

# The Structure of Raney Nickel

## IV. X-Ray Diffraction Studies

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Received March 30, 1971

X-Ray line broadening and adsorption studies on various types of Raney nickel prepared or treated at temperatures of 50, 80, and 107°C have shown an approximately linear relationship between surface area and the reciprocal of the crystallite size. The low-temperature preparations exhibited a greater concentration of residual crystalline alumina trihydrate. Removal of the crystalline alumina at 50°C, in some cases, led to increased porosity and surface area without changing crystallite size. More severe preparation or treatment in aqueous alkali gave catalysts of lower total aluminum and alumina trihydrate content. These conditions caused an increase in crystallite size, which was greater than that in catalysts from comparable heat treatment *in vacuo*, and emphasizes the importance of chemical as well as thermal processes in determining the nature of Raney nickel.

### INTRODUCTION

The manner of the Raney nickel preparation, by aluminum oxidation from a nickel-aluminum alloy using sodium hydroxide at moderate temperatures (1, 2), gives a product of extensive porosity which lends itself to examination by the classical nitrogen adsorption (BET) technique (3-9). This approach has revealed that the pore structure of the "completely activated" catalyst is relatively independent of the phase composition of the original alloy but is strongly dependent upon the temperature of aluminum oxidation. Raney nickels activated at 50°C had surface areas of  $110 \pm 10$  m<sup>2</sup>/g and a pore volume of  $.07 \pm .02$  cm<sup>3</sup>/g. Those prepared at 107°C, however, had lower surface areas and higher pore volumes of  $80 \pm 10$  m<sup>2</sup>/g and  $.12 \pm .02$  cm<sup>3</sup>/g, respectively. It was also observed that a change in the pore structure characteristic of a catalyst prepared

at 50°C to that typical of one in which the aluminum oxidation temperature was at 107°C could be effected by treating the low-temperature preparation in alkali at 107°C (10).

These findings would suggest that there was slight sintering or crystallite enlargement in the catalysts prepared at 107°C relative to those activated at 50°C. To examine the extent to which this and other factors are responsible for these differences in pore structure and on how they influence transitions between them, various preparations of Raney nickel were, therefore, examined by X-ray powder diffractometry, nitrogen adsorption (BET), and chemical analysis methods.

### EXPERIMENTAL

#### (a) Catalyst Preparation

The nature and composition of the various alloy precursors and the manner of various Raney nickel catalyst preparations were as described previously (10). In some cases, however, less concentrated alkali

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TABLE I  
ALLOY AND CATALYST NOMENCLATURE

Alloy			Catalyst	
Type	Composition		Type	Preparation method
	Ni %	Al %		
A	50	50	I	Alloy addition to alkali at 50°C
B	42	58	II	Alkali addition to alloy in distilled water at 50°C
			III	Alloy addition to boiling alkali. Reaction temperature is about 107°C.
			IV(11)	Alkali addition to alloy at 80°C. Quantity of alkali used is less than the stoichiometric amount for aluminum oxidation.

A commercial catalyst supplied by the Davison Chemical Company was also used. All catalysts were washed in distilled water prior to storage in ethanol at 0°C except for the commercial preparation which was stored in distilled water at 25°C.

*Catalyst nomenclature:* The nomenclature used to describe the catalyst type and the alloy from which it was activated is shown in the following examples. Type IIIA describes a Raney nickel catalyst prepared by the Type III preparation method from the alloy Type A; Type IIB describes a Raney nickel catalyst prepared by the Type II method from the alloy Type B.

solutions were used and the nomenclature and preparative methods used are summarized in Table 1.

#### (b) X-Ray Analysis

X-Ray-powder analysis were made on a Philips horizontal goniometer (type number P.W. 1380), a development of the instrument described by Parrish *et al.* (12). A catalyst sample was transferred from its storage medium to a 2% solution of cellulose nitrate in isoamyl acetate. A suspension of the catalyst was then dispersed over a clean glass slide and the plastic film formed on drying prevented air oxidation of the specimen.

Collimated unfiltered copper radiation (40 kV and 20 mA being the tube voltage and current, respectively) was diffracted from the mounted catalyst on to a bent lithium fluoride crystal monochromator set such that only the  $K\alpha$  component of the diffracted radiation was transmitted to a scintillation counter. Identification of weak reflections is facilitated by the enhanced signal-to-noise ratio afforded by such monochromating methods. Ratemeter outputs of the diffracted radiation, from scanning the sample (at an angular velocity of  $\frac{1}{2}^\circ$   $2\theta$ /min) between  $7.5^\circ$  (in  $\theta$ ) to  $73^\circ$  (in  $\theta$ ) with respect to the incident beam,

enabled the majority of the Raney nickel reflections to be recorded. The X-ray-diffraction spectra for all the catalyst samples were obtained under the same operating conditions.

Estimates of the mean crystallite dimensions were evaluated from the width of the profiles of the nickel reflections according to the classical Scherrer relation

$$L = K\lambda/B \cos\theta, \quad (1)$$

where  $L$  is the crystallite size in Å,  $\lambda$  is the X-ray wavelength in Å,  $K$  is a constant (taken as 0.9),  $B$  is the observed peak width at half maximum intensity for any given reflection, and  $\theta$  is the Bragg angle for that reflection.

For any given reflection, the observed value of  $B$  is governed by two factors. Not only does the poorly crystalline nature of the sample affect the peak profile of any given reflection but there are also such factors as the X-ray beam originating from a line source, the geometry of the specimen and X-ray absorption and scattering effects in the specimen. Such effects, termed as instrumental factors, have been discussed, e.g., by Alexander (13), and to differentiate between the two factors Warren's (14) relationship was used:

$$B^2_{\text{true}} = B^2_{\text{obsd}} - B^2_{\text{instr}}, \quad (2)$$

where  $B_{\text{true}}$  is the true width of any given reflection due to the structure of the sample only;  $B_{\text{obsd}}$  is the observed broadening at half the maximum intensity of any given reflection, and  $B_{\text{instr}}$  is the contribution to the observed peak width at half maximum intensity due to instrumental factors.

To obtain an estimate of the contribution to any given peak width by the instrumental factor, a suitable standard, in which there is virtually no line broadening due to its structure, is needed. One of good crystalline perfection is, therefore, required and quartz powder was used. For any Raney nickel reflection, the instrumental contribution to the observed profile was obtained from a neighboring quartz reflection recorded under the same conditions of analysis. As nickel is face-centered cubic, mean unit-cell-parameter evaluations were made from the interplanar spacings of all the recorded reflections by using the simple crystallographic relation between the two which holds for cubic structures.

### (c) Gas Adsorption and Chemical Analyses

Nitrogen isotherms were determined at  $-195^{\circ}\text{C}$ , and the methods of interpreting these data were the same as those used previously (10). Chemical analyses of catalysts for total nickel and total aluminum were made by W. R. Grace and Co. using standard procedures. Samples for adsorption studies and analyses were evacuated at  $130^{\circ}\text{C}$  for 24 hr, and the weight after this treatment was used in the determination of surface areas, pore volumes, and chemical analyses.

In the present paper, as in a previous publication (10), in estimating the composition of catalysts, nickel was assumed to be present as metallic nickel, and aluminum as either metal or  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . Any difference between the total weight and the sum of the weights of total nickel and total aluminum was taken as the  $\text{O}_3 \cdot 3\text{H}_2\text{O}$  component of the trihydrate, provided that the estimated amount of aluminum calculated as present in the trihydrate did not exceed the total aluminum content. Alumina trihydrates were identified as components of

the catalyst, and it has been shown that crystalline bayerite does not dehydrate appreciably during evacuation at  $130^{\circ}\text{C}$  (15).

## EXPERIMENTAL RESULTS

### (i) General Observations

X-Ray-diffractometer scans through the (111) and (200) reflections using the same instrumental conditions are shown in Fig. 1 for preparations from alloy A, and the mean crystallite sizes and the unit cell dimensions are given in Table 2. Sample IIA

TABLE 2  
EFFECT OF AQUEOUS AND ALKALI TREATMENT AT ELEVATED TEMPERATURES ON THE MEAN CRYSTALLITE AND UNIT CELL DIMENSIONS OF A IIA TYPE OF RANEY NICKEL

Catalyst type	Mean crystallite size (Å)	Mean unit-cell dimension (Å)
IIA <sup>a</sup>	36	3.535
IIA + 4 hr/ $100^{\circ}\text{C}/\text{H}_2\text{O}^a$	52	3.531
IIA + 4 hr/ $107^{\circ}\text{C}/\text{NaOH}$	55	3.532
IIIA <sub>1</sub>	58	3.528

<sup>a</sup> Alumina trihydrate reflections observed.

was prepared at  $50^{\circ}\text{C}$ , and portions of this material were subsequently treated with water and aqueous NaOH at 100 and  $107^{\circ}\text{C}$ , respectively. Sample IIIA<sub>1</sub> was activated with aqueous NaOH at  $107^{\circ}\text{C}$ . None of the reflections of the original alloy was found for these samples or in any of the preparations described in this paper. Samples activated at  $107^{\circ}\text{C}$  or treated at about this temperature had larger nickel crystallites than preparations made at  $50^{\circ}\text{C}$ . The unit-cell dimension for nickel in Raney nickel has been quoted as accurate to within  $\pm 0.01 \text{ \AA}$  (5) and  $0.004 \text{ \AA}$  (3) due to line broadening, but the values calculated for the catalysts in Table 2 are significantly larger than for crystalline nickel, which has been reported as  $3.5238 \text{ \AA}$  (16).

Reflections for alumina trihydrates were also found in some of the samples in Fig. 1, and these are shown more clearly for a IVA

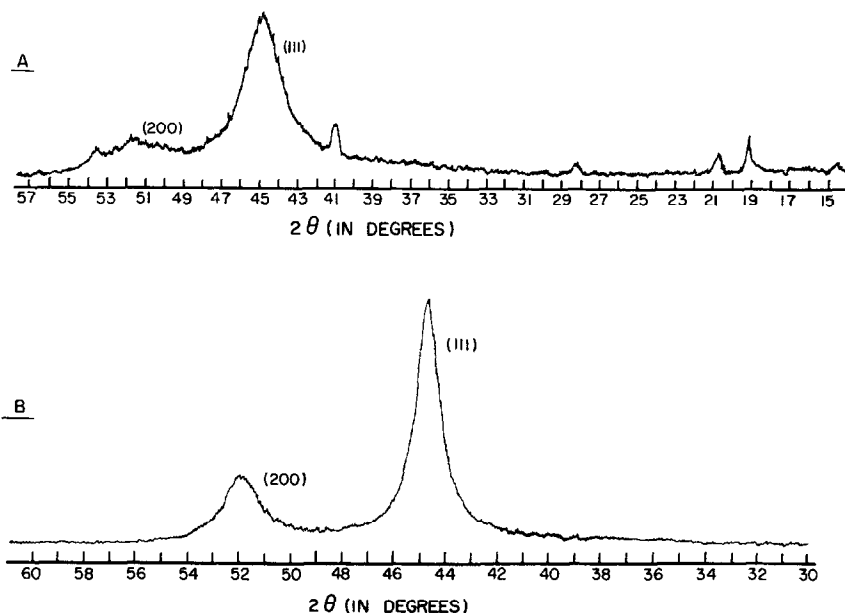


FIG. 1. A. X-Ray diffraction showing the (111) and (200) reflections from a Type IIA Raney nickel catalyst. The other reflections correspond to alumina trihydrate. B. X-Ray diffraction spectrum showing the (111) and (200) reflections from a Type IIIA Raney nickel catalyst.

preparation, containing a larger fraction of aluminum, in Fig. 2. These diffraction peaks can be interpreted as a mixture of bayerite (17) and gibbsite (18) as shown in Table 3. The diffraction patterns for the alumina trihydrate were always sharper than for nickel suggesting that the crystallites of the aluminas were larger than those of nickel. Similar alumina diffraction patterns were obtained from the solid in the grey-white suspension decanted from the catalyst in Type II preparations. Aluminas were not observed in preparations made at 107°C nor in samples treated with aqueous alkali at this temperature.

(ii) *Correlation between the Mean Crystallite Size of Nickel and Surface Area*

If nickel is the high-area component of the catalyst, the following equation should hold:

$$S = Kf 10^4 / \rho L, \quad (3)$$

where  $K$  and  $f$  are constants,  $K$  being a geometric factor (equal to 6 for spherical or cubic crystallites) and  $f$  being the fraction of crystallite surface available for gas adsorption,  $S$  is the surface area in  $\text{m}^2/\text{g}$ ,  $\rho$  the density in  $\text{g}/\text{cm}^3$ , and  $L$  is the mean

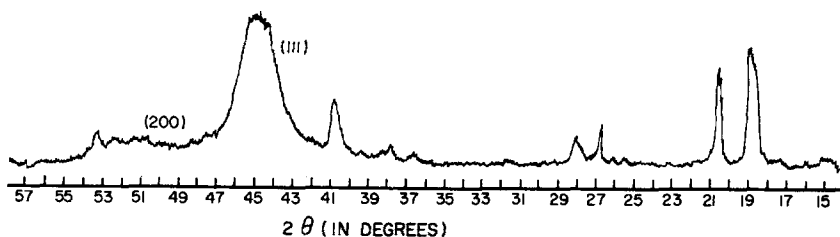


FIG. 2. X-Ray-diffraction spectrum showing the (111) and (200) reflections of a Type IVA Raney nickel catalyst. The other reflections correspond to alumina trihydrates.

TABLE 3  
X-RAY DIFFRACTION ANALYSIS OF THE CRYSTALLINE IMPURITY REFLECTIONS IN THE  
SPECTRA OF THE IVA AND IN SOME OF THE IIA TYPES OF RANEY NICKEL

Type IVA	Type IIA	Bayerite interplanar <i>d</i> spacing (Å) (17)	Index	Gibbsite interplanar <i>d</i> spacing (Å) (18)	Index
4.655	4.631	4.745	001		
4.305	4.298	4.381	100	4.37	110
	4.270			4.32	200
3.343				3.306	112
3.209		3.209	101		
3.187	3.164			3.187	11 $\bar{2}$
2.490				2.454	021
2.380		2.365	002	2.388	31 $\bar{1}$
2.213	2.203	2.222	111		
2.003		1.989	201	1.993	023
1.719	1.709	1.722	112		

size of the crystallites in Å. Plots of Eq. (3) in Figs. 3 and 4 show an approximately linear relationship between surface area and the reciprocal of crystallite size. In Fig. 3, the surface area per gram of catalyst is plotted, and here point 8, for the IVA sample with a large alumina content, falls far below the best fitting straight line. The surface area per gram of nickel is

plotted in Fig. 4 for catalysts with nickel analyses. The IVA preparation now lies in the cluster of points about the line (as point 5) but the linearity of the plot is not significantly improved for the other data. From the unit-cell dimensions, the density of nickel in the catalyst should be only slightly less than that of massive nickel, 8.9 g/cm<sup>3</sup>. Using this density and assuming

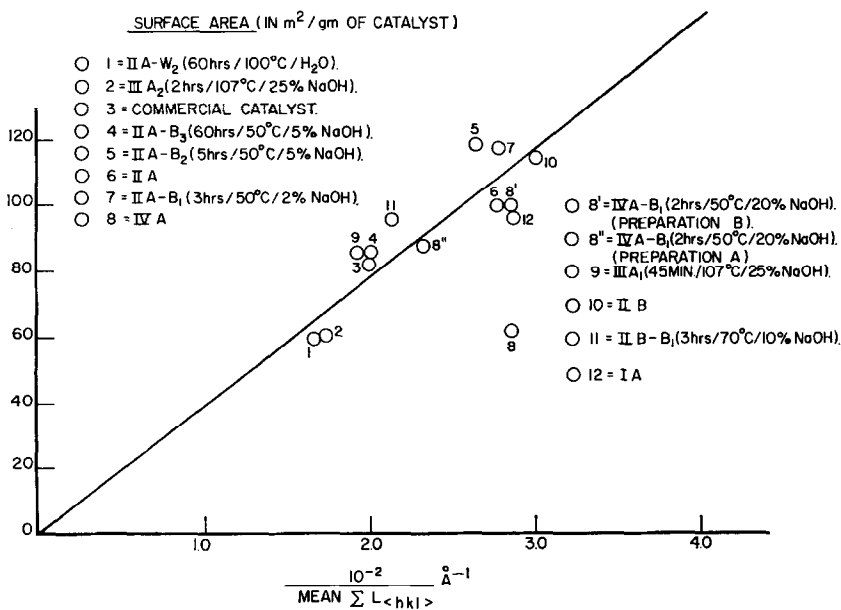


FIG. 3. Correlation between surface area in m<sup>2</sup>/g of catalyst and the reciprocal of the mean crystallite size for various types of Raney nickel.

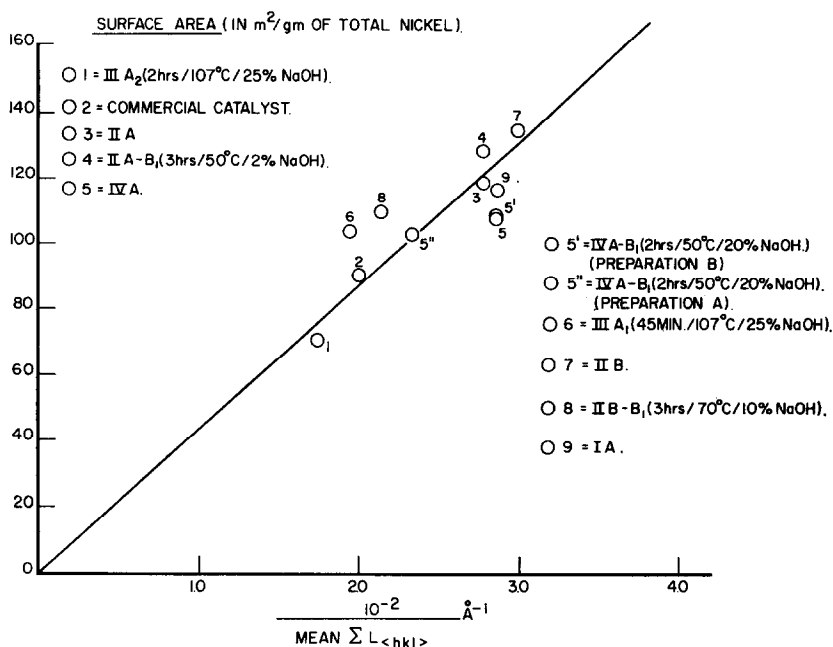


Fig. 4. Correlation between surface area in  $\text{m}^2/\text{g}$  of total nickel in the catalyst and the reciprocal of the mean crystallite size for various types of Raney nickel.

the crystallites to be spheres or cubes ( $K = 6$ ), the value of constant  $f$  is 0.65 from the correlation given in Fig. 4. For a given catalyst type the changes produced by alkali or water treatments are usually consistent with Eq. (3), but some marked deviation can be explained in various ways, e.g., the change from Type IIA (Point 6 in Fig. 3) to Type IIA- $B_1$  (Point 7) and Type IIA- $B_2$  (Point 5), in which there is an increased surface area for a constant crystallite size, could be explained by removal of crystalline, low-area alumina trihydrate, thought to block porous regions in the catalyst (10), thereby revealing fresh nickel areas for adsorption. The transition in surface from Type IVA (Point 8 in Fig. 3) to Type IVA- $B_1$  Preparation A and B (Points 8'' and 8', respectively) is probably due to the same effect of alumina removal. There has been surface topographical evidence from scanning electron microscopy for these observations (19).

Table 4 summarizes available data on crystal structure, pore geometry, and composition. The surface and pore-volume measurements were made on samples evacu-

ated at  $130^\circ\text{C}$ , and X-ray studies on specimens prepared without evacuation or heating. The changes caused by evacuation at  $130^\circ\text{C}$  are small as shown in the next section.

### (iii) X-Ray Examination of Vacuum-Heated Catalysts

Several catalysts were evacuated in glass adsorption tubes at temperatures from 130 to  $500^\circ\text{C}$ . The sample was transferred to ethanol without contacting air, and the catalyst in ethanol was prepared for X-ray diffraction. Crystallite size increased with increasing evacuation temperature (20) as shown in Table 5. The increase was most pronounced for the commercial catalyst which had the lowest content of alumina trihydrate. The unit-cell dimensions in all of the vacuum-heated catalysts are greater than that for crystalline nickel but they do not change regularly with temperature of evacuation.

## DISCUSSION

A difference of only about  $50^\circ\text{C}$  in the preparation or treatment temperature of

TABLE 4  
 SUMMARY OF STRUCTURAL AND COMPOSITIONAL DATA ON RANEY NICKEL

Catalyst type	Unit cell (Å)	Mean crystallite size (Å)	Surface area (m <sup>2</sup> /g)	Pore vol (cm <sup>3</sup> /g)	Mean pore diam (Å)	Total Al (%)	Total Ni (%)	Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O (%)
Low temperature or low temperature/short-time treated preparations generally have higher surface areas and smaller crystallite sizes								
IA	3.547	35	96	.055	23	9.55	81.66	14.13
IIA	3.532	36	99	.062	25	9.09	83.79	10.89
IIA-B <sub>1</sub> (3 hr/50°C/2% NaOH)	3.535	36	118	.098	33	6.67	91.31	3.10
IIA-B <sub>2</sub>	3.540	38	119	.098	33	9.25	59.54 <sup>a</sup>	
(5 hr/50°C/5% NaOH)						3.20	79.16	
IIIB	3.547	33	115	.082	29	7.71	85.31	10.68
IVA	3.535	35	62	.048	31	23.67	57.22	29.26
IVA-B <sub>1</sub> (2 hr/50°C/20% NaOH) (Preparation B)	3.529	35	100	.103	41	9.57	92.12	0
High-temperature or low-temperature/long-time-treated preparations generally have higher surface areas and larger crystallite sizes								
IIA-B <sub>3</sub>	3.529	50	86	.130	61	3.76	70.80 <sup>a</sup>	
(60 hr/50°C/2% NaOH)						3.36	69.14	
IIA-W <sub>2</sub>	3.532	52	60	.071	48			
(60 hr/100°C/H <sub>2</sub> O)								
IIIB-B <sub>1</sub>	3.535	47	96	.097	41	4.69	87.50	9.72
(3 hr/70°C/10% NaOH)								
IIIA <sub>1</sub>	3.538	52	86	.125	58	4.51	82.88	13.06
(45 min/107°C/25% NaOH)								
IIIA <sub>2</sub>	3.529	58	61	.145	96	4.00	86.31	11.57
(2 hr/107°C/25% NaOH)								
Commercial catalyst	3.532	50	82	.125	61	5.96	91.67	3.64
IVA-B <sub>1</sub> (2 hr/50°C/20% NaOH) (Preparation A)	3.532	43	88	.133	61	7.32	85.12	11.46

<sup>a</sup> Nickel estimates are anomalously low from both determinations and could be due to oxidation effects (see text). Estimates of alumina trihydrate content are, therefore, meaningless.

TABLE 5  
COMPARISON OF CRYSTALLITE DIMENSIONS ON ORIGINAL AND VACUUM-HEATED CATALYSTS

Catalyst type	Evacuation temp (°C)	Mean crystallite size (Å)	Unit cell dimension (Å)	Composition	
				Total Al(%)	Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O(%)
IIA	None	36	3.532	9.1	10.9
	310	40	3.547		
	500	57	3.533		
IIB	None	33	3.547	7.7	10.7
	130	36	3.559		
IIIA <sub>1</sub>	None	52	3.538	4.5	13.0
	130	57	3.531		
Commercial catalyst	None	50	3.532	6.0	3.6
	130	61	3.534		
	300	75	3.536		
	490	104	3.532		
IVA	None	35	3.535	23.7	29.3
	130	40	3.534		

Raney nickel can induce a noticeable change in the degree of crystallite enlargement even though these dimensions are less than 100 Å, values in keeping with other data reported in the literature for this catalyst (21-23). The absolute values of crystallite sizes from the Scherrer equation are not usually regarded as being very accurate, but in different samples of a given preparation, however, the relative sizes between the different samples are given accurately (22). A reasonable correlation was obtained between surface area and the average crystallite size, and assuming spherical or cubic crystallites and the normal density for nickel, 65% of the geometric area of the crystallites is available to gas adsorption. In other words, the surface areas reflect the particle sizes of a catalyst which can differ markedly from the crystallite sizes as estimated by X-ray line-broadening methods.

The alumina trihydrates found in Raney nickels result from the hydrolysis of aluminate ion. The solubility of alumina in aqueous solutions increases with increasing concentration of sodium ion and increasing temperature and decreases with increasing concentration of aluminate ion. X-Ray diffraction patterns for alumina trihydrates were found only for catalysts activated at 50°C, Type I and II, and 80°C, Type IV. These diffraction patterns had sharp peaks

suggestive of large crystallites. Subsequent treatment of samples of Types II and IV with aqueous alkali at 50°C removed effectively the alumina trihydrate reflections.

The concentration of alumina trihydrates calculated from the chemical analysis, however, in many cases remained as large as in the original sample, particularly for alkali treatments of long duration, as shown in Table 4. Some of these results, especially in the case of Types IIA-B<sub>2</sub> and IIA-B<sub>3</sub>, can be explained by part of the activated nickel being oxidized in prolonged alkali treatment at 50°C or in preparation at 107°C though no evidence of NiO was observed from X-ray diffraction.

Observation of both the gibbsite and bayerite modifications of alumina trihydrate in Raney nickel differs from that reported by Nishimura (24) who observed only bayerite. In the precipitation of aluminas from highly alkaline solutions, Oomes, de Boer and Lippens (25), however, found that gibbsite was favored at 50°C and bayerite at lower temperatures.

It has been reported (3, 4, 10) that the surface areas were almost unchanged in Raney nickel catalysts after evacuation at temperatures up to 250°C. This implied that some degree of thermal stability is associated with this catalyst type. A comparison of crystallite dimensions between the original and treated preparations (in



Table 5), however, illustrates that some crystallite development has occurred which is more marked at higher evacuation temperatures. The changes of crystallite size in catalysts heated *in vacuo* up to 130°C would, however, be expected to impart only a slight effect on surface area (5). Changes in crystallite dimensions with increasing evacuation temperature are most marked in the commercial catalyst, which has the lowest alumina trihydrate content. This could be suggestive of alumina imparting thermal stability to the catalyst.

Under aqueous conditions, increased reaction times, higher temperatures, and greater alkali concentrations give, in general, products of decreased surface area, increased pore volume and mean pore diameter. These changes are accompanied by an increase in crystallite size and a decrease in the total aluminum, and alumina trihydrate content. Changes induced in the crystallite structure of Raney nickel by differing preparation and treatment conditions in an aqueous environment are more marked than those caused by comparable thermal conditions *in vacuo*. This is illustrative of chemical as well as thermal processes being of profound importance in determining the nature of any given Raney nickel catalyst (26).

#### ACKNOWLEDGMENT

The authors acknowledge gratefully fellowship funds provided by the Davison Chemical Company Limited and thank Dr. F. G. Ciapetta, Dr. T. H. Cheavens, and N. E. Miller for helpful discussions and for furnishing catalyst samples. The assistance of the Washington Research Center of W. R. Grace and Co. in the provision of analytical data is also gratefully appreciated.

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