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EFFECT OF REDUCTION TEMPERATURE, CARBIDING, AND SULFUR POISONING ON THE METHANATION ACTIVITY OF RANEY NICKEL

DEPARTMENT OF ENERGY, PITTSBURGH, PA.
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EFFECT OF REDUCTION TEMPERATURE, CARBIDING AND SULFUR POISONING ON THE METHANATION ACTIVITY OF RANEY NICKEL

By

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ABSTRACT

The effects of reduction temperature, carbiding and sulfur poisoning on the methanation activity of Raney nickel were investigated. A combination of techniques such as BET surface area, H_2 and CO chemisorption, ESCA measurements and activity tests were used to characterize the catalyst before and after deactivation.

The following reductions in catalytic activity, as determined in a pulse microreactor at 320° C, were observed for the deactivated samples. Initial heating of the catalyst for 3-1/2 hours at 500° C and 1 hour at 600° C in 8 percent H_2 in helium lowered CO conversion by 12 and 24 percent, respectively, when compared to a sample that was reduced for 1 hour at 400° C. The methanation activity of Raney nickel at 320° C was drastically lowered following a precarbiding treatment at 263° C. Surface poisoning with H_2S caused a greater reduction in methanation activity than that attributed to the corresponding decrease in free nickel surface area.

A surface carbide and sulfur species were observed by ESCA measurements on samples that were deactivated by carbiding and H_2S poisoning.

INTRODUCTION

In the Department of Energy's SYNTHANE process, that is currently under development for the production of synthetic natural gas (SNG) from coal, a Raney nickel catalyst is being investigated for use in the methanator to convert CO and H_2 to CH_4. In order for the process to become technically and economically feasible, the catalyst should have a life expectancy of at least one year without significant loss of catalyst activity. To date, pilot plant investigations on three types of methanators; the tube wall reactor (3,4,6,7)[6], the hot gas recycle system, (5,8,9), and the hybrid reactor (14) have shown that catalyst deactivation is a serious problem.

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[1] Research chemist.

[2] Former physical scientist

[3] Former NRC post-doctoral fellow.

[4] Physical science technician

[5] Research Supervisor

[6] Numbers in parentheses refer to items in the list of references at the end of this report.

There are several possible causes of catalyst deactivation. Previous work (10) has indicated that loss of catalytic activity in pilot plant reactors is associated with loss of nickel surface area. This suggests that metal sintering has occurred due to localized hot spots on the catalyst surface resulting from the exothermic methanation reaction. Carbon laydown can also affect the life of Raney nickel by poisoning active sites or by plugging pores in the catalyst. Although under methanation conditions carbon deposition is thought to be avoided by keeping the H_2/CO ratio greater than three (10), carbon has been detected at the inlet end of the catalyst bed following termination of pilot plant runs (13). X-ray diffraction analysis of the spent catalyst suggests that carbon can occur in the forms of Ni_3C or a nickel carbide stabilized by iron. Sulfur compounds are known to poison nickel (11, 12). In the SYNTHANE process less than 0.1 PPM of H_2S will be allowed in the feed gas to the methanator.

In order to identify factors related to catalyst deactivation, a combination of techniques, such as BET surface area, H_2 and CO adsorption, electron spectroscopy for chemical analysis (ESCA) and activity tests were used to characterize Raney nickel before and after deactivation. The effects that high temperatures, sulfur poisoning and carbiding have on the methanation activity of Raney nickel will be discussed.

EXPERIMENTAL

Catalyst Preparation

Approximately 228 grams of a commercial Raney nickel alloy[7] obtained from W. R. Grace[8] was added to a solution of 50 percent NaOH. By controlling the rate of alloy addition and temperature of the water bath surrounding the reaction flask, the temperature of leaching was maintained at 70° C. Activation was continued until the evolution of H_2 could no longer be detected by a wet test meter. Calculations based on the volume of H_2 measured indicated 95 percent of the aluminum was leached from the alloy. The leached sample was thoroughly washed with deionized water, dilute (0.5 percent) acetic acid, and deionized water, respectively, and the pH of the final solution was 7.5. To stabilize the catalyst by mild oxidation, the aqueous slurry (900 ml) was treated with 16 ml of 30% H_2O_2, then separated from the water and dried under vacuum at 25° C. The stabilized nickel catalyst was divided into 10 approximately equal parts and stored in glass vials. Thermogravimetric analysis (TGA) of the stabilized sample resulted in a 14 percent weight loss after reduction in H_2 for approximately 8 hours at 400° C. Samples of the stabilized catalyst were used for various experiments as described below.

---

[7] The Raney alloy was identified as Batch 18 and had the following elemental composition: 61.1 percent Al, 38.3 percent Ni, 0.2 percent C, 0.1 percent Fe, 0.2 percent Na, and 0.1 percent S.

[8] Reference to specific brands is made for identification only and does not imply endorsement by the U.S. Department of Energy.

Catalyst Deactivation

Sintering. Raney nickel was sintered by heating the catalyst in the carrier gas (8 percent H_2 + 92 percent He) of the pulse microreactor to temperatures of 500° and 600° C. Following the sintering treatment, CO conversion was determined at 320° C. Samples used for nickel surface area measurements were sintered in the TGA apparatus.

Carbiding. Nickel carbide, identified by X-ray diffraction, can be prepared by passing CO over Raney nickel at temperatures less than 300° C at 1 atm. Bahr and Bahr (1) showed that below 270° C, CO reacted with nickel to form Ni_3C. The decomposition of CO continued until the Ni was completely transformed into Ni_3C.

Approximately 6.6 grams of the stabilized sample was reduced in H_2 at 400° C for 3-1/2 hours, then carbided by passing CO through the catalyst bed for 2 hours at 263° C. The sample was cooled to room temperature in N_2. The percent of nickel carbide, as determined by the amount of CO_2 absorbed in a soda lime trap and by the increase in catalyst weight, was 59 and 73 percent, respectively. An average value of 66 percent was used for the extent of nickel atoms carbided. The sample was stored in a glass vial under 1 atm. of N_2. A sketch of the apparatus used for carbiding is shown in Figure 1.

Sulfiding. Sulfiding was accomplished by passing H_2S through a bed of reduced Raney nickel at 400° C. As shown in Figure 2, H_2S was introduced into the H_2 stream by diffusion through a permeation tube containing liquid H_2S. The permeation rate for the 10 cm H_2S tube was 246 ng/min or 7.23×10^{-9} moles/min at 1° C. This value was determined by two methods. The first involved taking the following calibration data, supplied by the manufacturer, and plotting the logarithm of the permeation rate against temperature.

Temperature, °C	Permeation Rate, ng H_2S $cm^{-1}min^{-1}$
20	165
30	410
40	1000

Extrapolation to 1° C gave 25 ng H_2S $cm^{-1}min^{-1}$. In the second method the permeation rate at 1° C was calibrated by passing N_2 at flows of 150 to 200 cm^3/min over the tube and collecting the H_2S in a lead acetate solution. The concentration of absorbed H_2S was determined by analytical techniques. From nine runs over a period of from 30 to 70 minutes, the average rate for the 10 cm tube was 246 ng/min. Therefore, passing H_2 at a flow rate of 180 cc/min over the permeation

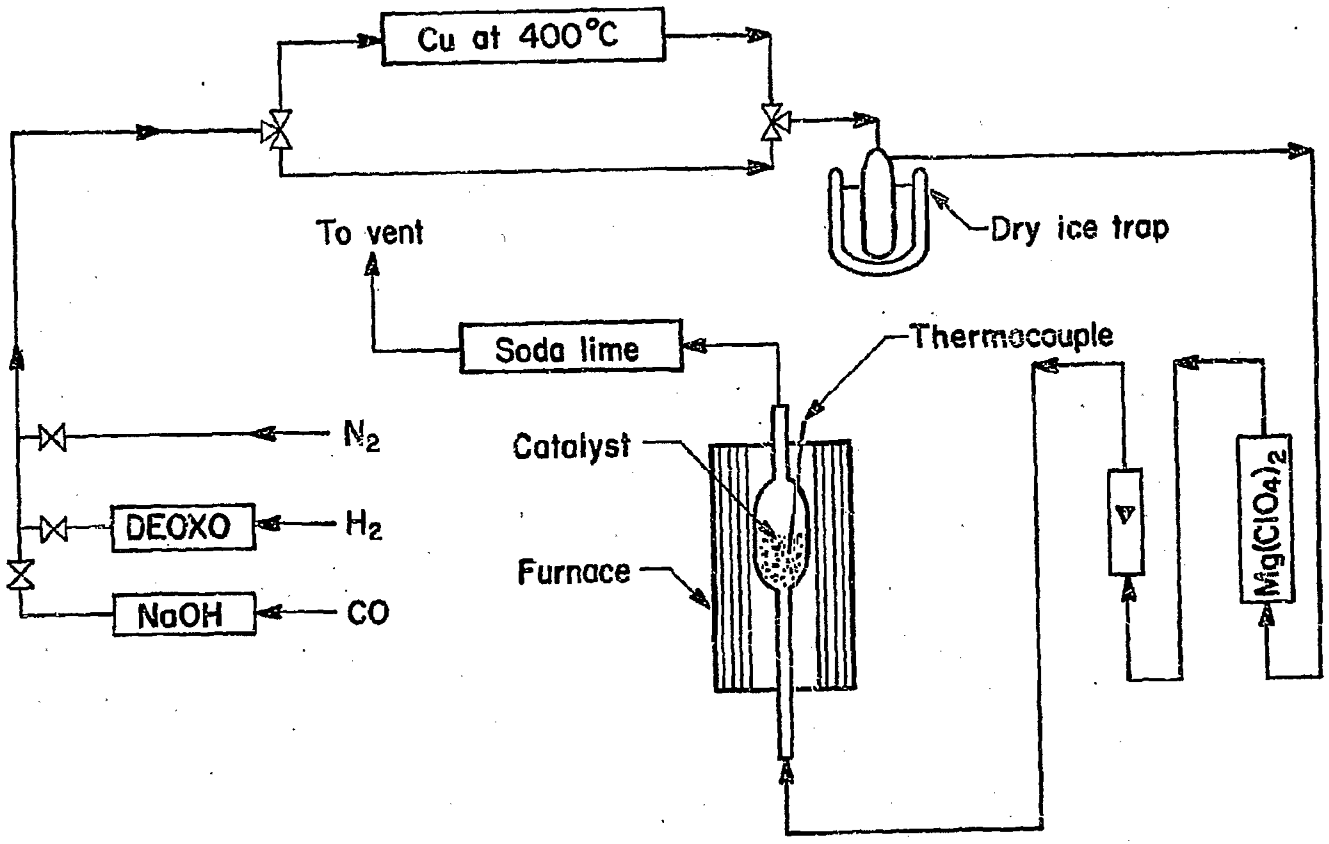

Figure 1—Carbiding apparatus

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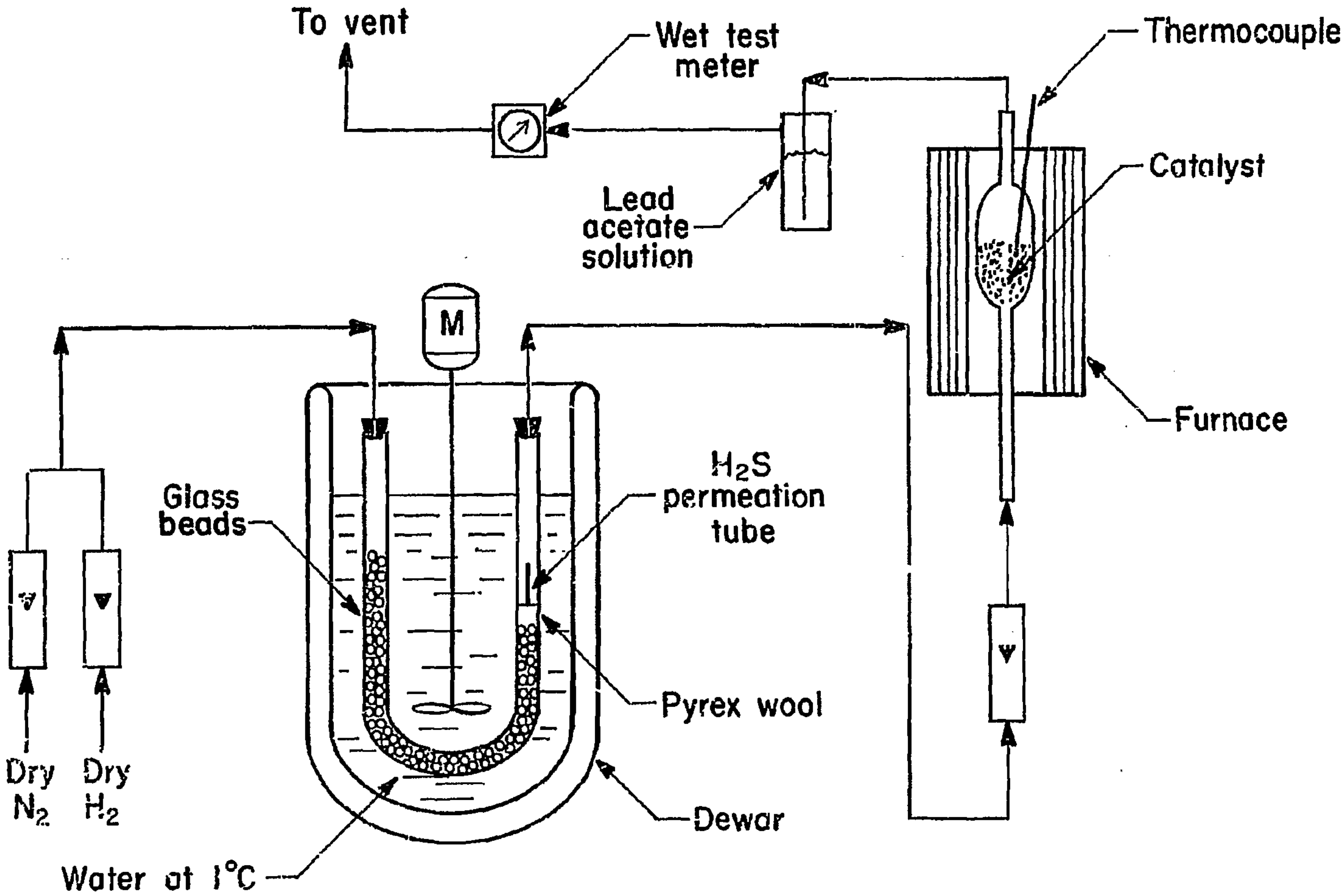

Figure 2 - Sulfiding apparatus

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tube at 1° C resulted in a feed containing 0.9 PPM H_2S in H_2 by volume. From the time internal of H_2S/H_2 flow through the samples, the amounts of H_2S that adsorbed on Ni sites were caluclated. Since a negligible amount of H_2S was absorbed in a lead acetate solution downstream from the catalyst, it was concluded that the sample adsorbed the H_2S nearly quantitatively. Assuming one molecule of H_2S adsorbed on three nickel sites, a monolayer coverage of sulfur, based on H_2 chemisorption measurements, was calculated as follows:

$$\frac{10.6\ m^2\ Ni}{g\ catalyst} \times \frac{1\ cm^3\ H_2}{3.64\ m^2 Ni} \times \frac{1\ mole\ H_2}{22{,}400\ cm^3 H_2} \times \frac{2\ moles\ Ni_{(S)}}{1\ mole\ H_2}^{9} \qquad (1)$$

$$= \frac{2.6 \times 10^{-4}\ moles\ Ni_{(S)}}{g\ catalyst}$$

Therefore, one monolayer coverage corresponds to 0.87 X 10^{-4} moles of H_2S per gram of catalyst. Nickel surface coverages of 15 and 51 percent were obtained by passing the H_2S/H_2 feed through 5.3 and 4.8 grams of reduced nickel for 157 and 485 hours, respectively.

Catalyst Testing

A pulse microreactor-gas chromatograph (GC) system, shown in Figure 3, was used to measure the initial activity and product selectivity of the Raney nickel catalysts. Catalyst weights ranging from 2.4 to 22.2 mg were placed in the center of a 6 mm O.D. by 4 mm I.D. pyrex glass reactor of approximately 31 cm length. For the carbided and sulfided catalysts, samples were transferred to the reactor via a glove bag filled with N_2. The reactor was then connected to the flow system and purged with carrier gas. Care was taken to prevent air from contacting the sample as the reactor was being connected. A horizontal tube furnace 20 cm in length was used to heat the glass reactor tube, and a chromel vs. alumel thermocouple inserted inside the reactor tube immediately before the catalyst bed measured the temperature. The carrier gas was passed through the reactor at 60 cm^3/min and 20 psig. Prior to methanation tests, the nickel catalyst was reduced in carrier gas for one hour at 400° C. Reactant gas consisting of 76.00 percent H_2, 23.76 percent CO, 0.08 percent CO_2, 0.10 percent N_2 and 0.06 percent CH_4 was introduced into the carrier gas stream via a 1.00 cm^3 sampling valve.

A Bendix Model 2230-2 gas chromatograph with a thermal conductivity detector was used with a Hewlett Packard 7123A recorder to analyze the gaseous products. A 3 foot column packed with 60/80 mesh 5A molecular sieve was used to separate CH_4 and CO, while a 5 foot column packed

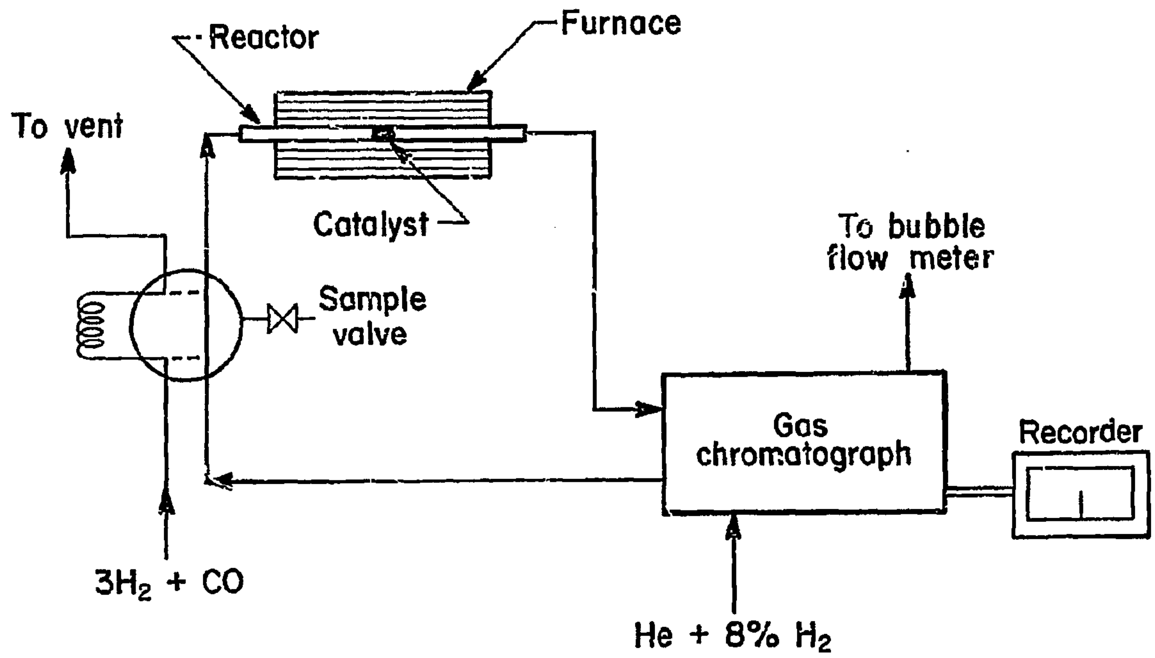

Figure 3—Pulse microreactor system

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with 80/100 mesh porapak-S was used to separate CO_2, C_2H_6 and H_2O. Both columns were made from 1/4-inch O.D. stainless steel tubing and were held at 60° C. A gas switching valve on the GC was used to prevent water and CO_2 from contacting the molecular sieve column. In most cases initial activity and product selectivity were determined at 320° C, but for some of the deactivated samples, temperatures ranging from 200° to 400° C were employed. The only hydrocarbon products detected were methane and ethane. Methanation activity was defined as the ratio of weight of standard catalyst to the weight of deactivated catalyst required to obtain a given CO conversion. CO conversion was defined by:

$$\text{Percent Conversion} = \frac{A}{A + B} \times 100 \qquad (2)$$

where A is the net moles of CO converted to CH_4, C_2H_6 and CO_2 and B represents the moles of CO leaving the reactor. The selectivity to product X was defined by the following equation:

$$\text{Percent Selectivity to X} = \frac{\text{moles of CO consumed to form X}}{A} \times 100 \qquad (3)$$

where X is CH_4, C_2H_6 or CO_2.

Surface Area Measurements

A volumetric BET adsorption apparatus was used to determine total surface areas by N_2 adsorption at -196° C and nickel surface areas by H_2 chemisorption at 250° C. In each case the sample was first reduced in hydrogen to 400° C. Nickel surface areas of the sintered catalysts were also determined in the TGA by CO chemisorption at 110° C. The latter method was used for small sample sizes, and results were comparable with the H_2 chemisorption method.

ESCA Measurements

ESCA spectroscopy is a surface analysis technique which involves irradiating a sample with X-rays and measuring the kinetic energy of the ejected core electrons. Binding energies of the ejected electrons are then obtained by subtracting the energy of the incident X-ray from the measured kinetic energies. Since binding energy is a function of chemical environment, identification of the element to which the electron was associated can be made. Shifts in the binding energy of several electron volts are common for different oxidation states.

In this investigation a Hewlett-Packard 5950A ESCA spectrometer was used to examine the surface of Raney nickel catalysts. An aluminum anode was used for the source of X-rays, and an electron flood gun was used to control charging effects. Spectra were recorded with the flood gun set to 0.4 mA and the initial or surface electron kinetic energy set to zero volts. Except for survey scans of 1,000 eV, a 20 eV range was recorded.

Two techniques were used for preparation of samples for analysis. In one, the reduced nickel was pressed into a strip of indium foil, and in the other, a press was utilized to form small pills. The samples were prepared in a glove bag and then transferred to the sample probe of the spectrometer. The following were examined for Ni, Al, C, Fe, Na and S:

(1) Raney nickel alloy prior to leaching

(2) reduced nonpyrophoric sample

(3) carbided sample

(4) sample poisoned with H_2S

RESULTS

Standards; Nondeactivated Sample

Carbon monoxide conversion and selectivity data for the nondeactivated samples are listed in Table A-1 in the Appendix. As illustrated in Figure 4, a slight decrease in CO conversion was observed for successive pulses of synthesis gas over the lower weight sample, but for samples of higher weight, the decrease in activity was not noticeable after the first few pulses of $3H_2/CO$. Heating the catalyst in carrier gas at 320° C overnight did not affect the CO conversion or product selectivity. With increased sample weight CO conversion increased, but no significant change was detected in product selectivity. Total BET (N_2 adsorption at -196° C) and Ni surface areas (H_2 adsorption at 250° C) of the reduced catalyst were 42.0 and 10.6 m^2/g, respectively.

Sintered Samples

To study sintering, CO conversion was measured at 320° C before and after heating the stabilized Raney nickel catalyst. The first three pulses listed in Table 1 give CO conversion following the standard reduction treatment at 400° C. Heating the sample for 2-1/2 hours at 500° C in the H_2-He mixture resulted in a loss in catalytic activity. A second reduction treatment for one hour at 500° C had no additional effect, but further deactivation did occur after heating to 600° C for one hour. Heating the sample to 500° and 600° C did not significantly affect the product selectivity. Nickel surface area, as determined by CO adsorption at 110° C, dropped from 15 m^2/g for a sample heated at 400° C to 6 m^2/g as a result of the combination of heating to 500° and 600° C in carrier gas.

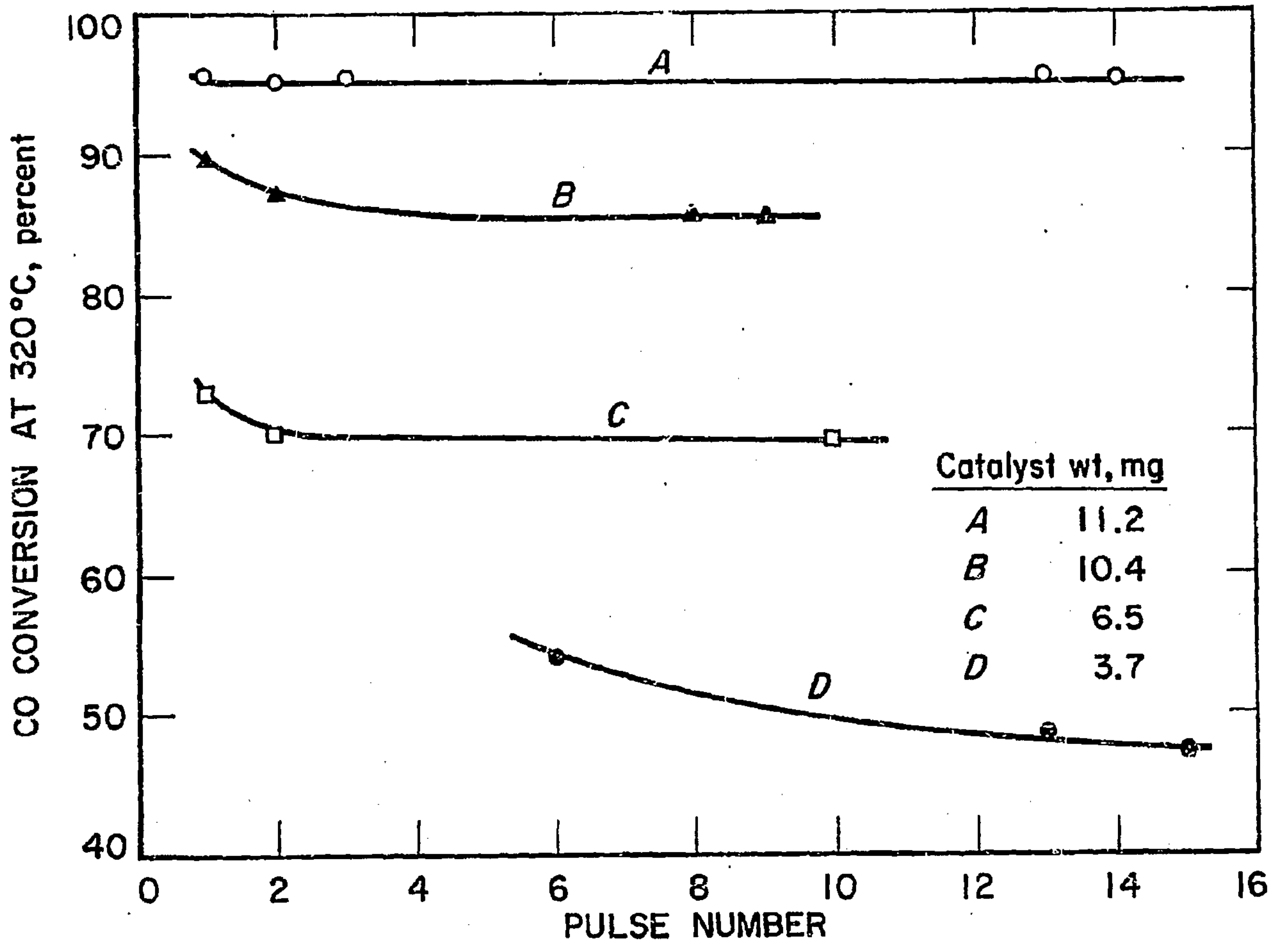

Figure 4—CO conversion on Raney nickel as a function of pulse number for various weights of catalyst.

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Table 1. - Effect of prereducing temperature on CO conversion

Pulse No.[1]	Treatment in 8 pct H_2 + He	CO conversion at 320° C, pct	Selectivity, pct			Nickel surface area, m^2/g
			CH_4	CO_2	C_2H_6	
	1 hr at 400° C					[2]15
1		95	91.2	8.8	0.1	
2		96	90.6	9.4	0.1	
3		93	89.6	10.3	0.1	
	2-1/2 hr at 500° C					
4		86	89.9	10.0	0.2	
5		83	86.3	13.4	0.2	
	1 hr at 500° C					
6		83	90.4	9.2	0.4	
	1 hr at 600° C					6
7		71	91.8	7.6	0.5	

---

[1] Sample weight was 11.5 mg and the carrier gas flow rate was 60 cm^3/min.
[2] Determined with CO, assuming linear adsorption. For a similarly treated sample, H_2 chemisorption resulted in a nickel surface area of 10.6 m^2/g.

Carbided Samples

The results from pulse microreactor testing of the carbided samples are given in Table A-2 of the Appendix. To prevent reduction of the sample, the carrier gas was changed to helium. Low but reproducible CO conversions were obtained at 300° C. Methane selectivity was low (30-65%) at 300° C, and the selectivity to CO_2 (30-66%) was much higher than with uncarbided Raney nickel catalyst. Doubling the sample weight resulted in only a slight increase in CO conversion. Following initial runs at 300° C, the temperature was varied from 200° to 400° C. Selectivity to products was erratic with respect to time and temperature. Temperatures below 300° C generally produced high CO_2 selectivity which is in keeping with conditions needed to react CO with metallic nickel to produce CO_2 and Ni_3C. Above 300° C, Ni_3C becomes unstable and decomposes to free nickel and carbon. The combination of these two reactions is the Boudouard reaction, the conversion of CO to CO_2 and carbon.

Table 2 compares CO conversion and product selectivity of a noncarbided to a carbided sample. Neglecting the possible GC detector response variation resulting from using 100 percent He as carrier in B-96 and 8 percent H_2 in helium in B-120, a loss in CO conversion of 39 percent resulted from the carbiding treatment. One would think that carbiding 66 percent of the total nickel would result in almost complete coverage

Table 2. - Effect of carbon laydown on CO conversion and product selectivity of Raney nickel

Sample	Carbided, pct.	Weight, mg	Pulse No.	CO Conversion at 320° C, pct	Selectivity CH_4	CO_2	C_2H_6
B-120	0	12.9[1]	13	96	87.5	11.7	0.8
B-96	66	14.5	13	57	62.4	37.5	0.1

[1] Since sample B-96 was not reduced prior to the methanation reaction, 12.9 mg is the weight before H_2 reduction.

of the nickel surface sites and that a greater reduction in CO conversion would have been observed. The decrease in nickel surface area as a result of carbiding was not known.

Past work at the Pittsburgh Energy Research Center has shown that deactivated Raney nickel catalysts from pilot plant runs when tested in a TGA gain weight during the methanation reaction. X-ray diffraction of the deactivated samples indicated a surface carbide to be present. On a non-deactivated or standard sample, no weight gain was detected when $3H_2$ + CO was passed over the catalyst at 380° C. This work suggests that carbon deposition occurs on deactivated pilot plant samples under methanation conditions. Therefore, it is believed that the high selectivity to CO_2 observed on the carbided samples in this investigation is the result of an enhancement in the Boudouard reaction. Wentrcek, et al, (16) using Auger spectroscopy observed a surface carbide on Ni/Al_2O_3 following exposure of the catalyst to pulses of CO at temperatures greater than 177° C. The resulting Ni-C species was very reactive to H_2 with quantitative conversion to methane at 277° C. At 400° C, the surface carbide was converted to graphitic carbon which had a very low reactivity towards H_2. In an earlier investigation Bahr and Bahr (1) showed that at temperatures between 270° and 380°C CO reacts with nickel to form Ni_3C and carbon. It is therefore postulated that in this investigation product CH_4 resulted from the reaction of H_2 from the pulse and surface Ni_3C and CO_2 form CO decomposition.

Sulfided Samples

Table A-3 in the Appendix lists the data for samples deactivated by sulfiding with H_2S. Very little, if any, loss in CO conversion with pulse number occurred for the various weights of samples tested. Overnight contact in carrier gas at various temperatures or contact with synthesis gas at methanation temperatures did not affect the methanation activity or product selectivity. CO conversion as a function of sample weight for the sulfided samples are compared to the nonsulfided (or standard) sample in Figure 5. For 8 mg samples, a decrease in CO conversion of approximately 20 and 52 percent resulted from sulfiding Raney nickel to nickel surface coverages of 15 and 51 percent, respectively.

Nickel surface areas for the 15 and 51 percent sulfided samples, as determined by H_2 chemisorption at 250° C, were 8.9 and 4.8 m^2/g, respectively. Using 10.6 m^2/g as the surface area for the nonsulfided sample, the corresponding percent reductions in nickel surface areas for the two sulfided samples were 16 and 55, respectively.

Comparison of Deactivated Samples

Carbon monoxide conversions and nickel surface or nickel bulk areas of approximately equal weights of standard and deactivated Raney nickel catalysts are compared in Table 3.

Table 3. - CO conversion and surface area of standard and deactivated Raney nickel

A. Sintered Sample

Sample	Wt, mg	Temp. in carrier gas, °C	CO conversion at 320° C, pct	Nickel surface area, m^2/g[1]
Standard	11.5	400	93	15
Deactivated	11.5	600	71	6

B. Carbided Sample

Sample	Wt, mg	Extent of carbiding, pct	CO conversion at 320° C, pct
Standard	12.9	0	96
Deactivated	14.5	66	57

C. Sulfided Sample

Sample	Wt, mg	Sulfur surface coverage, pct Ni_3S	CO conversion at 320° C, pct	Nickel surface area, m^2/g[2]
Standard	8	0	78	10.6
Deactivated	8	15	63	8.9
Deactivated	8	51	39	4.9
Standard	12	0	96	10.6
Deactivated	12	15	80	8.9
Deactivated	12	51	52	4.9

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[1] Nickel surface area determined by CO adsorption at 110° C.

[2] Nickel surface area determined by H_2 adsorption at 250° C.

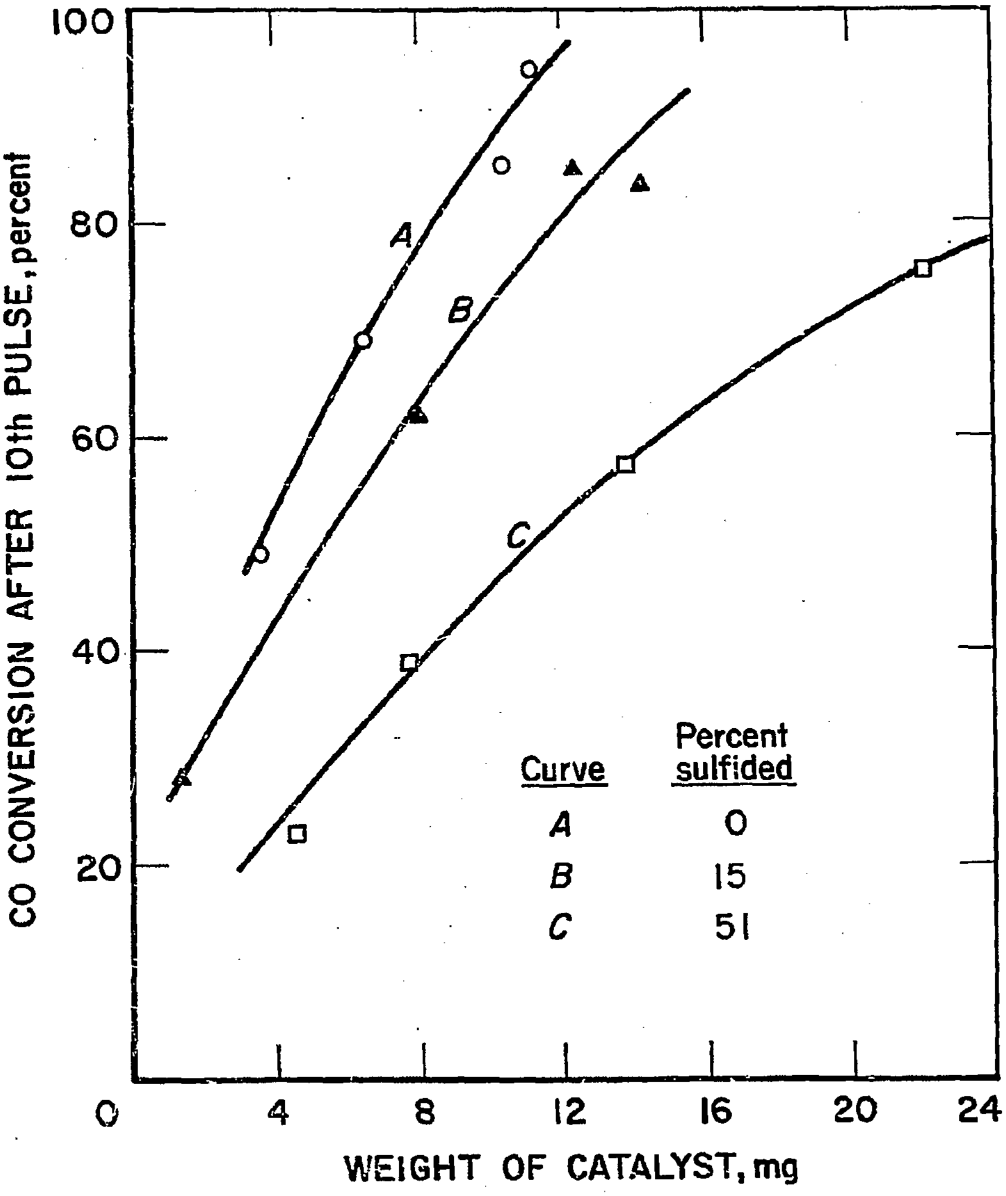

Figure 5–Effect of sulfiding on CO conversion at 320°C.

In order to compare the performance of a deactivated sample to that of the nondeactivated standard, the activity of the deactivated catalyst is related to the remaining nickel surface area in Table 4. Activity is defined as the ratio of the weight of standard to the weight of deactivated catalyst that would be required to give the same CO conversion as the standard. Figure 5 was used to determine the weight of standard (curve A) that would be needed to give the same CO conversion as the sintered and carbided samples listed in Table 3. For the two sulfided samples, Figure 5 was used to determine the activity for CO conversions of 60 and 80 percent.

Table 4. - Activity of deactivated samples and remaining nickel surface area

A. Sintered sample

Sample weight for 71% CO conversion, mg		Activity	Decrease in nickel surface area as a result of sintering at 600° C, pct
Deactivated	Standard		
11.5	6.8	0.60	60

B. Carbided sample

Sample weight for 57% CO conversion, mg		Activity	Bulk nickel not carbided, pct
Deactivated	Standard		
14.5	4.6	0.32	33

C. Sulfided sample

(a)

Sample weight for 60% CO conversion, mg			Activity		Remaining nickel surface area, pct	
SS-1[1]	SS-2[2]	Standard	SS-1	SS-2	SS-1	SS-2
7.3	14.9	5.0	0.68	0.33	85	49

(b)

Sample weight for 80% CO conversion, mg			Activity		Remaining nickel surface area, pct	
SS-1	SS-2	Standard	SS-1	SS-2	SS-1	SS-2
12.5	25.4	8.5	0.71	0.33	85	49

---

[1] SS-1 represents sulfided sample with 15 percent surface coverage.

[2] SS-2 represents sulfided sample with 51 percent surface coverage.

ESCA Measurements

A comparison between the ESCA spectra of Raney nickel before and after deactivation was made. Of particular interest was to identify surface carbide and deposited sulfur on the deactivated samples.

Survey scans of Raney nickel alloy and the reduced nonpyrophoric sample illustrate the usefulness of ESCA to detect elemental surface composition. Results from these scans are given in Table 5. Results of 20 eV scans over samples of Raney nickel alloy, a leached nonactivated reduced (LNDR) sample, the carbided and sulfided samples are given in Table 4-A in the Appendix.

In the Raney nickel alloy, the ratio of $Ni^{+2}/Ni^{0} = 2.0$, while in the LNDR sample the $Ni^{+2}/Ni^{0} = 0.8$. In the LNDR sample aluminum was observed which represents the nondissolvable Al, possibly from NiAl, and the absence of sodium indicates the completeness of the washing process. Very low concentrations of sulfur and nitrogen were observed in the two samples and are believed to represent surface S^{-2}, SO_4^{-2}, N_2 and NO_2^{-1} species. A large carbon peak in the alloy at 284.5 eV could represent either graphitic carbon ($E_B = 284.3$) or a paraffinic carbon (E_B=285.0) (2). In the LNDR sample possibly a CO_x species resulted in a peak at 289.0 eV as well as a large peak at 284.5 eV. Reduced iron was seen in both samples.

On the sample that was deactivated by carbon laydown, binding energy peaks at 283.2 and 282.4 eV were observed and are believed to represent surface carbides. Since a carbidic carbon will be expected to have a partially negative charge, it will appear at a lower E_B than would be observed for C_{1s} (285.0 eV).

Table 5. - Survey scans of Raney nickel alloy and a reduced nonpyrophoric sample

A. Raney nickel alloy

Elemental line	E_B, eV	Counts, K
Ni 3p	68	3.5
Al 2p	74	11.0
Ni 3s	112	1.0
Al 2s	119	12.5
S 2p	169	1.0
Cl 2p	199	0.5
C 1s	284	Very large peak
Ni 2p	858	19.0

B. Reduced nonpyrophoric sample

Elemental line	E_B, eV	Counts, K
Fe 3p	55	0.5
Ni 3p	67	7.0
Al 2p	73	6.0
Si 2p	100	0.5
Ni 3s	112	2.5
Al 2s	118	6.5
N 1s	398	0.8
C 1s	284	8.5
F 1s	688	1.0
Ni 2p	857	43.0

Samples sulfided with H_2S were examined for carbon, nickel and sulfur. About the same level of carbon was observed as was detected on the alloy and the LNDR samples. The ratio of Ni^{+2}/Ni^{o} increased with extent of sulfiding. For the 15 percent sulfided catalyst $Ni^{+2}/Ni^{o} = 1$, while for the 51 percent sulfided sample the ratio equaled 2. On the 15 percent sulfided sample only one sulfur peak at 162.4 eV was observed, while on the higher sulfided sample, a second peak at 170 eV appeared. The 162.4 eV peak is believed to represent a surface sulfide, while the 170 eV peak is an adsorbed SO_x species. One would expect the E_B for the sulfur S2p electron in NiS_x to be lower than 162 eV. Gaseous H_2S has a S2p E_B of 170 eV and the E_B for an adsorbed sulfate, $Fe_2(SO_4)_3$, is 169.3 eV (2). The observed 170 eV peak is not gaseous H_2S. It is possible that a surface NiS_x existed and was oxidized to a sulfate while being transferred to the spectrometer or while being stored in the glass vial.

Samples that were deactivated by heat treatment were not examined by ESCA.

Conclusions

The methanation activity of Raney nickel has been shown to be very sensitive to moderate deactivation conditions. A one hour exposure of the catalyst to a temperature of 600° C in an atmosphere of hydrogen-helium reduced nickel surface area by 60 percent and activity by 40 percent. Carbiding Raney nickel catalyst caused deactivation approximately in proportion to the amount of nickel which reacted with CO to form nickel carbide which is believed to be a fortuitous result. Possibly what occurred when synthesis gas was passed over the carbided sample was the reaction of H_2 with Ni_3C to produce CH_4 and the decomposition of CO to generate product CO_2. Raney nickel was extremely affected by H_2S which caused a greater reduction in methanation activity than in the corresponding decrease in nickel surface area. Calculated nickel surface areas, assuming a Ni_3S adsorbed species, correlated very well with the nickel surface area determined by H_2 chemisorption. The greater reduction in methanation activity than in nickel surface area suggests that nickel sites of different strengths existed and that H_2S selectively poisoned the more active sites.

ESCA survey scans on Raney nickel alloy and a leached reduced sample of the catalyst resulted in detection of surface Fe, S, C, N, Al and Ni. A small amount of surface carbide was observed on the sample that was deactivated by contacting with CO. A sulfur species was observed on the sample sulfided to 51 percent coverage and was identified as a sulfate. It is believed that a NiS_x species existed on the surface of the catalyst but was oxidized to the sulfate during sample storage or when transferred to the spectrometer.

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Appendix

Table A-1. - CO Conversion and Selectivity of Nondeactivated Raney Nickel at 320° C

Sample No.	Pulse No.	Catalyst wt,[1] mg	Flow Rate, cm^3/min	CO Conversion percent	Selectivity, percent		
					CH_4	CO_2	C_2H_6
B-73	1	3.7	30	86	85.6	14.2	0.1
			(overnight at 25°C)				
	2	3.7	30	83	90.3	9.5	0.2
	5	3.7	60	56	93.7	5.9	0.4
	6	3.7	60	54	94.2	5.2	0.6
	[2]7-12	3.7	60	—	—	—	—
	13	3.7	60	48	95.0	4.3	0.7
			(overnight at 320°C)				
	15	3.7	60	47	95.4	4.0	0.5
B-74	1	10.4	60	90	92.4	7.5	0.1
	2	10.4	60	87	91.2	8.9	0.1
	3-7	10.4	60	—	—	—	—
	8	10.4	60	85	90.9	9.0	0.1
	9	10.4	60	85	90.1	9.9	0
B-75	1	6.5	60	73	86.5	13.4	0.1
	2	6.5	60	70	88.3	11.2	0.5
	3-9	6.5	60	—	—	—	—
	10	6.5	60	69	93.4	6.5	0.1
	13	6.5	60	65	89.5	10.3	0.2
B-120	1	11.2	60	95	83.3	14.4	2.3
	2	11.2	60	95	79.4	17.4	2.9
	4-10	11.2	60	—	—	—	—
	11	11.2	60	97	85.1	13.9	1.0
	13	11.2	60	96	87.5	11.7	0.8
	14	11.2	60	96	90.0	9.3	0.8

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[1] Corrected for weight loss during H_2 reduction.

[2] Successive pulse over catalyst, product gases were not analyzed by GC.

[3] In 8 percent H_2 + He at very low flow rate.

Table A-2 - CO Conversion and Selectivity Data of Carbided Raney Nickel

Sample No.	Pulse No.	Sample wt, mg	Reaction temp, °C	CO Conversion, percent	Selectivity, percent,		
					CH_4	CO_2	C_2H_6
B-95	3	6.9	300	18	45.5	54.0	0.5
	4	6.9	300	15	60.5	38.0	1.5
	5	6.9	300	18	64.1	34.7	1.2
	6	6.9	300	16	61.0	38.5	1.5
	7	6.9	300	17	64.0	35.0	1.5
	8	6.9	300	19	68.5	30.2	1.3
			(overnight in He at 25° C)				
	9	6.9	300	17	32.7	66.2	1.0
	10	6.9	300	17	57.8	40.7	1.4
	11	6.9	350	60	48.0	52.0	0
B-96	1	14.5	300	22	50.5	49.0	0.5
	2	14.5	300	28	64.2	35.3	0.5
	3	14.5	300	23	48.7	50.7	0.6
	4	14.5	300	26	50.8	48.6	0.6
			(overnight in He at 25° C)				
	5	14.5	300	30	36.7	63.1	0.2
	6	14.5	200	1	—	—	—
	7	14.5	320	3	8.2	91.8	0
	8	14.5	240	4	8.8	91.2	0
	10	14.5	260	12	23.0	76.3	0.7
			(overnight in He at 25° C)				
	11	14.5	280	24	14.0	85.6	0.4
	12	14.5	300	40	65.0	34.6	0.4
	13	14.5	320	57	62.4	37.5	0.1
	14	14.5	340	67	71.9	28.0	0
	15	14.5	360	72	70.9	29.1	0
	16	14.5	400	80	72.9	27.1	0
			(overnight in He at 310° C)				
	17	14.5	320	53	68.0	31.9	0.2
	18	14.5	200	1	—	—	—

Table A-3. - CO Conversion and Selectivity of Sulfided Raney Nickel

A. 15 percent sulfided

Sample No.	Pulse No.	Sample wt, mg	Reaction temp., °C	CO Conversion, percent	Selectivity, percent		
					CH_4	CO_2	C_2H_6
B-129	1	8.0	320	61	87.0	11.5	1.5
	2	8.0	320	58	85.0	12.8	2.3
	3	8.0	320	61	87.0	11.5	1.5
	4-9	8.0	320	—	—	—	—
	10	8.0	320	62	—	—	—
	11	8.0	320	62	84.8	13.2	2.0
			(overnight at 320° C)				
	12	8.0	320	59	86.0	12.5	1.5
	13	8.0	320	59	87.0	11.6	1.3
	14	8.0	320	59	86.0	12.4	1.7
	15	8.0	330	66	81.4	17.4	1.1
	16	8.0	340	71	82.8	16.8	0.4
	17	8.0	350	77	82.3	17.4	0.3
	18	8.0	360	81	84.1	15.8	0.2
	19	8.0	370	84	82.8	16.9	0.2
	20	8.0	380	87	83.6	16.3	0.1
	21	8.0	390	90	85.2	14.7	0
	22	8.0	320	59	92.8	6.3	0.9
B-130	1	2.4	320	15	83.8	10.8	5.4
	2	2.4	320	25	81.9	12.6	5.5
	3	2.4	320	25	80.8	13.5	5.7
	4-9	2.4	320	—	—	—	—
	10	2.4	320	28	89.9	7.1	2.9
	12	2.4	320	26	82.6	12.0	5.4
	13	2.4	320	27	81.0	13.5	5.5
B-126	1	14.3	320	—	—	—	—
	2	14.3	320	84	77.4	20.9	1.7
	3	14.3	320	83	83.9	14.8	1.3
	4	14.3	320	84	86.1	12.9	1.0
	5-9	14.3	320	—	—	—	—
	10	14.3	320	83	85.4	13.6	0.9
	11	14.3	320	84	82.8	15.9	1.3
B-127	1	12.4	320	87	86.4	13.0	0.6
	2	12.4	320	86	86.5	12.6	0.9
	3	12.4	320	85	87.9	11.4	0.7
	4-9	12.4	320	—	—	—	—
	10	12.4	320	86	85.4	13.7	0.9
	11	12.4	320	85	85.8	13.5	0.8

(continued)

Table A-3. - CO Conversion and Selectivity of Sulfided Raney Nickel (continued)

B. 51 percent sulfided

Sample No.	Pulse No.	Sample wt, mg	Reaction temp, °C	CO Conversion, percent	Selectivity, percent		
					CH_4	CO_2	C_2H_6
B-131	1	22.2	320	74	87.9	11.0	1.1
	2	22.2	320	75	84.8	13.9	1.3
			(overnight at 25°C)				
	3	22.2	320	73	86.3	12.9	0.8
	4-9	22.2	320	—	—	—	—
	10	22.2	320	75	82.3	16.6	1.1
	11	22.2	320	74	84.9	13.8	1.3
	12	22.2	320	73	80.3	18.2	1.5
	13	22.2	320	72	84.2	14.7	1.1
	14	22.2	320	73	78.5	19.8	1.7
B-133	1	13.8	320	58	86.9	11.6	1.5
	2	13.8	320	57	88.8	9.8	1.4
	3	13.8	320	56	88.3	10.3	1.4
	4-9	13.8	320	—	—	—	—
	10	13.8	320	57	86.9	11.4	1.7
	11	13.8	320	55	95.1	4.2	0.8
			(overnight at 25°C)				
	12	13.8	320	55	89.7	8.9	1.3
	13	13.8	320	57	88.7	10.1	1.2
	14	13.8	330	62	84.0	14.4	1.5
	15	13.8	340	69	81.1	18.3	0.6
B-133	16	13.8	350	72	86.0	13.8	0.2
	17	13.8	360	76	85.8	14.1	0.2
	18	13.8	370	80	83.9	15.9	0.2
	19	13.8	380	82	83.7	16.2	0.1
	20	13.8	390	84	85.1	14.9	0
	21	13.8	320	55	89.1	9.5	1.4
	22	13.8	320	54	86.5	11.2	2.3
B-134	1	7.7	320	35	85.4	10.7	3.9
	2	7.7	320	37	85.4	10.8	3.8
	3	7.7	320	38	87.7	8.9	3.5
	4-9	7.7	320	—	—	—	—
	10	7.7	320	39	87.3	9.2	3.5
	11	7.7	320	39	86.6	9.5	3.9
			(over weekend at 250°C)				

(continued)

Table A-3. - CO Conversion and Selectivity of Sulfided Raney Nickel (continued)

B. 51 percent sulfided

Sample No.	Pulse No.	Sample wt, mg	Reaction temp., °C	CO conversion, percent	Selectivity, percent CH_4	CO_2	C_2H_6
B-134	12	7.7	330	40	87.3	10.4	2.0
	13	7.7	340	47	87.1	11.2	1.7
	14	7.7	350	49	85.3	13.6	1.0
	15	7.7	360	60	86.8	12.5	0.7
	16	7.7	370	66	84.3	15.4	0.3
	17	7.7	380	68	83.0	16.7	0.3
	18	7.7	390	74	78.3	21.4	0.3
	19	7.7	320	37	87.1	9.7	3.2
B-136	1	4.6	320	25	88.4	8.2	3.4
	2	4.6	320	24	92.3	4.9	2.8
	3-9	4.6	320	--	--	--	--
	10	4.6	320	23	87.0	8.6	4.4
	11	4.6	320	24	88.9	6.9	4.3

Table A-4. - ESCA Measurements (20 eV scans) Over Raney Nickel Alloy, Leached, Nondeactivated, Reduced Raney Nickel, and Carbided and Sulfided Raney Nickel

I. Raney nickel alloy

Elemental state	Tabulated E_B, eV (15)[1]	Reference compound (15)[1]	Observed E_B, eV	Counting time,[2] counts/min	Proposed species
Ni 2p	855	$K_2Ni(CN)_4$	853.2	81	Ni
			856.2	163	Ni^{+2}
Al 2s	120	Al_2O_3	118.6	126	[1]Al^{o}
C 1s	285	$(CH_2)_n$	A large C 1s peak was observed; no change in peak position upon turning off the electron flood gun.		
Fe 2p	710	$K_3Fe(CN)_6$	711.5	15	Fe^{+2}, Fe^{+3}
Na 1s	1071	Na_2SO_3	1071.0	20	Na^{+}
S 2p	163	WS_2	163.0	4	S^{-2}
	164.3(2)	$Fe_2(SO_4)_3$	168.2	8	SO_4^{-2}
N 1s	399	$(NH_4)_3AlF_6$	399.2	8	N_2
II. Leached, nondeactivated, reduced samples					
Ni 2p	855	$K_2Ni(CN)_4$	852.3	1412	Ni^{o}
			855.5	1088	Ni^{+2}
			[3]861.5	353	--
Al 2s	120	Al_2O_3	118.6	173	Al^{o}
C 1s	285	$(CH_2)_n$	284.5	162	C°
	289(2)	CH_3COONa (2)	289.0	44	CO_x
Fe 2p	710	$K_3Fe(CN)_6$	[4]711.2	147	Fe^{+2},Fe^{+3}
			[5]712.8	47	Fe^{+2},Fe^{+3}
Na 1s	1071	Na_2SO_3	No signal in 34 minutes		
S 2p	163	WS_2	163.0	4	S^{-2}
	169.3(2)	$Fe_2(SO_4)_3$	168.2	7	SO_4^{-2}
N 1s	399	$(NH_4)_3AlF_6$	399.0	21	N_2
	402.2(2)	$(CH_3)_3NO$(2)	403.5	6	NO_2^{-1}

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[1] E_B values and reference compounds taken from references (15) and (2).

[2] Since Ni and Fe were oxidized, would expect most of Al to be Al^{+3}

[3] Inelastically scattered electrons from Ni^{+2}

[4] Reduced sample.

[5] Nonpyrophoric sample that was not reduced.

Table A-4. - ESCA Measurements (20 eV scans) Over Raney Nickel Alloy, Leached, Nondeactivated, Reduced Raney Nickel, and Carbided and Sulfided Raney Nickel (continued)

III. Carbided sample of reduced Raney nickel

Elemental state	Tabulated E_B, eV(15)	Reference Compound (15)	Observed E_B, eV	Counting time, counts/min	Proposed species
C 1s	285	$(CH_2)_n$	282.4	6	C^-
(Flood gun on)	284.3(2)	graphite (2)	283.2	50	C^-
			284.6	132	C°
	289(2)	CH_3COONa(2)	289.0	38	CO_x
C 1s	285	$(CH_2)_n$	285.0	91	C°
(Flood gun off)	289(2)	CH_3COONa(2)	288.0	38	CO_x
IV. Sulfided sample of reduced Raney nickel					
A. Sulfided to 15 percent coverage					
S 2p	163	WS_2	162.4	7	S^{-2}
Ni 2p	855	$K_2Ni(CN)_4$	852.6 856.2	286 314	Ni° Ni^{+2}
B. Sulfided to 51 percent coverage					
S 2p	163 169.3(2)	WS_2 $Fe_2(SO_4)_3$(2)	163.0 170.0	7 10	S^{-2} SO_4^{-2}
Ni 2p	855	$K_2Ni(CN)_4$	853.0 856.5	410 787	Ni° Ni^{+2}
C 1s	285	$(CH_2)_n$	285.8	97	C°

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