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The Stoichiometry and Poisoning by Sulfur of Hydrogen, Oxygen and Carbon Monoxide Chemisorption on Unsupported Nickel[1]

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Hydrogen chemisorption and BET measurements (argon and nitrogen) have been used to determine the stoichiometry of hydrogen adsorption on nickel powder. The hydrogen adsorption isotherms were measured at room temperature and at 200°C. The experimental results indicate that the H/Ni_s ratio on unsupported nickel is 1:1 at both temperatures. Nickel powder samples were also poisoned with H_2S at a level of 5 ppm for 6 hr. The samples poisoned with H_2S suffer no loss in overall surface area determined by BET measurements; however, hydrogen chemisorption is substantially reduced, although less at 200°C than at 25°C.

Data for CO adsorption on a nickel powder at 25°C show a CO/H value of 2.09 suggesting surface carbonyl formation. After evacuation at 25°C, however, the ratio decreases to 1.16, showing that reversible adsorption–desorption occurs. At −83°C, a value of CO/H of 0.54 is obtained both before and after evacuation indicating no reversible adsorption. The number of CO molecules irreversibly adsorbed per surface nickel atom is 0.54. Data for adsorption of oxygen at 25°C show that three oxygen atoms adsorb for every nickel surface atom and that approximately one of three oxygen atoms can interact with but not be removed by titration with hydrogen at 25°C.

INTRODUCTION

Hydrogen chemisorption is used widely to selectively measure nickel surface areas of nickel catalysts. In the calculation of nickel surface area the hydrogen atom to nickel surface atom stoichiometry is usually assumed to be 1:1. In addition to hydrogen, carbon monoxide and oxygen adsorption have been used to measure nickel surface areas (*1*, *2*), although adsorption stoichiometries for these gases are not simple and may vary with experimental conditions. Previous studies (*3–6*) of the stoichiometries of hydrogen, carbon monoxide, and oxygen adsorption on nickel were performed using samples for which the surface purity was not determined. Moreover, some of this work (*3*) has been criticized (*7*) on the basis of calculated surface areas for the krypton atom. There is also lack of agreement in regard to the stoichiometries of oxygen and carbon monoxide adsorption on nickel (*4–6*). The study of CO adsorption on nickel is further complicated by formation of a volatile carbonyl (*4*, *5*, *8*, *9*), by formation of different bonds (bridged and linear) and by strong physical and chemical adsorption on the support.

This paper reports the application of hydrogen, oxygen, and carbon monoxide chemisorption measurements in combination with BET surface area measurements

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TABLE 1

H_2 Chemisorption and BET Surface Area Data for Inco Nickel Powder

Run	Preparation conditions	H_2 chemisorption (25°)		BET (−196°C)	
		Uptake (μmoles/g)	SA (m^2/g)	SA (m^2/g)	Absorbate
1	Reduced and evacuated at 400°C	3.46	0.283	0.284	Nitrogen
2		3.47	0.284		
3	Reduced and evacuated at 280°C	4.86	0.398	0.400	Argon
4		5.39	0.442	0.430	Argon

to elucidate the adsorption stoichiometries of these gases on a high purity nickel powder, the surface purity of which was verified by means of ESCA. In addition, the effects on hydrogen and carbon monoxide adsorption (on nickel) of exposure to dilute hydrogen sulfide are presented and discussed.

EXPERIMENTAL METHODS

Materials

The nickel powder used in this study was Inco type 287 (International Nickel Co.). This carbonyl nickel powder is of extremely high purity. ESCA analysis of the powder revealed that only oxygen and carbon impurities were present on the surface in concentrations greater than 1 atom.%. Argon cleaning to a depth of about 200 Å (10 Å = 1 nm) revealed that oxygen was situated primarily in the outer 50 Å layer of nickel while a small amount of carbon was present at depths greater than 50 Å from the surface.

Hydrogen gas was passed through an Air Products and Chemicals deoxygenation catalyst and dried by means of a molecular sieve trap at −83°C. Matheson ultrahigh purity CO (99.8%) was used as received. Both the hydrogen sulfide in hydrogen standard (prepared by Matheson) and oxygen (99.9%) were used as received.

Procedure

Isotherms were measured in a conventional Pyrex glass constant volume system, evacuated by means of oil diffusion and mechanical pumps. The pumps were isolated from the adsorption system by means of a liquid-nitrogen-cooled trap. The system pressure was monitored by means of Varian thermocouple and ionization gauges. Adsorption pressures were measured with a Texas Instruments quartz spiral Bourdon gauge with a 0–500 Torr (1 Torr = 133.3 $N\ m^{-2}$) range.

Catalyst samples were sealed in a Pyrex flow-through cell which could be isolated or evacuated by appropriate manipulation of attached stopcocks. Prior to the adsorption measurement, each nickel powder sample was reduced in flowing hydrogen for 2 hr at either 280 or 400°C and then evacuated to 1×10^{-5} Torr at the reduction temperature. The nickel surface areas were calculated assuming a site density of 6.77 $Å^2$/atom based on the arithmetic average of the planar densities of the (100), (110), and (111) planes. BET surface areas were calculated using argon and nitrogen

TABLE 2

Comparison of Hydrogen Chemisorption at Room Temperature and High Temperature (196–206°C)

Run[a]	Condition	Room temp uptake (μmoles/g)	High temp uptake (μmoles/g)
1	Fresh sample	5.39	5.67 (206°C)
2a	Fresh sample reduced 2.5 hr 250°C	4.76	—
2b	Same sample rereduced 2.5 hr 260°C	3.99	4.68 (200°C)
2c	Same sample rereduced at 280°C	4.15	4.61 (205°C)
2d	Same sample rereduced at 240°C	4.11	—
2[b]	Average	4.08 ± 0.08	4.65 ± 0.05
3a	Fresh sample	4.52	4.95 (196°C)
3b	H_2S poisoned 6 hr @5 ppm	3.01	4.48 (196°C)

[a] Three different samples of the Inco Ni powder were used in Runs 1–3.

[b] The uptake for Run 2a was not included in the average due to possible sintering between Runs 2a and 2b. (Note consistency of data for Runs 2b–2d.) If Run 2a is included the average is 4.25 ± 0.34.

areas of 16.88 and 16.2 Å^2/molecule, respectively.

RESULTS

Results for hydrogen chemisorption and nitrogen or argon BET data are shown in Table 1. Surface area data were obtained by nitrogen BET and hydrogen chemisorption measurements for samples reduced and evacuated at 400°C and by argon BET and hydrogen chemisorption measurements for samples reduced and evacuated at 280°C. For the sample treated at 400°C, the nitrogen BET surface area and the hydrogen chemisorption surface area are the same, namely 0.284 m^2/g. Hydrogen chemisorption and argon BET surface areas for the sample treated at 280°C are typically 0.442 and 0.430 m^2/g, respectively.

Hydrogen chemisorption data at 25 and 200°C are compared in Table 2 for both fresh and poisoned samples reduced and evacuated at 280°C. The hydrogen isotherms for Run 3 of Table 2 are shown in Fig. 1. The hydrogen uptake at 200°C is about 10–15% higher than the uptake at

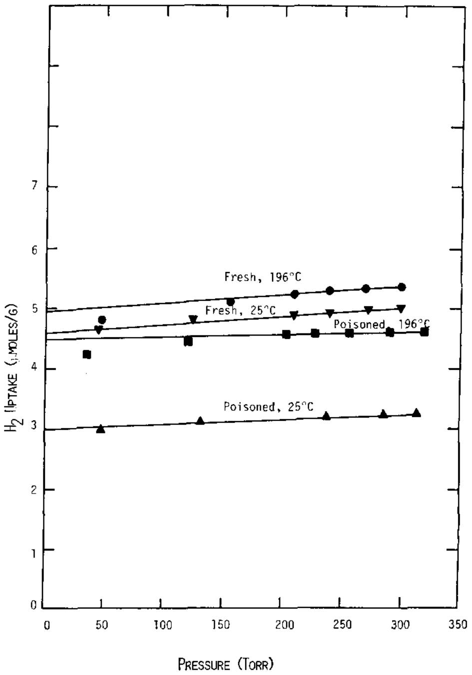

FIG. 1. H_2 chemisorption on Inco nickel powder: (●) H_2 chemisorption at 196°C; (▼) H_2 chemisorption at 25°C (■) H_2 chemisorption at 196°C after 6 hr 5 ppm H_2S; (▲) H_2 chemisorption at 25°C after 6 hr 5 ppm H_2S.

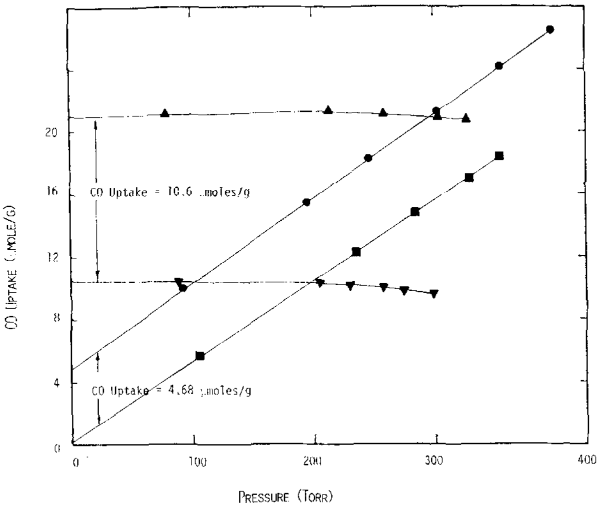

FIG. 2. CO chemisorption on Inco Ni: (●) CO isotherm No. 1 at −83°C; (■) CO isotherm No. 2 at −83°C; (▲) CO isotherm No. 1 at 25°C, (▼) CO isotherm No. 2 at 25°C.

25°C. Statistical analysis of the hydrogen uptake data for Run 2 indicates that this difference is probably significant within the observed experimental error of 1–5% between runs for the same sample. Larger differences in uptake (10–25%) were observed between different samples because of sintering effects during the initial reduction. After the nickel sample was poisoned for 6 hr with 5 ppm H_2S in H_2 (280°C), the hydrogen uptakes at 25 and 196°C were reduced 25 and 10% respectively; again these changes (for the same sample) are significant within experimental error. The amount of sulfur deposited on the sample was approximately 1.8 μmoles/g.

Carbon monoxide chemisorption isotherms are presented in Fig. 2. The carbon monoxide isotherms were determined by measuring CO adsorption on a sample evacuated at either 280 or 400°C and cooled to the adsorption temperature, evacuating the sample for 15 min at the adsorption temperature and then readsorbing CO. At 25°C, the irreversible CO uptake (difference between isotherm 1 and 2) is 10.6 μmoles/g while at −83°C, the CO uptake is 4.68 μmoles/g. The CO/H ratios at 25 and −83°C for unpoisoned and poisoned samples are presented in Table 3. Irreversible and total CO adsorption are equal at −83°C while total CO adsorption is double the irreversible adsorption at 25°C. The CO/H ratio decreases 35–40% upon poisoning with H_2S at both 25 and −83°C for irreversibly absorbed CO. However, at 25°C the CO/H ratio based on total CO adsorption almost doubles.

Oxygen adsorption data (the average of two different samples of the nickel powder) measured at 25°C are shown in Fig. 3. Since the hydrogen uptake for the freshly reduced and evacuated samples was 4.1–4.5 μmoles/g, the initial isotherm for the adsorption of oxygen on the clean nickel surface corresponds to about three oxygen atoms per surface nickel atom suggesting that bulk oxide plus chemisorbed oxygen are found at the surface. In the titration of the oxygen covered surface with hydrogen only half again as much hydrogen is adsorbed on the surface. In the final titration of the oxygen and hydrogen covered surface with oxygen the uptake is only about one third as much as the hydrogen uptake.

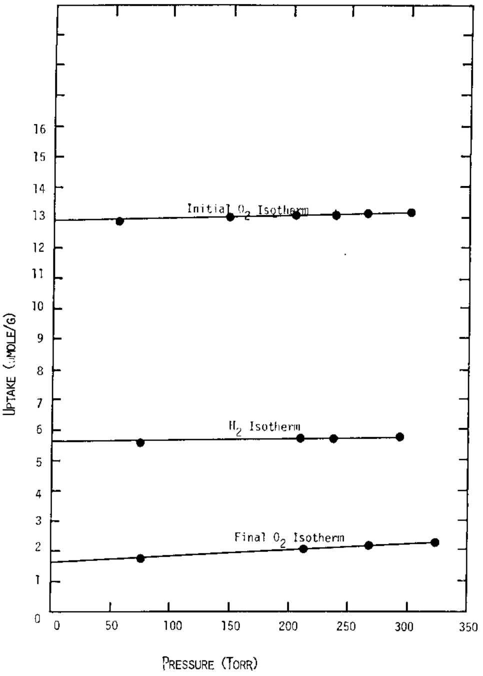

Fig. 3. O_2–H_2 titration on Inco nickel powder.

A separate oxygen adsorption run was carried out at −83°C; the oxygen uptake for the clean (high temperature evacuated) sample was 10.4 μmoles/g, and the corresponding hydrogen uptake at 25°C for this same sample was 4.76 μmoles/g. In other words about twice as much oxygen adsorbed at −83°C as hydrogen at 25°C.

DISCUSSION

The determination in this study of adsorption stoichiometries for hydrogen, carbon monoxide, and oxygen on nickel is significant because it establishes a basis for choosing a reliable technique for measuring nickel surface areas. Comparison of hydrogen chemisorption and BET data presented in Table 1 shows that hydrogen adsorbs dissociatively on nickel in a ratio of one hydrogen atom per nickel surface atom both at 25 and 200°C. The adsorption isotherm monolayer uptake is reasonably independent of pressure (see Fig. 1). Knor and Ponec (*7*) have criticized the BET measurements which were the basis of the results of Beeck and Ritchie (*3*). For the area of krypton, instead of the value of 14.6 Å^2/atom used by Beeck and Ritchie, Knor and Ponec used a value of 21 Å^2/atom which results in a nickel site density of 8.9 Å^2/atom. The results of this study, however, confirm the earlier work by Beeck and Ritchie (*3*) on a nickel film and by O'Neill (*4*) on a nickel powder suggesting that the adsorption stoichiometry of H/Ni is 1:1.

The stoichiometry of carbon monoxide adsorption, however, depends upon temperature, equilibration time, and equilibration pressure. Because of extensive physical (or reversible) adsorption it becomes necessary to determine chemical adsorption as the difference between two isotherms, the second corresponding to reversible adsorption after outgassing at the adsorption temperature. At −83°C the isotherm slopes and adsorption uptakes vary considerably with pressure as illustrated in Fig. 2; this pressure dependence is significantly greater than expected for simple physical adsorption, suggesting that reversible chemisorption plays an important role. A comparison of hydrogen and carbon monoxide adsorption uptakes (extrapolated to zero pressure) in Table 3 shows that at −83°C the ratio of carbon monoxide molecules to surface nickel atoms is 0.54. At 25°C the ratio (considering total reversible and irreversible adsorption) is 2.09 which suggests formation of volatile nickel carbonyl, consistent with observations by other workers (*4*, *5*, *8*, *9*) of nickel carbonyl formation in carbon monoxide atmosphere above 0°C and 3–5 Torr pressure.

The adsorption data following exposure to 5 ppm H_2S for 6 hr indicate that the hydrogen adsorption sites of the nickel powder are more readily blocked at 25°C than at 200°C with the same surface coverage. The decrease in hydrogen adsorption due to H_2S exposure is consistent with the observation by O'Neill (*4*) that hydrogen does not adsorb on a sulfided nickel surface. The increased hydrogen uptake at 200°C on the sulfided catalyst is in agreement with work by Griffith and coworkers (*10, 11*). It should be noted that the hydrogen isotherm obtained at 200°C was measured prior to the isotherm at 25°C; both measurements were preceded by evacuation at 280°C. Thus, if any sulfur is removed by evacuation at 280°C, the hydrogen isotherms obtained after poisoning would not reflect completely the extent to which sulfur had originally covered the surface. Moreover, it is possible that adsorbed sulfur may be removed during H_2 adsorption at 200°C. Nevertheless, Den Besten and Selwood (*12*) observed desorption of H_2 only in evacuating H_2S exposed nickel catalysts at temperatures up to 450°C; thus it appears from their investigation that adsorbed sulfur is not removed by evacuation. Moreover, attempts by O'Neill (*4*) to remove sulfur from the sulfided nickel surface by heating *in vacuo* and reducing in hydrogen at 350°C were reported to have failed. There is recent evidence, however, that adsorbed sulfur is partially removed by hydrogen at elevated temperatures. For example, Dalla Betta *et al.* (*13*) have shown that sulfur poisoned nickel and ruthenium catalysts recover methanation activity after 24 hr exposure to a CO/H_2 reactant stream. In this laboratory it has been observed, similar to Rostrup-Nielson (*14*) that 10–15% of the adsorbed sulfur can be removed from a nickel catalyst originally saturated in a H_2S/H_2 stream by exposing the sample to a stream of H_2 at 450°C.

Carbon monoxide adsorption data (at −83°C) after H_2S poisoning indicate similarly that adsorption sites are blocked. The data for carbon monoxide adsorption at 25°C, however, are most probably indicative of nickel carbonyl formation which occurs above a pressure of 3 Torr at this temperature and which has been shown to be catalyzed by H_2S (*4*).

TABLE 3

Hydrogen–Carbon Monoxide Adsorption Ratios (CO/H) on Inco Nickel Powder

	Irreversibly adsorbed CO	Irreversibly + reversibly adsorbed CO
Initial	0.54 (−83°C) 1.16 (25°C)	0.54 (−83°C) 2.09 (25°C)
H_2S poisoned 6 hr @ 5 ppm	0.35 (−83°C) 0.70 (25°C)	0.35 (−83°C) 3.85 (25°C)

The data in Fig. 3 indicate that oxygen adsorption on nickel occurs with a stoichiometry of three oxygen atoms for each nickel surface atom. O'Neill (*4*) and Buyanova *et al.* (*6*) reported considerably lower O/Ni_s values at 25°C of 1.2 and 1.8, respectively. The adsorption measurements of O'Neill were performed over a pressure range of 10–70 Torr compared to 100–400 Torr in this study. This difference in pressure might explain the differences in stoichiometry. Buyanova *et al.* did not report their adsorption pressure; however, their measurement of fast uptake compared to the measurement in this study of equilibrium uptake after 45 min might also account for differences in stoichiometry. Regardless of the explanation, the large discrepancies in stoichiometry for oxygen chemisorption on nickel at 25°C suggest the need for caution in using this technique. Moreover, in view of the pyrophoric nature of high surface area nickel catalysts, this technique may have severe practical limitations.

The results for oxygen adsorption in this study (Fig. 3) suggest that surface and bulk nickel oxides are formed at 25°C. Adsorbed oxygen is apparently not removed by titration with H_2 at 25°C since only half the amount of hydrogen was adsorbed needed to completely titrate the oxygen monolayer to form water and hydrogen covered nickel. The subsequent oxygen uptake was only one third as much as the hydrogen uptake which again shows that oxygen chemisorption at 25°C is not reversible. These data are consistent with the following hypothesized sequence of surface reactions in which s denotes surface and b denotes bulk nickel:

$$2\mathrm{Ni_s} + 4\mathrm{Ni_b} + 3\mathrm{O_2} \rightarrow 2\mathrm{Ni_s{-}O} + 4\mathrm{Ni_b{-}O}, \quad (1)$$

$$2\mathrm{Ni_s{-}O} + \tfrac{3}{2}\mathrm{H_2} \rightarrow \mathrm{Ni_s{-}OH} + \mathrm{Ni_s{-}H_2O}, \quad (2)$$

$$\mathrm{Ni_s{-}H_2O} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{Ni_s{-}O} + \mathrm{H_2O}\ \text{(physically adsorbed)}. \quad (3)$$

In the first reaction a surface oxide layer and two bulk oxide layers are formed. In Reaction 2 hydrogen reacts with the surface oxide layer to form an adsorbed hydroxyl group and weakly bound water. In Reaction 3 the weakly bound water is displaced by oxygen and the water is retained on the surface in a physically adsorbed state. Although there are probably other similar detailed mechanisms which might account for the data, the overall observations are constant, namely that oxygen chemisorbs forming a multilayer oxide and is not removed by hydrogen titration.

Oxygen adsorption at −83°C is similarly complicated in that twice as much oxygen is adsorbed as hydrogen at 25°C, in agreement with observations by Mueller (*15*). It is not obvious whether oxygen adsorbs dissociatively or nondissociatively at this lower temperature. Thus, because of the complex stoichiometry neither oxygen chemisorption nor the hydrogen–oxygen titration are deemed suitable for measuring nickel surface areas.

In summary, the adsorption data on nickel powder demonstrate that hydrogen chemisorption is a desirable method for measuring nickel surface areas because the adsorption stoichiometry is simple ($\mathrm{H/Ni_s} = 1$) and reasonably insensitive to temperature, equilibration time and pressure. For gravimetric adsorption on nickel, the use of D_2 is recommended. On the other hand, carbon monoxide adsorption is not recommended because the adsorption stoichiometry varies with temperature, equilibration time, and equilibration pressure, and because volatile nickel carbonyl is formed at 25°C. Oxygen adsorption is undesirable because of multilayer oxidation at 25°C and perhaps at −83°C. The results are significant in providing quantitative understanding of the adsorption of the three most important gases on unsupported nickel and in establishing a scientific basis for measuring nickel surface areas. Of course, it will be necessary in the continuation of this study to demonstrate that hydrogen adsorption on supported nickel is likewise as simple (i.e., $\mathrm{H/Ni_s} = 1$).

Finally, adsorption data after exposure to dilute H_2S establish that adsorbed sulfur blocks adsorption sites for carbon monoxide at −83°C and for hydrogen at 25°C. However, hydrogen chemisorption on poisoned samples is decreased less at 200°C compared to 25°C. Carbon monoxide adsorption at 25°C is increased by hydrogen sulfide poisoning most probably since nickel carbonyl formation is enhanced.

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