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The CO/H$_2$ Reaction over Nickel–Alumina Studied by the Transient Method

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The methanation of carbon monoxide over Ni/Al$_2$O$_3$ has been studied at atmospheric pressure and in the temperature range of 180–240°C using a once-through flow reactor at small conversions. When the steady-state reaction in CO/H$_2$ was switched to H$_2$ alone, a large peak of methane and a smaller peak of higher hydrocarbons were obtained. Considerable H$_2$O was also obtained indicating the presence of substantial chemisorbed CO. The methane response is composed of two parts: a sharp reactive peak followed by a long tailing part. Separate transient experiments, involving CO/H$_2$, CO/He, and C$_2$H$_4$/He, indicate that the tailing part of the response is associated with chemisorbed CO and the sharp, reactive peak is associated with free carbon.

INTRODUCTION

Although the details of the sequence of steps in the methanation reaction have been the subject of controversy since the discovery of the reaction by Sabatier (*1*), there is considerable recent evidence that the reaction proceeds via an active surface carbon intermediate formed by the dissociation of CO. The results of a variety of studies have perpetuated this viewpoint as recently reviewed by Ponec (*2*) and Bell (*3*).

Numerous recent studies have demonstrated the reactivity to H$_2$ of surface carbon formed by the disproportionation of CO on Ni:

$$2\mathrm{CO(g)} \rightarrow \mathrm{C}^* + \mathrm{CO_2(g)}$$

Wise and co-workers (*4, 5*), using the technique of temperature-programmed surface reaction, have observed the formation of basically two types of surface carbon (called α- and β-carbon by the authors) by CO disproportionation at temperatures of 225–325°C on a Ni/Al$_2$O$_3$ catalyst. It was postulated that the reactivity of the dispersed α-state indicates that it is a feasible intermediate in methanation. Araki and Ponec (*6*) have also shown the reactivity of surface carbon to hydrogen on Ni and Ni–Cu films. They have implicated surface carbon formed from the disproportionation of CO as a viable reaction intermediate by predepositing ^{13}C and then admitting ^{12}CO/H$_2$ and subsequently measuring the initial production of ^{13}CH$_4$ as much greater than that of ^{12}CH$_4$. This was also observed by Biloen *et al.* (*7*) on Ni, Co, and Ru.

Rabo *et al.* (*8*) have demonstrated the reactivity of surface carbon by observing that carbon deposited by CO at high temperature on Ni, Co, and Ru is reactive to form methane even at room temperature, but adsorbed CO is practically inert to hydrogen at room temperature. This is evidence that the more probable route to methanation is via the dissociation of CO and subsequent hydrogenation of surface carbon rather than the direct hydrogenation of adsorbed CO. Goodman *et al.* (*9*) have shown that the rate of carbon formation by CO disproportionation and the hydrogenation rate of carbon thus produced are comparable with the rate of methanation at 175°C indicating that not only is this a probable mechanism, but also that there is a possible balance in the carbon formation and carbon removal

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steps during methanation such that one is not solely rate-determining.

As can be seen numerous studies have demonstrated the reactivity of surface carbon; however, few have been concerned with determining the nature and composition of the active Ni surface under working methanation conditions. The transient response method is a technique appropriate for furnishing such information and that is the subject of this paper.

In earlier work on Fe catalysts (*10*) the technique has proven quite powerful. Van Ho and Harriott (*11*) have done some transient methanation experiments on Ni/SiO_2 catalysts and have interpreted their results in terms of the formation of active carbon by the aid of H_2. Happel *et al.* (*12–14*) have used transient isotope tracing in an attempt to determine the composition of the surface species present during reaction. Although the results are possibly complicated by a variety of exchange reactions, they have proposed that the most abundant surface species are C^* and CH^* (*14*) in agreement with Amenomiya *et al.* (*15*) for similar experiments.

For a Ru catalyst, Cant and Bell (*16*) have shown that after steady-state methanation, by switching the feed to the reactor to pure hydrogen, a large peak of methane is observed indicating a hydrogen deficient surface covered mostly by C-containing species, in this case CO^*.

The bulk of the experiments in this work concerns the hydrogenation of the surface species present during reaction in CO/H_2 by switching the reactor feed to pure hydrogen and observing the subsequent product response. Also a number of transient experiments were performed in an attempt to identify the surface species responsible for the observed hydrogenation product response.

In these experiments a once-through, quasi-differential reactor was used with a high fluid velocity and a very small residence time so that the surface phase quantities in the reactor relative to those in the gas phase are large. In this way, product responses observed during the transient experiments are largely a result of surface kinetic phenomena, not appreciably complicated by the reactor dynamics of the gas phase.

EXPERIMENTAL

Catalyst preparation. A 10 wt% $Ni/\gamma\text{-}Al_2O_3$ catalyst was prepared by impregnating Alon-C (DeGussa) to incipient wetness with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. The powder was pressed, crushed, and screened and then dried and reduced *in situ* in flowing hydrogen using a procedure similar to that recommended by Bartholomew (*17*). Prior to use in all cases the catalyst was reduced for at least 2 h at 450°C in flowing hydrogen before cooling in hydrogen to reaction temperature. For most of the experiments, where short reaction times were employed, it was found that flowing hydrogen for 15 min at reaction temperature was sufficient to regenerate a surface with reproducible activity.

Catalyst characterization. The BET surface area of the catalyst was measured in a flow sorption apparatus (Quantasorb Model QS-7) and was found to be 117 m^2/g.

The active metal surface was measured by H_2 chemisorption utilizing a flow technique similar to that used by Amelse *et al.* (*18*) for an Fe catalyst. The H_2 uptake of the catalyst was found to be 154 μmol/g of catalyst yielding a value of 308 μmol Ni surface atoms/g of catalyst. The metal particles were assumed to be cubes exposed on 5 sides. An average Ni atom area of 6.5 $Å^2$ (*17*) yielded a particle 44 Å on a side, in good agreement with a value of 47 Å as determined by X-ray diffraction line broadening analysis on the same sample.

Apparatus. A once-through flow reactor was employed with a typical catalyst charge of 8–25 mg. The 3.81-mm stainless-steel reactor and the catalyst support were found to have negligible catalytic activity. The reactor was typically operated with steady-state conversions of CO <5% and

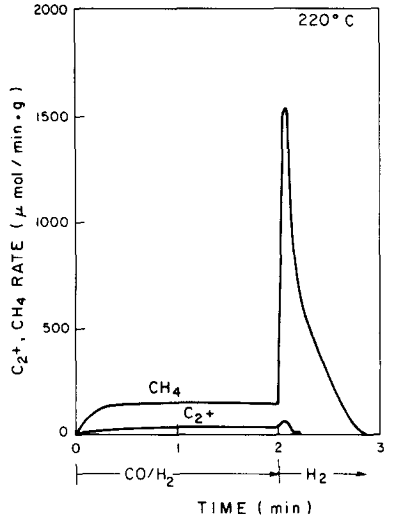

FIG. 1. He → CO/H_2 → H_2 transient, 220°C.

the flow rates of all gas streams were always 30 ml/min. Step changes in concentration were introduced to the reactor by two four-way switching valves (Carle Model 2011) that selected one of three streams of pure gases or premixed gases. Choke valves on the two streams not selected for the reactor feed were adjusted so as to maintain a constant pressure drop and to ensure minimal disruption of the flow rate upon switching. Gas concentration analysis was made by a sector-type mass spectrometer (Nuclide Model 3-60-G) equipped with a fast-response continuous inlet system. Mass/charge ratios of 15, 18, 27, 28, 29, 43, and 44 were used for the analysis of CO, CO_2, H_2O, and C_1–C_4 paraffins. Since the fragmenting patterns for these components overlap considerably, some experiments were necessarily repeated for each mass/charge to obtain a complete quantitative solution of the system of linear algebraic equations. In many cases it was possible to use the intensity of the mass/charge = 15 signal directly as a measure of the CH_4 concentration.

The hydrogen, carbon monoxide, ethylene, and helium (Matheson) were all standard grade and used with purification by passage through molecular sieves. Carbonyls in the CO were decomposed in the reactor preheater coil.

RESULTS AND DISCUSSION

CO/H_2 experiments. In Fig. 1 is represented a typical transient experiment at 220°C. In this case the reactor feed was switched from pure H_2 to pure He for 1 min to desorb the surface hydrogen. Then at time zero in Fig. 1 the feed was switched to 10% CO/H_2 and a steady methane formation rate was achieved within approximately 1 min. The activity was observed by longer experiments to decline only very slowly from that point on. The steady-state rate of production of CH_4 in 10% CO/H_2 was found to be 118 μmol/min-g at 220°C corresponding to a turnover frequency of 6.4E-3 s^{-1}. Using the kinetic parameters of Vannice (*26*) a turnover frequency of 8.1E-3 s^{-1} is obtained at 220°C and $H_2/CO = 9$ for a 8.8% Ni/Al_2O_3 catalyst, in good agreement with our results. An activation energy of 26 kcal/mol calculated from our data is in excellent agreement with Vannice (*26*) who reports the same value. At 2 min the feed was changed to pure hydrogen and the resulting product response was observed. As can be seen a large peak of CH_4 is obtained indicating that the surface is in fact hydrogen deficient during steady-state reaction as observed by Cant and Bell (*16*) for Ru/SiO_2 and Van Ho and Harriott (*11*) for Ni/SiO_2.

The switch to pure H_2 has the effect of hydrogenating all of the carbon-containing surface species to mostly CH_4 and a small amount of higher hydrocarbons, for if the temperature is then raised to 450°C in flowing H_2 no additional detectable CH_4 production is observed indicating that the carbon-containing species are essentially quantitatively hydrogenated at reaction temperature. There is probably no formation of carbonaceous residues associated with the metal that may be inactive to H_2 even at 450°C, for the initial activity is reproducible. Also only a very small quantity (<10 μmol/g) of adsorbed CO desorbs during the switch to H_2. Thus the sum of the areas under the CH_4 and C_2^+ curves approximately represents the amount of carbon-containing intermediates on the surface during steady-state reaction. This quantity, 292 μmol/g, is consistent with the number of available surface Ni atoms, 308 μmol/g, as determined by H_2 chemisorption, and this result also supports the earlier contention that the surface is covered mostly by C-containing intermediates.

It should be mentioned here that the other major product during reaction is, of course, H_2O. The mass spectrometer used has a slow response to H_2O so that little useful kinetic information is obtained from the rate vs time response. However, a reasonably accurate measure of the cumulative amount of H_2O formed after the switch to H_2 can be made. This quantity reflects the amount of oxygen-containing species present during steady-state reaction which can be hydrogenated. Approximately 180 μmol/g of H_2O was formed indicating the presence of considerably less oxygen than carbon on the surface.

The sum of the oxygen hydrogenated to H_2O and the carbon hydrogenated to CH_4 and higher HC's (282 + 180 = 472 μmol/g) compared with the total number of surface Ni atoms available for reaction (308 μmol/g) indicates that a considerable amount of carbon and oxygen are present undissociated. This hypothesis is supported by results which will be discussed later.

CO_2 is also formed at steady-state at a rate (1.2 μmol/min-g) considerably less than that of CH_4 (118 μmol/min-g) and upon switching to H_2 the CO_2 production immediately stops.

The CH_4 product response curve in Fig. 1 after the switch to H_2 at 2 min appears to be formed by two types of surface species: one sharp reactive peak which is produced first and a second tailing peak. It is expected that the various carbon-containing surface species of different reactivities or of various stages in the mechanistic pathway would contribute to the hydrogenation product response. The more reactive species or the species further along in the mechanistic pathway are removed faster and therefore result in an earlier response. The less-reactive species would contribute to the tailing effect. However, the observed response is not entirely consistent with this simple analysis as will be discussed later.

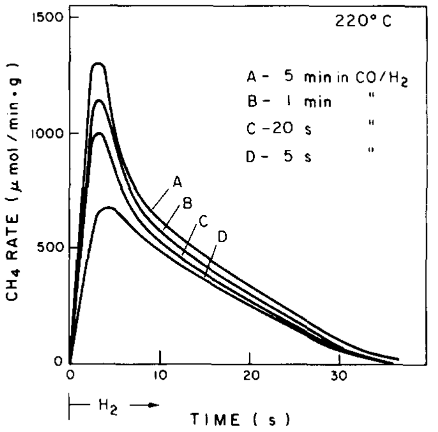

FIG. 2. Effect of time-on-stream of CO/H_2 on CH_4 response, 220°C.

In an attempt to observe the evolution of the steady-state surface species through changes in the CH_4 response during hydrogenation, switches to H_2 were made after various times on stream of CO/H_2. The results are presented in Fig. 2. After 5 min on stream the product response is essentially constant in shape and size. It is clear that the tail part of the CH_4 response is formed immediately and that the attainment of steady-state surface conditions is mostly controlled by the evolution of the sharper reactive peak, and this result is expected if the species responsible are in fact active intermediates in the reaction. This also suggests that the species responsible for the reactive peak are further along the mechanistic pathway from adsorbed CO.

Similar results are observed at 240, 200, and 180°C (*19*). Across this range of temperatures there appears to be a change in the relative population of the reactive peak and the tail. At 180°C, the amount of CH_4 formed in the reactive peak appears to be a

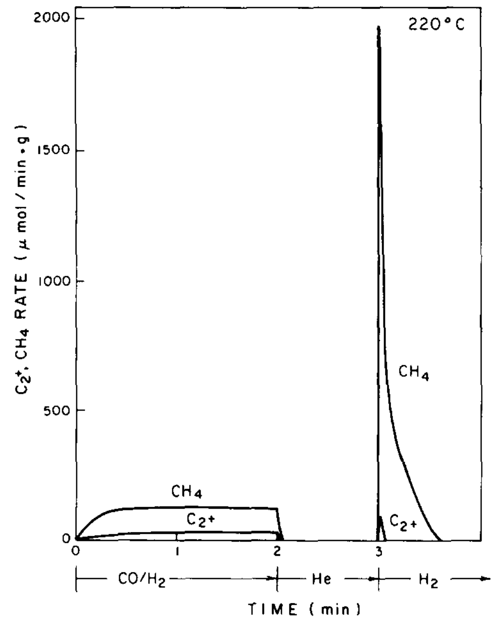

FIG. 3. He → CO/H_2 → He → H_2 transient, 220°C.

larger portion of the total CH_4 than at 240°C.

In an effort to see if there are any C-containing surface species present during reaction at 220°C that can be readily desorbed, the steady-state reactor feed was switched to He for 1 min before switching to H_2. The results are presented in Fig. 3 where it is seen that the He purge has the effect of rapidly quenching the methanation reaction. The desorption of less than 2 μmol/g of CH_4 is observed, and the immediate desorption of 60 μmol/g of CO is also measured. Upon switching to H_2, the area under the methane peak is found to be 181 μmol/g, considerably less than the amount formed after directly switching to H_2. The amount of H_2O formed corresponding to the CH_4 in Fig. 3 is 60 μmol/g reflecting the fact that adsorbed CO has desorbed. The desorption of CO stops after approximately 30 s but for longer He purges the amount of CH_4 formed after switching to H_2 is less. The results for various He purge times are depicted in Fig. 4 and similar results are observed at 200 and 240°C (*19*).

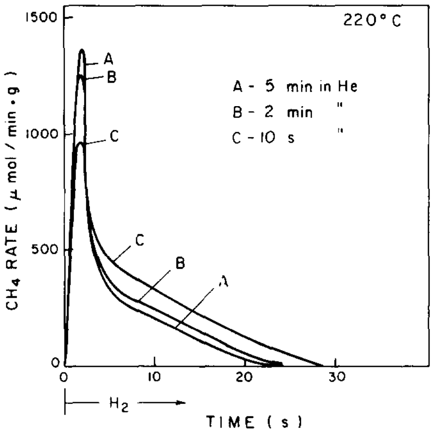

FIG. 4. Effect of He Purge time on CH_4 response, 220°C.

These results may be explained by the continued production of CO_2 when the switch to He is made as shown in Fig. 5 for 240°C, at which temperature the effect is most accentuated. The same phenomenon is observed at all temperatures studied. It is seen here that upon switching to He the CO_2 production drops below its steady-state value then begins to rise and goes through a maximum that is, in fact, higher than the steady-state rate. The CO_2 production then gradually tapers off. The amount of carbon lost by CO_2 during the He purge is consistent with the amount of carbon lost as reflected in the CH_4 production in Fig. 4 indicating that there is little or no deactivation in He of the C-containing intermediates.

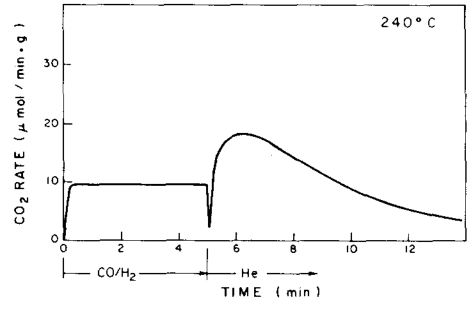

FIG. 5. Continued production of CO_2 in He, 240°C.

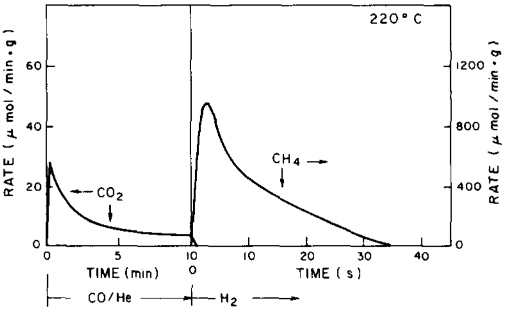

FIG. 6. CO/He experiment, 220°C.

The initial dip and the maximum in the CO_2 production can be explained in the following way if it is assumed that there is less free chemisorbed oxygen than CO* on the surface during steady-state methanation. The CO_2 production is most likely the result of the combination of undissociated adsorbed CO and adsorbed O atoms, since the continued production of CO_2 results in a substantial decrease in the tail part of the CH_4 hydrogenation response which has been associated with chemisorbed CO. So a simple rate expression is

$$r(CO_2) = k(CO^*)(O^*)$$

When the reaction in CO/H_2 is switched to He, CO immediately desorbs resulting in the immediate drop in the rate of CO_2 production in Fig. 5. If the rate of CO dissociation is faster than the rate of CO_2 production, and if O* is initially present in a smaller quantity, the rate of CO_2 production will increase. Eventually the CO* will be used-up resulting in a decrease in the rate thereby creating the maximum.

The continued production of CO_2 in He could also conceivably result from the recombination of C* and 2O* but this mechanism would most likely not result in the rate going through a maximum. Araki and Ponec (*6*) have observed that the recombination of C* and O* is very slow on Ni relative to reaction (*1*). Biloen *et al.* (*7*) have observed that the recombination of C* and O* is very slow by isotope-exchange experiments.

The reactive peak of the CH_4 hydrogenation response is higher and sharper in the 1-min He case (Fig. 3) than in the direct to H_2 case (Fig. 1), similar to the results of Cant and Bell (*16*) for Ru/SiO_2. It appears that the He purge has opened up additional surface sites via the desorption of CO and reaction to form CO_2 so that the rate of CH_4 production starts off from a higher value since there would then be a more favorable surface stoichiometry. In fact the reactive peak reaches a maximum at a time which is as fast as the response time of the detection system. The amount of CH_4 formed during the reactive peak, however, appears to remain essentially constant indicating that it is not associated with the CO that has desorbed with the He treatment and is not appreciably changed by the 1-min He treatment.

CO/He experiments. The interaction of CO with the catalyst in the absence of H_2 was also studied, mostly at 220°C. If 10% CO/He flows over the catalyst, CO_2 is formed via the disproportionation reaction at a rate considerably lower than that of CH_4 during reaction with CO/H_2 but initially much higher than that of CO_2 during reaction with CO/H_2. The results are shown in Fig. 6. Here the catalyst was reduced in H_2 then switched to He for 1 min to remove the surface hydrogen. Then the feed was switched to 10% CO/He and then back to H_2. As can be seen the CH_4 product response is similar to that obtained after reaction with CO/H_2. In an attempt to observe the evolution of the surface species, experiments were done for different times on stream of CO/He and the results are shown in Fig. 7. The development of the reactive peak is associated with the amount of time on stream of CO/He and therefore with the amount of C deposited by the disproportionation reaction. However, a much longer time on stream is required for the development of the reactive peak with CO/He than with CO/H_2. It appears from these experiments that C* formed by the disproportionation of CO is capable of forming a reactive

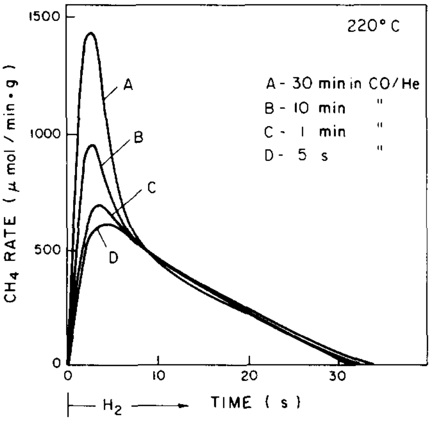

FIG. 7. Effect of time-on-stream of CO/He, 220°C.

peak similar to the one observed after reaction with CO/H_2. This is evidence that at least some of the reactive peak in Fig. 1 is associated with reactive surface C.

In Fig. 2 the attainment of steady-state reaction correlates with the development of the sharp, reactive peak in the CH_4 product response. For a very short time on stream of CO/He or CO/H_2 the reactive peak is apparently not observed at all, but for longer times its appearance indicates the time-dependent and apparently kinetically significant transformation of CO* into a more reactive form, probably the dissociated form. Since it takes longer for the development of the reactive response peak for CO reaction in the absence of H_2, this suggests that the deposition of reactive surface carbon is easier in the presence of H_2, in agreement with what was found by Bell *et al.* (*16, 20*) for Ru. This is probably a result of the effect of the removal of the reactive O* adatoms by the H_2. Mori *et al.* (*21*) have shown that O_2 is much more reactive to H_2 than CO. Also contributing to the reactive peak in the CO/H_2 case would be the partially hydrogenated carbon fragments.

C_2H_4/He experiments. In Fig. 8 is shown the response to H_2 of carbon deposited by the decomposition of ethylene. After a flow of 0.5% C_2H_4/He for 10 s the feed was switched to He for 1 min and then back to H_2. During the C_2H_4/He considerable CH_4 was formed indicating that carbon was deposited by the self-hydrogenation of ethylene:

$$C_2H_4(g) \rightarrow C^* + CH_4(g)$$

Upon switching to H_2 a peak very similar in shape and reactivity to the initial reactive peak formed by CO/H_2 is observed. In Fig. 8 both responses are plotted for comparison.

It should be mentioned here that both the CO/He experiments and the C_2H_4/He experiments are transient-state experiments, that is, experiments that do not, of course, represent a steady-state or working surface. However, useful information is obtained from the response peak shapes concerning the reactivity to H_2 of various carbonaceous surface species.

Ethylene hydrogenation. Hydrogenation of ethylene was carried out at 220°C on the same catalyst with a 10% C_2H_4/H_2 mixture. Complete conversion of ethylene to C_2H_6 with a small CH_4 and C_3H_8 production rate was observed. Upon switching to He for 1 min the rate quenches rapidly and then, when a switch to H_2 is made, only a very small peak of CH_4 was observed even though the rate of production of CH_4 was somewhat higher than that during CO/H_2 reaction. This indicates the presence of very little strongly held C (as in the reactive

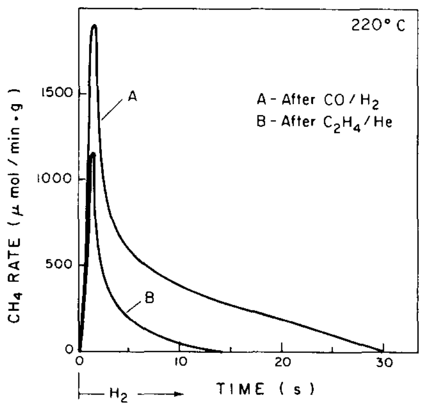

FIG. 8. Comparison of CH_4 response from CO/H_2 and C_2H_4/He, 220°C.

peak) on the surface during ethylene hydrogenation. No higher hydrocarbons were observed upon switching to H_2.

Oxygenation of the surface. An experiment was done in an attempt to find out how much hydrogen is contained in the surface species during reaction with CO/H_2. The catalyst was brought to steady state in 10% CO/H_2, then switched to He for 1 min similar to the experiment in Fig. 3. A switch to 1% O_2/He was made and a trace quantity of H_2O (<2 μmol/g) appeared in the product response suggesting that there is very little hydrogen in the reactive surface species. Also appearing in the product response was CO_2 (82 μmol/g) and CO (7 μmol/g). Switching back to H_2 and heating to 450°C resulted in the evolution of 91 μmol/g of additional C as CH_4. Thus the total carbon (180 μmol/g) removed by O_2 and then H_2 agrees with the amount from Fig. 3 for the hydrogenation experiment (181 μmol/g).

Comparison of the CH_4 response obtained with CO/H_2, CO/He, and C_2H_4/He suggests that the tail portion of the response is associated with chemisorbed CO since C_2H_4/He does not give the same distinctive tail. It is expected that the C_2H_4 would decompose on the surface to yield mostly surface carbon. McCarty and Madix (*22*) studied ethylene interaction with Ni(110) by flash desorption and found that all of the hydrogen is removed as H_2 before 225°C, and the resulting carbon is carbidic in nature. So a peak similar in shape and reactivity to the initial sharp hydrogenation peak after reaction with CO/H_2 is obtained from C deposited in the absence of CO thereby lending support to the contention that the reactive peak is associated with free carbon.

As stated earlier the amount of carbon lost by CO_2 production during the He flush is consistent with the amount lost as reflected in the CH_4 production upon switching to H_2. However, a mass balance on the oxygen is not consistent, that is, the oxygen lost as CO_2 is greater than the amount as determined by the H_2O response upon switching to H_2, particularly for long times in He. Galuszka *et al.* (*15*) have observed the reaction of oxygen, possibly from the support with C*, to give a second high-temperature peak of CO in TPD. Also, although the level of oxygen impurities in the He is low (too low to account for the observed rate of CO_2 production), for long periods of He flush such as 15–30 min, this trace oxygen could have a significant cumulative effect. However, the exact source of the oxygen is at this point unknown.

The O_2/He experiment resulted in the evolution of a trace amount of H_2O. Although the carbonaceous surface species were not completely titrated by the O_2, this experiment suggests that there is not a large portion of CH_x^* groups on the surface during steady state. This is in contrast to results obtained on a Fe/Al_2O_3 catalyst where considerable H_2O is observed upon switching to O_2 (*10a*). However, in the present work, since not all of the surface carbon species were oxygenated the results are limited quantitatively.

The C_2H_4/H_2 experiment supports this contention and suggests that the catalyst is not capable of retaining a large amount of CH_x^* groups in the presence of 90% gas phase H_2 due to the high reactivity of such groups. Certainly the complete conversion of ethylene by the same size sample as the methanation experiments attests to the high hydrogenation activity of Ni. However, the surface conditions, particularly the surface concentration of H*, are certainly different in the two experiments, but these results suggest that the surface is not mostly CH_x^* groups supporting the other results which indicate that there is a substantial amount of relatively unreactive chemisorbed CO.

CONCLUSIONS

The experimental results can be explained in terms of the following simplified mechanism:

$$H_2(g) + 2^* \rightleftarrows 2H^* \qquad (1)$$

$$CO(g) + * \rightleftarrows CO^* \tag{2}$$

$$CO^* + * \rightarrow C^* + O^* \tag{3}$$

$$C^* + H^* \rightarrow CH^* + * \tag{4}$$

$$CH^* + H^* \rightarrow CH_2^* + * \tag{5}$$

$$CH_2^* + H^* \rightarrow CH_3^* + * \tag{6}$$

$$CH_3^* + H^* \rightarrow CH_4 + 2^* \tag{7}$$

$$O^* + 2H^* \rightleftarrows H_2O + 3^* \tag{8}$$

$$CO^* + O^* \rightleftarrows CO_2 + 2^* \tag{9}$$

Various studies have attempted to identify the slow step in this reaction scheme, whether it be the scission of the CO bond (*11, 23, 24*), the hydrogenation of carbonaceous species (*7, 13, 14*), or a balance between the two steps (*9, 25*).

In summary, a number of important insights have been gained concerning the nature of the working methanation surface. It is evident that the surface is very much deficient in hydrogen during reaction because a very large peak of methane is observed upon switching the steady-state reaction to H_2. Also considerable H_2O is obtained indicating the presence of a substantial quantity of chemisorbed CO.

The shape of the CH_4 response curve upon switching the steady-state reaction to H_2 suggests surface heterogeneity since the response consists of a sharp, reactive peak followed by a long tail. The transient experiments involving CO/He and C_2H_4/He indicate that the tailing effect is caused by a kinetic process involving chemisorbed CO, but the exact nature of this process and the heterogeneity involved is still speculative. Also it appears from the other results that there is very little CH_x^* present during reaction so that the surface is largely covered by chemisorbed CO and reactive surface carbon.

Both C* and CO* cover important parts of the surface, and it appears that the rates of both CO dissociation and carbon hydrogenation are important in determining the global rate. There is no unequivocal rate-determining step.

REFERENCES

1. Sabatier, P., and Senderens, C. R., *C.R. Acad. Sci., Paris* **134,** 514 (1902).
2. Ponec, V., *Catal. Rev.-Sci. Eng.* **18** (1), 151 (1978).
3. Bell, A. T., *Catal. Rev.-Sci. Eng.* **23** (1), 203 (1981).
4. Wentrcek, P. R., Wood, B. J., and Wise, H., *J. Catal.* **43,** 363 (1976).
5. McCarty, J. G., and Wise, H., *J. Catal.* **57,** 406 (1979).
6. Araki, M., and Ponec, V., *J. Catal.* **44,** 439 (1976).
7. Biloen, P., Helle, J. N., and Sachtler, W. M. H., *J. Catal.* **58,** 95 (1979).
8. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53,** 295 (1978).
9. Goodman, D. W., Kelley, R. D., Madey, T. E., and White, J. M., *J. Catal.* **64,** 479 (1980).
10. (a) Bianchi, D., Borcar, S., Teulé-Gay, F., and Bennett, C. O., *J. Catal.* **82,** 442 (1983); (b) Matsumoto, H., and Bennett, C. O., **53,** 331 (1978); (c) Reymond, J. P., Mériaudeau, P., Pommier, B., Bennett, C. O., **64,** 163 (1980).
11. Van Ho, S., and Harriott, P., *J. Catal.* **64,** 272 (1980).
12. Happel, J., Suzuki, J., Kokayeff, P., and Fthenakis, V., *J. Catal.* **65,** 59 (1980).
13. Happel, J., Cheh, H. Y., Otarod, M., Ozawa, S., Severdia, A. J., Yoshida, T., and Fthenakis, V., *J. Catal.* **75,** 314 (1982).
14. Happel, J., Fthenakis, V., Suzuki, I., Yoshida, T., and Ozawa, S., "Proceedings, 7th International Congress on Catalysis, Tokyo, Japan."
15. Galuszka, J., Chang, J. R., and Amenomiya, Y., "Proceedings, 7th International Congress on Catalysis, Tokyo, Japan."
16. Cant, N. W., and Bell, A. T., *J. Catal.* **73,** 257 (1982).
17. Bartholomew, C. H., and Farrauto, R. J., *J. Catal.* **45,** 41 (1976).
18. Amelse, J. A., Schwartz, L. H., and Butt, J. B., *J. Catal.* **72,** 95 (1981).
19. Underwood, R. P., M.S. thesis, Univ. of Connecticut, Conn., 1982.
20. Ekerdt, J. G., and Bell, A. T., *J. Catal.* **58,** 170 (1979).
21. Mori, T., Masuda, H., Imi, H., Miyamoti, A., Shigeo, B., and Yuichi, M., *J. Phys. Chem.* **86,** 2753 (1982).
22. McCarty, J. B., and Madix, R. J., *J. Catal.* **48,** 422 (1977).
23. Dalla Betta, R. A., and Shelef, M., *J. Catal.* **49,** 383 (1977).
24. Zagli, A. E., Falconer, J. L., and Keenan, C. A., *J. Catal.* **56,** 453 (1979).
25. Gardner, D. C., and Bartholomew, C. H., *Ind. Eng. Chem. Fundam.* **20,** 229 (1981).
26. Vannice, M. A., *J. Catal.* **44,** 152 (1976).