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Hydrogen in a Commercial Raney Nickel

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A commercial Raney nickel evacuated at 25°C evolved about 23 cm^3 (STP)/g H_2, as measured by volumetric and temperature-programmed-desorption (TPD) methods. D_2 exchange at 25°C showed the total exchangeable elemental hydrogen and water to be 26 cm^3 (STP)/g. The maximum amount of chemisorbed H_2 was estimated to be 13 cm^3 (STP)/g, and this quantity could be replaced if TPD tests were stopped at 235°C. The TPD spectra had a broad peak at 200°C and a shoulder at 140°C. Adding water to the carrier gas in TPD experiments instantaneously increased the rate of H_2 evolution; water addition more than doubled the H_2 evolved to 700°C. Without H_2O addition hydrogen desorption was only slightly exothermic, but when H_2O was added, it was highly exothermic. The latter process appears to be the reaction of H_2O plus zero-valent aluminum; this reaction did not proceed to a large extent in the usual desorption tests. Thus, most of the hydrogen was present as chemisorbed and interstitial hydrogen.

The hydrogen evolved on heating Raney nickel usually exceeds substantially the amount that can be attributed to chemisorption. The extra hydrogen has been explained in two ways: (a) this hydrogen is "dissolved in the bulk of the nickel" (*1–13*), and (b) the H_2 is generated by the reaction of residual water with residual zero-valent aluminum (*14–17*). Due to the difficulties and inaccuracies of the analysis for zero-valent and oxidized aluminum, these problems have not been resolved. Fouilloux *et al.* (*18*) reported that catalysts, activated strenuously to remove virtually all the aluminum, contained only chemisorbed hydrogen; this paper also presents a brief summary of work to 1972.

The temperature-programmed-desorption, TPD, methods of Amenomyia and Cvetanovic (*19, 20*) are sensitive techniques for examining desorption processes, yielding differential rather than the integral data obtained by volumetric methods. Hungarian workers have used TPD in studies of conventional Raney nickel (*21–24*) and the nonpyrophoric catalyst (*25–28*). In TPD experiments on most Raney nickels only two to three peaks were observed, but these maxima were shown to be composites of a spectrum of different desorption processes.

The present paper describes measurements of the hydrogen "content" of a commercial Raney nickel as determined by four different methods.

EXPERIMENTAL

The Catalyst

Two samples of their activated commercial Raney nickel were kindly furnished by the Davison Chemical Company. The catalysts were stored under water in closed metal containers, and were designated as COM I and COM by us. Chemical analyses were made for Ni, Al, and Fe on samples that had been evacuated for 24 h at room temperature to obtain a weight on which to base the analyses. Ni was determined by standard volumetric and gravimetric methods and occasionally by atomic absorption spectroscopy (AAS); Al by a standard volumetric method, chelatometry, and AAS; and iron by AAS only. The analyses

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TABLE 1

Analyses of Raney Nickel

Sample	wt% determined		
	Ni	Total Al	Fe_2O_3
COM I	90.4 ± 0.3	6.2 ± 0.2	0.29 ± 0.02
COM	89.3 ± 0.3	5.8 ± 0.2	0.29 ± 0.02

are given in Table 1. The sum of Ni, total Al, and Fe_2O_3 is less than 100%; the remainder is water, hydrogen, and/or oxygen.

Powder X-ray diffraction patterns were obtained for catalyst COM using Mo radiation monochromatized with a Zr filter. Only broad peaks for a fcc structure were obtained and the unit cell dimension was 3.532 Å compared with 3.5238 Å for nickel; these results are similar to previous results on a similar commercial Raney Ni (*29*). For solid solutions of Al in Ni, Taylor and Floyd (*30*) found an increase of the unit cell dimension, a_0, in angstroms, according to $a_0 = 3.524 + 0.181 \cdot X_{Al}$, where X_{Al} is the atom fraction of Al. The value 3.532 Å corresponds to 2.1 wt% aluminum.

BET surface areas from nitrogen isotherms at −195°C for a number of samples of Davison commercial Raney nickel were about 80 m^2/g, and the area was not changed by storage in water for as long as 3 years. Heating and evacuating the sample decreased the area substantially as shown in Table 2.

Isobars for H_2 were determined at 300 Torr on a sample of COM initially evacuated at 25°C. The isobar was started at −196°C and after "equilibration" the adsorption was measured successively at −77, 0, and 25°C, and then the adsorption was measured at the same temperatures in a decreasing sequence. At least 30 min was allowed for "equilibration" at each point. Next, the same sample was evacuated at 106°C and increasing followed by decreasing temperature sequences were performed from −195°C to 106°C and down to −195°C again. Similar sequences were carried out for samples heated successively to 251, 400, and 580°C. All of the isobars showed "activated adsorption," i.e., the adsorption increased with increasing temperature in some regions, as shown in Fig. 1. Adsorption was always larger in decreasing rather than increasing temperature sequences. The sample evacuated at 106°C adsorbed the most H_2 in the descending temperature sequence followed by evacuation temperatures of 251, 25, 400, and 580°C. The largest H_2 adsorption at 300 Torr was 13.9 cm^3 (STP)/g at −196°C on a sample evacuated at 106°C.

The chemisorption of CO at −195°C was measured on some of these samples using

TABLE 2

Total and Nickel Areas of Raney Nickels

Temperature of treatment (°C)	Surface area (BET) (m^2/g)	V_m for N_2 (cm^3 (STP)/g)	Strongly chemisorbed CO (cm^3 (STP)/g)	Nickel area		Surface nickel % of total Ni
				m^2/g	% of BET area	
23[a]	80.1	18.3	19.8	69.2	86.3	5.7
580[b]	22.2	5.1				
570[c]	7.5	1.7	1.07	3.7	49.6	0.3

[a] Evacuated at room temperature.

[b] Sample used for H_2 isobars.

[c] Used in a TPD experiment.

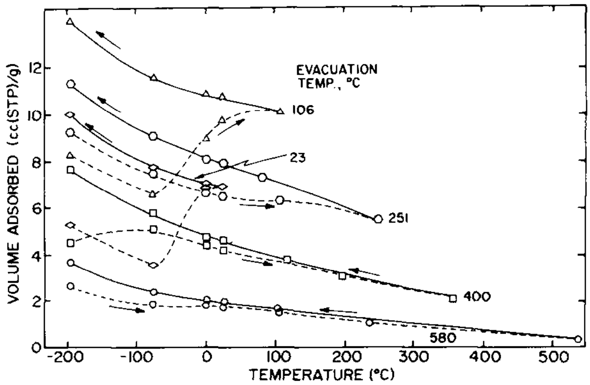

FIG. 1. Adsorption isobars at 300 Torr on Raney nickel COM evacuated at several temperatures. Increasing temperature sequences are denoted by dashed curves, decreasing sequences by solid curves.

the method described in an earlier paper from this laboratory (*31*). This procedure involved determining an initial isotherm for both strongly and weakly adsorbed CO, pumping off the weakly held molecules at −78°C for 30 min, and redetermining the isotherm at −195°C. The difference between the first and the second isotherms is the amount of strongly chemisorbed CO. The second CO isotherm is about equal to the first N_2 isotherm, when both isotherms are plotted as a function of relative pressure. Metal surface areas were calculated using surface coverages per molecule of 13 Å^2 for CO (*32*) and assuming $CO/Ni_S = 0.5$.

Thermodesorption Experiments

Gases evolved when Raney nickel was heated were measured in a volumetric system and in a TPD apparatus. In both methods the sample was evacuated overnight or longer at room temperature to a pressure of 10^{-5} Torr.

The first apparatus was a volumetric adsorption system with a manostat. The sample, 0.2 to 0.8 g, in a special quartz tube was connected to the volumetric system through a liquid-nitrogen trap to remove water vapor. The volumes of parts of the system were calibrated with helium using the calibrated burettes. The sample was heated at a rate of about 2°C/min to 700°C. The system was set to maintain the pressure constant after gas evolution started; several pressures from 20 to 300 Torr were used. The volume (STP) of gas evolved was independent of the pressure at which it was collected. The gas evolution was most rapid at about 200°C, but we did not try to obtain kinetic data in this system.

The TPD system is shown in Fig. 2. The carrier gas is passed over the sample, through a cold trap, and to a thermal conductivity cell (TC). Four modes of operation were used:

a. Argon as the carrier gas, cold trap in dry ice, H_2 and CH_4 detected in the TC cell.

b. Same as above but water at about 25 Torr was added from water saturator 11. H_2 and CH_4 detected.

c. H_2 as the carrier gas, cold trap in liquid nitrogen, only CH_4 detected.

d. H_2 as the carrier gas, cold trap at room temperature, CH_4 and H_2O detected.

The catalyst sample, 0.2 to 0.8 g, was placed on a fritted quartz disk in the quartz TPD tube. The TPD tube was placed in an electrical tube furnace with rapid thermal response characteristics. The linear temperature programming was obtained by using a clock motor to drive the control knob of a proportional controller activated by a thermocouple placed between the TPD cell and the furnace, as shown in Fig. 2. Heating rates of 4.2 to 12.8°C/min were used in these experiments. From changes of the

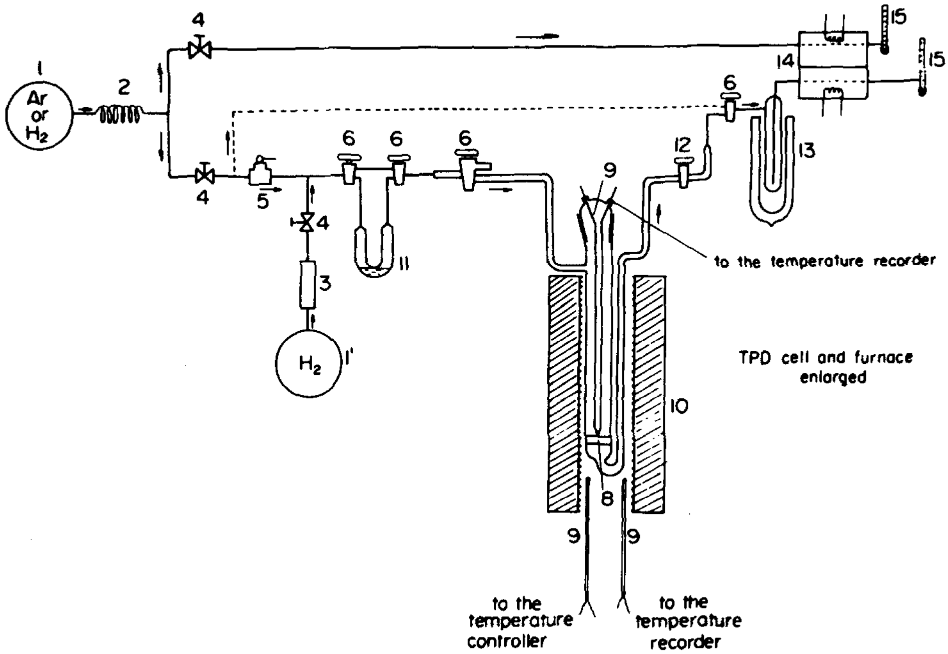

FIG. 2. Diagram of the temperature-programmed-desorption system.

relative responses of the thermocouples within the sample, 8, and outside the TPD tube, 9, exothermic or endothermic reactions could be detected; however, this system is a DTA unit of low sensitivity.

Exchange of Deuterium with Raney Nickel

Raney nickel was equilibrated with D_2 in a volumetric adsorption system modified to permit gas sampling. The catalyst was placed in a special 100-cm^3 glass bulb with a stopcock and a standard joint. The catalyst was evacuated at 25°C for 24 h or more, to a pressure of less than 10^{-5} Torr and weighed. The bulb was attached to the adsorption system and the system evacuated. An inlet of D_2 was taken into the volumetric system and measured, and subsequently the D_2 was introduced to the catalyst. After a period of "equilibration" of 18 or more h at 25°C, samples of known volume were removed for analysis.

The isotopic species, H_2, HD, and D_2, were determined by gas chromatography at −195°C using helium as a carrier gas and a 4-m column of alumina impregnated with $MnCl_2$ to equilibrate spin isomers. The separated species were converted to H_2O, HDO, and D_2O by passing over cupric oxide at 600°C, and their concentration determined by a thermal conductivity cell.

Dissolution in Aqueous HCl and Mercury Addition

The volumetric system used for thermal desorption was employed with special sample tubes in which the samples were evacuated at room temperature to less than 10^{-5} Torr. The sample tube had a special funnel and stopcock for introducing the aqueous HCl solution or the mercury.

In the acid dissolution tests the sample tube was large enough, 25 cm^3, to contain sufficient acid to dissolve the sample. A trap at −195°C prevented water and HCl from entering the volumetric system. The sample bulb was placed in a liquid-nitrogen bath, and the aqueous HCl was introduced and frozen. The temperature of the bulb was increased slowly to room temperature to maintain a moderate rate of gas evolution. When gas evolution stopped, the bulb was heated to about 50°C. At the end of the experiment the hydrogen was measured, and the amounts of Ni and Al in the solution were determined.

The amount of hydrogen preexisting in the catalyst is obtained by subtracting from the hydrogen evolved the volume of H_2 generated in dissolving zero-valent Ni and Al in the HCl solution to give the final composition of the solution. If the catalyst contains oxidized Ni or Al that dissolves in the HCl solution, the calculated volume of preexisting hydrogen will be lower than the actual value. Some Raney nickels contain hydrated alumina that has at least limited solubility in aqueous HCl.

The mercury addition experiments merely involved adding mercury to the evacuated sample and measuring the hydrogen evolved.

EXPERIMENTAL RESULTS

Thermal Desorption

The volumes of H_2 evolved in volumetric and temperature-programmed-desorption systems were identical within experimental error. The H_2 evolved as measured by both methods increased with time of storage of the sample in water, as shown in Table 3. At first the TPD spectra had only one peak at about 200°C, but after 23 months a second peak at 485°C appeared.

TABLE 3

Hydrogen Evolved from COM Catalyst in Thermodesorption as a Function of Age

Age (months)	Hydrogen evolved[a] (cm^3 (STP)/g) Volumetric	TPD
5	20.5	
10		21.8
17		23.2
19	23.4	
23		29.1
30	29.8	

[a] Corrected for the presence of 3.7% CH_4 in H_2.

In the first 23 months the TPD spectra for commercial Raney nickel with argon as a carrier gas and a dry-ice trap following the sample, had one broad maximum at about 200°C and a shoulder at 140°C, as shown by curve a of Fig. 3; gas evolution began at about 70°C. Analyses of the entire gas sample from the volumetric experiments were 3.7% CH_4 and 96.3% H_2. Tests were not highly reproducible as indicated by comparing curve a with the first part of curve b in Fig. 3. Exotherms were not observed with the usual size samples, about 0.6 g, but were detected for samples of about 1.2 g. Linear heating rates of 4.2, 6.2, and 12.8°C/min were used. The heating rate did not change the position of the peak maximum significantly.

Similar TPD experiments were made using hydrogen as a carrier gas, in one instance with the trap at room temperature to detect the evolution of H_2O and CH_4, and in the other with a liquid-nitrogen trap to observe CH_4. The evolution of H_2O had a maximum at 100 to 120°C and was complete by 300°C. Methane evolution started at 108°C and had a maximum at about 200°C; CH_4 follows the same pattern as hydrogen. The water desorbing at 100–120°C may be the "adherent water" mentioned in the Raney nickel literature. A sample of bayerite ($Al_2O_3 \cdot 3H_2O$) in the present apparatus started to evolve water at 150°C and the dehydration was completed at 220°C.

Weight loss in a TPD test with 0.6185 g Raney nickel was 5.0 mg. From the TPD curves, 1.0 cm^3 (STP) or 0.71 mg CH_4 was evolved, 3.5 cm^3 (STP) or 2.82 mg H_2O, and from another experiment, 17.7 cm^3 or 1.59 mg H_2 to give a calculated weight loss of 5.1 mg.

TPD tests were also used to study the readsorption of H_2. As shown in curve b of Fig. 3, the temperature was increased only to 232°C to desorb 14.1 cm^3 (STP)/g H_2. The sample was then cooled to 23°C in flowing H_2, held in H_2 at 23°C for 20 h, evacuated at 23°C to 10^{-5} Torr, and a second TPD test was performed, this time

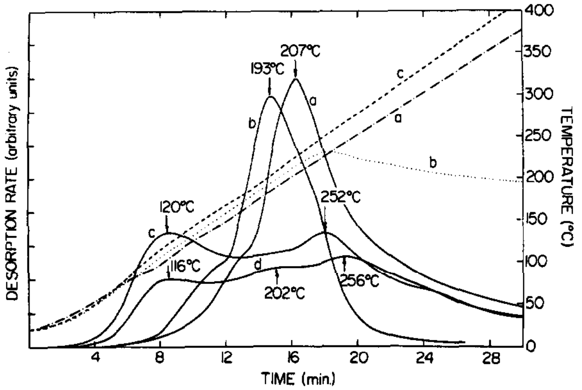

FIG. 3. Temperature-programmed-desorption curves (solid) for Raney nickel COM. Broken curves show temperatures. (a) Standard TPD test on a fresh sample. (b) Same as (a) except that the temperature increase was stopped at 232°C. (c) TPD for the sample from (b) that was cooled to room temperature in hydrogen. (d) Repeat of experiment in (c).

to 700°C, to give curve c. Curve c has maxima at 120 and 252°C, the latter probably representing evolution of the original H_2 not removed in the TPD test to 232°C. The peak at 120°C in curve c was not found in the original spectra a and b but may be related to the small shoulder in a and b. Table 4 shows that after heating to 230°C, 50 to 60% of the H_2, 12–13 cm^3 (STP)/g, can be readsorbed, but after heating to 700°C only 20%, 4.5 cm^3 (STP)/g, is readsorbed.

Experiments were arranged so that water vapor could be introduced into the argon carrier gas. The argon was passed through a U-shaped trap containing liquid water at room temperature to introduce about 25 Torr of water vapor. The water in the gas stream was removed by a cold trap ahead of the detector. Usually the temperature in the TPD test was held constant until the H_2 evolution was slow, before the water was introduced. The evolution of H_2 immediately increased and the process was *exothermic* with the temperature increasing about 3°C. The ratio p_{H_2O}/p_{H_2} in the argon was always substantially smaller than required for the oxidation of bulk nickel. In TPD tests with H_2O addition, the total amount of H_2 evolved to a final temperature of 700°C always increased substantially.

After some TPD tests to 700°C, a second TPD experiment to 700°C was performed on the same sample using H_2 as a carrier gas and with the cold trap removed so that water could be detected, if reducible oxides such as NiO were present. For samples from regular TPD tests, no water vapor was found. Samples used with intermittent water additions yielded small amounts of water in the TPD with H_2. In one test the H_2 evolved to 700°C increased from 24 to 77 cm^3 (STP)/g on water addition. The H_2O evolved in the subsequent TPD with H_2 corresponded to the oxidation of 0.6 wt% of the total nickel or 12% of the surface nickel; however, this amount of oxidation of Ni would contribute to the H_2 evolved only 2.4 cm^3 (STP)/g.

In another experiment, intermittent wa-

TABLE 4

Readsorption Experiments with COM Catalysts[a]

H_2 evolved (cm^3 (STP)/g)			H_2 put back into catalyst	
Regular TPD to 700°C	To 230°C	To 700°C after re-adsorption	cm^3 (STP)/g	% of "total"
22.5	14.11	20.00	11.61	51.60
22.5	17.87	18.42	13.79	61.30
22.9	—	4.52	4.52	19.76

[a] In these experiments it was assumed that only hydrogen was evolved.

ter addition increased H_2 evolution to 700°C from 25.1 to 45.3 cm^3 (STP). In the TPD with water, the sample gained 13 mg, and the water produced in the subsequent TPD with H_2 corresponded to 1.4 mg of oxygen in NiO and to 2.0 cm^3 (STP) H_2. The extra H_2 in the TPD with water, 20.2 cm^3, minus that produced by oxidizing Ni, 2.0 cm^3, has been attributed to the oxidation of aluminum. The weight gain in producing 18.2 cm^3 H_2 from Al is 13.0 mg, and the H_2 lost from the sample is 25.1 cm^3 and weighs 2.2 mg. Thus, the calculated weight gain = 13.0 − 2.2 + 1.4 = 12.2 mg compared with 13 mg observed. These data provide a reasonably strong argument that most of the extra H_2 produced by adding H_2O may be attributed to the oxidation of Al.

Hydrogen–Deuterium Exchange

In these tests deuterium is introduced to an evacuated catalyst in a volumetric gas-handling system. If all processes involving exchange proceed rapidly and if there are no isotope effects, the amount of exchangeable hydrogen initially in the catalyst may be estimated from the deuterium inlet and the ratio of hydrogen to deuterium atoms in the gas phase after "equilibration."

The sample of Raney nickel was evacuated at room temperature for 24 h to 10^{-5} Torr in a special glass tube. A measured volume of D_2 was then introduced to the sample at 25°C. After "equilibration" at 25°C, small gas samples were taken and analyzed for H_2, HD, and D_2 by gas chromatography. Several gas samples were taken and analyzed; appropriate corrections were made for the amount and composition of the gas removed. In other experiments the adsorption of H_2 and D_2 was shown to be practically the same on Raney nickel at 25°C, about 9 cm^3 (STP)/g at 200 Torr, which is in agreement with the work of Taylor and Pace (*34*) for nickel on kieselguhr.

Table 5 describes exchange on COM Raney nickel. The system reached "equilibrium" in less than 18.5 h, including the isotopic species found in the gas. The values of 25.7 cm^3 (STP)/g agree with the amounts of H_2 measured in thermal desorption in either volumetric or TPD measurements. The deuterium should exchange with accessible hydrogen and water in the catalyst. According to the TPD experiments the COM catalyst after evacuation at 25°C contains the precursor of 1.6 cm^3 (STP)/g CH_4 and water vapor in the amount of 5.6 cm^3 (STP)/g plus additional water that might have reacted with the catalyst to produce H_2.

Dissolution in Aqueous HCl and Mercury Addition

The acid dissolution method for determining preexisting hydrogen may be complicated by oxidized Ni or Al, preexisting in the sample, dissolving in the acid solution and being counted as metallic. For this reason the preexisting hydrogen determined in this way must be regarded as a

TABLE 5

Exchange of Deuterium at 25°C with Commercial Raney Nickel

Catalyst sample	Equilibration time (h)	Final gas composition[a] (mole %)			Equilibrium constant	Hydrogen content
		H_2	HD	D_2	K^b	(cm^3 (STP)/g)
1	63.5	28.3	47.4	24.3	3.27 ±0.05	25.7 ±0.3
2	18.5	28.2	47.1	24.8	3.17 ±0.05	25.8 ±0.1

[a] Average of six analyses for each sample.

[b] Equilibrium constant for $H_2 + D_2 = 2HD$. From Ref. (*35*) at 25 °C, $K = 3.225$.

lower limit of the amount actually present. The preexisting hydrogen is the small difference between a large experimental value and a large calculated value. Our results were not very reproducible; two samples of COM I dissolved in 4 *N* HCl solution had 24.2 and 17.2 cm^3 (STP)/g preexisting hydrogen, and for COM in 1 *N* and 4 *N* HCl, 27.0 and 16.8 cm^3 (STP)/g, respectively. Our conclusion is that the minimum value for preexisting hydrogen is about 20 cm^3 (STP)/g; this amount seems larger than can be accommodated by chemisorption.

Addition of Hg to COM at 23°C displaced 14 cm^3 (STP)/g H_2 and mild heating of the sample bulb increased the H_2 to 16 cm^3 (STP)/g.

DISCUSSION

In the first year after its activation our samples of Davison commercial catalyst "contained" from 20 to 25 cm^3 (STP)/g H_2; our discussion will define "contained" and "hydrogen content." The hydrogen content as measured by thermal desorption increased with time of storage in water to 30 cm^3 (STP)/g at 30 months. The extra hydrogen was associated with the appearance of a new TPD peak at 485°C. Kramer and Andre (*38*) found a TPD peak for hydrogen on alumina at 480°C that was produced only by adsorption of atomic hydrogen on alumina or by hydrogen spillover on nickel-on-alumina. Possibly this species could be produced along with a slow reaction of elemental aluminum with water during storage. In the first year after activation the hydrogen contents as measured by different methods were:

Method	Hydrogen content (cm^3 (STP)/g)
Acid dissolution	>20
Thermal desorption, volumetric	20–23
TPD	22–23
Deuterium exchange	25.7
Immersion in Hg	14–16

An important problem is to define the source of this hydrogen. The hydrogen may preexist in the Raney nickel as chemisorbed and interstitial hydrogen, or it may be produced by the reaction of water and aluminum. The amounts of hydrogen that are strongly chemisorbed at 25°C or that readsorbed at 25°C after the TPD test to 232°C, 10–13 cm^3 (STP)/g, seem to be minimum values for the chemisorbed plus interstitial hydrogen. D_2 exchange may occur with preexisting hydrogen associated with the nickel, adsorbed or adherent water, water in hydrates, and the precursors of CH_4. We may infer that D_2 exchange will occur with chemisorbed or hydrate water on alumina associated with active nickel on the basis of results of Iida and Tamaru (*36*); water chemisorbed on platinum-on-alumina exchanged readily with D_2 at temperatures as low as 229 K. Coverage of 10% of the Pt surface by CO stopped the exchange reaction.

In a typical TPD experiment with a 2-year-old catalyst 5.7 cm^3 (STP)/g H_2O was evolved along with 28.6 cm^3 of H_2. If all of the H_2 were produced by the reaction of H_2O plus Al, the total water in the catalyst would be 34.3 cm^3/g or 27.6 mg/g. TPD tests with water addition demonstrated that the catalyst contains zero-valent aluminum that reacts with H_2O by an exothermic reaction; exotherms as large as 3°C were observed on water addition. The desorption without H_2O addition was only slightly exothermic. Exotherms were not observed in the usual experiments, but were found when larger samples of catalyst were used. These observations suggest that the reaction of H_2O with residual Al is not an important step in the evolution of H_2 from the present catalyst.

Thermodesorption by the volumetric and TPD methods yielded the same volumes of H_2 and these are in agreement with the D_2 exchange and acid dissolution experiments. The TPD curves had a shoulder at 140°C and a broad peak at about 200°C. The temperature of the peak maximum did not change significantly when the heating rate was increased from 4.2°C to 12.8°C/min. This result was unexpected because for simple desorption processes the maximum temperature should increase with heating rate. Possibly desorption from a number of different "sites" with different activation energies could respond in this fashion as the heating rate is changed.

The broad maximum at 200°C was composed of a spectrum of different desorption events. In TPD tests stopped at 232°C and the sample cooled to room temperature in H_2, about 12 cm^3 (STP)/g H_2 was readsorbed. In subsequent TPD tests a spectra with three broad peaks in the temperature range 100–250°C was obtained. The peak at about 120°C was substantially larger than the shoulder at 140°C obtained from the original catalyst. This low-temperature hydrogen either was not formed on the catalyst in its activation or was lost subsequently by desorption or by reaction with oxygen from the atmosphere.

The Hungarian workers examined a number of conventional Raney nickel catalysts. Usually their TPD spectra had two maxima at about 110 and 240°C, and a total of about 60 cm^3 (STP)/g was desorbed (*23*). At least part of the substantial differences between the Hungarian data and ours results from the pretreatment procedures, particularly the amounts of water remaining in the sample. Our catalysts were evacuated in the TPD cell at 25°C for more than 18 h to a pressure of 10^{-5} Torr; the Hungarians introduced the wet catalyst into the TPD system and dried it in flowing argon at the start of the TPD experiment. In special experiments the Hungarian workers showed that the observed peaks were composites of several desorption events (*37*).

We conclude that the present Raney nickel, evacuated at 25°C, contains about 13 cm^3 (STP)/g chemisorbed hydrogen and nearly as much interstitial hydrogen. Only a small portion of the H_2 is produced by the reaction of water and aluminum; this conclusion is based on the observation that the evolution of H_2 is not highly exothermic.

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