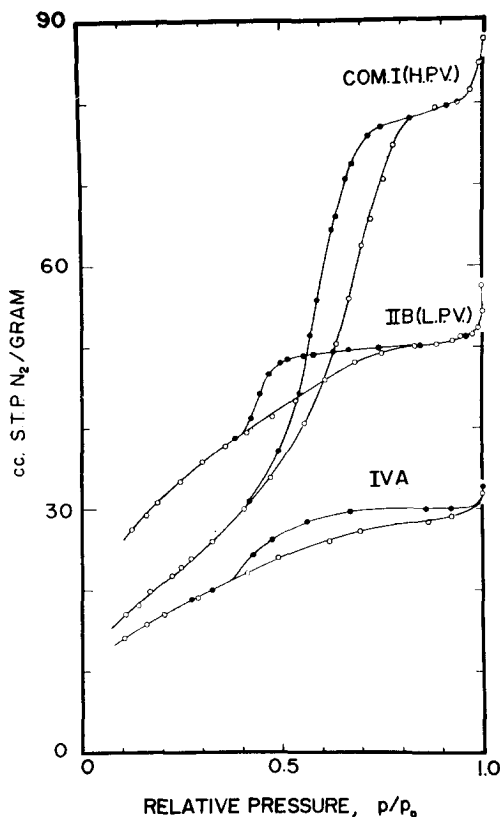


FIG. 2. Nitrogen isotherms at -195°C for typical low (IIB) and high (Com. 1) temperature preparations, and for the alumina-rich IVA catalyst; \circ adsorption; \bullet desorption.

where d is the diameter in cm and A , the surface area in cm^2 .

The notation of samples in Fig. 1 and Table 2 is derived from the method of preparation (I to IV) and the starting alloy (A, B, or C), so that the data at present under consideration are those for samples IIA, IIB, and IIC.

This LPV type of isotherm was found to be characteristic of all fresh catalysts "fully" extracted at 50°C . Methods I and II applied to each alloy for various times of reaction corresponding to 80–95% aluminum oxidation, gave catalysts which adsorbed nitrogen in a similar manner with minor variations in pore volume. Typical data for a type I preparation reacted for 90 min (90% aluminum oxidation) are given as IA_1 in Table 2. A type I preparation reacted for only 10 min (50% alumi-

num oxidation) gave an isotherm of the same shape with smaller area and pore volume per gram of solid (IA_3 in Table 2). Prolonged digestion at 50°C in the reactant liquid had little effect on the pore geometry of the preparations, a type I preparation extracted for $2\frac{1}{2}$ hours (90% extraction in 1 hour) giving similar data to the IA_1 material (IA_2 in Table 2).

For comparative purposes, the helium and mercury densities of a IIA catalyst were measured at 25°C . The mercury density was determined at a pressure of about 1.1 atm; visual examinations indicated that mercury did not wet the solid. Values of 5.78 and 4.08 g/cc were obtained for the helium and mercury densities, respectively. The corresponding pore volume ($1/\rho_{\text{Hg}} - 1/\rho_{\text{He}}$) is 0.072 cc/g. The IIA preparation, in common with all catalysts prepared at 50°C , had a particle size of the same order of magnitude as the starting 30- to 50-mesh alloy. Therefore, little interparticle void space is likely to be included in this figure.

The density of alloy A, determined in ethanol at 25°C , was 4.22 g/cc. The volume change during extraction, calculated per gram of final catalyst, is given by $(1/x\rho_{\text{alloy}}) - (1/\rho_{\text{He}})$, where x is grams of catalyst obtained from 1 g of alloy, and ρ_{alloy} and ρ_{He} are, respectively, the density of the alloy and the helium density of the catalyst. The volume change was 0.23 cc/g of catalyst, which is substantially larger than the pore volume. Therefore, some of the pores generated during extraction are large enough to be penetrated by mercury or the overall size of particles decreases.

Total nickel and total aluminum analyses were obtained for several catalysts. Each catalyst was assumed to contain only nickel, aluminum, and alumina trihydrate (1) and the content of each was calculated as shown in Table 2.

Catalysts of type IV, which contain much alumina, gave isotherms of somewhat lower pore volume and the adsorption-desorption hysteresis loop was significantly different, as shown by the data for a type IVA preparation given in Fig. 2 and Table 2. This material required much longer times of evacuation at 130°C , suggesting the slow

dehydration of alumina hydrates (19). Changes in the BET area of this catalyst accompanying various thermal treatments were studied in an attempt to examine the contribution of aluminas to the total areas measured. Results are given in Table 3.

TABLE 3
BET AREA OF A TYPE IVA CATALYST AFTER
EVACUATION UNDER VARIOUS CONDITIONS

Evacuation temp. (°C)	Duration (hr)	BET area (m ² /g)
25	72	89
130	24	74
130	48	67
130	72	62
250	16	67
400	16	38
450	4	50

High pore volume preparations. Nitrogen isotherms for the two commercial catalysts, one extracted from 50 wt % nickel alloy (Com. I), the other from 42 wt % nickel alloy (Com. II), were very similar, but significantly different from those described above. This second type of isotherm, of higher pore volume (HPV), is typified by that shown in Fig. 2 and by the data for these catalysts in Table 2.

Commercial Raney nickel is normally prepared at the boiling point of the aqueous alkali solution. Type III preparations were made under these conditions and isotherms similar to those from the commercial catalysts were obtained, IIIA₁ and IIIA₂ in Table 2. In contrast to the preparations at 50°C (IA₁ and IA₂) the longer extraction in IIIA₂ led to an increase in pore volume and decrease in surface area compared with IIIA₁.

Conversion of LPV nickel to the HPV form. Increased porosity as a result of extraction at higher temperature may be tentatively ascribed to (i) the reaction of additional alloy, (ii) the removal by solution of larger amounts of residual alumina, or (iii) some action of the aqueous solution at the higher temperature.

Samples of newly prepared LPV catalysts were therefore treated with fresh solutions of aqueous sodium hydroxide at 50°C.

The type of isotherm obtained is illustrated by the IIA-B and IIB-B data in Table 2. A small amount of hydrogen was evolved during these treatments but was complete in a few hours. Catalysts removed and washed at this stage had increased surface area and pore volume with little change in the mean pore diameter. Prolonged treatment at 50°C or short periods at 70°C produced catalysts having isotherms of the HPV type, although the changes produced were not readily reproducible (IIB-B₁ and IIB-B₂ in Table 2). Type III catalysts were largely unaffected by storage in fresh sodium hydroxide (IIIA₂-B in Table 2).

The effect of hot water on a IIA catalyst was also studied. Adsorption isotherms (Fig. 3) and calculated data (Table 2) are given for catalysts treated for 20 hr at 70°C (IIA-W₁) and for 60 hr at 100°C (IIA-W₂). Sample IIA-W₂ was not pyrophoric and had a very low activity in the hydrogenation of cyclohexene in ethanol.

Catalysts prepared by method III and LPV catalysts given extensive treatment in fresh NaOH, to a large degree became

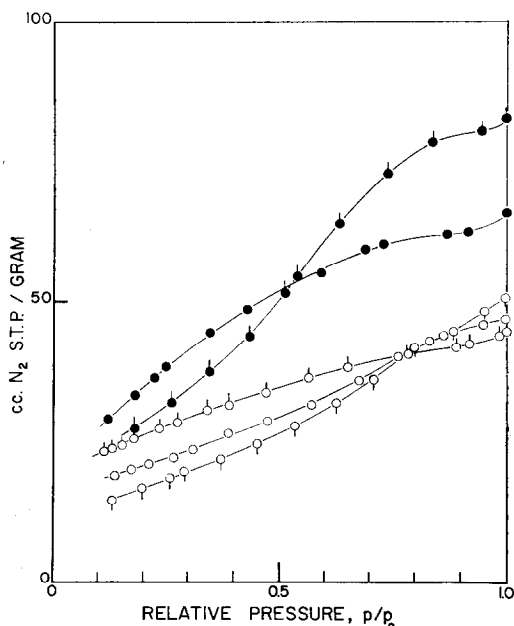


FIG. 3. Nitrogen adsorption isotherms at -195°C for catalysts: ● IIA-B₁, ○ IIA, ○ IIA-W₁, ○ IIA-W₂, and ● IIB-B₁.

finely divided. Therefore, density measurements were not made.

Pore distributions in LPV and HPV Raney nickel. The isotherms in Fig. 2 were analyzed by de Boer's t -plot method (20) and pore distribution curves were derived for our own version of the Barrett, Joyner, and Halenda methods (21).

t Plots for several isotherms are shown in Fig. 4. Surface areas from the t plots were usually within $\pm 2\%$ of those from the BET equation. t Plots for HPV catalysts curved above the initial linear portion at a relative pressure about 0.35, probably attributable to capillary condensation. Plots for the LPV catalysts, however, deviated from initial linearity in the opposite direction, which may be due to the filling of very fine pores at low relative pressures. At least a second straight line may be passed through subsequent points and for catalyst IIB breaks occurred at 5 and 8 Å.

For catalyst IIB, detailed calculations of pore size indicated a bimodal distribution with maxima at pore diameters 20 and 34 Å from the desorption isotherm and at 15 and

25 Å from the adsorption isotherm. The mean pore diameter from the ratio of pore volume to area for cylindrical pores was 25 Å. The pore distribution for the HPV catalyst Com. 1 showed a small maximum or plateau at small diameters, followed by a large broad maximum. These features occurred at 24 and 48 Å in calculations based on the desorption isotherm and at 18 and 38 Å in those from the adsorption curves. The mean diameter from the volume-to-area ratio was 61 Å. The alumina-rich catalyst IVA gave a singular maximum in pore distribution curves, which occurred at diameters of 24 and 16 Å from the desorption and adsorption isotherms, respectively. The mean pore diameter in this case was 31 Å.

The absence of nitrogen chemisorption. Kokes and Emmett (2) showed that certain supported nickel catalysts would chemisorb nitrogen weakly at -195°C while others would not. Clearly, the higher BET area of the LPV catalyst could be due to such nitrogen chemisorption. Subsequent to the above experiments, therefore, a new IA preparation, of somewhat higher area than that reported in Table 2, was used for experiments in which the sample was evacuated 1 hr at -78°C after the determination of a nitrogen isotherm and a second nitrogen isotherm then measured. The two isotherms were identical and yielded a BET area of $118\text{ m}^2/\text{g}$. An argon isotherm was determined on the same sample. A BET area of $134\text{ m}^2/\text{g}$ was calculated using an extrapolated value for the liquid vapor pressure of argon at -195°C and assigning a value of 15.2 \AA^2 to the cross sectional area of the adsorbed argon atom (22, 23).

We conclude that in the determination of surface area by the physical adsorption of nitrogen, the higher area of the LPV nickel is not due to nitrogen chemisorption.

DISCUSSION

Raney nickel alloys investigated in the present work contained three phases: a eutectic precipitate of aluminum with 0.05 wt % nickel in solid solution and NiAl_3 , β -phase NiAl_3 , and γ -phase Ni_2Al_3 . Metallographic and electron-microprobe studies,

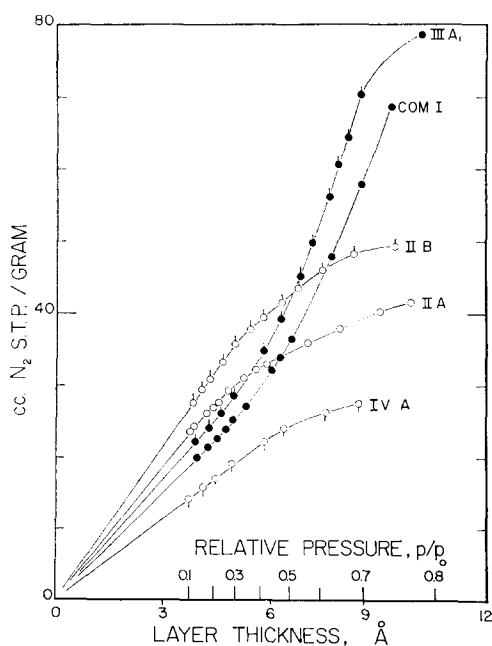


Fig. 4. t Plots for typical LPV (IIB; IIA) and HPV (IIIA₁; Com. 1) preparations, and for the alumina-rich IVA catalyst.

to be described in a later paper, showed that in extraction with aqueous NaOH the eutectic phase disappeared leaving large cavities but the β - and γ -phases remained and retained many of their optical characteristics so that these grains could be recognized in the extracted catalyst.

The extraction of Raney nickel has some similarities to the activation of promoted magnetite for the ammonia synthesis by reduction in hydrogen. The particles of the magnetite catalyst retain (24) their original size during reduction; however, the volume of Raney nickel seems to decrease during extraction. If the gross volume of catalyst A remained constant the pore volume of preparation IIA should be 0.23 cc/g compared with values of 0.072 and 0.062 cc/g from Hg/He densities and adsorption isotherms, respectively. Other preparations from catalyst A had pore volumes from adsorption isotherms as large as 0.14 cc/g.

The pore geometry appeared to be strongly dependent upon the temperature of extraction, 50° or 100°C in the present work, and relatively independent of Ni/Al ratio or distribution of phases in the original alloy; the catalysts extracted at 50° and in boiling alkali are designated as low (LPV) and high (HPV) pore volume types in the present paper. Catalysts extracted at 50°C had surface areas of 100–115 m²/g, while those extracted at the boiling point of the alkali solution (107°C) had areas of about 80 m²/g.

Surface areas of several LPV catalysts per gram of original alloy were approximately constant, but the pore volumes increased with increasing values of the ratio of the volume fraction of NiAl₃ over the fraction of NiAl₃ + Ni₂Al₃.

Preparation	Per g original alloy		Ratio volume fraction NiAl ₃ / (NiAl ₃ + Ni ₂ Al ₃)
	Surface area (m ²)	Pore volume (cc)	
IIA	60	0.038	0.41
IIB	56	0.039	0.43
IIC	59	0.045	0.84
IVA	62	0.048	—

Sample IVA has about the same area per gram of original alloy as IIA but a larger

pore volume, despite the aluminum in this preparation being only 80% oxidized and the weight percent alumina calculated as the trihydrate being 43%.

Sample IA₃ was extracted only 50%. Metallographic studies showed that this catalyst contained almost exclusively extracted NiAl₃ and unreacted Ni₂Al₃, and based on phase analyses this sample should contain about 20 wt % of activated catalyst. The area and pore volume per gram of activated catalyst would then be about 80 m² and 0.05 cc, respectively. This approximate calculation suggests that surface area and pore volume are generated directly in the oxidation and dissolution of aluminum and the formation of the final porous structure does not involve major changes of the material produced initially. Electron microprobe studies showed that at least on a scale of microns sharp concentration gradients for Ni and Al exist at the interface between the extracted and original material.

Subsequent treatment of the LPV catalyst with fresh alkali solution at 50°C for 3 to 5 hr increased both area and pore volume. Prolonged treatment at 50°C increased pore volume appreciably and decreased area. A 3-hr alkali treatment at 70°C yielded a catalyst with smaller area and larger pore volume than typical HPV catalysts.

Changes typical of the LPV to HPV transformation did not occur on treatment with water at 70° or 100°C. This treatment decreased surface area but did not increase the pore volume appreciably. Hence, formation of the HPV type catalyst may be attributed to exposure of the LPV catalyst to the alkali solution for prolonged periods at moderate temperatures or short periods at temperatures above 50°C.

The pore distributions of LPV and HPV Raney nickel calculated from the desorption isotherms show a dual maximum (pore diameters 20–24 and 34–48 Å) for each type. However, while almost the entire porosity of the HPV type is formed by the larger pores, the smaller pores form a major part of the LPV pore structure. Thus the transformation from LPV to HPV

Raney nickel apparently involves an increase in the volume of large pores at the expense of small pores and perhaps a small increase in the diameter of pores of both sizes. Together with the fact that the IVA catalyst, containing 42 wt % alumina, gave a singular maximum at the lower pore diameter, these results suggest that variations in the surface area and pore volume of Raney nickel are related to the content of alumina trihydrate.

However, the removal of a high-area material from the pore structure is not an adequate explanation of the data. An increase of pore volume of 0.07 cc/g requires the removal of more than 14% of a material of density of 2.4, such as gibbsite; however, present data (IIB and IIIA₁) indicate only a 5% decrease in alumina. Nevertheless, the alumina could block pores and decrease the pore volume by a larger amount than its volume. If the difference in area between IIB and IIIA₁ is attributed to removal of 5% of high-area alumina, the area of the alumina removal equals about 540 m²/g alumina. Most alumina hydrates have relatively low surface area after evacuation at 130°C, however; for example, bayerite has an area of 20–30 m²/g after this treatment (19). Further, the alumina in IVA had a small surface area, and this material, which may

of course not be typical of alumina in conventional catalysts, did not activate during evacuation at higher temperatures.

Apparently, therefore, treatment of LPV catalysts with aqueous alkali involves removal of alumina blocking and filling pores, but the volume of alumina removed seems smaller than the increase in pore volume. Brief alkali treatment at 50°C increases both surface area and pore volume, but prolonged alkali treatment at 50°C or brief periods at 70°C decreases surface area, but increases pore volume. The more severe alkali treatments must, in addition, cause sintering (25) as well as enlarging pores. The pore geometry of HPV type catalysts was unaffected by prolonged storage in water and for at least short periods in alkali.

In the preceding paragraph we have ignored additional oxidation of aluminum during subsequent treatments of the LPV catalysts because the oxidation of aluminum seems small based on the few chemical analyses available. Treatment with water at 70° and 100°C probably also oxidizes some aluminum, but here the surface area decreases significantly with at most a small increase in pore volume.

There have been many attempts (2, 15, 16, 17) to prepare Raney nickel of optimum activity by varying the conditions of

TABLE 4
SUMMARY OF LITERATURE DATA

References	Alloy	Extraction and storage conditions	BET area (m ² /g)	Pore volume	Mean pore diameter (Å)
(7)	50/50	W-6 preparation, fresh	142	0.092 ^a	26
(5)	42/58	25% KOH at 75°C, fresh	70–90	—	—
		Stored in alkali solution	161	—	—
(6)	50/50	30% NaOH at 85°C	120	—	—
(11)	Not specified	W-4 preparation	90–100	—	—
(9)	50/50	W-6 preparation, stored 10 months in water	86	0.181 ^a	84
(10)	—	Classical catalyst ^b	72	0.097 ^a	54
(10)			59	0.13	86
(10)		} These alloys activated in 4 steps, as described } in footnote ^c	36	0.10	112
(10)			45	0.14	128

^a Calculated from authors data.

^b Author's notation.

^c 6N NaOH at 15°C, 6N NaOH at b.p., washed in 2N NaOH at b.p. and 6N NaOH at b.p. for 4 hr.

aluminum leaching. As a consequence, much work concerning the properties of the catalyst has been carried out with Raney nickels prepared by a variety of procedures, the effects of which are not sufficiently understood. One aspect of the structural changes accompanying different methods of catalyst preparation has been examined in the present work and it is found that significant changes in the pore geometry of the catalyst occur as additional alumina is removed from the already "fully" leached material. Other workers (25) have observed pronounced crystallite growth under similar circumstances and it seems probable that the changes observed between the LPV and HPV pore structures are related to both sintering of this sort and to the removal of alumina trihydrate from the pores of the LPV type. It may be noted that both the LPV and HPV type of isotherm belong to the same shape group (A or E) in de Boer's (26) classification, suggesting a basic similarity in pore shape.

These data provide a basis for the correlation of previous work, as may be seen in Table 4. Catalysts prepared under mild conditions, have, in general, high area and narrow pores, while the samples of Prettre (10), after a severe leaching process, are low-area materials with larger pores. The catalyst of Kokes and Emmett (9) appears to contravene this trend, but here one must consider also the effect of 10 months storage in water.

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