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Alkali Promotion of Nickel Catalysts for Carbon Monoxide Methanation

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Differential reactor studies of carbon monoxide hydrogenation have been carried out on a series of 8% Ni/SiO_2–Al_2O_3 catalysts in which the supports have been impregnated with increasing amounts of sodium. Magnetic measurements show that the extent of reduction and the nickel crystallite size are not influenced by the sodium on the support. Hydrogen adsorption measurements reveal that the exposed surfaces are in agreement with the crystallite sizes and are not significantly poisoned by the alkali. The turnover number increases with sodium content and passes through a maximum at 0.3% Na with an enhancement by a factor of 6. Kinetic data best fit the surface reaction mechanism for which rate $= kK_{CO}P_{CO}P_{H}^{\frac{1}{2}}/(1 + K_{CO}P_{CO})^2$. For K_{CO}, the pre-exponential factor and heat of adsorption are unchanged by Na, but the parameters of k are not. The pre-exponential factor passes through a maximum and the activation energy decreases as the Na level increases. These results are best explained by an initial decrease in acidity, which keeps the nickel surface clean, followed by a poisoning via direct metal interaction or support modification by the alkali.

INTRODUCTION

The mechanism of carbon monoxide hydrogenation over a commercial nickel–kieselguhr catalyst has been reported in a previous communication from this laboratory (*1*). A proposed mechanism is shown in Table 1. Below 473°K, the slow step was found to be the dehydration reaction [6], between 473 and 573°K the surface reaction [3] was rate determining, and above 573°K there were indications of carbon monoxide adsorption limitations. This paper extends the investigation to include the effect of alkali promotion on the kinetics predicted from the surface reaction [3]. Nickel concentration and support modifications are also discussed.

Industrial methanation processes use supported nickel catalysts for the hydrogenation of carbon monoxide (*2*) because of its uniquely high activity and economic availability. Supports such as alumina, aluminates, and silicates are preferred since these minimize sintering. Alkali promoters, most commonly potassium, are added to either poison support acidity or to catalyze coke removal via hydrogen or steam reactions (*3*). Alkalis have been reported as promoters of the intrinsic activity of the nickel itself in hydrocarbon steam reforming (*4*).

Very little systematic research on the effect of alkalis on methanation activity has been reported. Schoubye recently demonstrated that several percent of K_2O decreased the activity of nickel catalysts by a factor of about 25 although the sulfur capacity remained unchanged (*5*). These observations imply an effect other than direct poisoning of the nickel sites.

We have conducted an investigation on the effect of support acidity on hydrogena-

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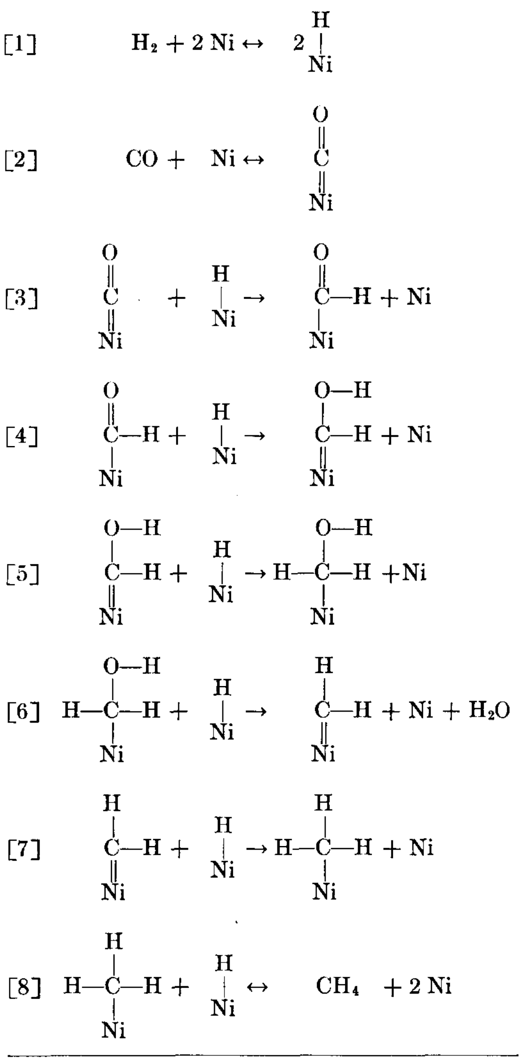
TABLE I

Proposed Mechanism



$$[1]\quad H_2 + 2\,Ni \leftrightarrow 2\begin{array}{c}H\\|\\Ni\end{array}$$

$$[2]\quad CO + Ni \leftrightarrow \begin{array}{c}O\\\|\\C\\\|\\Ni\end{array}$$

$$[3]\quad \begin{array}{c}O\\\|\\C\\\|\\Ni\end{array} + \begin{array}{c}H\\|\\Ni\end{array} \rightarrow \begin{array}{l}O\\\|\\C\text{—}H + Ni\\|\\Ni\end{array}$$

$$[4]\quad \begin{array}{l}O\\\|\\C\text{—}H\\|\\Ni\end{array} + \begin{array}{c}H\\|\\Ni\end{array} \rightarrow \begin{array}{l}O\text{—}H\\|\\C\text{—}H + Ni\\\|\\Ni\end{array}$$

$$[5]\quad \begin{array}{l}O\text{—}H\\|\\C\text{—}H\\\|\\Ni\end{array} + \begin{array}{c}H\\|\\Ni\end{array} \rightarrow H\text{—}\begin{array}{l}O\text{—}H\\|\\C\text{—}H + Ni\\|\\Ni\end{array}$$

$$[6]\quad H\text{—}\begin{array}{l}O\text{—}H\\|\\C\text{—}H\\|\\Ni\end{array} + \begin{array}{c}H\\|\\Ni\end{array} \rightarrow \begin{array}{l}H\\|\\C\text{—}H + Ni + H_2O\\\|\\Ni\end{array}$$

$$[7]\quad \begin{array}{l}H\\|\\C\text{—}H\\\|\\Ni\end{array} + \begin{array}{c}H\\|\\Ni\end{array} \rightarrow H\text{—}\begin{array}{l}H\\|\\C\text{—}H + Ni\\|\\Ni\end{array}$$

$$[8]\quad H\text{—}\begin{array}{l}H\\|\\C\text{—}H\\|\\Ni\end{array} + \begin{array}{c}H\\|\\Ni\end{array} \leftrightarrow CH_4 + 2\,Ni$$

tion and hydrogenolysis reactions. Identical samples of approximately 5 to 10% nickel on silica–alumina were prepared with progressive amounts of sodium added to the support prior to impregnation. Catalysts were characterized by magnetic, hydrogen adsorption, and nitrogen adsorption measurements and by activity tests for acidity. Results of this research will be reported at a later time. In view of the current interest in methanation process and catalyst design, we are prompted to present our findings on the kinetics of carbon monoxide hydrogenation over these catalysts.

EXPERIMENTAL

Catalyst preparation. Extrudates of Davison Chemical SMR-7-3598 silica–alumina (25% Al_2O_3) were crushed to 100- to 120-mesh particles and divided into 0.06-kg aliquots. Each sample of silica–alumina was treated for 2 days with 100 cm^3 of H_2O containing increasing amounts of NaCl. They were then dried in an oven at 413°K for an additional day and calcined at 723°K in flowing air for 3 hr. This procedure was found by Maatman *et al.* to be effective in removing all of the chloride ions with a deposition of Na on the catalyst surface (*6*).

Portions (0.03 kg) of each sample were further treated with 50 cm^3 of H_2O containing 0.015 kg of $Ni(NO_3)_2 \cdot 6H_2O$, corresponding to a nickel loading of approximately 10%. These were contacted for a week, dried at 373°K for 1 day, crushed to 48–60 mesh, and stored for use. Prior to each subsequent experiment, each catalyst was reduced at 623°K for 16 hr in flowing hydrogen as a standard procedure.

Magnetic measurements. Samples were reduced *in situ* and characterized magnetically with a Faraday apparatus using a Model 4800 Alpha Scientific magnet with constant gradient pole pieces. Weight losses and induction forces were recorded with a Cahn 2000 RG Electrobalance. Magnetizations at 298°K were measured for the reduced samples up to a magnetic field of 6 kOe. The data were typical of highly dispersed superparamagnetic nickel systems. Saturation magnetizations, M_s, were found by extrapolation to high fields. Selwood has shown this procedure to be adequate within an accuracy of 5%, especially for dispersions that are not too high (*7*). Weight percentage of reduced nickel for each sample was calculated from M_s. The average crystallite diameter was calculated using the low field approximation of the Langevin function (7).

Adsorption measurements. Adsorption measurements were made with a conventional volumetric apparatus using a MKS Baratron Type 144 pressure indicator. Reduction was completed at standard conditions with a special flow-through cell.

The usual BET procedures were carried out with nitrogen at 77°K to measure total surface areas.

Hydrogen adsorption was measured at 298°K, and the usual calculations made to give nickel surface area (*1*).

Methanation rates. Methanation rates were measured with a continuous flow, differential microreactor. The catalyst charge of about 0.0002 kg was equally mixed with inert α-Al_2O_3 in a stainless steel tube (0.6-cm diameter) contained in a controlled furnace. The feed was a mixture of individually adjusted flows of helium, hydrogen, and carbon monoxide. Total flow rates varied from 20 to 200 cm^3/min at a total pressure of 100 kPa. Catalyst bed temperatures were measured with a shielded chromel–alumel thermocouple in the bed. Furnace temperatures were controlled by a thermocouple outside the reactor tube.

Rates were measured in the temperature range 523–603°K with conversions below 5%. In most cases the carbon monoxide pressure was varied from 10 to 40 kPa with the balance of the feed hydrogen. No deactivation with either time or temperature was observed. Rates were calculated from the measured conversions and flow rates and were reproducible within 5%.

TABLE 2

Effect of Sodium on Reducibility, Crystallite Size, and Total Surface Area

Na (wt%)	Ni (wt%)	d_{Ni} (nm)	BET surface ($Sg \times 10^{-5}$, m^2/kg)
0	7.6	8.8	1.74
0.12	6.3	7.6	1.82
0.44	8.0	8.8	1.78
0.73	8.0	8.8	1.68
2.37	8.0	9.0	1.52

TABLE 3

Effect of Sodium on Nickel Surface Site Concentration

Na (wt%)	Nickel surface site concentration (sites/kg(cat) $\times 10^{-22}$)		N_H/N_M
	N_H	N_M	
0	7.23	7.73	0.94
0.12	7.20	7.42	0.97
0.44	8.42	8.13	1.04
0.73	7.43	8.13	0.91
2.37	6.65	7.95	0.84

RESULTS AND DISCUSSION

Table 2 shows the amount of reduced nickel, the mean crystallite diameter, and the total BET surface area for each catalyst. There is very little significant difference between the samples. These results indicate that the presence of sodium on the support does not influence the amount of nickel reduced nor does it induce sintering of the nickel crystallites. There is a slight drop in total surface area at the high levels of sodium loading. This may be due to physical blockage of the smallest micropores or to general surface loss of the support.

Table 3 gives surface nickel concentrations calculated from the hydrogen surface areas, N_H, and from the crystallite diameters, N_M. The last column in Table 3 shows the ratio of N_H to N_M. With the exception of the last catalyst, both N_H and N_M are relatively constant and the N_H/N_M ratio varies from 0.91 to 1.04, indicating very good agreement between the two techniques. This not only supports the accuracy and consistency of the two methods but also justifies the assumptions of spherical shape for the crystallites,

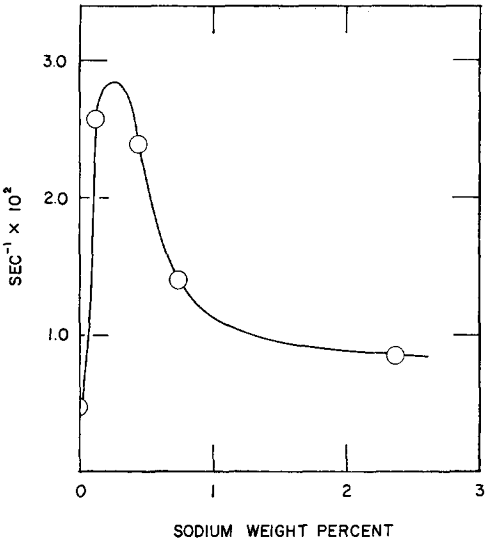


FIG. 1. Turnover numbers for sodium-treated catalysts. 543°K, $P_{CO} = 20$ kPa., $P_H = 80$ kPa.

H–Ni stoichiometry, and full coverage of hydrogen at 298°K (*8*). Furthermore we conclude the absence of substantial bonding with the support and sodium poisoning of the nickel. However, poisoning may be responsible for the lower N_H/N_M ratio of the 2.37% Na sample and even, to some extent, for 0.73% Na. Even at these values, the extent of surface poisoning is small.

These conclusions imply that changes in catalytic behavior come not from a loss of sites but from changes in surface atoms themselves, caused by either solution of sodium into the nickel metallic structure or induced effects from the support. It is not clear which since we have no measurement of how much sodium is associated with the nickel during the impregnation process or through subsequent surface diffusion.

Our sodium-impregnated supports show a loss of surface acidity similar to that reported by Maatman *et al.* (*6*). The nickel, therefore, is exposed to supports of decreasing Bronsted acidity. Richardson (*9*) has documented specific activities for benzene hydrogenation and ethane hydrogenolysis which decrease sharply as the acidity of different types of supports increases. This may be due to the initial formation of poisoning carbonaceous residues by the more acidic supports or to a poisoning effect due to surface hydroxyl groups migrating to the nickel surface. In addition, acidity may change the character of the nickel through electron transfer across the metal–support interface (*10*).

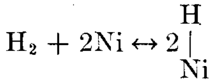
The influence of sodium is shown in Fig. 1. Here the turnover numbers have been calculated from measured rates and the values of N_H taken from Table 3. There is a maximum value of the turnover number at 0.3% Na with an enhancement by a factor of 6 over the sodium-free catalyst. The turnover number becomes less sensitive at higher sodium levels.

In order to further accent the effect of support sodium, we conducted a study of kinetic parameters over the temperature range 523–603°K. Seeking mechanisms through the fitting of kinetic data is a doubtful and dangerous procedure. At best, experimental conditions and accuracy are such that certain mechanisms are only excluded. The proposed mechanism in Table 1 leads to any number of rate equations depending on which step is assumed to be slow. These are generally of the type

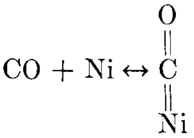
$$\text{rate} = \frac{kK_{CO}P_{CO}P_H^n}{(1 + K_{CO}P_{CO})^m}, \quad (1)$$

if strong hydrogen or product adsorption are excluded. We have fitted our data to various values of n and m. The results of $m = 1$ all lead to negative coefficients and are eliminated. Of the others, all give reasonably good fits, with best results for $n = 0.5$, $m = 2$, and $n = 1$, $m = 2$. In a previous report from this laboratory (*1*), pulsed thermokinetic (PTK) measurements (*8*) were used to determine the slow steps. Between 473 and 573°K, Step [3] of the mechanism in Table 1 appeared to be rate determining. This leads to a rate equation with $n = 0.5$, $m = 2$ consistent with our results.

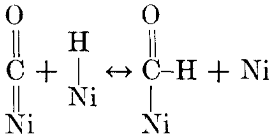
Vannice (*11*) explains kinetic data over alumina-supported Group VIII metals by a modification of the mechanism in Table 1. He assumes Steps [3] and [4] are in equilibrium and the slow step is the combination of Steps [5] and (6) as follows.

[1] 

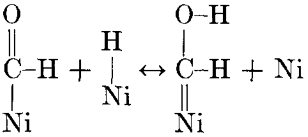
$$H_2 + 2Ni \leftrightarrow 2\,\underset{Ni}{\overset{H}{|}}$$

[2] 

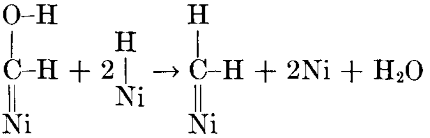
$$CO + Ni \leftrightarrow \underset{\underset{Ni}{\|}}{\overset{\overset{O}{\|}}{C}}$$

[3] 

$$\underset{\underset{Ni}{\|}}{\overset{\overset{O}{\|}}{C}} + \underset{Ni}{\overset{H}{|}} \leftrightarrow \underset{\underset{Ni}{|}}{\overset{\overset{O}{\|}}{C}}\text{–}H + Ni$$

[4] 

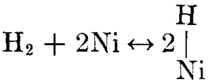
$$\underset{\underset{Ni}{|}}{\overset{\overset{O}{\|}}{C}}\text{–}H + \underset{Ni}{\overset{H}{|}} \leftrightarrow \underset{\underset{Ni}{\|}}{\overset{\overset{O\text{–}H}{|}}{C}}\text{–}H + Ni$$

[5] 

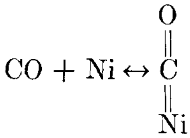
$$\underset{\underset{Ni}{\|}}{\overset{\overset{O\text{–}H}{|}}{C}}\text{–}H + 2\,\underset{Ni}{\overset{H}{|}} \rightarrow \underset{\underset{Ni}{\|}}{\overset{\overset{H}{|}}{C}}\text{–}H + 2Ni + H_2O$$

This leads to a rate equation with $n = 2$, $m = 3$ which is a less accurate fit of our data but nevertheless gives reasonable results. The three-species reaction in this slow step is less likely than either Step [5] or [6]. Furthermore, the results are not consistent with PTK measurements, at least on Ni/SiO_2 catalysts. The possibility remains, however, that with Al_2O_3 the slow step found by PTK below 473°K, i.e., Step [6], may extend to higher temperatures, thus approximating Vannice's mechanism.

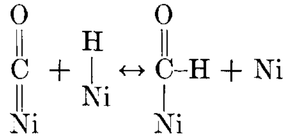
Fontaine and Harriott (*12*) likewise assume equilibrium in Step [3], Table 1, but introduce the subsequent slow step [4]:

[1] 

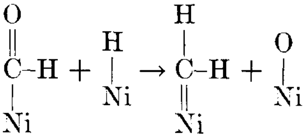
$$H_2 + 2Ni \leftrightarrow 2\,\underset{Ni}{\overset{H}{|}}$$

[2] 

$$CO + Ni \leftrightarrow \underset{\underset{Ni}{\|}}{\overset{\overset{O}{\|}}{C}}$$

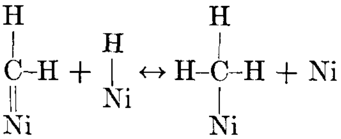
[3] 

$$\underset{\underset{Ni}{\|}}{\overset{\overset{O}{\|}}{C}} + \underset{Ni}{\overset{H}{|}} \leftrightarrow \underset{\underset{Ni}{|}}{\overset{\overset{O}{\|}}{C}}\text{–}H + Ni$$

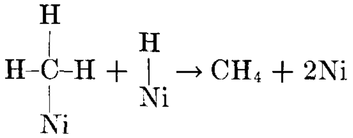
[4] 

$$\underset{\underset{Ni}{|}}{\overset{\overset{O}{\|}}{C}}\text{–}H + \underset{Ni}{\overset{H}{|}} \rightarrow \underset{\underset{Ni}{\|}}{\overset{\overset{H}{|}}{C}}\text{–}H + \underset{Ni}{\overset{O}{|}}$$

For this sequence, it follows that $n = 1$, $m = 2$, a reasonably good fit to our data. Fontaine and Harriott, however, find that for low CO partial pressures (<10 kPa) the rate-versus-P_{CO} curves pass through a much broader maximum than can be explained by this rate expression. This, they explain, by introducing a second slow step:

[5] 

$$\underset{\underset{Ni}{\|}}{\overset{\overset{H}{|}}{C}}\text{–}H + \underset{Ni}{\overset{H}{|}} \leftrightarrow H\text{–}\underset{\underset{Ni}{|}}{\overset{\overset{H}{|}}{C}}\text{–}H + Ni$$

[6] 

$$H\text{–}\underset{\underset{Ni}{|}}{\overset{\overset{H}{|}}{C}}\text{–}H + \underset{Ni}{\overset{H}{|}} \rightarrow CH_4 + 2Ni$$

Most experience with hydrocarbon hydrogenation or hydrogenolysis involving methyl groups reduced the possibility of this as a slow step. Also, the presence of bridged adsorbed CO groups at low pressures offers alternate routes which can explain the zero-order dependence in these regions.

On the basis of all current evidence, we believe that the mechanism of Table 1,

TABLE 4

Kinetic Constants of Alkali-Promoted Catalysts

Na (wt%)	k_0 (molecules/ s·site·Pa)$^{\frac{1}{2}}$	E (kJ/mol)	$K_0 \cdot 10^2$ (MPa^{-1})	Q (kJ/mole)
0	1.11×10^7	116	1.13	42.7
0.12	3.77×10^7	113	1.20	40.2
0.44	1.12×10^6	98	0.48	44.8
0.73	1.32×10^5	91	0.55	44.8
2.37	1.95×10^4	84	1.37	40.8

with slow Step [3] leading to Eq. (1) and $n = 0.5$, $m = 2$, is a reasonable basis on which to examine the changes brought about by the sodium on the support. The activation energy, E, and heat of adsorption, Q, were found from the temperature dependence of the parameters

$$k = k_0 e^{-E/RT} \tag{2}$$

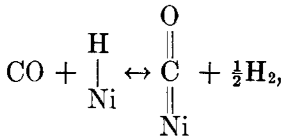
and

$$K_{\mathrm{CO}} = K_0 e^{Q/RT} \tag{3}$$

measured over the range 523–603°K.

These results are given in Table 4.

The most striking result in Table 4 is the relatively constant values of K_0 and Q. The kinetic parameters are similar to these reported by others (*13*). The initial heat of adsorption of carbon monoxide on nickel films has been reported at about 167 kJ/mol (*14*). However, Wedler *et al.* (*15*) found heterogeneity, with the heat of adsorption decreasing from an initial value of 126 kJ/mol to less than 17 kJ/mol at full coverage. McGill and Richardson (*1*) are in agreement with this and conclude from PTK measurements that the higher heats at low coverage are associated with the bridged mode of absorption, whereas the high coverage linear mode has a heat of adsorption of 67 kJ/mol. The values of Q in Table 4 are constant at about 41–45 kJ/mol, suggesting the involvement of an even more weakly bound molecule of carbon monoxide. Baker and Rideal (*16*) found that when carbon monoxide was added to a hydrogen-covered surface, adsorption occurred with the displacement of adsorbed hydrogen. Vlasenko *et al.* (*17*) showed the adsorption to be the linear type. McGill and Richardson (*1*) confirmed these results and obtained a heat of adsorption of 42–50 kJ/mol. If we interpret the Q values in Table 4 as an indication of this type of adsorption, then Step [2] of Table 1 must be modified to

[2] 

$$\mathrm{CO} + \overset{\mathrm{H}}{\underset{\mathrm{Ni}}{|}} \leftrightarrow \overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{Ni}}{\|}}{\mathrm{C}}} + \tfrac{1}{2}\mathrm{H}_2,$$

but the kinetic rate equation remains unchanged.

The main differences are found in the parameters k_0 and E. The effect of increasing sodium content is to lower the activation energy with k_0 passing through a maximum. The shape of the curve in Fig. 1 is determined by these changes in k_0 and E. From 0.12% Na upward, the relationship between $\ln k_0$ and E is linear as found in the classical compensation effect.

A closer examination of the rate constant, k, shows that it contains both the rate constant of Step [3], and K_{H}, the adsorption coefficient for hydrogen. Changes in k may be due to differences in k_3 and/or K_{H}. We have postulated in the mechanism of Table 1 and the rate equations derived from it that hydrogen and carbon monoxide compete for equivalent sites. Since the

TABLE 5

Turnover Numbers on Nickel Catalysts[a]

Catalyst	Turnover number (molecules/ s·site) × 10^2)	Reference
Raney Ni	3.83	Dalla Betta *et al.* (*18*)
5% Ni/ZrO_2	7.9	Dalla Betta *et al.* (*18*)
2% Ni/Al_2O_3	7.7	Dalla Betta *et al.* (*18*)
5% Ni/Al_2O_3	3.5	Vannice (*11*)
8.8% Ni/Al_2O_3	8.2	Vannice (*19*)
16.7% Ni/SiO_2	3.5	Vannice (*19*)
7.3% Ni/SiO_2-Al_2O_3	0.5	This work

[a] 543°K, $P_{\mathrm{CO}} = 20$ kPa, $P_{\mathrm{H}} = 80$ kPa.

energetics of CO adsorption do not change significantly, it is reasonable to assume no large changes in the nature of hydrogen adsorption and accordingly, K_H. This leads to the conclusion that the observed effects result from changes in k_3.

The exact nature of the interaction is difficult to define from these results alone. The promotion may be due to the effect of sodium on the nickel itself or on the acidity of the support.

It is informative to compare the turnover numbers at the same conditions for nickel on supports with different acidities. This is done in Table 5 using data from recent publications.

Comparisons of these turnover numbers derived from different laboratories shows a remarkable consistency (within a factor of 2) for supports of low acidity but with a decrease by a factor of 10 for the more acidic support. Addition of 0.12 wt% Na increases the rate by a factor of about 6. These observations suggest that a decreasing support acidity results in less metal poisoning via acid catalyzed carbonaceous species from polymerization of the CH_x groups. Kreindel *et al.* (*20*) found no effect of support on methanation activity at 3.0 MPa, but at higher pressures the ease in maintaining a clean surface is increased. Alternatively, a model based on electron transfer could be used. Vannice (*21*) found that increasing the acidity of a supported Pd catalyst increased the methanation activity. He postulated that a transfer of electrons from the Pd to the support, as suggested by Della Betta and Boudart (*10*), makes the metal more like Ru and thus more active. Vannice further predicts that in the case of Ni, the transfer to the support results in a Co-like metal with decreased activity. This prediction is in agreement with results given here. However, infrared measurements (22) imply that electron transfer is in the opposite direction, i.e., from the more acidic support. Moreover, we have also shown that ethane hydrogenolysis and benzene hydrogenation is independent of support acidity when only *initial* activity is considered (*23*).

Thus we conclude that the higher activity of the less acidic support, if related to acidity directly, is most probably due to less poisoning by carbonaceous material. The opposite results of Vannice in the case of Pd cannot be reconciled with this conclusion, but it should be noted that his experiments were made with SiO_2 and Al_2O_3 and not with the much more acidic silica–alumina used here.

Increased sodium content results in a decreasing methanation activity. Here the promotion discussed above is superseded by some poisoning function of the alkali, either directly via the metal or metal–support interface or via the support itself. We cannot distinguish between local (within the metal) or long-range (induced from the support) effects since we have no direct knowledge of the degree of sodium incorporation in the metal.

CONCLUSIONS

This work has shown that for 8% Ni/SiO_2–Al_2O_3 catalysts, prior impregnation of sodium on the support leads to a maximum in the turnover number of CO methanation at 0.3% Na with an enhancement by approximately a factor of 6. Kinetic measurements show that the mechanism is unchanged and that the rate constant of the slow step, a surface reaction, is the only parameter effected. We cannot differentiate definitely between direct metal promotion or support-induced effects. However, the overall evidence implies that small amounts of alkali result in a cleaner support with less nickel deactivation, but the improved activity is overcome by alkali poisoning as the sodium content increases.

ACKNOWLEDGMENT

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