# The Structure of Raney Nickel

## III. The Chemisorption of Hydrogen and Carbon Monoxide

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The chemisorptions of hydrogen and carbon monoxide at −195°C were measured on several different preparations of Raney nickel, and the fraction of the surface as nickel was estimated. From carbon monoxide chemisorption, assuming a cross-sectional area of CO of 13 Å², the fraction of the surface as nickel varies from 55 to 85% for conventional preparations. The fraction of surface as nickel decreased with increasing alumina content. Prolonged heating of a catalyst in boiling water decreased the nickel area to ⅙ of the original value with the total area decreasing to ⅔. No correlation was found between nickel area and activity in the hydrogenation of cyclohexene in ethanol at 30°C except that activity of the sample treated with boiling water was low.

## INTRODUCTION

In addition to the nickel phase, thought to contain some 4 wt % aluminum in solid solution (1, 2), Raney nickel may also contain unreacted alloy, β-alumina trihydrate (1, 3) and trace amounts of residual alkali (4). Many of the unusual properties of the Raney catalyst, for example, the thermal stability of the high area nickel below 400°C (2, 4) are probably due to these residual materials. Recent work also indicates (2) that the large volumes of hydrogen evolved when Raney nickel is heated, and formerly considered as evidence for a hydride (5, 6) or nickel-dissolved hydrogen (1, 7) structure, may be explained on the basis of reaction between residual aluminum and water bound as alumina trihydrate.

The composite nature of Raney nickel must also be reflected in the surface of the catalyst and several workers have attempted to measure the amount of metallic nickel present in the surface. Kokes and

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Emmett (8) report a nickel area about 20% of the BET value; Huff et al. (4) estimated that some 50% of the total available area was nickel metal; and Mars et al. (2) concluded that the catalyst surface was predominantly (80–90%) metallic.

We have therefore reexamined the composition of the Raney nickel surface by the low temperature chemisorption of hydrogen and carbon monoxide. Since inconsistencies in the literature might have been due to differences in the catalysts used, Raney nickel prepared in several ways including two commercially activated samples, has been studied. The degree to which such measurements may be related to catalytic activity has also been examined.

## EXPERIMENTAL METHODS

Two batches of commercial catalyst from the Davison Chemical Company, are referred to as samples COM I and COM II throughout. Our own catalyst preparations are designated by the method of extraction (I, II, or IV) and the starting alloy (A, B, or C). Catalysts of types I and II were prepared at 50°C by adding alloy to 20%

aqueous NaOH or by adding 40% NaOH to a suspension of the alloy in distilled water, respectively. Type IV, an alumina-rich catalyst, was prepared by the method of Dirksen and Linden (3). These methods of catalyst preparation and the procedure for outgassing and weighing samples are described in detail in a previous paper (9). Many of the catalysts used in the present work were samples of the same preparations as described previously (9); however, they had been stored under ethanol at 0°C for 2 to 4 months before use. To evaluate the effect of prolonged storage in ethanol at 0°C, two additional samples of catalyst IIA were prepared.

Catalyst activity was evaluated within a month of preparation using the hydrogenation of cyclohexene in ethanol at 30°C and 1 atm of hydrogen in a well-stirred, constant pressure microreactor (10).

## RESULTS

Samples were evacuated (9) at 130°C, which corresponds to the maximum in the hydrogen chemisorption versus evacuation temperature data of Mars et al. One sample of the catalyst was used for
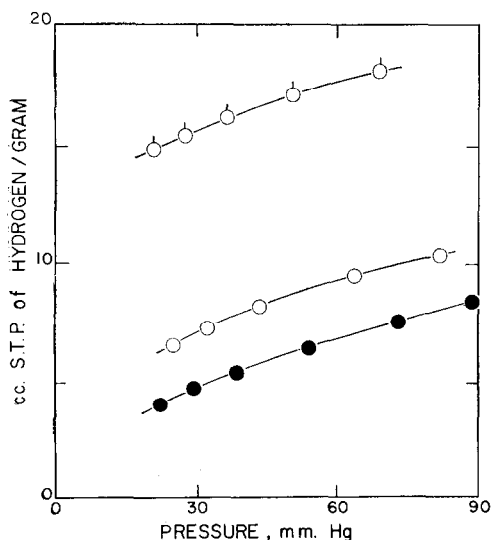
hydrogen chemisorption and another sample for adsorption of carbon monoxide. The chemisorption of hydrogen was measured as described by these authors (2). An isotherm $H_2{}^I$ was measured at −195°C on the original evacuated catalyst; then the sample was evacuated 2 hr at −195°C and a second isotherm, $H_2{}^{II}$ determined. The type of isotherm obtained is illustrated by the data for a IIB catalyst shown in Fig. 1. An isotherm $H_2{}^{III}$, measured after performing the intermediate evacuation at −78°C is included for comparison. The volumes of strongly chemisorbed hydrogen determined as $(H_2{}^I − H_2{}^{II})$ and $(H_2{}^I − H_2{}^{III})$ were 10.8 and 8.5 ml STP/g, respectively.

The adsorption of carbon monoxide was estimated in a similar way by the determination of two isotherms at −195°C, $CO^I$ and $CO^{II}$, with intermediate evacuation of physisorbed gas at −78°C. Data of this type for catalyst IIB, are given in Fig. 2, which includes the isotherms $N_2{}^I$ and $N_2{}^{II}$, the former nitrogen isotherm obtained on the original evacuated catalyst, the latter
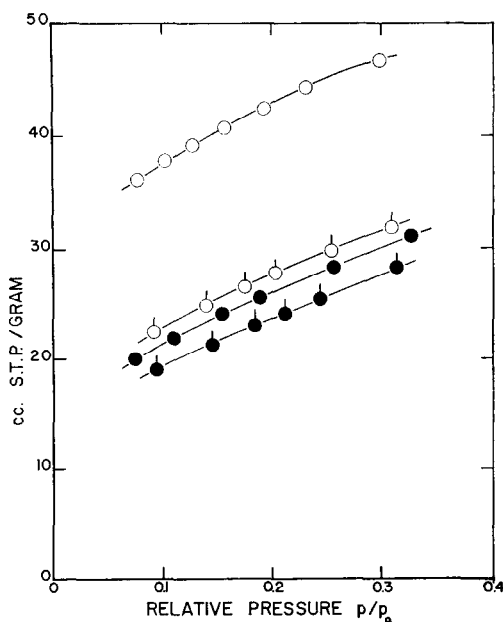


FIG. 1. Adsorption of hydrogen on Raney nickel IIB at −195°C: Ȯ, on catalyst evacuated at 130°C, $H_2{}^I$; ●, previous sample after evacuation at −195°C, $H_2{}^{II}$; ○, sample above (●) after evacuation at −78°C, $H_2{}^{III}$.



FIG. 2. Adsorption of CO and $N_2$ on Raney nickel IIB at −195°C: ● $N_2$ at −195°C on sample evacuated at 130°C, $N_2{}^I$; ○ CO on sample above after evacuation at 30°C, $CO^I$; CO Ȯ on previous sample (○) after evacuation at −78°C, $CO^{II}$; ◖ $N_2$ on (Ȯ) after evacuation at −78°C, $N_2{}^{II}$.

TABLE 1

SUMMARY OF EXPERIMENTAL AND CALCULATED DATA

Except as noted, all samples were stored in ethanol at 0°C or water at 25°C for about 3 months before use.

| Sample notation | Temp. of evacuation (°C) | Storage medium | $N_2\text{-}V_m$ (ml STP/g) | BET Area (m²/g) | $\Delta H_2{}^a$ (A) | $\Delta CO^b$ (B) | $\Delta CO/\Delta H_2$ (C) | Nickel area (%) | | Catalytic activity (arbitrary units) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $(D)^c$ | $(E)^d$ | |
| COM I | 200 | Water | 16.5 | 72 | | 13.7 | | 42.6 | 66.4 | 1.0 |
| COM I | 130 | Water | 18.8 | 82 | 9.6 | 17.6 | 1.83 | 40.8 | 74.9 | 1.0 |
| COM I | 130 | Water | 18.8 | 82 | 9.2 | 17.7 | 1.92 | 41.0 | 75.3 | 1.0 |
| COM II | 130 | Water | 17.8 | 78 | 8.8 | 19.0 | 2.15 | 41.7 | 85.0 | 0.8 |
| IA | 130 | Ethanol | 22.0 | 96 | 11.0 | 16.3 | 1.48 | 37.1 | 59.3 | 3.0 |
| IIA | 130 | Ethanol | 21.1 | 92 | 9.4 | 14.4 | 1.53 | 33.9 | 54.6 | 2.5 |
| IIA$^e$ | 130 | Ethanol | 18.9 | 83 | | 14.1 | | | 59.3 | |
| IIA$^f$ | 130 | Ethanol | 19.7 | 87 | 8.1 | 15.7 | 1.94 | | 63.0 | |
| IIB | 130 | Ethanol | 22.9 | 100 | 10.8 | 16.1 | 1.49 | 39.3 | 56.2 | 2.5 |
| IIA-W₂ | 130 | Water | 13.7 | 60 | 1.55 | 2.75 | 1.77 | 9.4 | 16.0 | 0.29 |
| IVA | 130 | Ethanol | 14.3 | 62 | 4.75 | 7.2 | 1.52 | 27.9 | 40.5 | 2.5 |
| IVA | 130 | Ethanol | 15.2 | 66 | 3.6 | 6.9 | 1.91 | 19.8 | 36.5 | 2.5 |

$^a$ $(H_2{}^I - H_2{}^{II})$ (ml STP/g).

$^b$ $(CO^I - CO^{II})$ (ml STP/g).

$^c$ Fraction of nickel in surface as estimated by hydrogen chemisorption.

$^d$ Fraction of nickel in surface as estimated by CO chemisorption.

$^e$ Chemisorption measured 14 days after preparation.

$^f$ CO chemisorption measured 1 day after preparation; hydrogen chemisorption after 7 days.

on a surface containing chemisorbed CO. These isotherms indicate a CO chemisorption of 16.1 ml STP/g when calculated as $(CO^I - CO^{II})$ and 18.0 ml STP/g calculated as $(CO^I - N_2^{II})$, the method preferred by Kokes and Emmett (8). Both $N_2^I$ and $N_2^{II}$ yielded linear BET plots with monolayer values of 22.5 and 20.0 ml $N_2$ STP/g, respectively. As shown in Figs. 1 and 2, the different isotherms for a given gas were displaced by equal amounts at all pressures studied.

Isotherms for nitrogen, hydrogen, and carbon monoxide adsorption were measured for many of the Raney catalysts described in Part I (9). Nitrogen monolayer coverages were, in some cases, slightly different than those found for the fresh catalysts, possibly due to several months of storage. Isotherms for different samples from the same batch of catalyst at a given time were satisfactorily reproducible ($\pm 4\%$). Consistent adsorption data ($\pm 7\%$) were obtained for 4 preparations of IIA and two of IIB. Less reproducible adsorption data ($\pm 20\%$) were obtained with sample IV.

Volumes of hydrogen ($H_2^I - H_2^{II}$) and carbon monoxide ($CO^I - CO^{II}$) chemisorbed by the various samples are given in Table 1, together with an estimate of catalytic activity for cyclohexene hydrogenation. Activities are expressed in arbitrary units per unit weight of catalyst, based on the assignment of unit activity to the COM I catalyst.

## RELATED STUDIES

(a) After evacuation of COM I at 130°C, the surface was saturated with chemisorbed hydrogen by the usual adsorption–evacuation cycle at $-195$°C and $(CO^I - CO^{II})$ was measured as described in the previous section. 12.5 ml of CO STP/g were chemisorbed compared with 17.6 ml STP/g on the original evacuated sample.

(b) A similar procedure used to measure $(H_2^I - H_2^{II})$ after initial chemisorption of carbon monoxide resulted in the adsorption of hydrogen of only 0.24 ml STP/g compared with 9.6 ml STP on the original evacuated sample.

(c) After evacuation for 16 hr at 200°C, catalyst COM I chemisorbed less carbon monoxide than after evacuation at 130° (Table 1).

## DISCUSSION

The adsorption data of the present study compare well with much of the previous work. Catalyst IIA, for example, chemisorbed 9.4 and 14.4 ml STP/g of hydrogen and carbon monoxide, respectively. After similar pretreatment, the preparation of Mars et al. (2) chemisorbed ca. 10 ml of STP hydrogen/g, while Huff et al. (4) report carbon monoxide chemisorption of 14.1 ml STP/g, after evacuation at 200°C. These results indicate little dependence on the method of catalyst preparation, and indeed, the volumes of both hydrogen and carbon monoxide chemisorbed by the various catalysts studied in the present work, excluding only those catalysts treated in water and the alumina-rich, preparation IV, were broadly similar ($\pm 15\%$).

For all samples studied, the ratio between the volumes of carbon monoxide and hydrogen chemisorbed, remained approximately constant, about 1.7, (Table 1, column C). Thus, changes in the sorptive capacity of the catalysts are reflected in the same way by both gases. Catalysts I and II usually gave lower values, about 1.5, and the commercial catalysts higher values, about 1.9. These differences may result from the lower alumina content of the commercial catalysts or from storage of commercial catalysts in water and preparations I and II in ethanol.

A ratio of 2 CO to 1 $H_2$ would be expected if each surface Ni atom adsorbed 1 CO molecule or 1 hydrogen atom. On a steric basis the presence of residual alumina or chemisorbed species might be expected to affect the chemisorption of CO more than $H_2$. In addition, the chemisorption of both gases may be influenced by residual hydrogen remaining on the Raney nickel after evacuation at 130°C.

Interaction of the catalyst and storage liquid may be expected to occur during storage and evacuation at 130°C. For ex-

ample, infrared bands assigned to chemisorbed CO were observed on a nickel catalyst exposed to ethanol and heated and evacuated (11). In storage of samples of IIA in ethanol at 0°C for 3 months, the chemisorbed carbon monoxide per unit area decreased about 10%, and the chemisorbed hydrogen increased slightly. These data can not be explained only on the basis of accumulating chemisorbed carbon monoxide during storage, because the chemisorbed CO should drastically decrease the chemisorption of hydrogen.

With the exception of the alumina-rich preparations the ratios of chemisorbed $H_2$ to $V_m$ for nitrogen varied from 0.41 to 0.51, and the ratios of chemisorbed CO to $V_m$ were about 0.95 for the commercial catalysts and 0.75 for preparations I and II. Thus, a substantial fraction of the surface is metallic nickel.

Nickel areas, calculated from hydrogen chemisorption and expressed as a percentage of the total BET area, are given in column D of Table 1. These values were calculated by the method of Mars *et al.* (2) in which they assumed that equal portions of the most densely packed (111, 110, and 100) planes are exposed and that 1 hydrogen atom is adsorbed on each nickel atom on the surface. In this case 1 ml of chemisorbed hydrogen (STP) corresponds to 3.64 $m^2$ of nickel surface. Data in column D were not corrected for residual chemisorbed hydrogen. A similar calculation, taking one carbon monoxide molecule per metal atom, has been used in studies of carbon monoxide chemisorption on supported metal catalysts at ambient or higher temperatures. Since the average ratio of the volumes of carbon monoxide and hydrogen chemisorbed was about 1.7 in the present work, nickel areas calculated in this way would be smaller than those estimated from hydrogen chemisorption.

However, because the chemisorbed CO molecule is larger than Ni atoms in closely-packed arrays, an alternative procedure, in which the metal area is calculated by assigning a cross-sectional area to the carbon monoxide molecule, has been employed; a calculation similar to that used

in determining total surface area from the physical adsorption of nitrogen at −195°C. For values of 13 (8) and 16 $Å^2$ (4) for the cross sectional area of the CO molecule, catalyst IA, for example, has nickel areas 59.3 and 73.0% of the BET area, respectively. Percentage values based on the lower estimate of molecular size (13 $Å^2$) are given in column E of Table 1.

The fractions of the surface as nickel estimated from hydrogen chemisorption (column D) are significantly lower than those from carbon monoxide (column E). The Dutch group (2) suggested that about ⅓ of the chemisorbed hydrogen remains after evacuation at 130°C for 24 hr. On this basis the areas estimated from hydrogen adsorption should be increased by a factor of about 1.5. This correction substantially improves the agreement between values of fraction of surface as nickel given in columns D and E.

For several reasons given in the text the fractions of the surface as metallic nickel given in column E of Table 1 seem the least uncertain. These nickel areas seem remarkably large in view of the origin of these surfaces in hot aqueous alkali and subsequent storage in water or ethanol. Smaller nickel areas were obtained for the alumina-rich catalysts. Although other work in this laboratory indicates that the alumina in Raney nickel has a low surface area (9) and part or all of it is more crystalline than the nickel (12), it is possible that some of the nickel area is blocked by alumina. Treating the activated catalyst in boiling water decreased the chemisorption of both CO and $H_2$ to about ⅙ of the original values, although the surface area was not decreased as severely. Coverage of the surface with nickel oxide or alumina is possible.

Activity data for the hydrogenation of cyclohexene in ethanol at 30°C (Table 1) did not correlate with nickel or total surface areas; however, the catalyst treated with boiling water had the lowest nickel and total areas and lowest activity. Catalyst types I, II, and IV had activities of about 2.5 compared with 1.0 for commercial preparations. The methods of activat-

ing the laboratory and commercial preparations were significantly different, and the commercial catalysts were stored in water rather than ethanol.

The low nickel area (20%) reported by Kokes and Emmett (8) appears to have been due to the high evacuation temperature, 400°C, rather than to a particular type of catalyst preparation. The hydrogen-chemisorption data of Mars et al. (2) indicate that the nickel areas decrease more rapidly with increasing evacuation temperature than does the BET area, and a relative nickel area of about 20% after evacuation at 400°C, may be estimated from their graphs.

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