

## Chemistry of Nickel-Alumina Catalysts

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A study of the chemistry involved in preparation, pretreatment, and reduction of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts was carried out using hydrogen chemisorption, thermal gravimetric analysis, and chromatographic analysis. Data showing effects on nickel surface area of calcination, heating rate during reduction, nickel loading, and passivation are presented and discussed. The results indicate that controlled decomposition of alumina-supported nickel nitrate in hydrogen atmosphere (without prior calcination) tends to maximize nickel surface area, dispersion, and reduction to nickel metal. Nickel surface area and the fraction of nickel reduced to the metallic state both increase as the hydrogen space velocity during reduction is increased. Upon increasing the reduction temperature from 300 to 500°C, the percentage reduction to nickel metal is increased from 40 to 100% whereas nickel surface area changes relatively little.

### I. INTRODUCTION

Supported nickel catalysts find wide application in many important industrial hydrogenation processes including methanation of coal synthesis gas. Yet there is little quantitative information in the literature dealing with the chemistry of nickel catalyst preparation. In such preparations one is confronted with the difficult problem of understanding and controlling in a reproducible manner many different steps such as drying, calcination, reduction, etc., and in each step such variables as time, temperature, heating rate, and gas flow rate. Naturally the goal in such preparations is to maximize the surface area and activity of each catalyst. It would be highly desirable, therefore, to understand

the chemical reactions occurring in each preparation step and the effects of controllable variables on the resultant catalytic surface.

In laboratory or commercial preparation of catalysts by impregnation or coprecipitation of metal salts, it is common procedure to decompose the metal salts to the oxide by calcination in air at 400-500°C followed by reduction in flowing hydrogen at 400-500°C to obtain well-dispersed metals. However, previous studies (1-11) indicate that nickel supported on alumina is not completely reduced under typical reducing conditions to the metallic state, but rather only after many hours of exposure to hydrogen at very high temperatures (10, 11). The degree of reduction of nickel in alumina-supported catalysts prepared in various ways generally increases with

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increasing reduction temperature and increasing nickel content (9, 11). Samples prepared by impregnation generally achieve a higher degree of reduction than samples prepared by precipitation (7, 8). Increasing the temperature of the calcination step prior to reduction significantly decreases the reducibility of nickel on alumina (2, 4, 5, 7, 8). Indeed, data in this study suggest that more complete reduction to metallic nickel is possible, if the supported nickel salt is not calcined at all but is decomposed in hydrogen rather than air.

This study of nickel-alumina catalysts was undertaken first, to determine the effects of various pretreatment steps and controllable preparation variables such as reduction temperature, space velocity, and heating rate on nickel surface area and on the extent of reduction to nickel metal, and second, to unravel the chemistry of catalyst calcination and reduction.

## II. EXPERIMENTAL

### A. Apparatus and Procedure

Adsorption measurements were performed using a conventional Pyrex glass volumetric adsorption apparatus capable of  $10^{-6}$  Torr (1 Torr =  $133.3 \text{ N m}^{-2}$ ) vacuum. The catalyst sample was placed in a flowthrough cell to permit reduction in

flowing hydrogen prior to the adsorption measurement. The amount of gas adsorbed by the catalyst was determined by means of a calibrated gas buret connected to a manometer backed with a metrically calibrated mirror. Following reduction of catalyst samples in flowing hydrogen (50  $\text{cm}^3/\text{min}$ ) at 450–500°C and evacuation at 400–500°C nickel surface areas were measured using hydrogen chemisorption at room temperature (12). The amount of hydrogen adsorbed by the catalyst was measured after allowing 45 min for the adsorption to approach equilibrium. Naturally, this does not represent the maximum possible  $\text{H}_2$  uptake since there is a slow, activated or diffusion-controlled adsorption over a period of hours. Nevertheless, it does serve as a reproducible property of these surfaces.

Figure 1 shows a typical room temperature adsorption isotherm for hydrogen adsorbed on  $\text{Ni}/\text{Al}_2\text{O}_3$ . The data show that the gas taken up by the sample approaches saturation at about 10 cm Hg pressure (1 cm Hg =  $1333 \text{ N m}^{-2}$ ) and that physical adsorption on the support is small (in view of the almost zero slope of the isotherm). The uptake due to chemisorption was found by extrapolating to zero pressure the straight-line portion of the isotherm above the saturation pressure. Catalyst surface areas were calculated assuming  $\text{H}/\text{Ni}_{(s)} = 1$  and a surface area of  $6.5 \text{ \AA}^2$  per nickel atom ( $10 \text{ \AA} = 1 \text{ nm}$ ), based on an average of the areas for the (100), (110), and (111) planes.

The extent of reduction to nickel metal (reduced catalysts) was determined after hydrogen chemisorption by evacuating the sample to 450°C and pressures of  $10^{-4}$  to  $10^{-5}$  Torr followed by measuring the uptake of pure oxygen at 400–430°C. It was assumed that in the reduced catalyst all unreduced nickel was in the form of NiO and that at 400–430°C in the presence of oxygen all nickel in the metallic form would be oxidized to NiO. Comparison of the actual oxygen uptake with amount needed

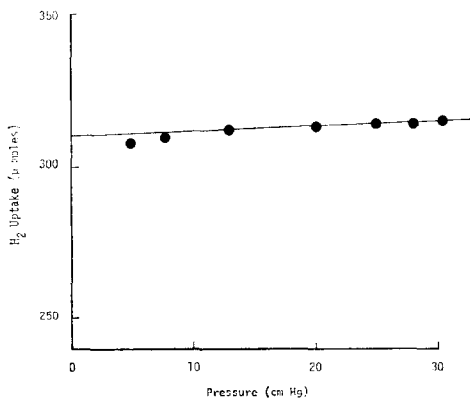


FIG. 1.  $\text{H}_2$  chemisorption 9 wt%  $\text{Ni}/\text{Al}_2\text{O}_3$ ; reduced, 7 hr, 420°C; evac. 2 hr, 420°C.

if all of the nickel were assumed to be initially in the metallic state constituted the basis for calculating the percentage reduction to the metal.

Selected samples were also analyzed for metallic nickel by passing CO over previously reduced catalysts at 80°C and a space velocity of 300 hr<sup>-1</sup> (5, 6). The Ni(CO)<sub>4</sub> thus formed was collected during 24 hr by decomposition to a nickel mirror in a preweighed glass tube at 350°C. Two of the samples were exposed to 7 and 25 ppm H<sub>2</sub>S in H<sub>2</sub> at 450°C for 3-4 hr prior to cooling and exposure to CO.

The decomposition products formed by passing air or hydrogen through alumina-supported nickel nitrate samples were analyzed with a Hewlett-Packard 5830 chromatograph using a Poropak Q column. In each of the chromatographic runs hydrogen or air was passed at a flow of 500 cm<sup>3</sup>/min through a 10-g sample placed in a stainless steel reactor as the temperature was slowly increased from 25 to 300°C.

Sample weight versus temperature measurements were performed using a Dupont 951 Thermal Gravimetric Analyzer with a 990 control. Selected nickel samples were analyzed chemically by x-ray fluorescence spectroscopy.

### B. Materials

Analytically pure Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Baker) was used in the TGA experiments and in preparation of supported nickel catalysts. Solutions of this salt were impregnated to incipient wetness into SA Med. Alumina (Kaiser), SAS Med. Alumina Pellets (Kaiser), and 100 S Pellets (Houdry). After impregnation the samples were dried in air at 80-100°C followed by either calcination at 400°C for 1 or 2 hr and subsequent reduction in flowing hydrogen or by direct reduction in hydrogen. Hydrogen gas (99.96%) was purified by passing through a palladium Deoxo purifier (Engelhard) and dehydrated molecular

sieve or a liquid nitrogen trap. The carbon monoxide (C. P. Grade, Matheson) was passed through a molecular sieve prior to use.

## III. RESULTS AND DISCUSSION

### A. Effect of Calcination on Nickel Surface Area

The effect of calcination at 400°C on nickel surface area is demonstrated by hydrogen chemisorption data in Table 1. Six different catalysts were prepared by impregnation of alumina with nickel nitrate after which three of these catalysts were calcined in air at 400°C for 1 hr and then reduced in flowing hydrogen at 500°C for 12 hr. The other three catalysts were reduced in hydrogen without prior calcination. The resulting nickel surface areas and dispersions (dispersion defined as the fraction of total nickel atoms found at the surface) are significantly larger for samples reduced without prior calcination compared to samples calcined prior to reduction. In other words, the calcination at 400°C is clearly detrimental to preparing a high nickel surface area. Similar observations have been reported for Ni/SiO<sub>2</sub> catalysts (13) and carbon-supported iron and platinum-iron alloy catalysts (14).

The observation of lower hydrogen surface areas for calcined samples has at least three possible explanations which are

TABLE I  
Effect of Calcination on Nickel Surface Area

Wt% Ni/Al <sub>2</sub> O <sub>3</sub>	Calcined at 400°C, 1 hr	Reduced at 500°C, 12 hr	Surface area (m <sup>2</sup> /g)	Percentage dispersion <sup>a</sup>
9	No	Yes	10.0	15.9
9	Yes	Yes	4.3	6.9
15	No	Yes	14.6	13.8
15	Yes	Yes	5.2	5.0
27	No	Yes	18.6	10.7
26	Yes	Yes	10.3	5.7

<sup>a</sup> Dispersion is the fraction of total nickel atoms found at the surface.

not mutually exclusive:

(i) The extent of reduction to nickel metal is less for a precalcined sample compared to a sample prepared by direct decomposition of the metal salt in hydrogen; in addition, any unreduced NiO at the surface does not chemisorb hydrogen.

(ii) Calcination produces via a sintering mechanism relatively large particles of nickel oxide which are reduced (by some unknown mechanism) to metal crystallites of approximately the same size and are larger than nickel crystallites produced by direct decomposition of supported nickel nitrate in hydrogen.

(iii) In high temperature calcination of nickel-alumina catalysts NiO interacts with Al<sub>2</sub>O<sub>3</sub> to form a very stable NiAl<sub>2</sub>O<sub>4</sub> spinel, which cannot be reduced even under very severe, high temperature reducing conditions.

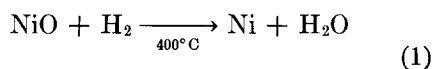
The first explanation is reasonable in view of previous studies (2, 4, 5, 7, 8) which show that for progressively higher temperatures of calcination prior to reduction, a significantly lower fraction of the total nickel is reduced to the metallic state. In this study the percentage reduction to nickel metal for noncalcined samples varied from 45–100%, whereas corresponding values for calcined samples reduced under equivalent conditions of time and temperature in other studies (2, 5) ranged from 3–60% depending upon the calcination temperature as well as reduction time and temperature. Moreover, it was observed in this study that hydrogen chemisorption on NiO is indeed negligible compared to adsorption on nickel metal.

The second explanation of larger nickel oxide particles finds a precedent in a previous X-ray study (14) of carbon-supported iron in which very large oxide particles (500–1000 Å) were observed following calcination, whereas the decomposition of the supported nitrate in hydrogen produced significantly smaller particles

of iron metal (200–400 Å in diameter). On the other hand, Bicek and Kelley (4) have suggested that in reduction of calcined nickel-alumina, nickel crystallites are formed by growth from nickel ions or atoms; however, this particular inference was not apparently supported by experimental evidence. Unfortunately, X-ray diffraction scans of nickel-alumina catalysts in this study showed considerable overlap of the lines for Ni, NiO, and alumina making it practically impossible to differentiate various phases and to estimate crystallite sizes.

The third explanation involving a high temperature solid state reaction of nickel oxide with Al<sub>2</sub>O<sub>3</sub> to form a Ni Al<sub>2</sub>O<sub>4</sub> spinel is well documented in the literature (4, 15–19).

To better understand the chemical changes in the calcination and reduction processes, the decomposition of unsupported and supported Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in air followed by reduction in hydrogen was studied by means of thermal gravimetric analysis (TGA). The weight loss versus temperature curve from the TGA experiment for the unsupported nitrate is shown in Fig. 2. Decomposition of the nitrate to NiO in air is complete at 400°C as indicated by an observed weight loss of 75% compared with a calculated value of 74.3% for conversion of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O to NiO. If hydrogen is then passed through the sample at 400°C, the oxide is completely reduced to the metallic state as evidenced by an observed weight loss of 22.1% which compares favorably with a calculated value of 21.5% predicted for the decomposition of NiO to Ni metal,



$$\Delta H^\circ_{25^\circ\text{C}} = 0.4 \text{ kcal/mole.}$$

In the corresponding TGA experiment with supported nickel nitrate it was not possible to determine quantitatively the extent of oxidation and reduction in the

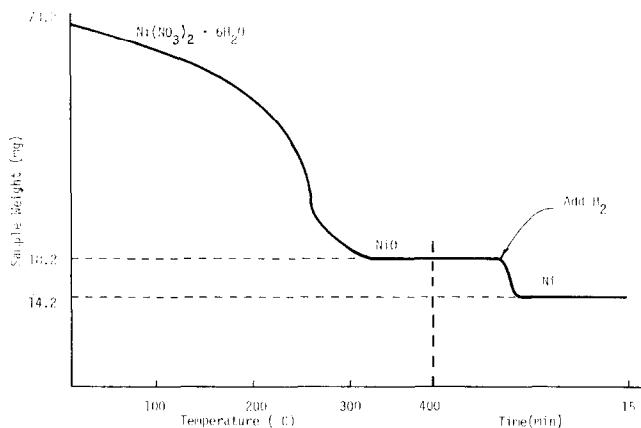


FIG. 2. Thermal gravimetric analysis of decomposition of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in air or helium, then hydrogen.

presence of air and hydrogen, respectively, mainly because after impregnation to incipient wetness and drying in air, the catalyst when heated continued to lose physically held water from the support and chemically held water from the hydrated nitrate. Therefore, attempts to establish an initial stoichiometric weight and quantitatively differentiate between partially or fully oxidized or reduced states were not successful. Nevertheless, it was determined, based on experiments discussed in a later section of this paper, that supported nickel samples (in this study) exposed to air at  $400^\circ\text{C}$  were oxidized to NiO.

#### B. Effect of Heating Rate during Reduction on Nickel Surface Area

The rate of temperature rise in hydrogen reduction of alumina-supported nickel ni-

trate or nickel oxide affects significantly the amount of nickel surface area obtained for a given catalyst as illustrated by data in Table 2. Nickel surface areas and dispersions are shown for two different catalyst pairs, for which the only difference in preparation for a given pair was the rate of temperature increase during reduction. Both 9% Ni/ $\text{Al}_2\text{O}_3$  catalysts were calcined at  $400^\circ\text{C}$  and then reduced in hydrogen at heating rates of approximately 15 and  $5^\circ\text{C}/\text{min}$ , respectively. The nickel surface area and dispersion are about 25% greater for the catalyst reduced with a slower rate of temperature increase. Neither of the 15% Ni/ $\text{Al}_2\text{O}_3$  catalysts were calcined, but rather prepared by decomposition of the nickel salt in hydrogen at heating rates of 5 and  $15^\circ\text{C}/\text{min}$ , respectively. The surface area and dispersion are twice as large for

TABLE 2  
Effect of Heating Rate in Reduction of Ni/ $\text{Al}_2\text{O}_3$

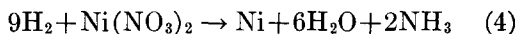
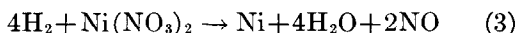
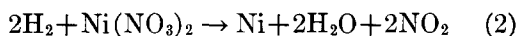
Wt% Ni/ $\text{Al}_2\text{O}_3$	Calcined at $400^\circ\text{C}$	Rate of temperature Rise in reduction	Surface area ( $\text{m}^2/\text{g}$ )	Percentage dispersion
9	Yes	Fast, $\sim 15^\circ\text{C}/\text{min}$	3.2	5.1
9	Yes	Slow, $\sim 5^\circ\text{C}/\text{min}$	4.3	6.9
15	No	Fast, $\sim 15^\circ\text{C}/\text{min}$ (No hold)	6.5	6.1
15	No	Slow, $\sim 5^\circ\text{C}/\text{min}$ (4 hr hold at $230^\circ\text{C}$ )	14.6	13.8

the catalyst reduced with a low heating rate. There is clearly a larger effect for catalysts reduced without prior calcination.

The chemistry of nickel oxide reduction (see Eq. 1 above) is fairly straightforward, although the precise mechanisms are not known. Hydrogen interacts with nickel oxide to produce water, which if not removed from the catalyst, aids in transport and growth of nickel crystallites. The low enthalpy for reaction of nickel oxide with hydrogen suggests that overheating effects are not expected; however, a slow heating rate does allow water to be driven off and transported from the catalyst by the flowing stream of hydrogen, thus minimizing the effects of sintering. In fact, it is possible to control catalyst dispersion by controlling either the amount of water removed by drying prior to reduction (20) or by controlling the heating rate and partial pressure of water during reduction (19).

In the decomposition of nickel nitrate in hydrogen atmosphere, there is also considerable water formed plus an additional heating effect which can influence the ultimate dispersion. Three possible decomposition reactions for nickel nitrate in

hydrogen are:



The heats of reaction at 25°C are 11.9, -86.5, and -261.2 kcal/mole, respectively. Since Reactions 3 and 4 are very exothermic, a fast heating rate could possibly result in a temperature runaway and extensive sintering at a temperature where the rates of the reactions are significant.

This exothermic effect was actually observed during TGA measurements involving the decomposition of 82 mg of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in flowing hydrogen. The thermogram in Fig. 3A shows a smooth weight loss with increasing temperature up to about 250°C (probably loss of water) at which point there was a rapid temperature rise in a matter of seconds to almost 800°C, followed by a rapid weight loss at almost constant temperature, and then a very rapid cooling at constant weight. Figure 3B shows the same reaction under similar conditions for alumina-supported nickel nitrate. The exotherm is much smaller in

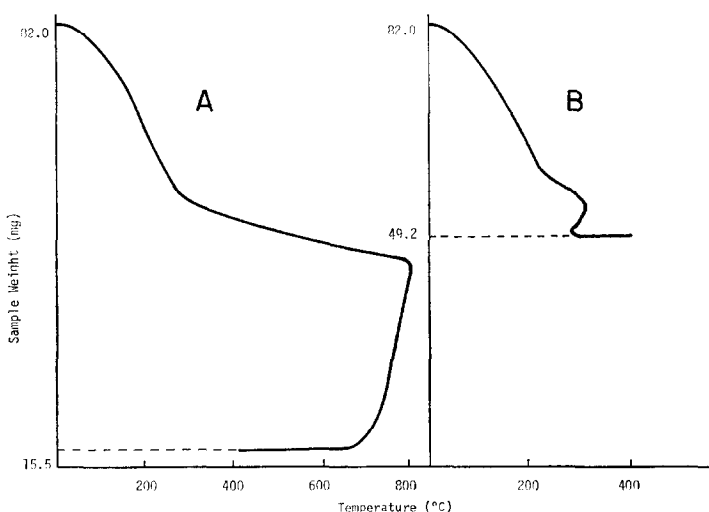


FIG. 3. Thermal gravimetric analysis of decomposition of (A) unsupported and (B) supported  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2$ .

magnitude since the amount of nitrate is smaller and the support functions as a heat sink. Nevertheless, the heat effect might be of disastrous proportions in a large bed of catalyst of industrial capacity. It is possible, however, to minimize the exothermic heat release and obtain a highly dispersed nickel catalyst by controlled temperature decomposition in hydrogen atmosphere. TGA analysis and chemisorption measurements indicate that a low heating rate coupled with an intermittent hold at about 230°C for 1 hr eliminates any detrimental heat effects and assures reasonable dispersion of nickel on alumina. Diluting hydrogen with an inert gas to obtain better heat removal during reduction may result in lower surface areas unless trace contaminants are removed from the inert gas. For example, reduction with an 8% H<sub>2</sub>, 92% N<sub>2</sub> mixture consistently produced catalysts with lower surface areas compared to reduction of the same samples with pure hydrogen. Nevertheless, reduction of alumina-supported nickel nitrate with a 20% H<sub>2</sub>, 80% N<sub>2</sub> mixture purified by passing through a palladium catalyst and zeolite trap produced a 15 wt% Ni/Al<sub>2</sub>O<sub>3</sub>, with 19.1 m<sup>2</sup>/g nickel area compared to 16.2 m<sup>2</sup>/g for an identical sample reduced in pure hydrogen.

Although it is clear that the decomposition of nickel nitrate in hydrogen is very exothermic and that the decomposition rate is very rapid at a temperature approaching 250°C, it is not obvious which of Reactions 2-4 predominates at any given set of conditions. The stoichiometries of Reaction 2-4 are such that differing amounts of hydrogen are required for each reaction. Hence, the decomposition rate and mechanism may also depend upon the hydrogen flow rate, especially at temperatures where the reactions are very fast.

Chromatographic analysis and pH measurement of the decomposition products for nickel nitrate heated in flowing hydrogen as a function of time and temperature

were undertaken to determine by inference the most important reactions. Measurements of pH were made during reduction of a dozen different 15 wt% Ni/Al<sub>2</sub>O<sub>3</sub> samples by placing Hydrion paper in the gaseous product stream from a small Pyrex reactor containing 1-2 g of catalyst. The measurements showed a pH of 1 as the sample was heated from about 100 up to 250°C at which temperature the pH changed rapidly to 7, then very rapidly to 8-10. Acidic products were heaviest in the temperature range from about 200 to 250°C. The basic products were predominant from about 270 to 360°C. In the range from 360 to 420°C the pH decreased to 7.

Chromatographic analysis of the decomposition products from a stainless steel reactor indicated NO and NO<sub>2</sub> formation observed initially at 218°C which increased in magnitude up to about 250°C. Upon reaching 246°C there was a temperature excursion to 275°C (duration of about 2-3 min), followed by a decrease in temperature over 10 min to 247°C. Then as the temperature increased gradually from 250 to 275°C, the concentration of NO and NO<sub>2</sub> decreased; there was no significant NO<sub>2</sub> formation above 275°C. The NO concentration remained small until the temperature reached 330°C and then increased again. During the chromatographic measurements a strong acid smell was detected in the range of 218 to 230°C and a brown gas (presumably NO<sub>2</sub>) was observed at 240-250°C. A smokey white vapor was observed in the reduction gas products just prior to and during the transition from acidic to basic products. No NH<sub>3</sub> was detected chromatographically; however, it was likely absorbed by water in our reactor condenser trap.

The pH and chromatographic data together suggest that the reactions to produce NO and NO<sub>2</sub> are important up to about 250°C at which temperature the reaction to produce ammonia becomes important. Because this latter reaction is so exothermic

the reaction can run away if the heating rate is sufficient.

*C. Effects of Reduction Temperature on Nickel Surface Area and Percentage Reduction to Nickel Metal*

The determination of percentage reduction of nickel to the metallic state using  $O_2$  chemisorption at 400–430°C requires that the stoichiometry of the oxide thus formed be precisely known. Hill and Selwood (10) explained  $H_2$  consumption values in excess of those required for reduction of NiO by assuming the existence of higher oxidation states for surface nickel (e.g.,  $Ni_2O_3$ ). They argued that for small nickel oxide crystallites, present in dilute catalysts, the surface represents a significant fraction of the total nickel oxide and consequently one measures an average oxidation state higher than +2. Indeed, in nickel-alumina samples containing 3–4 wt% nickel, the average oxidation state after calcination at 450°C was 2.6–2.7 (10). Nevertheless, oxidation states of 2.0 were observed for catalysts having nickel loadings in excess of about 5 wt% (10). Moreover, Holm and Clark (7) observed Ni valences of 2.55, 2.14, 2.04, and 1.91 for a 3% Ni/ $Al_2O_3$  calcined in air at 300, 400, 500, and 700°C, respectively, showing that NiO is formed above 400°C. Since bulk phases of  $Ni_2O_3$  or  $NiO_2$  are not stable in the anhydrous state (21) and since the nickel catalyst loadings in this study were considerably greater than 5%, it is reasonable to assume an average stoichiometry of NiO.

Nevertheless the nickel oxide stoichiometry and the validity of the method used for measuring extent of reduction to metallic nickel were checked in two independent experiments. First, a 0.52-g sample of 14.0% Ni/ $Al_2O_3$  which had been reduced 10 hr at 485°C (space velocity of 2000  $hr^{-1}$ ) was reduced an additional 135 hr at 450°C and 2000  $hr^{-1}$ . Since Hill and Selwood (10) found a reduction time of 130 hr adequate for complete reduction of a 6.5% Ni/ $Al_2O_3$

previously calcined at 450°C, there is little doubt that the 14.0% Ni/ $Al_2O_3$  catalyst prepared (in this study) without precalcination and reduced for 145 hr contained only completely reduced nickel. In fact, the percentage reduction to metallic nickel increased from 93% (10 hr reduction) to 98% (145 hr reduction) assuming stoichiometric formation of NiO upon exposure to  $O_2$ ; the  $H_2$  adsorption uptake increased proportionately from 203.5 to 211.1  $\mu mol/g$ . These data are consistent within experimental error with a stoichiometry for nickel oxide of NiO and an oxidation state for nickel of 2.0, assuming complete reduction to nickel.

The second set of experiments involved independent determination of the extent of reduction using the selective removal of metallic nickel with CO (80°C) to form nickel carbonyl (5, 6). The nickel carbonyl thus formed was decomposed in a preweighed glass tube at 350°C. The results including calculated extents of reduction compared with calculations from the  $O_2$  titration are listed in Table 3. The data show good agreement between percentage reduction values determined by nickel carbonyl extraction and by  $O_2$  uptake; the effective nickel valence for the oxide formed at 400–430°C is 2.12–2.16, assuming the  $Ni(CO)_4$  extraction technique is 100% efficient. Apparently, presulfidation had no effect on the results within the time frame of the extractions, although sulfur has been reported as a catalyst for  $Ni(CO)_4$  formation (22).

Data presented in Figs. 4 and 5 illustrate the effects of reduction temperature on measured nickel surface area and percentage reduction to nickel metal, respectively. Each of the impregnated and dried (but uncalcined) samples of a 13.5 wt% Ni/ $Al_2O_3$  catalyst was reduced approximately 16 hr in flowing hydrogen at a space velocity of 1500–2000  $hr^{-1}$ , and the heating rate was held to less than 5°C/min, interrupted only by a 1 hr hold at 230°C to prevent undesir-



TABLE 3  
Extent of Reduction Determined by Nickel Carbonyl Extraction

Run no.	Weight of sample (g)	Weight of Ni expected (g) for complete removal	Weight of Ni measured (g)	Percentage reduction	Percentage reduction based on O <sub>2</sub> titration	Effective Ni valence
1 <sup>a</sup>	2.0373	0.2852	0.2427	85.1	92.5	2.16
2 <sup>b</sup>	6.8852	0.9639	0.8358	86.7	92.5	2.12
3 <sup>c</sup>	3.9506	0.5531	0.3889	70.3	74.2	2.12

<sup>a</sup> Catalyst presulfided with 7 ppm H<sub>2</sub>S for 260 min; CO exposure, 16.5 hr at 80°C.

<sup>b</sup> Catalyst presulfided with 25 ppm H<sub>2</sub>S for 105 min; CO exposure, 24 hr at 80°C.

<sup>c</sup> No presulfidation; CO exposure, 26.5 hr at 80°C.

able heating effects otherwise due to the exothermic decomposition reactions above 250°C.

The surface area data plotted as a function of reduction temperature (see Fig. 4) from 300 to 500°C form a very flat convex parabola with a maximum in the nickel surface area of 20 m<sup>2</sup>/g occurring at about 350 to 400°C and minimum values of 14.3 and 15.3 m<sup>2</sup>/g occurring at the temperature extremes, 300 and 500°C, respectively. This modest variation in surface area is in contrast to the relative drastic increase in

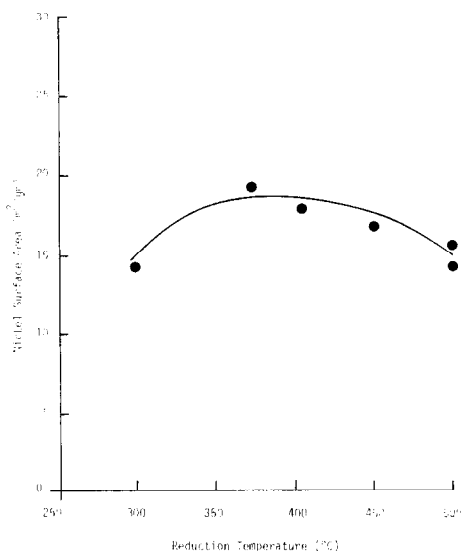


FIG. 4. Effect of reduction temperature on nickel surface area, 13.5 wt% Ni/Al<sub>2</sub>O<sub>3</sub> (H<sub>2</sub> GHSV = 1500–2000 hr<sup>-1</sup>).

percentage reduction to nickel metal (from 43 to 100%) over the same range of temperature (see Fig. 5). Dzis'ko *et al.* (9) observed that in supported nickel catalysts, the mean crystallite size of nickel is increased as the degree of reduction to the metal is increased. Our data are consistent with their observation; that is, the relatively small variation in surface area with

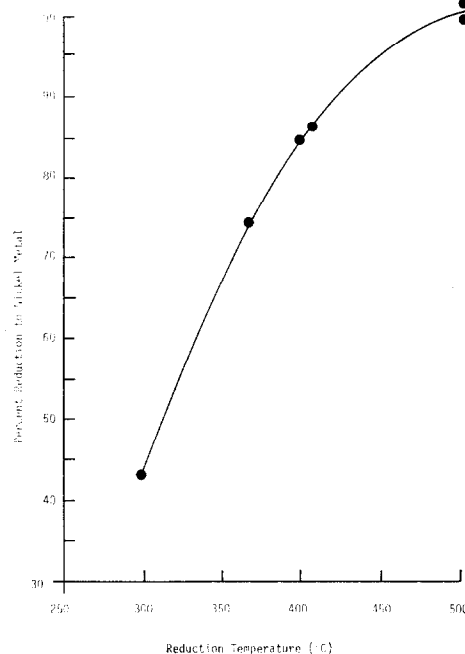


FIG. 5. Effect of reduction temperature on percentage reduction to nickel metal, 13.5 wt% Ni/Al<sub>2</sub>O<sub>3</sub> (H<sub>2</sub> GHSV = 1500–2000 hr<sup>-1</sup>).

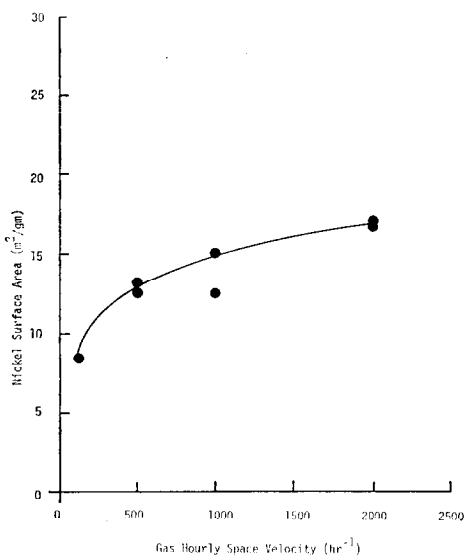


FIG. 6. Effect of hydrogen space velocity on surface area 14.0 wt% Ni/Al<sub>2</sub>O<sub>3</sub> (reduced at 485°C, 10–12 hr).

increasing temperature is a result of two opposing effects:

(i) The fraction of nickel reduced to the metal increases with increasing temperature. This metallic nickel thus formed chemisorbs hydrogen whereas unreduced nickel does not.

(ii) At the same time, however, the average crystallite size increases with temperature which means the fraction of surface nickel metal available for hydrogen chemisorption decreases.

Given a choice of reducing conditions for a nickel-alumina catalyst, it appears advantageous to reduce at 500°C so as to maximize the extent of reduction to nickel metal while at the same time assuring an equilibrium particle size which is stable against sintering, especially at use temperatures lower than 450°C. Accordingly, these advantages are achieved without sacrificing appreciable catalytic surface area.

What is the time requirement to reach a final state of reduction if no calcination is used in the preparation? The experience from preparation of many catalysts in this

study is that for a given reduction temperature and space velocity approximately a minimum of 8–10 hr is required to reach reasonably constant values of surface area and fractional reduction to nickel metal starting with a freshly impregnated and dried sample. If the reduction is taken beyond this minimum time requirement, the surface area and extent of reduction are expected to increase very little, assuming temperature and space velocity are fixed. This 8–10 hr minimum reduction time for uncalcined impregnated samples is apparently less than the 15–20 hrs required for Ni/Al<sub>2</sub>O<sub>3</sub> catalysts which were previously calcined (2).

#### D. Effects of Hydrogen Space Velocity on Nickel Surface Area and Percentage Reduction to Nickel Metal

Nickel surface area and extent of reduction measurements are shown in Figs. 6 and 7 as a function of hydrogen space

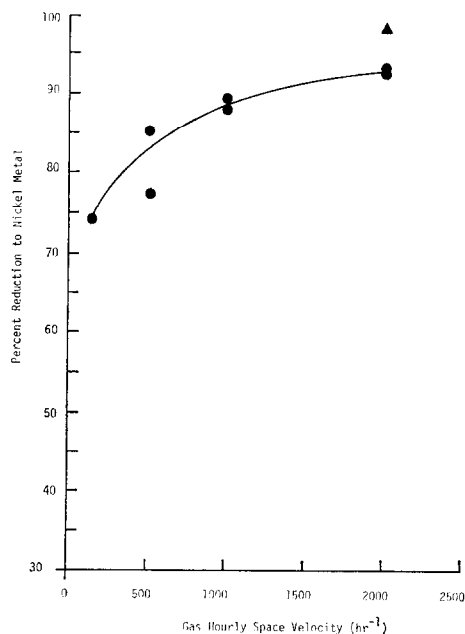


FIG. 7. Effect of hydrogen space velocity on percentage reduction to nickel metal, 14.0 wt% Ni/Al<sub>2</sub>O<sub>3</sub>. ●, reduced at 485°C, 10–12 hr; ▲, reduced an additional 135 hr at 450°C.

velocity. The data correspond to various samples of the same 14.0 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, each reduced in a large ceramic combustion tube approximately 10 hr at 490°C. Nickel surface areas were measured for a portion of each sample after passivation, transfer to a glass cell, and rereduction at 450°C for 6 hr. Nickel surface area increases significantly from 8 to 17 m<sup>2</sup>/g as the space velocity is increased from 100 to 2000 hr<sup>-1</sup> (see Fig. 6). This increase is likely a result of two effects: (i) More effective transport of water (which aids in the sintering process) from the sample at higher space velocities and (ii) more effective removal of heat generated by exothermic decomposition reactions at higher flow rates, thus minimizing temperature excursions and hot spots in the catalyst.

The increased extent of reduction of nickel to the metal (from 74 to 93%) with increasing space velocity (from 100 to 2000 hr<sup>-1</sup>), as shown in Fig. 7, very likely results from (i) increased transport of water and decomposition products, which are oxidizing agents, from the nickel surface, and (ii) a related increased efficiency of hydrogen transport to the surface due to increased turbulence and mixing. In other words, there is an increased effective partial pressure of hydrogen at the nickel surface.

An apparent saturation effect is observed in Figs. 6 and 7 in the higher space velocity range (1500–2000 hr<sup>-1</sup>). In other words, there is not considerable improvement to be expected in either nickel surface area or the extent of reduction by increasing the hydrogen space velocity during reduction beyond 2000 hr<sup>-1</sup>.

#### *E. Effect of Nickel Loading on Nickel Surface Area*

Nickel surface areas and dispersions are shown in Table 4 for a variety of alumina-supported samples, some of which were calcined at 400°C prior to reduction and others prepared by hydrogen decomposition of nickel nitrate. Again the surface areas

TABLE 4  
Effect of Ni Loading on Ni Surface Area

Wt% Ni/Al <sub>2</sub> O <sub>3</sub>	Precalcined at 400°C	Surface area (m <sup>2</sup> /g)	Percentage dispersion
9	Yes	4.3	6.9
15	Yes	5.2	5.0
26	Yes	10.3	5.7
34	Yes	10.5	4.5
9	No	10.0	15.9
15	No	14.6	13.8
27	No	18.6	10.7
36	No	17.2	6.8

and dispersions are larger for the latter group. The results for either group of catalysts are consistent with the generally accepted observation that metal dispersion decreases with increased metal loading. The nickel surface area, on the other hand, increases with increased nickel loading up to a value of 25 wt% nickel and then increases only very slightly or remains constant. In other words, the nickel utilization is very poor for the incremental addition above 25 wt%.

#### *F. Passivation of Reduced Nickel*

Finely dispersed nickel metal spontaneously oxidizes to nickel oxide (NiO and possibly Ni<sub>2</sub>O<sub>3</sub>) at room temperature with a large negative enthalpy of the reaction (–58.4 kcal/mole for NiO). Therefore, one should expect large temperature excursions when a sample of reduced catalyst is exposed to air. These heat effects if not controlled cause local and/or bulk sintering of the catalyst. The process of preventing the bulk oxidation of a reduced catalyst by oxidizing only the metal crystallite surface to achieve a “passive” monolayer coating is referred to here as passivation.

Possible effects of the passivation treatment on the surface area of a nickel catalyst were determined in the following way: (i) a sample was prepared by hydrogen

reduction of alumina-supported nickel nitrate at 480°C (the metal area was 15.32 m<sup>2</sup>/g), (ii) the sample was exposed to 10% air in helium at room temperature, and a small heat effect was noted initially, (iii) subsequent reduction under identical conditions followed by a surface area determination at room temperature gave 14.94 m<sup>2</sup>/g. Other catalysts in this study exposed initially to 1% air in nitrogen, showed no change in surface area within experimental error. Hence, passivation need not lead to any alteration in exposed area due to the Ni/NiO/Ni cycle, provided the bed temperatures are controlled to avoid sintering. This is particularly important for large catalyst beds where considerably larger temperature excursions could occur by rapid exposure to air.

#### CONCLUSIONS

The following conclusions are based on the results and discussion above:

(i) Decomposition of alumina-supported nickel nitrate in pure flowing H<sub>2</sub> (at 300–500°C) results in about 60–100% reduction to the metal and reasonably large nickel areas and dispersions. Nickel metal surface area and percentage reduction to nickel metal are maximized by reducing at hydrogen space velocities above 1500–2000 hr<sup>-1</sup> and at temperatures in the range of 450–500°C. These results are valid for nickel nitrate impregnated on a gamma-alumina support which is a common starting material for preparation of nickel catalysts. It would also be desirable to study other nickel salts and different supports as starting materials, although some of these results undoubtedly apply to other systems.

(ii) Calcination in air prior to the reduction step is detrimental to obtaining high reducibility, metal surface area, and metal dispersion. This does not mean that calcination of nickel catalysts is always undesirable. It may be desirable, for example, to heat a sample of Ni/Al<sub>2</sub>O<sub>3</sub> in air at high

temperatures (above 600°C) in order to form NiAl<sub>2</sub>O<sub>4</sub> which itself is a very stable noninteracting support for nickel (18, 23).

(iii) A slow heating rate during reduction of alumina-supported nickel nitrate prevents exothermic temperature excursions which may badly sinter the catalyst. The recommended preparative scheme to obtain well-dispersed Ni/Al<sub>2</sub>O<sub>3</sub> is to heat the supported nitrate slowly (less than 5°C/min) to 230°C in H<sub>2</sub> (space velocity of 1500–2000 hr<sup>-1</sup>) holding at 230°C for 1 hr. This is followed by heating slowly to 480°C and holding there for at least 10 hr.

(iv) Oxygen titration at 450°C can be used to measure the extent of reduction of nickel to the metallic state in nickel catalysts having metal loadings greater than about 5 wt%. This technique gives results comparable to the Ni (CO)<sub>4</sub> extraction technique and is faster, safer, and otherwise more convenient than the latter method.

(v) Nickel dispersion decreases with increased nickel loading. Surface area increases with increased nickel loading up to 25 wt% nickel and then increases only very slightly at higher loadings.

(vi) Nickel catalysts can be passivated with no significant loss of surface area provided over-heating is prevented. Controlled exposure of reduced nickel-alumina catalysts to 1% air in nitrogen at room temperature prevents sintering and bulk oxidation upon further exposure to the atmosphere.

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