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Effects of Additives on Methanation Activity of Raney Nickel Catalysts

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EFFECTS OF ADDITIVES ON METHANATION ACTIVITY OF RANEY NICKEL CATALYSTS

by

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ABSTRACT

The Bureau of Mines, U.S. Department of the Interior, in cooperation with the Department of Energy, has attempted to increase the activity of nickel catalysts for converting synthesis gas, derived from coal, to a substitute natural gas. This report describes the effects of low-level additions of B, Ca, Ce, Co, Mn, Mo, Pd, Re, Ti, Y, Zn, and Zr on the methanation activity of Raney nickel. The methanation rate at 320° C and the resistance to poisoning by 2 ppm H_2S were used to compare catalysts. The effects of the additions were small, and the experimental variances were large, necessitating the use of statistical methods to identify significant effects. Co, Ti, Y, and Zn improved the resistance to H_2S poisoning, but only Co improved the methanation rate. In some individual catalysts containing Ca, Mo, or Mn, both the methanation rate and resistance to H_2S poisoning were improved.

INTRODUCTION

The Bureau of Mines, U.S. Department of the Interior, as part of an ongoing effort to reduce the requirements for critical and strategic minerals through conservation and substitution, cooperated with the U.S. Department of Energy to improve Raney[3] nickel catalysts for methanation of synthesis gas derived from coal.

Partial combustion of coal in the presence of steam yields a synthetic gas of low heating value, which is useful in many industrial applications. This gas is unsuitable for residential use because it contains carbon monoxide. Also, the economics of transmission by pipeline favor a gas with higher heat content, such as methane. Methanation of synthesis gas, although highly exothermic, requires catalytic assistance. Nickel is preferred for that purpose because of its high activity, relatively low cost, and chemical-reaction selectivity.

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[3] Reference to specific trade names is made for information only and does not imply endorsement by the Bureau of Mines.

Raney nickel is often used as a methanation catalyst, and was chosen for use in the Synthane coal gasification demonstration plant at Bruceton, Pennsylvania. The synthane plant used coatings of Raney nickel applied to the inside of heat-exchange tubes or on support plates (1-4, 10).[4] Cast Raney nickel inserts have also been tested with considerable success (6, 9).

Investigators began adding various metals to Raney nickel soon after it was invented to improve its catalytic properties (8). Most of the improvements made by these additions were in the areas of reduction or hydrogenation of various organic compounds.

The concept of making a high-BTU gas from coal-derived gas was not pursued for many years because of cheap, abundant natural gas. However, as natural gas becomes less abundant and more expensive, the process becomes more attractive. Therefore this study was initiated to find additives to improve Raney nickel as a methanation catalyst. The objectives were to increase the rate of the catalytic methanation reaction and to improve the resistance of the catalyst to poisoning by low levels of H_2S (1 to 3 parts per million). The additives were selected for testing based mostly on the results of previous research; they were B, Ca, Ce, Co, Mn, Mo, Pd, Re, Ti, Y, Zn, and Zr.

EXPERIMENTAL PROCEDURE

Alloy Preparation

Catalysts were prepared from fused alloys, which were consolidated by nonconsumable electrode-arc melting in an inert atmosphere. The starting metals, usually in the form of thin sheet, were weighed and placed in alternating layers on a section of the water-cooled hearth of the arc-melting furnace in a sandwich-like arrangement. The furnace was evacuated and backfilled with argon, and a titanium button was melted to clean the atmosphere of any reactive gases. The alloy stack was then melted using a nonconsumable electrode. The resultant button was turned on its side and remelted, and the procedure repeated until the sample had been melted at least six times.

The 50-gram button was then cut into quarters and one-quarter was sealed in a quartz tube, in vacuo, and heat-treated to obtain equilibrium of the phases. The usual procedure was to hold the specimen at 840° C just below the peritectic temperature for formation of $NiAl_3$, for 20 to 24 hours.

In some cases, Ca, Ce, or Pd additives formed a ternary eutectic with the Ni-Al alloy that melted below 840° C. In such cases, the alloys were heat-treated at a lower temperature for a longer time (usually 760° C for 48 to 72 hours).

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[4] Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

Alloy Evaluation

Each alloy was examined metallographically to observe the phases present. Electron microprobe analysis was used to identify the phases and to estimate their chemical composition. Wet chemical analyses were often employed to confirm the bulk chemical composition of the alloys. These evaluations are included in the tables of appendix A.

Catalyst Preparation

A catalyst was prepared by leaching 1 gram of pulverized alloy (minus 80- plus 200-mesh) in 200 ml of 2 pct NaOH solution for 4 hours at 100° C, washing with 200 ml of 2 pct NaOH solution to avoid precipitation of hydrous aluminum oxides, and then rinsing with 500 ml of water to remove the NaOH.

Catalysts were stable when stored under water, but pyrophoric when dried in air. The small samples of catalysts tested (2.5 mg) could not be weighed reproducibly under water, so it was desirable to dry and weigh them in air. The catalysts were passivated with 100 ml of 1 pct H_2O_2 for 1 hour and then washed with 300 ml of water and 150 ml of alcohol. They were then dried in air. Prior to use, the catalysts were reactivated by heating to 400° C for 1 hour in flowing hydrogen.

Catalyst Evaluation

Surface-Area Measurement

The surface areas of the catalysts were measured by adsorption of gases from a flowing gas stream. The total surface area was determined by adsorption of nitrogen from a mixture of nitrogen and helium at liquid nitrogen temperature (-195.8° C). The surface area was calculated using the one-point Brunauer-Emmett-Teller (BET) equation. The "active area" was determined by adsorption by hydrogen from a hydrogen-nitrogen mixture as the sample was cooled from 400° C to room temperature. The number of catalytically active sites in the sample was assumed to be the number of hydrogen atoms absorbed at room temperature. (This is also assumed to be the number of exposed nickel atoms in the sample.) This procedure was described in detail in a previous publication (5).

Methanation Activity

The activity of each catalyst was determined by measuring the rate of methanation between 300° and 360° C at atmospheric pressure in a reactant gas comprised of 8 pct H_2; 1 pct CO; and the balance, helium. The methanation temperature was kept above 209° C to avoid formation of nickel carbonyl or bulk nickel carbide, but below 400° C to minimize sintering of the catalyst. The reactant gas composition was selected to minimize carbon deposition, formation of higher hydrocarbons, and local overheating because of the exothermic reaction. The apparatus and procedures are described in a previous publication (5). Catalyst activities were then compared on the basis of a "turnover number" (molecules of CH_4 produced per active site per second) at 320° C and an apparent activation energy.

Hydrogen Sulfide (H_2S) Poisoning

The resistance of the catalysts to poisoning by H_2S was measured by adding a low level of H_2S to the reacting gas in the methanation equipment and observing the rate of decrease in methanation activity. (The concentration of H_2S in the gas stream was about 2 ppm.) This test was usually made at 360° or 400° C where the methanation reaction rate was high. In all cases, deactivation was nonlinear at the outset because of an excess of active sites. However, when the excess sites were deactivated, the decrease of activity with time became linear. When the activity became very low, the deactivation curve again departed from linearity, probably because much of the H_2S passed through the catalyst bed without contacting any active catalyst sites. The quantity of H_2S that would completely deactivate the catalyst was estimated by extrapolating the linear portion of the curve to zero activity. The resistance of the catalyst to H_2S poisoning was calculated as the number of H_2S molecules required to deactivated one active site. The results of this test were clear-out for most of the catalysts, but catalysts based on a stoichiometric Ni_2Al_3 precursor alloy apparently have two kinds of sites where about half of the total sites deactivate more slowly than the others. Less than 15 pct of the catalysts studied in this investigation showed a dual response, and the effect has been neglected. However, it offers an interesting area for future research.

Figure-of-Merit

An additive which improves catalytic activity will not necessarily improve resistance to poisoning by H_2S, so a figure-of-merit was derived to compare all catalysts. If one catalyst had twice the initial activity but the same resistance to H_2S as another catalyst, it would produce about twice the amount of CH_4 in a synthesis gas stream containing small amounts of H_2S. Similarly if two catalysts had the same initial activity but one had twice the resistance to H_2S, the more resistant catalyst would produce about twice the amount of CH_4. Thus, the product of the methanation turnover number and the number of H_2S molecules required to poison an active site was chosen as the figure-of-merit. The larger the figure-of-merit, the better the catalyst.

RESULTS

The methanation activity and resistance to H_2S poisoning for the various catalysts are plotted in figures 1 and 2. Figure 1 summarizes the results for catalysts prepared from various alloys in the series $NiAl_3$-Ni_2Al_3. Figure 2 summarizes the results obtained for the catalysts containing additives. In the figures, the methanation activity is plotted logarithmically along the ordinate, and resistance to H_2S is plotted logarithmically along the abscissa. Figure-of-merit values of 0.1, 0.2, and 0.4 are indicated by the dashed diagonal lines.

Statistically, an individual catalyst can be considered to be significantly better (with 90 pct confidence) than Raney nickel without additives if its figure-of-merit is about 0.4 or greater. Figure 2 clearly shows that only five of the catalysts tested meet this criterion--three containing Ca, one with Co, and one with Mo.

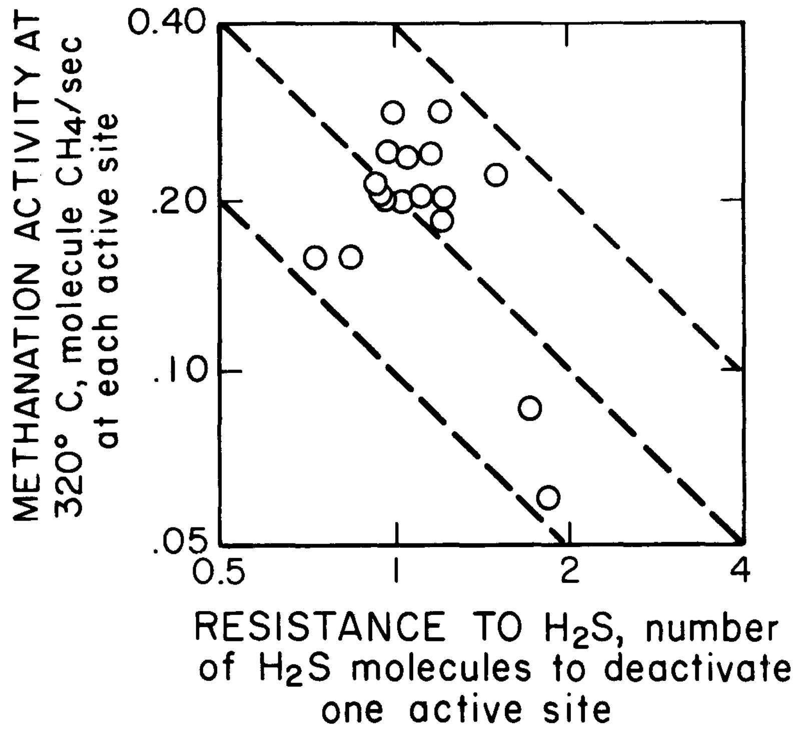

FIGURE 1. - Methanation activity and resistance to H_2S poisoning of Raney nickel catalysts prepared from alloys in the system $NiAl_3$-Ni_2Al_3, without additives. The diagonal dashed lines indicate values of 0.1, 0.2, and 0.4 for the product of methanation activity and H_2S resistance. (The lowest diagonal line indicates 0.1.)

Discussions of the observed results for each additive, together with the conclusions, are presented in the following sections. In most cases, the results were so variable that statistical methods had to be used to reach the conclusions. The test of significance was set at the 90 pct confidence level. In the following discussions, the average or mean of an effect for an additive refers to the unweighted arithmetic mean of all the values measured for that effect in the alloys containing that additive, unless some further limitation is specified. The discussions of the various additives are arranged according to the respective groups of the periodic table. For the interested reader, the experimental data have been included in appendix A, and the statistical evaluations of the data in appendix B.

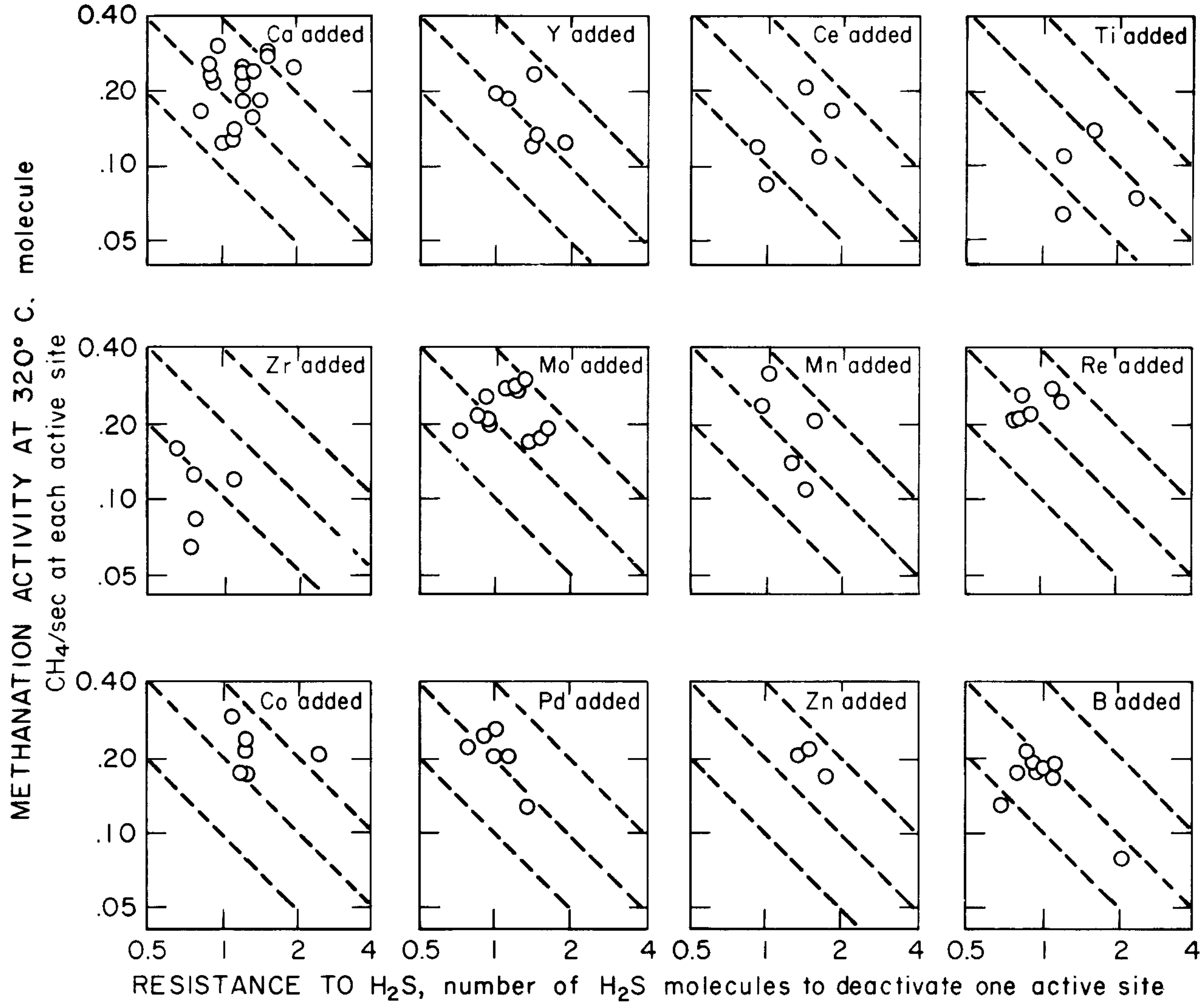

FIGURE 2. - Methanation activity and resistance to H_2S poisoning of Raney nickel catalysts containing various additives. The diagonal dashed lines in the plots indicate values of 0.1, 0.2, and 0.4 for the product of methanation activity and H_2S resistance. (The lowest diagonal line indicates 0.1.)

Group IIA - Calcium

Precise additions of calcium to Raney nickel are difficult to duplicate, because some of the calcium vaporizes during melting. Usually less than half of the added calcium remains in the alloy. However, almost none of the calcium is removed with the aluminum during activation of the Raney nickel. Fifteen calcium-containing alloys were prepared, with the calcium contents ranging from about 0.7 to over 6 wt-pct and the nickel contents, from 38 to 53 wt-pct. Two calcium-containing phases were identified--$CaAl_2$ and a ternary phase determined by microprobe analysis to be approximately $NiCa_{0.5}Al_{3.5}$. Many of these calcium-containing catalysts had measured methanation rates (per gram of catalyst) somewhat greater than the rates measured for the unmodified Raney nickel catalysts. Although these were not evaluated statistically, this effect was usually the result of a slightly increased (but not statistically significant) turnover number combined with a slightly increased active area. Methanation turnover numbers of two calcium-containing catalysts were significantly greater than those of the unmodified Raney nickel catalysts, and three were significantly smaller. Alloy composition had a significant effect, with a maximum turnover number at about 1 to 2 at. pct (1.4 to 2.4 wt-pct) calcium in the alloy, followed by lower values at higher calcium concentrations.

The mean of the apparent activation energies was significantly higher for catalysts containing calcium, although only two samples individually had significantly higher activation energies. However, among the calcium-modified catalysts studied, neither composition nor condition of the alloy had a significant effect on the activation energy.

There was a significant variation of resistance to H_2S poisoning with alloy composition, and the individual results suggest that a composition midway between $NiAl_3$ and Ni_2Al_3, approximately $NiAl_{2.176}$, may be a good starting alloy for a sulfur-resistant calcium-modified methanation catalyst.

The figure-of-merit roughly parallels the resistance to H_2S. Three catalysts, all based on $NiAl_{2.176}$, show a significant improvement, but the average of all the catalysts is about the same as that for the unmodified catalysts.

Group IIIB

Yttrium

Three alloys were prepared, based on the composition $NiAl_{2.176}$ and containing 0.8 to 3.0 wt-pct yttrium. Relatively little yttrium was lost during melting of the alloy, but about one-quarter of the added yttrium was lost in activating the catalyst. In general, the addition of yttrium resulted in reduced methanation activity without significantly changing the resistance to H_2S. However, the heat-treated sample containing 1.3 at pct (3.0 wt-pct) yttrium had both a reasonable methanation activity and improved resistance to H_2S, although the improvement in the figure-of-merit was not significant. Heat-treating the alloys generally improved the resistance of the catalysts to poisoning by H_2S.

Cerium

Additions of cerium were readily made to Raney nickel alloys, and little was lost during melting but as much as 50 pct was lost during activation. Three alloys were prepared based on the $NiAl_3$ composition containing 3 to 13 wt-pct cerium. A ternary phase was observed which had the approximate composition $NiCe_{0.8}Al_{4.5}$.

The addition of cerium to the catalyst significantly reduced the methanation activity without affecting the average resistance to H_2S. Increasing amounts of cerium seemed to improve the resistance to H_2S, and catalysts prepared from heat-treated alloys were more active than those from as-cast alloys.

The figure-of-merit was about the same or less than the unmodified catalysts, with low-level additions of cerium producing the lowest figures-of-merit.

The apparent activation energy for catalysts containing cerium was generally less than for the unmodified catalysts. Heat-treated alloys produced catalysts with significantly lower activation energies in two of the three compositions tested.

Group IVB

Titanium

From 4 to 13 wt-pct titanium was added to three $NiAl_3$ Raney nickel alloys with no loss during melting and around 20 pct loss during activation. $TiAl_3$ was the only titanium-containing phase identified.

Addition of titanium to the Raney nickel catalyst reduced the methanation activity but increased the resistance to H_2S poisoning. The average figure-or-merit, however, was well below that for the unmodified catalyst. The resistance to H_2S is a function of both the composition and condition of the precursor alloy, with both heat treatment and increasing titanium producing more resistant catalysts. One catalyst was over three times more resistant to H_2S poisoning than the unmodified catalyst.

Titanium additives pose a problem in that the methanation activity rapidly deteriorates at temperature below 320° C. Reliable methanation rate data were not obtained, and these catalysts probably would not be commercially useful.

Zirconium

Zirconium was readily added to the Raney nickel alloy. None was lost during the melting, but around 40 pct was lost during activation. Three alloys were prepared, based on $NiAl_3$, with 3 to 12 wt-pct zirconium. The only zirconium-containing phase found was identified by microprobe analysis to be approximately $NiZr_{0.8}Al_{3.7}$. Zirconium reduced the methanation activity, apparent activity energy, and the resistance to H_2S poisoning, and thus reduced the figure-of-merit. Zirconium was the only additive tested that produced catalysts with an average resistance to H_2S poisoning significantly lower than that of the unmodified Raney nickel catalyst. Composition of the alloy seemed to have an effect on the methanation activity; the middle composition, about 3 at. pct (8 wt-pct) zirconium added to $NiAl_3$, had the lowest activity.

Group VIB - Molybdenum

Six alloys were prepared by adding 0.4 to 11 wt-pct molybdenum to the $NiAl_3$ composition. No difficulties were encountered in adding molybdenum to Raney nickel. No molybdenum was lost during melting, but over two-thirds was lost by activation of the catalyst. One ternary phase was identified by microprobe analysis to have the approximate composition Ni_2MoAl_8.

On the average molybdenum had no effect on either the methanation activity or resistance to H_2S poisoning of the Raney nickel. Catalysts prepared from heat-treated alloys were more active than those prepared from as-cast alloys. Catalysts containing very low levels of molybdenum were more resistant to H_2S than those with higher levels of molybdenum or the unmodified catalysts. The catalyst containing 0.1 at. pct (0.4 wt-pct) molybdenum, made from the heat-treated alloy, had a significantly better figure-of-merit than the unmodified catalysts. The apparent activation energy was generally higher than the unmodified catalysts, and the activation energy increased with increasing amounts of molybdenum.

Group VIIB

Manganese

Manganese was added to the Raney alloy without difficulty. Three alloys were prepared with 2 to 8 wt-pct manganese in $NiAl_3$. A ternary phase with the approximate composition $NiMn_{0.9}Al_{5.2}$ was formed. No manganese was lost during melting but more than one-third was lost while activating the catalyst.

Low levels of manganese, about 1 at. pct (2 wt-pct) improved the methanation activity of the catalyst, but higher levels caused a decrease. Catalysts containing higher levels of manganese lost activity rapidly when the temperature was less than 320° C. The mechanism of deactivation has not been studied. Increasing levels of manganese improved resistance to H_2S, but the figure-of-merit remained in the range of the unmodified catalysts.

Minor additions of manganese to the Raney nickel lower the apparent activation energy, but greater amounts increase it. However, the difficulty in obtaining reliable methanation results at temperatures below 320° C casts doubt on these conclusions.

Rhenium

Three alloys were prepared containing 1 to 8 wt-pct rhenium in $NiAl_3$. Additions of rhenium to the Raney alloy were readily made, and several ternary phases were formed. Phases identified had approximate compositions $Ni(Al, Re)_2$, $NiReAl_8$, and $NiRe_2Al_8$.

The presence of rhenium in the catalyst had no significant effect on the methanation activity, the apparent activation energy, or the resistance to H_2S.

Group VIII

Cobalt

The addition of cobalt to the Raney nickel was studied over a fairly wide range of composition (3 to 21 wt-pct cobalt, based on the $NiAl_3$ composition). No cobalt was lost during melting but 20 to 30 pct was lost during activation. X-ray diffraction indicated almost exclusively an $NiAl_3$-type phase, even when the cobalt concentration equaled that of nickel. Electron microprobe analysis of this alloy indicated phases of approximate compositions $NiCo_{0.6}Al_{4.5}$, $NiCoAl_6$, and $NiCo_{1.9}Al_{11}$, but these could represent an incompletely homogenized sample in which all phases were of the type $(Ni, Co)Al_3$.

The addition of cobalt to the catalyst had no effect on the methanation rate or apparent activation energy. (Cobalt is reported to be less selective toward the production of CH_4 than nickel, but the conditions in this experiment strongly favored formation of CH_4. Selectivity was not studied because the equipment was not designed to measure formation of higher hydrocarbons.) However, cobalt did increase the resistance to poisoning by H_2S. The average figure-of-merit for these catalysts is significantly better than the average for the unmodified catalysts. The catalyst containing approximately equal amounts of Co and Ni was particularly resistant to H_2S poisoning and had an unusually large figure-of-merit (about 2.5 times the respective values for the unmodified catalysts).

Palladium

From 0.1 to 39 wt-pct palladium was added to the $NiAl_3$ Raney nickel alloy. The phases observed were mostly $NiAl_3$ and Ni_2Al_3, presumably with palladium in solid solution. A ternary phase of the Heusler type (crystal structure similar to $AlCu_2Mn$) was encountered for the alloy with the highest palladium concentration; the atomic ratio of palladium to nickel in this ternary phase was 1.32.

Addition of palladium had no significant effect on the resistance to H_2S poisoning, and small amounts had no effect on the methanation activity. However, the catalyst prepared from the alloy containing 5 wt-pct palladium had about half the methanation activity of the unmodified catalysts at 320° C with a 30 pct greater activation energy, and the catalyst prepared from the alloy containing 39 wt-pct palladium had no methanation activity at all. The mean of the methanation activities for those catalysts that could be measured was not significantly less than that for the unmodified catalyst, but the mean of the apparent activation energies increased significantly with the palladium addition.

Group IIB - Zinc

Vaporization of zinc and spattering of the molten alloy were encountered during melting. Only about 10 percent of the zinc added was finally incorporated into the alloys that were not heat-treated, for fear of losing even the small amount of zinc remaining. Three alloys based on $NiAl_{2.176}$ were obtained containing 0.1 to 0.4 wt-pct zinc. No ternary phases were detected by X-ray diffraction.

The small amount of zinc in the catalyst had no effect on the methanation activity or the apparent activation energy. Zinc increased the resistance to H_2S poisoning significantly; however, figures-of-merit were well within the range for unmodified catalysts.

Group IIIA - Boron

Boron was added to the Raney alloys with little difficulty. About one-half the boron was lost during melting and often more was lost during activation of the catalyst. Six alloys were prepared that had base compositions ranging from NiAl to $NiAl_3$. The boron contents ranged from 0.1 to 0.3 wt-pct. No boron-containing phase was detected by X-ray diffraction, although a small amount of some unidentified phase was observed by metallographic examination.

Nickel boride is reported to be a good hydrogenation catalyst (7), but the presence of boron in the Raney nickel catalyst lowered both the methanation activity and the apparent activation energy. In most cases, boron had no effect on the resistance to H_2S poisoning. The alloy designated $NiB_{0.168}Al_{1.50}$ produced a catalyst with a low methanation rate but high resistance to H_2S poisoning; the figure-of-merit, however, was low. Higher boron additions produced alloy phases of an NiAl type that could not be leached and showed no activity.

CONCLUSIONS

Statistically significant improvements in the resistance to H_2S were obtained by adding Co, Ti, Y, or Zn to Raney nickel, but only additions of Co generally improved the figure-of-merit. Some individual catalysts containing Ca, Mo, or Mn improved methanation activity, but no general relations between alloy composition and catalytic activity were observed.

REFERENCES

1. Demeter, J. J., A. J. Youngblood, J. H. Field, and D. Bienstock. Synthesis of High-Btu Gas in a Raney-Nickel-Coated Tube-Wall Reactor. BuMines RI 7033, 1967, 17 pp.

2. Forney, A. J., R. J. Demski, D. Bienstock, and J. H. Field. Recent Catalyst Developments in the Hot-Gas Recycle Process. BuMines RI 6609, 1965, 32 pp.

3. Haynes, W. P., J. J. Elliott, and A. J. Forney. Experience with Methanation in Catalysts. Am. Chem. Soc., Div. Fuel Chem., Preprints, v. 16, No. 2, 1972, pp. 47-63.

4. Haynes, W. P., A. J. Forney, J. J. Elliott, and H. W. Pennline. Synthesis of Methane in Hot-Gas-Recycle Reactors, Pilot Plant Tests. Am. Chem. Soc., Div. Fuel Chem., Preprints, v. 19, No. 3, 1974, pp. 10-42.

5. Oden, L. L., and J. H. Russell. Methanation Activity of Raney Nickel Catalysts: Effect of Proportion of $NiAl_3$ and Ni_2Al_3 in Precursor Alloys. BuMines RI 8272, 1978, 15 pp.

6. O'Hare, S. A., and J. E. Mauser. Melting and Casting of Raney Nickel Alloy. BuMines RI 8210, 1977, 9 pp.

7. Paul, R., P. Buisson, and N. Joseph. Catalytic Activity of Nickel Borides. Ind. Eng. Chem., v. 44, No. 5, May 1952, pp. 1006-1010.

8. Rea, A. E. Raney Nickel and Related Nickel Alloy Catalysts. Part I. Preparation and Properties. Selected References with Abstracts. International Nickel Co., Inc., New York, 1958, 75 pp.

9. Schehl, R. R., H. W. Pennline, J. P. Strakey, and W. P. Haynes. Pilot Plant Operation of a Nonadiabatic Methanation Reactor. Am. Chem. Soc., Div. of Fuel Chem., Preprints, v. 21, No. 4, 1976, pp. 2-21.

10. Strakey, J. P., A. J. Forney, and W. P. Haynes. Methanation in Coal Gasification Processes. Energy Res. and Devel. Admin. (now the Department of Energy) PERC/IC-75/1, 1975, 17 pp.

APPENDIX A.--TABLES OF DATA

The following tables summarize the results obtained from the various measurements of the alloys and the catalysts prepared from them. When replicate measurements were made, the average of the results was tabulated. Not all measurements were made on all samples, and a blank space in the tables indicates that the measurement was not made.

The various phases present in the alloys were identified by X-ray diffraction analysis. Rough estimates of the amounts of each phase were made from the intensities of the diffraction peaks. A primary phase usually constitutes more than 40 pct of the sample; a secondary phase, about 20 to 60 pct; a minor phase, from 5 to about 30 pct of the sample; and a trace phase, less than 10 pct of the sample. Phases constituting less than 1 or 2 pct of the sample usually cannot be detected.

Electron microprobe analysis was used to estimate the chemical composition of the various phases, especially those phases which could not be identified by X-ray diffraction analysis. The number of samples analyzed by electron microprobe was small, so the results of these analyses are included as footnotes in the tables.

TABLE A-1. **Effect of composition of the precursor alloy in the series $NiAl_3$-Ni_2Al_3**

Alloy composition[1] nominal	Condition[2]	Catalyst composition	Total area, m^2/g	Active area, m^2/g	Turnover No.[3]	Activation energy, kcal/mole	Resistance to H_2S[4]	Figure-of-merit[5]	Phases found by X-ray diffraction[6]		
									$NiAl_3$	Ni_2Al_3	Al
$NiAl_3$	AC		31.8	14.7	0.197	19.0	1.02	0.201			
Do........	HT	$NiAl_{0.07}$	29.0	16.6	.209	19.5	.92	.193			
$NiAl_3$	AC	$NiAl_{0.08}$	33.5	16.0	.236	18.9	1.05	.248			
Do........	HT	$NiAl_{0.06}$	32.2	16.5	.239	19.4	.97	.232			
$NiAl_{2.60}$....	AC	$NiAl_{0.15}$									
Do........	HT	$NiAl_{0.10}$	37.5	17.6	.209	20.2	.94	.196	P	P	
$NiAl_{2.59}$....	AC		30.1	17.8	.198	18.8	.97	.197			
Do........	HT	$NiAl_{0.08}$	27.7	16.6	.280	20.8	.99	.277			
$NiAl_{2.26}$....	AC	$NiAl_{0.16}$							M	S	T
Do........	HT	$NiAl_{0.11}$	41.6	18.3	.279	18.8	1.25	.349	S	P	
$NiAl_{2.17}$....	AC		34.7	18.2	.157	21.1	.71	[7].111			
Do........	HT	$NiAl_{0.09}$	32.0	17.6	.241	21.2	1.15	.277			
$NiAl_{1.99}$....	AC								M	P	T
Do........	HT	$NiAl_{0.11}$	41.4	19.8	.204	18.6	1.12	.229	M	P	
$NiAl_{1.76}$....	HT	$NiAl_{0.13}$	48.5	21.5	.220	16.6	1.47	.323			
$NiAl_{1.76}$....	AC		37.8	19.0	.183	19.4	1.19	.218			
Do........	HT	$NiAl_{0.11}$	38.6	19.7	.201	19.6	1.22	.245			
$NiAl_{1.50}$....	AC									P	
Do........	HT	$NiAl_{0.26}$	56.4	25.4	[7].060	[7]9.2	[8]1.85	[7].111		P	
Do........	AC		46.4	21.4	.159	16.3	.83	.132			
Do........	HT	$NiAl_{0.35}$	50.3	24.1	[7].086	[7]13.8	[8]1.72	.148			

[1] These alloys were not analyzed because the nominal composition is as accurate as chemical analysis would be.

[2] AC = As-cast alloy; HT = heat-treated alloy.

[3] Methanation activity at 320° C, molecules CH_4/sec/active site.

[4] Molecules H_2S/active site.

[5] Product of turnover number and effect of H_2S.

[6] P = primary, S = secondary, M = minor, T = trace.

[7] Significantly less than the average value.

[8] Significantly greater than the average value.

TABLE A-2. - Effect of calcium addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m^2/g	Active area, m^2/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H$_2$S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]				
Nominal	Analyzed									NiAl$_3$	Ni$_2$Al$_3$	Al	CaAl$_2$	Unidentified
NiCa$_{0.02}$Al$_{2.178}$		AC		46.4	21.3	0.241	21.7	1.18	0.283					
Do...........	NiCa$_{0.005}$Al$_{2.25}$	HT		45.6	20.6	.225	19.7	1.19	.268	P	M	T		
NiCa$_{0.04}$Al$_{3.08}$		AC	NiCa$_{0.028}$Al$_{0.14}$	49.3	19.1	.238	19.1	1.28	.305	S	M	M		
Do...........	NiCa$_{0.014}$Al$_{2.93}$	HT	NiCa$_{0.022}$Al$_{0.09}$	35.3	18.2	.260	20.6	.89	.232	P	T	T		T
NiCa$_{0.04}$Al$_{2.176}$		AC		48.6	21.4	.277	20.7	[6]1.54	[6].426					
Do...........	NiCa$_{0.022}$Al$_{2.41}$	HT		45.1	20.5	[6].305	22.8	1.45	[6].441	M	P	T		
NiCa$_{0.04}$Al$_{1.84}$		AC	NiCa$_{0.021}$Al$_{0.16}$	58.7	23.1	.184	22.4	1.18	.216					
Do...........	NiCa$_{0.012}$Al$_{2.22}$	HT	NiCa$_{0.012}$Al$_{0.14}$	51.9	21.3	.161	[6]23.9	1.28	.206	M	P			T
NiCa$_{0.085}$Al$_{3.18}$		AC	NiCa$_{0.054}$Al$_{0.16}$	48.0	18.8	.218	18.9	.93	.204	M	M	M		T
Do...........	[7]NiCa$_{0.05}$Al$_{2.93}$	HT	NiCa$_{0.045}$Al$_{0.11}$	33.1	16.0	[6].308	19.0	.95	.293	P		T		M
NiCa$_{0.08}$Al$_{2.176}$		AC		56.5	23.9	.260	21.3	[6]1.59	[6].413					
Do...........	NiCa$_{0.047}$Al$_{2.22}$	HT		47.5	21.9	.252	20.2	1.20	.303	M	P	T		
NiCa$_{0.075}$Al$_{1.91}$		AC	NiCa$_{0.040}$Al$_{0.28}$	70.9	26.1	[8].130	19.7	1.06	.138					
Do...........	NiCa$_{0.032}$Al$_{2.23}$	HT	NiCa$_{0.027}$Al$_{0.15}$	39.3	21.4	.194	[6]27.9	1.37	.265	T	P		T	T
NiCa$_{0.15}$Al$_{3.30}$		AC	NiCa$_{0.090}$Al$_{0.17}$	45.5	19.4	.171	22.4	.82	.140	M	M	T		M
Do...........	[9]NiCa$_{0.085}$Al$_{2.98}$	HT	NiCa$_{0.084}$Al$_{0.12}$	33.8	18.2	.229	20.9	.90	.206	P		T		M
NiCa$_{0.15}$Al$_{2.06}$		AC	NiCa$_{0.085}$Al$_{0.31}$	66.2	24.8	[8].125	20.4	1.04	.130					
Do...........	NiCa$_{0.081}$Al$_{2.17}$	HT	NiCa$_{0.085}$Al$_{0.22}$	54.8	24.5	[8].131	20.5	1.12	.147		P		T	M

[1] AC = As-cast alloy; HT = heat-treated alloy.
[2] Methanation activity at 320° C, molecules CH$_4$/sec/active site.
[3] Molecules H$_2$S/active site.
[4] Product of turnover number and effect of H$_2$S.
[5] P = primary, S = secondary, M = minor, T = trace.
[6] Significantly larger than for unmodified catalysts.
[7] Composition of phases observed by electron microprobe = NiAl$_3$, Ni$_2$CaAl$_7$.
[8] Significantly smaller than for unmodified catalysts.
[9] Composition of phases observed by electron microprobe = NiAl$_3$, Ni$_2$CaAl$_7$, NiCaAl$_8$.

TABLE A-3. - Effect of yttrium addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m^2/g	Active area, m^2/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H$_2$S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]			
Nominal	Analyzed									NiAl$_3$	Ni$_2$Al$_3$	Al	Unidentified
NiY$_{.010}$Al$_{2.20}$		AC	NiY$_{0.008}$Al$_{0.086}$	39.6	18.2	0.194	17.9	1.00	0.194	S	P	T	T
Do.........	NiY$_{0.012}$Al$_{2.44}$	HT	NiY$_{0.008}$Al$_{0.068}$	31.4	17.0	.135	19.0	1.45	.196	S	P	T	T
NiY$_{.020}$Al$_{2.22}$		AC	NiY$_{0.018}$Al$_{0.080}$	40.1	18.7	.187	18.5	1.14	.212	M	P	M	M
Do.........	NiY$_{0.022}$Al$_{2.44}$	HT	NiY$_{0.016}$Al$_{0.066}$	26.9	15.6	.227	19.1	1.43	.324	M	P	T	M
NiY$_{.042}$Al$_{2.27}$		AC	NiY$_{0.032}$Al$_{0.101}$	42.3	19.6	[6].123	18.9	1.37	.168	M	P	M	M
Do.........	NiY$_{0.041}$Al$_{2.53}$	HT	NiY$_{0.030}$Al$_{0.078}$	27.7	17.5	[6].125	17.0	[7]1.89	.236	M	P	M	M

[1] AC = As-cast alloy; HT = heat-treated alloy.
[2] Methanation activity at 320° C, molecules CH$_4$/sec/active site.
[3] Molecules H$_2$S/active site.
[4] Product of turnover number and effect of H$_2$S.
[5] P = primary, S = secondary; M = minor; T = trace.
[6] Significantly smaller than for unmodified catalyst.
[7] Significantly larger than for unmodified catalyst.

TABLE A-4. - Effect of cerium addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m^2/g	Active area, m^2/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H$_2$S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]				
Nominal	Analyzed									NiAl$_3$	Ni$_2$Al$_3$	Al	NiCeAl	Unidentified
NiCe$_{0.029}$Al$_{2.96}$		AC	NiCe$_{0.013}$Al$_{0.20}$	35.5	22.4	[6]0.087	22.6	1.00	[6]0.087	S	S	T	T	T
Do...........	NiCe$_{0.026}$Al$_{2.91}$	HT	NiCe$_{0.021}$Al$_{0.23}$	27.5	13.5	[6].123	[6]14.6	.91	[6].112	P	M	T		T
NiCe$_{0.075}$Al$_{2.96}$		AC	NiCe$_{0.04}$Al$_{0.35}$	32.7	13.5	[6].062	16.9			M	S	T	T	T
Do...........	[7]NiCe$_{0.05}$Al$_{2.54}$	HT	NiCe$_{0.03}$Al$_{0.32}$	17.7	10.1	.207	19.4	1.37	.284	S	S			T
NiCe$_{0.149}$Al$_{2.88}$		AC	NiCe$_{0.08}$Al$_{0.57}$	23.9	12.6	[6].110	17.0	[8]1.64	.180	M	S	T	T	T
Do...........	[9]NiCe$_{0.13}$Al$_{3.09}$	HT	NiCe$_{0.10}$Al$_{0.83}$	14.9	8.0	.173	[6]12.9	[8]1.79	.309	M	M			M

[1] AC = As-cast alloy; HT = heat-treated alloy.
[2] Molecules CH$_4$/sec/active site at 320° C.
[3] Molecules H$_2$S/active site.
[4] Product of turnover number and effect of H$_2$S.
[5] P = primary, S = secondary, M = minor, T = trace.
[6] Significantly smaller than for unmodified catalyst.
[7] Compositions of phases observed by electron microprobe: NiAl$_3$, Ni$_2$Al$_3$, NiCe$_{0.7}$Al$_{3.8}$.
[8] Significantly greater than for unmodified catalyst.
[9] Compositions of phases observed by electrom microprobe: NiAl$_3$, Ni$_2$Al$_3$, NiCe$_{0.84}$Al$_{4.5}$.

TABLE A-5. - Effect of titanium addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m^2/g	Active area, m^2/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H_2S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]			
Nominal	Analyzed									$NiAl_3$	Ni_2Al_3	Al	$TiAl_3$
$NiTi_{0.107}Al_{2.98}$	[7]$NiTi_{0.13}Al_{3.43}$	AC	$NiTi_{0.09}Al_{0.15}$	45.3	13.9	[6]0.03	[6]9.1	1.22	[6]0.077	M	S	T	M
Do...........		HT	$NiTi_{0.10}Al_{0.16}$	32.2	14.1	[6].109	19.6	1.22	.133	P	M		M
$NiTi_{0.209}Al_{2.99}$	$NiTi_{0.25}Al_{3.57}$	AC	$NiTi_{0.15}Al_{0.18}$	58.4	13.5	.136	20.2	[8]1.59	.216	M	S	T	M
Do...........		HT	$NiTi_{0.16}Al_{0.16}$	39.3	13.0			[8]2.04		S	M		M
$NiTi_{0.447}Al_{3.00}$	[7]$NiTi_{0.49}Al_{3.36}$	AC	$NiTi_{0.33}Al_{0.43}$	58.9	10.5	[6].074	[8]28.5	[8]2.27	.168	M	S	T	M
Do...........		HT	$NiTi_{0.32}Al_{0.41}$	38.2	12.6			[8]3.43			S		S

[1] AC = As-cast alloy; HT = heat-treated alloy.
[2] Methanation activity at 320° C, molecules CH_4/sec/active site.
[3] Molecules H_2S/active site.
[4] Product of turnover number and effect of H_2S.
[5] P = primary, S = secondary, M = minor, T = trace.
[6] Significantly smaller than for unmodified catalyst.
[7] Composition of phases observed by electron microprobe: $NiAl_3$, Ni_2Al_3, $TiAl_3$.
[8] Significantly greater than for unmodified catalyst.

TABLE A-6. - Effect of zirconium addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m^2/g	Active area, m^2/g	Turn over No.[2]	Activation energy, kcal/mole	Resistance to H_2S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]			
Nominal	Analyzed									$NiAl_3$	Ni_2Al_3	Al	Unidentified
$NiZr_{0.042}Al_{3.15}$	$NiZr_{0.044}Al_{3.4}$	AC	$NiZr_{0.027}Al_{0.092}$	31.6	15.9	[6]0.122	19.3	1.11	0.135	M	S	M	T
Do...........		HT	$NiZr_{0.032}Al_{0.13}$.	28.5	14.8	[6].085	19.4	.78	[6].066	P	T	T	M
$NiZr_{0.138}Al_{3.41}$	[7]$NiZr_{0.144}Al_{3.9}$	AC	$NiZr_{0.071}Al_{0.077}$	26.5	14.4	[6].047	16.5			M	M	M	M
Do...........		HT	$NiZr_{0.089}Al_{0.18}$.	19.0	11.9	[6].066	16.7	.74	[6].049	S		T	S
$NiZr_{0.250}Al_{3.74}$	[8]$NiZr_{0.25}Al_{4.4}$.	AC	$NiZr_{0.075}Al_{0.10}$.	25.8	13.2	[6].126	17.9	.75	[6].095	M	M	M	M
Do...........		HT	$NiZr_{0.144}Al_{0.33}$.	20.7	11.4	.159	[6]13.9	[6].65	[6].103	S		T	P

[1] AC = As-cast alloy; HT = heat-treated alloy.
[2] Methanation activity at 320° C, molecules CH_4/sec/active site.
[3] Molecules H_2S/active site.
[4] Product of turnover number and effect of H_2S.
[5] P = primary, S = secondary, M = minor, T = trace.
[6] Significantly smaller than for unmodified catalyst.
[7] Composition of phases observed by electron microprobe: $NiAl_3$, $NiZr_{0.8}$, $Al_{3.7}$, Al.
[8] Composition of phases observed by electron microprobe: $NiAl_3$, $NiZr_{0.8}Al_{3.8}$ to $Ni_{0.5}Zr_{1.1}Al_{3.9}$, Al.

TABLE A-7. - Effect of molybdenum addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m^2/g	Active area, m^2/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H_2S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]				
Nominal	Analyzed									$NiAl_3$	Ni_2Al_3	Al	Ni_3Al	Unidentified
$NiMo_{0.005}Al_{3.02}$	$NiMo_{0.007}Al_{3.67}$	AC	$NiMo_{0.002}Al_{0.07}$.	40.8	18.3	0.191	18.8	[6]1.59	0.303	M	M	M		
Do...........		HT	$NiMo_{0.0015}Al_{0.06}$	28.2	15.0	[6].304	19.6	1.33	[6].406	P	T	T		
$NiMo_{0.011}Al_{3.02}$	$NiMo_{0.012}Al_{3.32}$	AC	$NiMo_{0.003}Al_{0.08}$.	35.2	16.9	.179	19.5	[6]1.49	.267	M	M	M		
Do...........		HT	$NiMo_{0.003}Al_{0.05}$.	27.8	15.4	.291	15.8	1.22	.355	P		T		
$NiMo_{0.020}Al_{3.06}$	$NiMo_{0.023}Al_{3.29}$	AC	$NiMo_{0.004}Al_{0.07}$.	24.7	15.7	.173	20.5	1.43	.247	S	M	M		T
Do...........		HT	$NiMo_{0.004}Al_{0.05}$.	28.7	14.4	.282	20.4	1.18	.332	P	T			T
$NiMo_{0.042}Al_{3.12}$	(7)	AC		31.5	15.7	.219	20.7	.85	.185	S	S	M		T
Do...........		HT	$NiMo_{0.007}Al_{0.05}$.	28.3	15.7	.263	[6]26.0	.92	.242	S	T			M
$NiMo_{0.087}Al_{3.25}$	(7)	AC		36.6	16.6	.201	[6]23.1	.95	.191	S	S	T		T
Do...........		HT	$NiMo_{0.01}Al_{0.05}$..	34.4	18.5	.192	[6]24.4	.71	.137	P	T			M
$NiMo_{0.191}Al_{3.57}$		AC		28.4	14.0	.208	[6]27.3	.93	.192	M	M	T		M
Do...........		HT	$NiMo_{0.03}Al_{0.04}$..	18.7	8.7	.276	[6]23.5	1.08	.297	M	M		T	S

[1] AC = As-cast alloy; HT = heat-treated alloy.
[2] Methanation activity at 320° C, molecules CH_4/sec/active site.
[3] Molecules H_2S/active site.
[4] Product of turnover number and effect of H_2S.
[5] P = primary, S = secondary, M = minor, T = trace.
[6] Significantly greater than for unmodified catalyst.
[7] Composition of phases observed by electron microprobe: $NiAl_3$, Ni_2MoAl_8.

TABLE A-8. - Effect of manganese addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m²/g	Active area, m²/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H_2S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]				
Nominal	Analyzed									$NiAl_3$	Ni_2Al_3	Al	Mn_5Al_8	Unidentified
$NiMn_{0.054}Al_{3.14}$		AC	$NiMn_{0.03}Al_{0.09}$	49.8	16.5	0.240	20.2	0.93	0.224	M	S	M	T	
Do...........	$NiMn_{0.06}Al_{3.44}$	HT	$NiMn_{0.04}Al_{0.11}$	34.5	17.3	[6].318	[7]13.7	.98	.311	P				T
$NiMn_{0.112}Al_{3.34}$		AC	$NiMn_{0.07}Al_{0.10}$	43.2	16.5	.210	[7]13.1	[6]1.47	.309	M	S	T	T	
Do...........	$NiMn_{0.11}Al_{3.52}$	HT	$NiMn_{0.07}Al_{0.09}$	41.9	15.5	[7].112	[7]11.6	1.41	.158	P				M
$NiMn_{0.251}Al_{3.77}$		AC	$NiMn_{0.14}Al_{0.10}$	62.2	17.8			1.25		M	M	T	T	
Do...........	[8]$NiMn_{0.21}Al_{4.03}$	HT	$NiMn_{0.15}Al_{0.11}$	54.8	14.3	.138	[6]30.9	1.26	.175	P				M

[1] AC = As-cast alloy; HT = heat-treated alloy.
[2] Methanation activity at 320° C, molecules CH_4/sec/active site.
[3] Molecules H_2S/active site.
[4] Product of turnover number and effect H_2S.
[5] P = primary, S = secondary, M = minor, T = trace.
[6] Significantly greater than for unmodified catalyst.
[7] Significantly smaller than for unmodified catalyst.
[8] Composition of phases observed by electron microprobe: $NiMn_{0.02}Al_{2.9}$, $NiMn_{0.9}Al_{5.2}$, Al.

TABLE A-9. - Effect of rhenium addition to Raney nickel

Alloy composition		Condition[1]	Total area, m²/g	Active area, m²/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H_2S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]					
Nominal	Analyzed								$NiAl_3$	Ni_2Al_3	Al	Heusler-type	$Ni(Al,Re)_2$	Unidentified
$NiRe_{0.010}Al_{3.03}$	(6)	AC	41.7	17.1	0.245	23.2	1.18	0.288	M	P	M			
Do...........		HT	28.4	17.6	.260	18.8	.84	.218	P					T
$NiRe_{0.031}Al_{3.10}$		AC	37.5	18.2	.206	19.9	.78	.161	M	P	T	T	T	
Do...........		HT	28.6	18.3	.217	20.6	.92	.199	P					M
$NiRe_{0.064}Al_{3.20}$		AC	26.8	14.6	.284	20.2	1.14	.323	M	P	M	T	T	
Do...........	(7)	HT	27.5	17.8	.208	17.6	.81	.169	P					M

[1] AC = As-cast alloy; HT = heat-treated alloy.
[2] Molecules CH_4/sec/active site at 320° C.
[3] Molecules H_2S/active site.
[4] Product of turnover number and effect of H_2S.
[5] P = primary, S = secondary, M = minor, T = trace.
[6] Compositions of phases observed by electron microprobe: $NiAl_3$, Ni_2Al_3, $NiReAl_6$, $NiRe_2Al_8$.
[7] Compositions of phases observed by electron microprobe: $NiAl_3$, $NiRe_{2.6}Al_{0.5}$.

TABLE A-10. - Effect of cobalt addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m²/g	Active area, m²/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H_2S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]			
Nominal	Analyzed									$NiAl_3$	Ni_2Al_3	Al	Unidentified
$NiCo_{0.081}Al_{3.24}$		AC	$NiCo_{0.14}Al_{0.06}$	25.6	14.4	0.176	19.6	1.15	0.202	M	S	T	T
Do...........	$NiCo_{0.17}Al_{3.61}$	HT	$NiCo_{0.13}Al_{0.06}$	31.6	15.7	.220	19.8	1.22	.268	P			
$NiCo_{0.176}Al_{3.53}$		AC	$NiCo_{0.06}Al_{0.06}$	32.3	15.6	.287	22.8	1.11	.318	S	S	T	
Do...........	$NiCo_{0.08}Al_{3.44}$	HT	$NiCo_{0.06}Al_{0.06}$	31.6	15.4	.169	20.6	1.23	.208	P	T		
$NiCoAl_6$........		AC	$NiCo_{0.69}Al_{0.09}$	17.6	7.1	.207	18.5	[6]2.44	[6].502	P			T
Do...........	[7]$NiCo_{0.97}Al_{6.04}$	HT	$NiCo_{0.63}Al_{0.07}$	23.7	10.0	.235	20.6	1.19	.280	P			T

[1] AC = As-cast alloy; HT = heat-treated alloy.
[2] Molecules CH_4/sec/active site at 320° C.
[3] Molecules H_2S/active site.
[4] Product of turnover number and effect of H_2S.
[5] P = primary, S = secondary, M = minor, T = trace.
[6] Significantly greater than for unmodified catalyst.
[7] Compositions of phases observed by electron microprobe: $NiCo_{0.6}Al_{4.5}$, $NiCo_{1.2}Al_{5.9}$, $NiCo_{1.9}Al_{11}$.

TABLE A-11. - Effect of palladium addition to Raney nickel

Alloy composition		Condition[1]	Total area, m²/g	Active area, m²/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H_2S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]					
Nominal	Analyzed								$NiAl_3$	Ni_2Al_3	Al	Heusler-type	Ni_3Al	Unidentified
$NiPd_{0.0013}Al_{3.02}$		AC	39.0	16.0	0.180	19.6			S	S	T			T
Do............		HT	33.0	15.6	.212	21.1	1.07	0.227	P	T	T			
$NiPd_{0.0016}Al_{3.00}$		AC	38.4	17.3	.263	20.6	1.03	.271	M	S	M			
Do............		HT	32.6	16.2	.226	21.9	[6].68	.153	P	T				
$NiPd_{0.0064}Al_{3.01}$		AC	35.2	17.4	.211	17.3	.97	.204	M	S	M			
Do............		HT	28.4	15.9	.252	22.4	.93	.235	P					
$NiPd_{0.072}Al_{3.21}$.		AC	40.9	12.3	[6].129	[7]26.2			S	S	T			
Do............	(8)	HT	42.1	13.0	[6].127	[7]24.1	[7]1.65	.210	P	P	T			
$NiPd_{1.32}Al_{6.02}$..		AC	31.0	9.8	[6]0									P
Do............	(9)	HT	27.4	11.1	[6]0							M	T	M

[1]AC = As-cast alloy; HT = heat-treated alloy.
[2]Molecules CH_4/sec/active site at 320° C.
[3]Molecules H_2S/active site.
[4]Product of turnover number and effect of H_2S.
[5]P = primary, S = secondary, M = minor, T = trace.
[6]Significantly smaller than for unmodified catalyst.
[7]Significantly greater than for unmodified catalyst.
[8]Compositions of phases observed by electron microprobe: $NiAl_3$, Ni_2Al_3, Al.
[9]Compositions of phases observed by electron microprobe: $NiPd_{0.04}Al_{1.5}$, $NiPd_{0.08}Al_{2.5}$, Al, $NiPd_{0.4}Al_{0.4}$.

TABLE A-12. - Effect of zinc addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m²/g	Active area, m²/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H_2S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]		
Nominal	Analyzed									$NiAl_3$	Ni_2Al_3	Al
$NiZn_{0.026}Al_{2.23}$	$NiZn_{0.0023}Al_{2.25}$	AC	$NiZn_{0.002}Al_{0.15}$	30.1	14.9	0.220	20.0	[6]1.49	0.329	P	P	T
$NiZn_{0.053}Al_{2.30}$	$NiZn_{0.0032}Al_{2.22}$	AC	$NiZn_{0.003}Al_{0.14}$	30.2	15.9	.205	22.2	1.45	.297	S	P	T
$NiZn_{0.111}Al_{2.42}$	$NiZn_{0.015}Al_{2.62}$.	AC	$NiZn_{0.007}Al_{0.13}$	34.9	14.1	.172	20.4	[6]1.75	.302	P	P	T

[1]AC = As-cast alloy; HT = heat-treated alloy.
[2]Molecules CH_4/sec/active site at 320° C.
[3]Molecules H_2S/active site.
[4]Product of turnover number and effect of H_2S.
[5]P = primary, S = secondary, M = minor, T = trace.
[6]Significantly larger than for unmodified catalyst.

TABLE A-13. - Effect of boron addition to Raney nickel

Alloy composition		Condition[1]	Catalyst composition	Total area, m²/g	Active area, m²/g	Turnover No.[2]	Activation energy, kcal/mole	Resistance to H_2S[3]	Figure-of-merit[4]	Phases found by X-ray diffraction[5]			
Nominal	Analyzed									$NiAl_3$	Ni_2Al_3	Al	NiAl
$NiB_{0.035}Al_{2.71}$	$NiB_{0.015}Al_{2.88}$	AC	$NiB_{0.009}Al_{0.12}$	37.5	17.5	0.175	17.2	0.78	0.137	S	S	M	
Do..........		HT		34.5	17.0	[6].128	17.5	[6].66	[6].084	P	M		
$NiB_{0.034}Al_{1.96}$	$NiB_{0.022}Al_{2.08}$	AC	$NiB_{0.021}Al_{1.80}$	52.0	19.9	.215	15.8	.86	.185	M	P		
Do..........		HT		49.2	20.5	.184	[6]15.0	.99	.182	M	P		
$NiB_{0.086}Al_{2.25}$	$NiB_{0.035}Al_{2.41}$	AC		45.3	18.3	.192	17.1	1.07	.206	M	P	T	
Do..........		HT	$NiB_{0.005}Al_{0.09}$	43.1	20.6	.164	17.2	1.09	.178	M	P		
$NiB_{0.089}Al_{1.63}$		AC		56.8	21.6	.175	15.6	.94	.165	T	P		
Do..........	[7]$NiB_{0.014}Al_{1.61}$	HT	$NiB_{0.023}Al_{0.35}$	48.9	19.7	.193	16.8	.91	.175	T	P		
$NiB_{0.168}Al_{1.50}$	(9)	AC	$NiB_{0.012}Al_{0.38}$	50.3	19.6	[6].079	[6]14.5	[8]2.08	.164		P		
Do..........	$NiB_{0.037}Al_{1.158}$	HT		50.1	20.8	[6].035	16.1	[8]1.70	[6].059		P		
$NiB_{0.168}Al_{1.09}$		AC		0.4	0.0	[6]0	-	-	-				P
Do..........		HT		.6	.4	[6]0	-	-	-				P

[1]AC = As-cast alloy; HT = heat-treated alloy.
[2]Molecules CH_4/sec/active site at 320° C.
[3]Molecules H_2S/active site.
[4]Product of turnover number and effect of H_2S.
[5]P = primary, S = secondary, M = minor, T = trace.
[6]Significantly smaller than for unmodified catalyst.
[7]Compositions of phases observed by electron microprobe: $Ni_2Al_{3.4}$, $NiAl_3$, $Ni_{0.07}Al_{0.93}B_{12}$.
[8]Significantly greater than for unmodified catalyst.
[9]Compositions of phases observed by electron microprobe: $Ni_2Al_{2.93}(Al, Ni)B_{12}$.

APPENDIX B.--STATISTICAL EVALUATION

The experimental variations were larger than desired (the relative standard deviation for replicate measurements of methanation activity was 20 to 30 percent of the average activity), at least in part because of the small samples (about 2.5 mg) used in the tests. The effects of the additives were generally small, so it was necessary to use statistical methods of evaluation to determine which effects appear to be significant and which were probably random fluctuations.

The data were evaluated separately for each additive, and each response (methanation activity, activation energy, resistance to H_2S poisoning, and figure-of-merit) was investigated by a two-way analysis of variance. The analysis was based on the factors composition (amount of additive in the alloy) and whether the alloy was heat-treated before use or not. The residual variance was generally considered to be the error variance, and the error variances for a particular response were pooled for most additives to obtain a greater number of degrees of freedom for the error variance. There were a few cases in which the residual variance was unusually large, indicating perhaps a true interaction effect, and these numbers were not included in the pool of the error variance.

The following tables are abbreviated tables of the analyses of variance for each response. The indicated significant effects are reported at the 95-percent-confidence level.

TABLE B-1. - Statistical analysis of methanation activity of Raney nickel catalysts with additives

Additive	No. of samples	Methanation activity		Source of variance					
		Mean	Standard deviation	Composition		Condition		Residual	
				DF[1]	Variance	DF[1]	Variance	DF[1]	Variance
None......	14	0.21	0.034	8	0.00077	1	0.0032	4	0.0015
Calcium...	18	.21	.057	8	[2].0059	1	.0027	8	.00077
Yttrium...	6	[3].17	.043	2	.0034	1	.000048	2	.00125
Cerium....	6	[3].13	.054	2	.00075	1	[2].0099	2	.0016
Titanium..	4	[3].10	.033						
Zirconium.	6	[3].10	.042	2	[2].0037	1	.000038	2	.00069
Molybdenum	12	.23	.048	5	.00068	1	[2].0159	5	.0012
Manganese.	5	.20	[2].082	2	[2].0086	1	.0012	1	[2].0088
Rhenium...	6	.24	.032	2	.00097	1	.00042	2	.0013
Cobalt....	6	.21	.043	2	.00049	1	.00035	2	.0040
Palladium.	8	.20	.051	3	[2].0054	1	.00014	3	.00063
Zinc......	3	.20	.025						
Boron.....	8	.18	.025	3	.00080	1	.00097	3	.00039
Pooled variances			.047					34	.0014

[1] DF = degrees of freedom.
[2] Significantly greater than the error variance.
[3] Significantly smaller than for the unmodified catalyst.

TABLE B-2. - Statistical analysis of apparent activation energy of methanation on Raney nickel catalysts with additives

Additive	No. of samples	Apparent activation energy		Source of variance					
		Mean	Standard deviation	Composition		Condition		Residual	
				DF[1]	Variance	DF[1]	Variance	DF[1]	Variance
None......	14	19.4	1.2	8	1.42	1	0.0006	4	1.75
Calcium...	18	[2]21.2	2.2	8	4.74	1	4.40	8	4.68
Yttrium...	6	18.4	.8	2	.37	1	.007	2	1.29
Cerium....	6	[3]17.2	3.4	2	7.92	1	[4]15.36	2	[4]14.09
Titanium..	4	19.4	[4]7.9						
Zirconium.	6	[3]17.3	2.1	2	6.65	1	2.28	2	2.87
Molybdenum	12	[2]21.6	3.3	5	[4]17.92	1	.003	5	5.86
Manganese.	5	17.9	[4]8.0	2	[4]73.96	1	4.17	1	[4]102.58
Rhenium...	6	20.1	1.9	2	2.27	1	6.62	2	3.35
Cobalt....	6	20.3	1.4	2	2.88	1	.002	2	2.32
Palladium.	8	[2]21.7	2.7	3	[4]11.56	1	4.21	3	4.33
Zinc......	3	20.9	1.2						
Boron.....	10	[3]16.3	1.0	4	1.82	1	.58	4	.45
Pooled variances			2.2					32	3.38

[1] DF = degrees of freedom.
[2] Significantly larger than for the unmodified catalyst.
[3] Significantly smaller than for the unmodified catalyst.
[4] Significantly greater than the error variance.

TABLE B-3. - Statistical analysis of resistance to H_2S poisoning of Raney nickel catalysts with additives

Additive	No. of samples	Resistance to poisoning by H_2S		Source of variance					
				Composition		Condition		Residual	
		Mean	Standard deviation	DF[1]	Variance	DF[1]	Variance	DF[1]	Variance
None.......	14	1.1	0.18	8	0.0281	1	0.0365	4	0.0438
Calcium....	18	1.2	.23	8	^{2}.0816	1	.0041	5	.0265
Yttrium....	6	1.3	.18	2	.0106	1	^{2}.0913	2	.0260
Cerium.....	5	1.0	^{2}.55	2	^{2}.3019	1	.0280	1	.0485
Titanium...	6	^{3}2.0	^{2}.84	2	^{2}1.361	1	^{2}.4320	2	^{2}.1710
Zirconium..	5	^{4}.8	.18	2	.0315	1	.0417	1	.0202
Molybdenum.	12	1.1	.28	5	^{2}.1421	1	.0533	5	.0181
Manganese..	6	1.2	.22	2	^{2}.1198	1	.0	2	.00155
Rhenium....	6	1.0	.17	2	.0142	1	.0468	2	.0376
Cobalt.....	6	^{3}1.4	^{2}.52	2	^{2}.2711	1	^{2}.1873	2	^{2}.3018
Palladium..	6	1.1	.32	3	^{2}.1025	1	.0021	1	^{2}.2116
Zinc.......	3	^{3}1.6	.16						
Boron......	8	^{4}.9	.14	3	.0436	1	.0	3	.0054
Pooled variances			.22					25	.0245

[1] DF = degrees of freedom.
[2] Significantly greater than the error variance.
[3] Significantly larger than for the unmodified catalyst.
[4] Significantly smaller than for the unmodified catalyst.

TABLE B-4. - Statistical analysis of figure-of-merit of Raney nickel catalysts with additives

Additive	No. of samples	Figure-of-Merit		Source of variance					
		Mean	Standard deviation	Composition		Condition		Residual	
				DF[1]	Variance	DF[1]	Variance	DF[1]	Variance
None........	14	0.24	0.060	8	0.0022	1	0.0094	4	0.0049
Calcium.....	18	.26	.097	8	^{2}.0170	1	.0006	8	.0028
Yttrium.....	6	.22	.055	2	.0032	1	.0055	2	.0015
Cerium......	5	.19	.100	2	.0135	1	.0099	1	.0028
Titanium....	4	^{3}.15	.059						
Zirconium...	5	^{3}.09	.033	2	.00061	1	.0017	1	.0015
Molybdenum..	12	.26	.079	5	.0096	1	.0123	5	.0018
Manganese...	5	.24	.072	2	.0020	1	.0026	1	.0144
Rhenium.....	6	.23	.066	2	.0032	1	.0058	2	.0046
Cobalt......	6	^{4}.30	.110	2	.0138	1	.0118	2	.0105
Palladium...	6	.22	.039	3	.00005	1	.0010	1	.0022
Zinc........	3	.31	.017						
Boron.......	8	^{3}.16	.038	3	.0027	1	.00068	3	.00039
Pooled variances			.074					27	.0052

[1] DF = degrees of freedom.
[2] Significantly greater than the error variance.
[3] Significantly smaller than for the unmodified catalyst.
[4] Significantly larger than for the unmodified catalyst.

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