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The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures over the Group VIII Metals

IV. The Kinetic Behavior of CO Hydrogenation over Ni Catalysts

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The catalytic behavior of unsupported nickel and nickel dispersed on a variety of supports has been studied in the CO/H_2 synthesis reaction. The catalysts were characterized by chemisorption and X-ray diffraction measurements. Specific activities and product distributions were determined and kinetic parameters for the methanation reaction were obtained. The specific activity is sensitive to the support material but the variation in activity is less than an order of magnitude. There is also evidence that maximum activity may occur over a certain nickel particle size range. The kinetic parameters are relatively insensitive to the support; however, dispersing nickel on any of the supports studied enhanced the formation of higher molecular weight hydrocarbons compared to unsupported nickel. These differences in catalytic behavior are attributed to changes in the adsorbed state of CO on nickel surfaces which are a result of metal–support interactions or variations in nickel crystallite size.

INTRODUCTION

Nickel is the state-of-the-art methanation catalyst and much interest presently exists in the characterization and improvement of its catalytic properties in CO/H_2 reactions. Although nickel has long been recognized as one of the most active catalysts in the methanation reaction, only recently have studies been conducted which determined the *specific activity* of different nickel catalysts (*1–4*). Since significant differences can exist in nickel loading and in the dispersion of the metal component, the most legitimate comparison of activity among catalysts is that normalized to unit metal surface area or to the number of reduced metal surface atoms, i.e., turnover numbers. This investigation compares a number of nickel catalysts on a variety of typical support materials. Some catalysts were commercially available while others were prepared in this laboratory. Chemisorption and X-ray diffraction measurements allowed the calculation of specific activities and apparent metal dispersions.

By establishing specific activity as a basis of comparison for these catalysts, any effects on catalytic behavior attributable to metal crystallite size or to the support can be more clearly ascertained. A recent study showed that these two factors greatly alter the specific activity of Pt and Pd in the methanation reaction (*5*). Variations in crystallite size and support material have been reported to alter the catalytic activity of nickel in other reactions (*6–8*) and it was of interest to see if similar changes occur in the methanation reaction. If such effects were present, they should be reflected by

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differences in specific activity, kinetic parameters, and product selectivity; properties which are measured and compared in this study.

EXPERIMENTAL METHODS

As in the previous studies in this series, all catalysts were compared at 103 kPa (1 atm) total pressure in a differential flow microreactor. Product analysis was achieved by gas chromatography utilizing subambient temperature programming and Chromosorb 102 columns. Typically, CO conversions to all hydrocarbon products were 5% or less to minimize or eliminate heat and mass transfer effects. Further details on the reactor have been given earlier (*1*).

Both hydrogen and CO chemisorption measurements were conducted on all used catalyst samples and usually on the fresh reduced samples also. The glass chemisorption unit and the experimental procedure have been described before (*1*). The 42% Ni/α-Al_2O_3 (200) sample was reduced 1 hr at 270°C prior to the adsorption measurements.

The X-ray diffraction measurements were conducted in this laboratory and the average Ni particle sizes were determined by a standardized procedure (*9*).

The 42% Ni/α-Al_2O_3 catalyst is a commercial sample (G87RS) available from the Chemetron Corp. The 20% Ni/graphite catalyst is commercially available from the Ventron Corp. while the 30% Ni/α-Al_2O_3 sample is a coprecipitated catalyst sent to us courtesy of Catalyst Consulting Services, Louisville, Ky. The uncalcined nickel oxide was precipitated at 25°C from an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ using NH_4HCO_3. Both the 5% Ni/η-Al_2O_3 and the 8.8% Ni/η-Al_2O_3 catalysts were prepared by impregnating the Al_2O_3 with an aqueous solution of $Ni(NO_3)_2$ using typical incipient-wetness techniques. Initial dispersions of both fresh samples were close to 30%. The 16.7% Ni/SiO_2 catalysts were prepared in this laboratory by impregnating Cab-O-Sil obtained from the Cabot Corp. with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. One sample, designated 16.7% Ni/SiO_2 (27), had an initial dispersion of 27% while the other, 16.7% Ni/SiO_2 (11), had a lower initial dispersion of 11%. All samples prepared in this laboratory were dried overnight at 120°C.

Except for the NiO and the 42% Ni/α-Al_2O_3 (200°) sample, all catalysts were given a standard pretreatment and stepwise reduction in flowing H_2 which concluded with a 1 hr period at 450°C as described in Ref. (*1*). The NiO sample was reduced at 300°C for 1 hr in flowing hydrogen and the 42% Ni/α-Al_2O_3 (200°) catalyst was reduced at only 200°C since it is supposed to be prereduced and passivated thereby requiring only mild reduction conditions to activate the catalyst. As described (*1*), samples were analyzed after 20 min on stream, then pure H_2 was flowed over the catalyst for 20 min before CO was again introduced in the feed stream. This procedure is similar to that used by Sinfelt (*10*) and repeatedly gave reproducible results indicating little or no change in catalytic activity as total time on stream increased.

RESULTS AND DISCUSSION

Chemisorption and X-Ray Measurements

The chemisorption data for these nickel catalysts are listed in Table 1. With nickel catalysts one must always be aware of the potential problem of carbonyl formation when room temperature CO adsorption measurements are conducted. Indeed, in many cases a considerable drift was observed in the CO pressure during the isotherm measurement and it was assumed that this was due to surface carbonyl

TABLE 1

Chemisorption Measurements on Ni Catalysts

Catalyst	Uptake (μmole/g)				Used sample	
	Fresh sample		Used sample		CO/Ni	H/Ni
	CO	H_2	CO	H_2		
5% Ni/η-Al_2O_3	235	115	110	48	0.14	0.12
8.8% Ni/η-Al_2O_3	—	225	101	19	0.14	0.025
42% Ni/α-Al_2O_3	358	123	210	65	0.029	0.018
42% Ni/α-Al_2O_3 (200°)	—	—	220[a]	75[a]	0.031	0.021
30% Ni/α-Al_2O_3	506	338	591	318	0.12	0.12
16.7% Ni/SiO_2 (27)	—	384	456	121	0.16	0.085
16.7% Ni/SiO_2 (11)	—	157	179	110	0.063	0.077
20% Ni/graphite	11.4	38.5	24.0	19.8	0.0070	0.012
	41.6[b]	52.0[b]			0.012	0.031
NiO (reduced)	53	18.2	26	29.5	0.0015	0.0035

[a] Reduced 1 hr @270°C prior to adsorption measurements.

[b] Uptake measured @200°C.

formation with more than 1 CO molecule being adsorbed per surface Ni atom. However, slow irreversible CO adsorption on the support could also produce this behavior (*4*). This drifting did not always occur and a number of the CO uptake measurements were very well behaved. Frequently the CO uptake listed in Table 1, determined by the dual isotherm difference method (*1*), is not in bad agreement with the hydrogen uptake if the linearly bonded CO species is assumed to predominate on the Ni surface. Because of the possibility of carbonyl formation, though, the hydrogen uptakes are believed to be more representative of the true reduced nickel surface area and will normally be used for specific activity calculations in this paper.

TABLE 2

Comparison of Calculated Average Ni Particle Sizes for Used Catalysts

Catalyst	Diameter (nm) from:		
	X-Ray	$H_{(ad)}$	$CO_{(ad)}$
5% Ni/η-Al_2O_3	—	9	7.5
8.8% Ni/η-Al_2O_3	—	40	7.5
42% Ni/α-Al_2O_3	—	55	34
42% Ni/α-Al_2O_3 (200°)	16	47	32
30% Ni/α-Al_2O_3	—	8.5	8.5
16.7% Ni/SiO_2 (27)	10	11.5	6
16.7% Ni/SiO_2 (11)	11	13.0	16
20% Ni/graphite	22	32[a]	83[a]
NiO (reduced)	>200	280	660

[a] Based on adsorption @200°C.

For the used samples, the comparisons between average Ni particle sizes calculated from chemisorption data and sizes determined from X-ray diffraction data are shown in Table 2. X-Ray line-broadening measurements were not made on all used catalysts, but for those so characterized the agreement between X-ray and H_2 adsorption is quite satisfactory for all samples except the 42% Ni/α-Al_2O_3 (200°) catalyst. However, as mentioned in Refs. (*3*, *7*), not all the Ni on alumina supports may be reducible due, for instance, to surface spinel formation. Although this can cause discrepancies in particle size calculations, such nonreducible Ni atoms should not be active in the methanation reaction thereby retaining turnover numbers as a valid representation of specific activity on reduced Ni surfaces. The CO adsorption values appear to be less meaningful for particle size calculations.

Highly dispersed nickel catalysts are difficult to prepare using common supports and even more difficult to maintain in a state of high dispersion. For instance, both the Ni/Al_2O_3 and Ni/SiO_2 catalysts lost Ni surface area under reaction conditions. Even though the initial H/Ni ratio was 0.3 for the Ni/Al_2O_3 catalysts, which gave no discernible X-ray peaks, the H/Ni ratio of the used samples had dropped to half that value. The H_2 uptake on the 8.8% Ni/Al_2O_3 sample may be anomalously low since the CO uptake indicates a final dispersion very close to that of the 5% Ni/Al_2O_3 sample. A similar decrease in metal surface area occurred with the two 16.7% Ni/SiO_2 catalysts as both final dispersions were close to 0.08. Both new samples gave broad X-ray peaks indicative of crystallite sizes in excellent agreement with those calculated from H_2 chemisorption. However, silica does not interact with nickel in the same manner as alumina so the problems mentioned above are not encountered, and the growth in Ni crystallite size was clearly shown. With all the catalysts involved in this study, the nickel in the used samples existed in a final state of low dispersion.

Some difficulty was encountered in characterizing the 20% Ni/graphite catalyst. The room temperature uptakes on the fresh reduced sample appeared to be low, especially CO adsorption, and the switch in the CO/H_2 adsorption ratio for the used sample was irregular. If the Ni were truly intercalated between layers of graphite, as claimed by the manufacturers, it is possible that rapid adsorption equilibrium cannot be achieved due to diffusional effects. Both CO and H_2 adsorption on Ni are typically nonactivated and monolayer coverages at temperatures above 25°C would be expected to decrease. However, if diffusion to any intercalated Ni were limiting the adsorption process, uptakes determined at higher temperatures would be expected to be larger than uptakes at 25°C. The results in Table 1 show that both CO and H_2 adsorption, particularly the former, are enhanced at 200°C providing an indication that not all the Ni surface is readily accessible for adsorption at 25°C. Although the possibility exists that the larger H_2 uptake at the higher temperature may be due to H_2 spillover (*11*), the concomitant increase in CO uptake and the relatively low temperature of 200°C, compared to that used in Ref. (*11*), tend to discount the importance of this possibility. It is the author's opinion that the H_2 uptake at 200°C is the more representative measure of catalytically active metal surface sites since complications due to CO disproportionation could exist at this temperature.

Although it is possible that the adsorption values at 200°C are not completely representative of the catalytically active Ni surface area, these values were used for specific activity calculations. The turnover numbers obtained on this basis were consistent with those of other Ni catalysts, whereas a choice of adsorption on the used sample would have produced anomalously high turnover numbers.

Catalytic Behavior

The catalytic behavior of these catalysts is shown in Table 3. Here all Arrhenius and partial pressure dependency data have been interpreted to give the parameters in a power rate law of the form,

$$N_{CH_4} = Ae^{-E_{CH_4}/RT}P_{H_2}^{X}P_{CO}^{Y},$$

where N_{CH_4} is the turnover number for

TABLE 3

Kinetic Behavior in the Synthesis Reaction[a]

Catalyst	N_{CH_4} (sec$^{-1}\times10^3$)		E_{CH_4} (kJ/mole)	X	Y	N_{CO} (sec$^{-1}\times10^3$)		E_{CO} (kJ/mole)	Rate/g Ni	
	—[b]	—[c]				—[b]	—[c]		CH_4 (μmole/sec)	CO (μmole/sec)
5% Ni/η-Al_2O_3	37	32	105 ± 5	0.8	−0.3	44	38	98 ± 5	70	83
8.8% Ni/η-Al_2O_3	85	32	109 ± 3	0.8	−0.2	128	48	110 ± 3	37	55
42% Ni/α-Al_2O_3	43	27	138 ± 2	0.7	−0.5	109	68	154 ± 2	13	34
42% Ni/α-Al_2O_3 (200°)	22	15	134 ± 3	—	—	84	57	162 ± 4	7.9	30
30% Ni/α-Al_2O_3	18	19	116 ± 4	—	—	35	37	123 ± 5	36	71
16.7% Ni/SiO_2 (27)	34	18	127 ± 4	—	—	47	25	130 ± 2	50	69
16.7% Ni/SiO_2 (11)	45	55	116 ± 7	—	—	62	76	111 ± 8	9.8	13
20% Ni/graphite	51	127	139 ± 5	0.8	−0.5	79	198	147 ± 5	27	41
NiO (reduced)	16	37	114 ± 2	0.6	−0.3	~18	~42	103 ± 1	1.0	1.1

[a] $H_2/CO = 3$; rates compared @275°C; P = 103 kPa.
[b] Based on H_2 adsorption.
[c] Based on CO adsorption.

methane formation expressed as molecules of CH_4 formed per second per metal site, A is the preexponential factor, E_{CH_4} is the activation energy, and P_{H_2} and P_{CO} are the partial pressures of hydrogen and carbon monoxide, respectively. The activation energy for total CO conversion to all hydrocarbon products, E_{CO}, is also listed. The activation energy values along with their standard deviations were determined by least squares fitting of the experimental points using a standard computer program. For convenience, turnover numbers are calculated based on both CO uptakes and H_2 uptakes. This not only allows a direct comparison with the data in Refs. (*1*, *5*) but also shows that the turnover numbers on any particular Ni catalyst usually agree to within a factor of 2 regardless of the choice of adsorbate. As mentioned earlier, the preferable choice of Ni surface sites with these catalysts will be that determined by hydrogen chemisorption.

With these specific activity data the intrinsic activity of the catalysts can be compared directly; however, also in Table 3 are listed the rates per gram of nickel in the catalyst which gives a good representation of the effectiveness of Ni utilization. Comparing the turnover numbers at 275°C, which were obtained both by direct measurement and by extrapolation of Arrhenius plots, it can be seen that some variation occurs in specific activity as methanation rates differ by a factor close to 5. A similar spread occurs in the specific activities for CO conversion. This variation in specific activity for Ni catalysts is much smaller than the changes observed earlier for Pt and Pd catalysts (*5*). Although the effect is less pronounced, the generalization can be made here that large unsupported Ni crystallites have a lower specific activity than smaller supported crystallites, particularly for total CO conversion.

TABLE 4

Relative Activities for CH_4 Formation @205°C

Catalyst	N_{CH_4}[a] (sec^{-1} × 10^3)	Rate (μmole CH_4/sec·g cat)
8.8% Ni/η-Al_2O_3	2.48	0.094
5% Ni/η-Al_2O_3	1.24	0.119
16.7% Ni/SiO_2 (11)	1.10	0.240
20% Ni/Graphite	0.62	0.064
16.7% Ni/SiO_2 (27)	0.55	0.135
42% Ni/α-Al_2O_3	0.52	0.060
30% Ni/α-Al_2O_3	0.43	0.275
NiO (reduced)	0.38	0.023
42% Ni/α-Al_2O_3 (200°)	0.28	0.042

[a] Based on H_2 adsorption.

When these catalysts are compared at 205°C, at which temperature turnover numbers for all catalysts can be compared directly with no extrapolation, some changes occur in the ordering of relative activities due to variations in activation energies. This is shown in Tables 4 and 5. The comparison of activity on a gram catalyst basis is included here since it is a good representation of the total activity that can be achieved per unit volume of catalyst bed in a methanation reactor. The more highly dispersed alumina-supported catalysts still have the highest turnover numbers but there is now an even wider spread in specific activity. It is possible that the low activity of 42% Ni/α-Al_2O_3 (200°) was due to incomplete reduction of the nickel and additional reduction occurred during the subsequent chemisorption pretreatment at 270°C to give a larger value for the reduced Ni surface area than that existing under reaction conditions. The spread in specific activities is outside of experimental error and cannot be attributed to diffusional limitations since values calculated from the Weisz criterion (*12*) are 2 to 3 orders of magnitude smaller than unity. This variation in activity indicates that factors due to Ni crystallite size or to the support itself may have a detectable effect on catalytic behavior. The overall influence on activity appears to be less that an order of magnitude, though, and not so pronounced as with Pt or Pd.

TABLE 5

Relative Activities for CO Conversion @205°C

Catalyst	N_{CO}[a] (sec^{-1} × 10^3)	Rate (μmole CO/sec·g cat)
8.8% Ni/η-Al_2O_3	3.79	0.144
5% Ni/η-Al_2O_3	1.79	0.172
16.7% Ni/SiO_2 (11)	1.79	0.379
20% Ni/Graphite	0.79	0.083
42% Ni/α-Al_2O_3	0.76	0.088
16.7% Ni/SiO_2 (27)	0.71	0.170
30% Ni/α-Al_2O_3	0.67	0.426
NiO (reduced)	0.54	0.032
42% Ni/α-Al_2O_3 (200°)	0.42	0.065

[a] Based on H_2 adsorption.

No major trends were observed in the reaction parameters measured. Although apparent E_{CH_4} values varied between 105 and 138 kJ/mole, most values were around 113 kJ/mole and no correlation could be clearly established between the support used and the activation energy measured. The exponential dependence on H_2 partial pressure was between 0.6 and 0.8 while the dependence on CO pressure was between -0.2 and -0.5. The consistency of these pressure dependencies is a strong indication that no major change in the microscopic reaction path occurs in the methanation reaction although Ni is dispersed on a number of support materials with widely differing physical and chemical properties.

Different activation energies were reported in Refs. (*3*, *13*, *15*). Dalla Betta *et al.* (*3*) reported E_{CH_4} values of 117–130 kJ/mole which are in excellent agreement with values found in this study. However, lower values of 84 and 73–80 kJ/mole were reported by Bousquet and Teichner (*13*) and Fontaine (*15*), respectively. Bartholomew (*4*) did not determine E_{CH_4} values. Compared in the same pressure regime, the partial pressure dependencies of 0.6 for H_2 and -0.3 for CO determined from Ref. (*15*) agree well with those values reported here. Even with the variation in activation energy, it is interesting to note that the N_{CH_4} values do not vary greatly.

Only recently have studies appeared in the open literature in which specific activities of Ni in the methanation reaction have been calculated (*1–4*). In addition, two other studies have included both adsorption measurements and kinetic data to allow the estimation of turnover numbers (*13–15*). When the data of Dalla Betta

TABLE 6

Comparison of Specific Activity from Different Studies[a]

Catalyst	Temp (°C)	$N_{CH_4} \times 10^3$ (sec^{-1})	Ni[b] crystallite size (nm)	Dispersion[c] (%)	$N_{CO} \times 10^3$ (sec^{-1})	Ref.
5% Ni/Al$_2$O$_3$	275	37	9.0	11	44	(*1*)
15% Ni/Al$_2$O$_3$	275	35	—	—	43	(*4*)
Ni/Al$_2$O$_3$	275	35–75	8.5	12	—	(*13, 14*)
Raney Ni	275	45	32.0	3.1	115	(*3*)
8.8% Ni/Al$_2$O$_3$	275	85	39.5	2.5	128	This study
3% Ni/Al$_2$O$_3$	275	99	12.0	8.4	119	(*4*)
2% Ni/Al$_2$O$_3$	275	90	30.0	3.3	220	(*3*)
5% Ni/ZrO$_2$	275	91	12.5	7.9	170	(*2*)
16.7% Ni/SiO$_2$ (11)	212	1.7	13.0	7.7	—	This study
16.7% Ni/SiO$_2$ (27)	212	0.89	11.5	8.5	—	This study
12.2% Ni/SiO$_2$	212	0.61	6.5[d]	10.0[e]	—	(*15*)
5.3% Ni/SiO$_2$	212	0.56	5.5[d]	11.8[e]	—	(*15*)
2.0% Ni/SiO$_2$	212	0.29	4.5[d]	14.6[e]	—	(*15*)

[a] $P = 103$ kPa; $H_2/CO = 3$.

[b] Calculated assuming spherical Ni particles.

[c] Represented as H/Ni ratios.

[d] Estimated from CO desorption assuming a 1:1 ratio between linear and bridged CO. This ratio appears to be a reasonable estimate based on the ir spectra in Ref. (*8*).

[e] Expressed as CO/Ni ratios.

et al. (*2*, *3*) and Bartholomew (*4*) are corrected to the same H_2 and CO pressures used in this study and compared at 275°C, excellent agreement exists with the values reported in this study for the Ni/Al$_2$O$_3$ catalysts with comparable metal loadings. When the rate data of Bousquet and Teichner (*13*, *14*) are corrected to these standard conditions and turnover numbers are calculated, again a consistent N_{CH_4} value is obtained. Since the exact average temperature of the gas mixture is not known for the recirculating batch reactor used in Ref. (*13*), only upper and lower limits can be calculated for N_{CH_4}; however, the value is most likely nearer the upper limit. These comparisons are listed in Table 6. Despite these uncertainties, the turnover numbers for methane formation on Ni/Al$_2$O$_3$ catalysts with low metal loadings agree within a factor of about 2. Such consistency in the N_{CH_4} values from four different laboratories is quite gratifying and the increasing trend toward the reporting of specific activities in CO hydrogenation reactions is certainly welcome.

This agreement in turnover numbers determined for similar Ni catalysts support the point of view that the spread in activity observed in this study is due to the properties of the catalysts themselves rather than experimental artifacts. The similarity in E_{CH_4} values shown in this study also supports this contention. The inclusion of the commercial catalysts does widen the difference in N_{CH_4} values, but since the exact composition of these catalysts is not known, the existence of effects due to impurities or promoters cannot be discounted. Although it is too early to know if the distinction is real, it is interesting to note that two groups of Ni/Al$_2$O$_3$ catalysts appear to exist: one with a N_{CH_4}

value near 0.04 sec^{-1} and another with a value close to 0.09 sec^{-1}.

From the work of Fontaine (*15*), turnover numbers can be estimated if the amount of CO desorbed during transient response experiments is assumed to be a good representation of the number of Ni surface sites. These calculated values at 212°C for three Ni/SiO_2 catalysts are compared directly in Table 6 with the two 16.7% Ni/SiO_2 catalysts reported in this work. Very good agreement exists between the two studies when the two catalysts with the most similar Ni particle sizes are compared (16.7% Ni/SiO_2 (27) vs 12.2% Ni/SiO_2). However, with silica-supported nickel a trend in activity seems to occur—the smaller Ni crystallites (ca. 4.5 nm) have a lower N_{CH_4} than the larger crystallites, at least up to ~13 nm (130 Å) particles.

It was proposed in Ref. (*5*) that an enhancement of the more weakly bound CO species on Pt and Pd surfaces results in higher activity. This proposal was a consequence of the correlation between activity and CO heat of adsorption which was presented in Ref. (*1*). Since that correlation was first plotted, the heat of adsorption of CO on Ru has been measured for the first time (121 kJ/mole) (*16*) and new values of ~126 and ~155 kJ/mole have been obtained for this property on Ni (*17*) and Pd (*18*), respectively. Replotting the activity data on these new values alters the correlation little and the same conclusion is reached—the most active metal surface is that which adsorbs CO the least strongly. This conclusion is consistent with the idea that hydrogen adsorbs more competitively with CO on the surface with the more weakly bound CO thereby enhancing the rate since hydrogen is involved in the rate determining step. An alternative interpretation that a major change occurs in the chemistry involving the reactive CO intermediate does not seem applicable since the kinetic parameters in the methanation reaction vary little from catalyst to catalyst.

It is enticing to forward this same explanation to account for the variation in activity found in these nickel catalysts. For SiO_2-supported Ni, Van Hardeveld and Hartog (*8*) have shown that a decrease in Ni crystallite size from 21 to 4 nm, based on H_2 chemisorption, favored the formation of a more strongly bound CO species. This effect of particle size on CO adsorption is opposite to that which has been observed for Pt and Pd and therefore predicts that smaller Ni crystallites would have a *lower* N_{CH_4} or N_{CO} value than the larger Ni crystallites, at least within this range of Ni crystallite size. Such an effect would account for the trend observed with the Ni/SiO_2 catalysts. Since large unsupported Ni crystallites also have a low specific activity, a range of crystallite sizes may exist where maximum activity occurs.

However, there is enough spread in the specific activities measured for these catalysts to suggest that the support itself can also influence the catalytic behavior of the Ni particles. This proposal is not unfounded since O'Neill and Yates (*19*) have clearly shown that the support can markedly affect the adsorptive behavior of CO on nickel. If the simple premise is again made that any effect which weakens the M–CO adsorption bond will result in a higher activity, then the presence of the support becomes a factor to be considered. That the perturbation on specific activity is not particularly large for Ni may well be due to the fact that the heat of adsorption of CO on Ni is already one of the lowest of the Group VIII metals. If the correlation in Ref. (*1*) does represent the right-hand portion of a volcano plot, then continued weakening of the M–CO bond will begin at some point to decrease catalytic activity.

TABLE 7

Selectivity of Nickel Catalysts[a]

Catalyst	T (°C)	% Conversion to:		Hydrocarbon product (mole%)					CO_2 (mole%) in total carbon product
		Hydrocarbons	CO_2	C_1	C_2	C_3	C_4	C_5^+	
Bulk Ni	229	2.8	0.039	90	10	—	—	—	2.0
42% Ni/α-Al_2O_3	236	2.1	0.030	76	14	5	3	1	1.9
30% Ni/α-Al_2O_3	229	8.2	0.32	81	11	5	2	1	4.6
8.8% Ni/η-Al_2O_3	230	3.1	0.058	81	14	3	2	—	2.3
5% Ni/η-Al_2O_3	235	4.9	0.054	87	9	3	1	—	1.3
16.7% Ni/SiO_2	220	3.3	0.011	92	3	3	1	—	0.41
20% Ni/graphite	218	7.0	0.13	88	9	2	1	0.5	2.1

[a] $H_2/CO = 3$; $P = 103$ kPa.

Nickel may have a position close to the optimum in activity.

Product Selectivity

The support also has an observable effect upon the product distribution obtained from the synthesis reaction as shown in Table 7. In agreement with the open literature describing the behavior of nickel on typical supports such as Al_2O_3 and SiO_2, methane comprises 80–90 mole% of the product which is almost completely paraffinic in nature. However, the supported Ni catalysts have a greater capability of forming higher molecular weight hydrocarbons, especially C_3^+ species. This characteristic is shown in Table 3 where the N_{CH_4}/N_{CO} ratio is consistently higher at 275°C for unsupported Ni than for the supported catalysts. This ratio merely represents the fraction of reacted CO molecules which is converted into methane with the remainder going to C_2^+ hydrocarbons. Even though this distinction between supported and unsupported nickel can be noted, no significant difference in selectivity among the supported Ni catalysts is apparent. Small quantities of CO_2 were always present, but concentrations in the product stream were usually around 2% or less as shown in Table 7. The 30% Ni/α-Al_2O_3 catalyst may contain promoters which are responsible for the greater-than-normal CO_2 formation.

An interesting aspect of this study is the behavior of the Ventron 20% Ni/graphite catalyst. Ventron describes this as an intercalated material with $NiCl_2$ initially being situated between the graphite layers (*20*). However, the X-ray pattern obtained in this study not only showed the presence of Ni crystallites larger than 20 nm but also the existence of the graphitic structure and not the intercalate. In addition, the catalytic behavior also indicated that most, if not all, of the active nickel must reside outside the graphite layers since significant amounts of C_2^+ hydrocarbons are formed. Were all the nickel residing between the C layers, a change in selectivity might be expected because both reactants and products would have to diffuse through the graphite layers. Since the van der Waals gap between C layers in this metal intercalate is ~ 2.7 Å, CO, H_2, H_2O, and CH_4 could conceivably diffuse easily between the C planes, but larger hydrocarbons with effective diameters >3 Å would be expected to diffuse with much more difficulty. This consideration, coupled with the fact that both the product distribution and specific activity are comparable to that of other supported Ni catalysts (see Table 6), leads to the conclusion that little, if any, nickel exists between the layers after the pretreatment employed in this study. If some nickel still remains intercalated between the C layers, it appears to play no major role in the catalysis of the synthesis reaction, most likely due to diffusional limitations which occur between the carbon layers.

CONCLUSION

Nine different supported and unsupported nickel catalysts were characterized by chemisorption measurements and studied in the methanation reaction. Both commercial catalysts and samples prepared in this laboratory were investigated and it was found that although huge differences did not exist among any of these catalysts, specific activities in the methanation reaction did vary by a factor of 5. This spread is outside of experimental error and not completely understood at this time; however, there is evidence in the literature to support the contention that this relatively small alteration of activity is attributable to the material on which the nickel is dispersed. In addition, data from this study and one other suggest that a crystallite size effect may occur for Ni although changes in activity due to this factor also appear to be less than an order of magnitude. None of these variations with Ni catalysts is as pronounced as those found earlier with Pt and Pd catalysts; however, the explanation relating an increase in specific activity to an increase in the more weakly bound adsorbed CO species also seems applicable to Ni catalysts. The smaller effect on activity, compared to Pt or Pd, may be due to the inherently weaker CO adsorption on Ni.

The catalytic parameters determined for the catalysts in this study were quite consistent. This infers that the methanation reaction proceeds in a similar series of kinetic steps on the nickel surface which are not significantly altered by the support. However, the overall product distribution is more sensitive to the presence of the support and the reactions governing the growth of longer-chain hydrocarbons may be more susceptible to effects due either to crystallite size or perhaps in some way to the support itself.

This study gives meaningful comparisons between a large number of nickel catalysts since specific activities based on metal surface areas represent the only way to directly compare intrinsic activity. It shows that nickel catalysts prepared by different methods on typical supports can differ somewhat in their catalytic behavior but that these variations are relatively small compared to differences observed in other metal catalysts. When catalysts with similar supports are compared, the consistency in turnover numbers measured in this laboratory and four others is indeed remarkable. The increasing trend toward reporting specific activities under well-defined conditions is certainly welcome and will facilitate future catalytic comparisons.

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