JOURNAL OF CATALYSIS **125,** 35–44 (1990)

Dependence of Temperature-Programmed Methanation on H_2 Pressure

BISHWAJIT SEN AND JOHN L. FALCONER

Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309-0424

Received September 7, 1989; revised April 10, 1990

The effect of H_2 partial pressure (0.1–2 atm) on the temperature-programmed reaction (TPR) of adsorbed CO in flowing H_2/He was studied for Ni catalysts supported on SiO_2, Al_2O_3, and TiO_2. On Ni/SiO_2, as H_2 partial pressure decreased, the methanation rate decreased. The methanation rate of CO adsorbed on Ni/SiO_2 was approximately first order in H_2 pressure below 0.8 atm and zero order between 0.8 to 2 atm. On Ni/TiO_2 and Ni/Al_2O_3 catalysts, two CH_4 peaks form; one is due to hydrogenation of CO that is adsorbed on Ni and the other is due to hydrogenation of a H–CO complex (most likely CH_3O) that is adsorbed on the TiO_2 and Al_2O_3 supports. Formation of CH_4 from CO on Ni has the same dependence on H_2 pressure as that seen on Ni/SiO_2. However, hydrogenation of the H–CO complex is negative order in H_2 partial pressure; the peak temperature of CH_4 decreases with a decrease in the H_2 partial pressure. Apparently, H_2 inhibits hydrogenation of the complex by occupying surface sites that are needed for other species. A possible explanation is that the H–CO complex diffuses to vacant sites on the Ni surface to decompose and be hydrogenated, and at higher H_2 pressures, more of these sites are occupied by hydrogen. © 1990 Academic Press, Inc.

INTRODUCTION

Temperature-programmed reaction (TPR) is able to resolve reactions occurring on specific sites on the catalyst surface and hence can provide greater insight into catalytic mechanisms than can steady-state kinetic measurements (*1*). Consequently, a number of investigators (*2–12*) have used TPR on supported metal catalysts to study the kinetics of methanation. In these experiments, TPR was usually carried out by adsorbing CO at room temperature and then heating the catalyst in H_2 at atmospheric pressure while detecting the CH_4 product as a function of temperature. This approach has proven successful for a number of metals on a variety of supports because CO adsorbs more strongly than H_2, and the methanation rate is faster than the rate of CO desorption. Since CH_4 does not readily adsorb on the metal or the support, CH_4 curves obtained from TPR are relatively narrow for most catalysts studied, and thus the CH_4 peak temperature is a good measure of the specific activity of the catalyst. For most TPR studies of methanation, the catalyst surface was initially saturated with CO, although a few studies used interrupted reaction or CO_2 adsorption to vary the initial coverage and study the dependence of methanation on CO coverage (*7, 13, 14*). The dependence of methanation rate on H_2 partial pressure during TPR has been less studied, however, and is the subject of the present study.

The effect of H_2 partial pressure on TPR of adsorbed CO is presented for Ni catalysts dispersed on three supports: SiO_2, Al_2O_3, and TiO_2. The Ni/Al_2O_3 and Ni/TiO_2 catalysts have approximately the same metal loading, 5%, as one of the Ni/SiO_2 catalyst studied. However, a 9.5% Ni/SiO_2 was also included in the study to rule out differences that might result from changing the metal loading. On both Ni/SiO_2 catalysts, a single, well-defined CH_4

0021-9517/90 $3.00

peak is observed during TPR and the peak temperature increases with a decrease in H_2 pressure.

On Ni/TiO_2 and Ni/Al_2O_3, two distinct CH_4 peaks are observed because of a reactive spillover process (*15, 16*). As shown by TPR and TPD studies employing isotopes (*15–18*), these two peaks are due to hydrogenation of CO that is adsorbed on two distinct sites. One site is on Ni metal and the other is on the TiO_2 or Al_2O_3 support. The CO on Ni hydrogenates at a faster rate than the CO on the supports, and thus during steady-state methanation studies at atmospheric pressure and above, hydrogenation of CO on Ni is the route to CH_4 formation. The CO on Ni dissociates before being hydrogenated. However, some CO can also combine with adsorbed H to form H–CO complexes such as CH_3O and HCOO. Our studies show that the H–CO complex, which is stable on TiO_2 and Al_2O_3, can also be hydrogenated to CH_4. Hydrogenation of the H–CO complex probably requires dissociation back to CO and H.

During CO exposure at 300 K, CO adsorbs mostly on the Ni surface; during the subsequent TPR some of the adsorbed CO transfers to the TiO_2 or Al_2O_3 support to form a H–CO complex. Isotope studies (*15*) and isothermal treatments (*16, 19*) have shown that CO first adsorbs on Ni and then transfers to the oxide support. The H–CO complex appears to be a CH_3O species on TiO_2 and Al_2O_3 (*16–18, 20*), although we do not have direct observations of CH_3O on supported Ni catalysts. Infrared studies on Pt/Al_2O_3 catalysts, however, have directly detected a CH_3O species on the surface of Al_2O_3 under similar conditions (*21*). Temperature-programmed desorption studies have shown that H_2 and CO desorb simultaneously from Ni/Al_2O_3 (*17*) and Ni/TiO_2 (*16*) when CO was adsorbed in H_2 flow at 385 K. The locations of the H_2 and CO desorption peaks were quite different from those obtained for CO adsorption in H_2 at 300 K. The H : CO ratios during TPD for both Ni/Al_2O_3 and Ni/TiO_2 were consistent with the presence of a CH_3O species. Studies with catalyst mixtures (*22*) indicated that the H–CO complex was on the support.

Spillover to form a H–CO complex does not occur on Ni/SiO_2 catalysts under the conditions used for Al_2O_3 and TiO_2 supported catalysts (*18*), and thus TPR on Ni/SiO_2 enabled us to determine how the hydrogenation of CO on Ni crystallites depends on H_2 pressure. At H_2 partial pressures of 0.8 atm, more than half the CO that adsorbs on Ni/Al_2O_3 at 300 K spills over to form a H–CO complex during TPR, and the effect of H_2 pressure on the spillover process was studied. The spillover process is much slower on Ni/TiO_2, and less than 5% of the CO adsorbed at 300 K spills over during the TPR experiment. Although spillover is slow during TPR, the spillover process is activated (*16*), and thus coverage of the H–CO complex on the TiO_2 support is increased by CO adsorption at 385 K in ambient pressure H_2 flow. Because not much CO spills over onto the TiO_2 support *during* TPR, the effect of H_2 partial pressure on methanation of the H–CO complex could be studied independently of spillover from the Ni to the TiO_2. Thus, by studying these three catalysts, the effects of H_2 pressure were measured for hydrogenation of CO adsorbed on Ni, for hydrogenation of the H–CO complex adsorbed on the support, and for the transfer process between the two sites.

EXPERIMENTAL METHODS

The experimental system and procedures are similar to those described previously (*1, 13, 23*). A 100-mg sample of catalyst was located in a quartz downflow tubular reactor, which was heated by an electric furnace. A small thermocouple, whose tip was in the catalyst sample, measured the catalyst temperature. Temperature-programmed reaction (TPR) was carried out by first adsorbing CO at either 300 K (Ni/SiO_2 and Ni/Al_2O_3) or 385 K (Ni/TiO_2) in 100% H_2 flow at ambient pressure. A pulse valve was used to inject CO into the H_2 carrier gas. To obtain TPR spectra, the catalyst was heated at 1 K/s in either a pure H_2 stream or a H_2/He mixture to 775 K for Ni/SiO_2 and Ni/Al_2O_3, and to 725 K for Ni/TiO_2. The effluent from the reactor was continuously analyzed immediately downstream with a quadrupole mass spectrometer. A computer system, which allowed multiple mass peaks to be detected simultaneously, recorded the mass signals and the thermocouple voltage as a function of time. The mass signals for CH_4(15), CO(28), CO_2(44), and H_2O(18) were monitored. For the Ni/Al_2O_3 catalyst, the mass signal at 31 was also recorded to monitor methanol formation. However, no detectable signal was observed. The dominant product during temperature-programmed hydrogenation of adsorbed CO is CH_4, and thus the data presented show the rate of CH_4 formation as a function of temperature. For the initial TPR experiments, the Ni/SiO_2 and Ni/Al_2O_3 catalysts were pretreated in H_2 for 2 h at 775 K. The Ni/TiO_2 was pretreated for 1 h at 725 K. Before each subsequent TPR, the catalysts were held in H_2 for 15–30 min at 775 (Ni/SiO_2, Ni/Al_2O_3) or 725 K (Ni/TiO_2). The catalysts were then cooled in H_2 from the final reduction temperature in preparation for the next TPR.

Carbon monoxide was adsorbed on each catalyst by injecting 0.5-cm^3 pulses of 10% CO/He into ambient pressure H_2. Pulses were used instead of continuous CO flow in order to minimize formation of nickel carbonyl. A 0.5-cm^3 pulse was injected, upstream of the catalyst, every 30 s. For Ni/Al_2O_3 and Ni/SiO_2, our previous studies (*15, 18*) have shown that the Ni is saturated with CO quickly at 300 K. The first few pulses were completely adsorbed and most of subsequent pulses passed through the catalyst bed. Thus, more than sufficient CO exposure was used to obtain saturation coverages for Ni/SiO_2 (20 min exposure) and Ni/Al_2O_3 (11 min exposure). The activated process to form a H–CO complex on Ni/Al_2O_3 is slow and temperatures higher than 300 K are required to obtain significant H–CO coverages.

For Ni/TiO_2, the 0.5-cm^3 pulses were injected every 30 s for longer times (60 min) and the catalyst was held at 385 K during adsorption. In this procedure, the Ni surface was quickly saturated and most of the CO in subsequent CO pulses passed through without adsorbing. However, as shown previously (*16*), CO on Ni can transfer to the TiO_2 to form a H–CO complex. As this transfer occurred, the subsequent pulses saturated the Ni. Thus, the TiO_2 surface was slowly occupied by the H–CO complex. After CO adsorption, the catalyst was cooled to 300 K.

After CO adsorption, the carrier gas was switched from ambient pressure H_2 to a H_2/He mixture. Separate streams of pure He and H_2 gases were controlled by separate Tylan mass flow controllers and the gases were mixed upstream of the reactor. The total pressure was monitored downstream of the reactor and controlled by a back pressure regulator. For all experiments the total flow rate was above 100 standard cm^3/min, and thus thermocouple lag or CH_4 readsorption are not expected to influence the peak temperatures (*23*). The percentage H_2 was varied from 11 to 100%. Even at the lowest H_2 flow rate (11 standard cm^3/min on 9.5% Ni/SiO_2), the molar rate of H_2 flow over the catalyst surface was more than 100 times the maximum rate of CH_4 formation during TPR. Thus the H_2 partial pressure changed by approximately 5% (three H_2 molecules are required for each CH_4 formed) from the inlet to the outlet of the reactor, even at the lowest H_2 flow rate. Because methanation rates on the Ni/TiO_2 and Ni/Al_2O_3 catalysts were higher than those on the Ni/SiO_2 catalysts, the lowest H_2 flow rate used for Ni/Al_2O_3 and Ni/TiO_2 was 37 standard cm^3/min. Thus, an excess of H_2 was present in all TPR experiments, and the H_2 partial pressure was assumed constant during a TPR experiment.

The catalysts, (9.5% Ni/SiO_2, 5% Ni/SiO_2, 5% Ni/TiO_2, and 5.5% Ni/Al_2O_3), were prepared by impregnation to incipient wetness with an aqueous solution of nickel

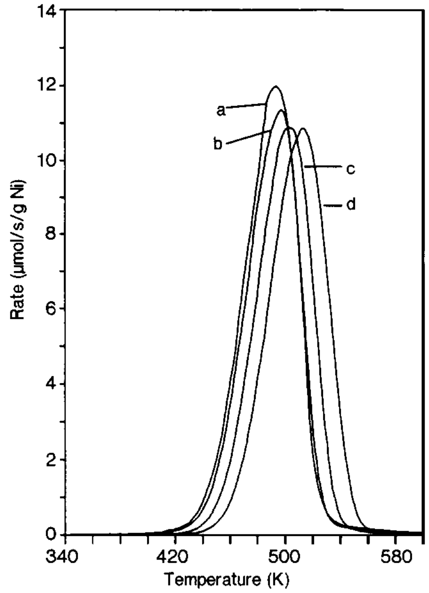

FIG. 1. Methane spectra for temperature-programmed reaction of CO adsorbed on a 5% Ni/SiO_2 catalyst. Carbon monoxide (40 pulses) was adsorbed at 300 K in 100% H_2 flow at ambient pressure, and the catalyst was heated in a H_2/He mixture. Total pressure is 0.82 atm. Partial pressure of H_2 (atm): (a) 0.82, (b) 0.64, (c) 0.34, (d) 0.14.

nitrate. After being dried in a vacuum oven, the catalysts were directly reduced in H_2. The complete procedure is described elsewhere (*8, 13, 23*). The final reduction temperature was 775 K for Ni/SiO_2 and Ni/Al_2O_3, and 725 K for Ni/TiO_2. Weight loadings were measured by atomic absorption.

RESULTS

Nickel/Silica Catalysts

As has been reported previously (*3, 7*) in pure H_2 flow near atmospheric pressure, adsorbed CO is hydrogenated to CH_4 on Ni/SiO_2 in a single narrow peak. The CH_4 peak temperature is relatively insensitive to initial CO coverage (*7*). In this study we examined the effect of varying the H_2 partial pressure on peak temperature, peak shape, and amount of CH_4 product on 5% Ni/SiO_2 and 9.5% Ni/SiO_2. As shown in Fig. 1 for the 5% Ni/SiO_2 catalyst, a monotonic increase in the CH_4 peak temperature was observed with a decrease in the H_2 partial pressure from 0.82 to 0.14 atm. For a H_2 partial pressure of 0.14 atm, the peak temperature was 515 K, an increase of 20 K over that obtained with pure H_2 (Table 1).

The results obtained on 9.5% Ni/SiO_2 are reported in Table 1. The CH_4 peak temperature was almost invariant at 485 ± 1 K as H_2 partial pressure decreased from 2 to 0.56 atm. The methane peak temperature increased by 11 K as H_2 pressure decreased from 0.56 to 0.09 atom. The increase in methane peak temperature signifies a decrease in methanation rate with a decrease in H_2 pressure.

TABLE 1

Variation of Methane Peak Temperatures with Hydrogen Pressure

Catalyst	H_2 pressure (atm)	Peak temperature (K)
5% Ni/SiO_2	0.82	495
	0.64	498
	0.34	504
	0.22	509
	0.14	515
9.5% Ni/SiO_2	2.00	485
	1.60	484
	1.10	487
	0.56	484
	0.40	487
	0.20	492
	0.09	496
5% Ni/TiO_2	0.82	460,525
	0.64	467,521
	0.52	470,514
	0.45	470,508
	0.34	485
	0.22	497
5.5% Ni/Al_2O_3	2.00	440,519
	1.75	440,510
	0.81	443,496
	0.71	443,495
	0.50	448,493
	0.34	456,487
	0.21	480

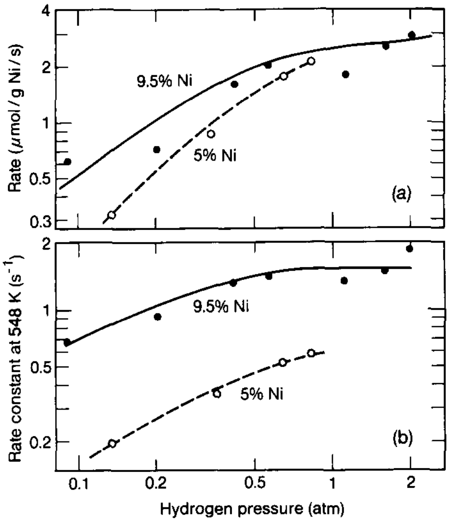

FIG. 2. (a) Methanation rate at 450 K, measured from the amplitude of the TPR curves as a function of H_2 pressure, for Ni/SiO_2 catalysts. The CO coverage is greater than 90% of saturation at this temperature. (b) Methanation rate constant at 548 K, as estimated from peak temperatures and peak halfwidths, for Ni/SiO_2 catalysts. In both (a) and (b), the open circles are 5% Ni/SiO_2 and the solid circles 9.5% Ni/SiO_2.

For the two Ni/SiO_2 catalysts, the CH_4 peak halfwidths (40 ± 2 K for 9.5% Ni/SiO_2, 46 ± 1 K for 5% Ni/SiO_2) were independent of H_2 pressure. The amount of CH_4 produced (524 ± 17 μmol/g Ni for 5% Ni/SiO_2 and 426 ± 41 μmol/g Ni for 9.5% Ni/SiO_2) was also independent of the H_2 partial pressure; this indicates that the rate of methanation was faster than the rate of CO desorption at the H_2 pressures studied. The amount of unreacted CO desorbing during TPR for the 9.5% Ni/SiO_2 catalyst was 124 ± 9 μmol/g Ni.

The apparent order of the methanation reaction in H_2 was estimated from log–log plots of the specific activity versus H_2 pressure (Fig. 2). Two methods were used to estimate the specific activities. The amplitudes of the initial rises of the CH_4 curves correspond to rates of methanation. These rates were measured at 450 K so that the CO coverage was above 90% for each measurement. Thus this comparison was made at essentially the same coverage of CO for each partial pressure of H_2. The high CO coverage is representative of methanation under steady-state conditions; CO has been reported to be the most abundant species on Ni (*24*) and 85–95% of the surface of Ni was concluded to be covered by CO during methanation (*25*). Since CO is more strongly adsorbed than H_2 (*26*), the high coverage of CO corresponds to approximately the same fraction of sites available for H_2 adsorption.

Figure 2a shows the log–log plots for rates measured from the TPR curves at a temperature of 450 K. Two regimes can clearly be distinguished. At H_2 partial pressures greater than 0.8 atm, the formation of CH_4 does not depend on H_2 pressure; below H_2 pressures of 0.8 atm, the formation of CH_4 is approximately first order in H_2 partial pressure (1 ± 0.1 for 5% Ni/SiO_2; 0.7 ± 0.2 for 9.5% Ni/SiO_2).

For the second method of analyzing the data for Ni/SiO_2, rate constants were estimated at 548 K, since this is a common temperature for steady-state measurements of methanation. Activation energies were estimated from the peak temperatures and the halfwidths (full width at half height) of each CH_4 curve (*27*). The three-quarter widths (full width at three-quarter height) and the peak temperatures were also used to estimate activation energies (*27*), and the two activation energies agreed for each CH_4 curve. Preexponential factors were estimated from the Redhead equation. These values of activation energies and preexponential factors were then used to estimate rate constants at 548 K for each H_2 partial pressure. Using rate constants yielded lower partial pressure dependencies for H_2 (0.6 ± 0.1 for 5% Ni/SiO_2, 0.5 ± 0.1 for 9.5% Ni/SiO_2) than obtained from the direct measurements of rates at high CO coverages.

Nickel/Titania Catalyst

As has been reported (*8*, *13*, *28*), when CO is adsorbed at 300 K on Ni/TiO_2 a narrow CH_4 peak is seen during TPR and essentially all the adsorbed CO is hydrogenated to CH_4. This peak at 460 K is at a lower temperature than is the CH_4 peak on Ni/SiO_2, and this observation is consistent with steady-state experiments, which report that Ni/TiO_2 is more active than Ni/SiO_2 (*29*). A peak is also seen at 525 K, but its amplitude is less than 10% of the amplitude of the CH_4 peak at 460 K. The peak at 525 K is due to hydrogenation of a H–CO complex that forms on the TiO_2 support by spillover from the Ni surface (*16*). The spillover process is slow at room temperature and does not occur to a large extent during TPR. However, the spillover process is activated, and a significant concentration of H–CO complex was obtained on the TiO_2 surface by exposure to CO pulses in H_2 flow for 1 h at 385 K. When a TPD experiment was carried out following CO adsorption in H_2 at 385 K, H_2 and CO desorbed simultaneously and the amount of desorption increased when the adsorption time increased at 385 K (*16*). Since the amplitude of the CH_4 peak that formed at 525 K during TPR also increased with adsorption time, this TPR peak was concluded to be the result of hydrogenation of a H–CO complex on the surface. The TPR spectrum obtained following CO adsorption for 1 h at 385 K is shown in Fig. 3a for heating in ambient pressure H_2; two distinct peaks are present. The amount of CH_4 in the peak at 525 K does not correspond to saturation coverage, and even 3 h of CO exposure at 385 K does not saturate the oxide surface (*16*). The Ni surface is saturated under these conditions. One hour of CO exposure is a convenient coverage, however, for comparing the effects of H_2 pressure on the two CH_4 peaks.

Figure 3 also shows the CH_4 spectra obtained during heating in lower H_2 partial pressures. As the H_2 pressure decreased, the peak originally at 460 K shifted to higher temperatures, and the peak originally at 525 K shifted to lower temperatures (Table 1). At sufficiently low partial pressures of H_2 (0.22 atm), the two peaks overlapped and appeared as a single broad peak (Fig. 3f).

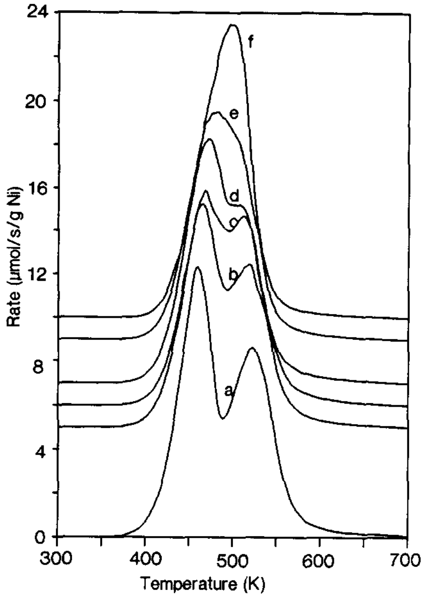

FIG. 3. Methane spectra for temperature-programmed reaction of CO adsorbed on a 5% Ni/TiO_2 catalyst. Carbon monoxide (120 pulses) was adsorbed at 385 K in 100% H_2 flow at ambient pressure, and the catalyst was heated in a H_2/He mixture. Total pressure is 0.82 atm. Partial pressure of H_2 (atm): (a) 0.82, (b) 0.64, (c) 0.52, (d) 0.45, (e) 0.34, (f) 0.22. The curves are displaced vertically for clarity.

The low-temperature peak showed a dependence on H_2 pressure that was similar to that seen for the single CH_4 peak from Ni/SiO_2; the activity decreased as the H_2 pressure decreased. Rates measured from the leading edges of the TPR curves at 420 K (which corresponds to CO coverages above 90%) as a function of H_2 partial pressure indicate that the formation of CH_4 from adsorbed CO is approximately first order (1.0 ± 0.1) in the H_2 pressure in the range 0.22 to 0.82 atm (Fig. 4). When CO was adsorbed at 300 K, so that the peak at 525 K was small, the peak temperature of the low-temperature peak increased by 24 K as the H_2 pressure was decreased from 0.8 to 0.1 atm (*18*).

In contrast to the behavior of the low-temperature peak, the peak temperature of the high-temperature peak decreased as the H_2 pressure decreased (Fig. 3). That is, the activity for CH_4 formation in the high-temperature peak *increased* as the H_2 pressure decreased; thus, the rate of methanation of the H–CO complex is negative order in H_2 pressure. The total amount of CH_4 produced in both peaks (940 ± 70 μmol/g Ni) was relatively independent of the partial pressure of H_2, but the peaks appeared to broaden as the H_2 pressure decreased. For adsorption at 385 K, more than 200 μmol/g of unreacted CO also desorbed (*16*).

Nickel/Alumina Catalyst

As reported previously (*11, 12, 15*), two distinct CH_4 peaks are seen during TPR in ambient pressure H_2 following CO adsorption at 300 K in H_2. Most of the adsorbed CO was hydrogenated to CH_4 (1360 μmol/g Ni) so that the amount of unreacted CO was small (70 μmol/g Ni). For the 5.5% Ni/Al_2O_3, the H_2 partial pressure was varied from 0.21 to 2 atm. At 2 atm H_2 pressure (Fig. 5a), the two CH_4 peaks were well separated, and the majority of the CH_4 was in the high-temperature peak. The CH_4 peak at 440 K is due to hydrogenation of CO adsorbed on Ni and the peak at 519 K is due to hydrogenation of the H–CO complex, which is adsorbed on the Al_2O_3 support. The H–CO complex forms much more rapidly on the Al_2O_3 surface than on the TiO_2 surface, and thus a majority of the CO, which was adsorbed on Ni at 300 K, spills over onto the Al_2O_3 surface during the TPR experiment (*11, 15*). As the H_2 pressure decreased from 2 to 0.21 atm, the relative amplitude of the low-temperature peak increased and that of the high-temperature peak (from the complex) decreased.

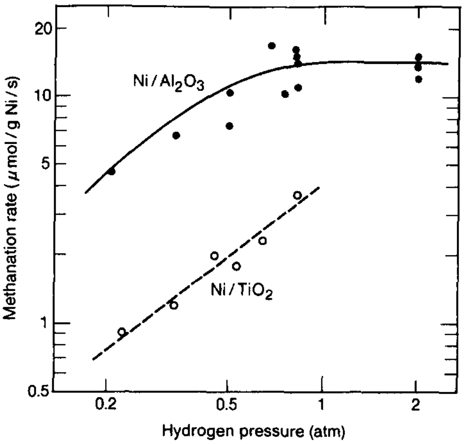

FIG. 4. Methanation rate, measured from the leading edge of the TPR curves, as a function of H_2 pressure. The rates were measured at 420 K for 5% Ni/TiO_2 and at 435 K for 5.5% Ni/Al_2O_3. The CO coverage is greater than 90% of saturation at these temperatures.

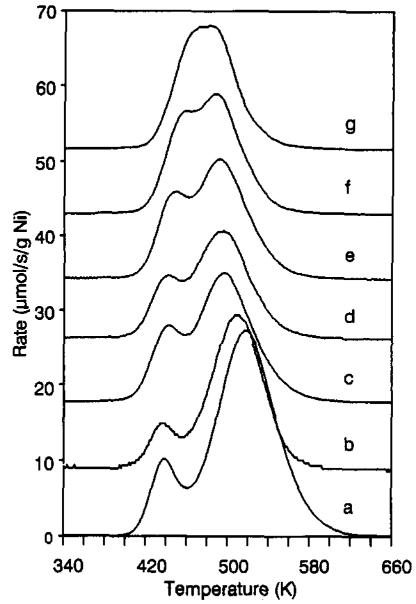

FIG. 5. Methane spectra for temperature-programmed reaction of CO adsorbed on a 5.5% Ni/Al_2O_3 catalyst. Carbon monoxide (22 pulses) was adsorbed at 300 K in 100% H_2 flow at ambient pressure, and the catalyst was heated in a H_2/He mixture. Total pressure (atm) and partial pressure of H_2 (atm): (a) 2, 2; (b) 2, 1.75; (c) 0.8, 0.8; (d) 0.8, 0.71; (e) 0.8, 0.50; (f) 0.8, 0.34; (g) 0.8, 0.21. The curves are displaced vertically for clarity.

The hydrogenation activities of the two forms of adsorbed CO each have a dependence on H_2 pressure similar to those observed for Ni/TiO_2; the low-temperature peak shifted to higher temperatures and the high-temperature peak shifted to lower temperatures as the H_2 pressure decreased (Table 1). The peaks coalesced into one broad peak at a H_2 pressure of 0.21 atm (Fig. 5g).

The formation of CH_4 in the low-temperature peak was approximately first order (0.9 ± 0.1) in H_2 partial pressure in the range

0.21 to 0.81 atm (Fig. 4). Rates were obtained from the leading edge of the TPR curves at 435 K, which corresponds to a CO coverage greater than 90%. At H_2 partial pressures greater than 0.81 atm, the rate does not seem to depend appreciably on the partial pressure of H_2. This is similar to the kinetic behavior of the Ni/SiO_2 catalysts.

DISCUSSION

In this study, the effect of H_2 partial pressure on the CH_4 spectra obtained during temperature-programmed hydrogenation of adsorbed CO was examined for Ni catalysts of similar weight loadings but on different supports. Except at the lowest partial pressures of H_2 (0.2 atm), two CH_4 peaks were observed from the Ni/TiO_2 and Ni/Al_2O_3 catalysts, but only one was present on Ni/SiO_2. The low-temperature peaks on Ni/TiO_2 and Ni/Al_2O_3 and the single peak on Ni/SiO_2 have been attributed to hydrogenation of CO adsorbed on Ni metal, and the high-temperature peaks on Ni/TiO_2 and Ni/Al_2O_3 have been attributed to hydrogenation of a H–CO complex, which is adsorbed on the supports (*15–18, 26*). Adsorption at elevated temperatures, isotope studies, and TPD studies have shown that a H–CO complex does not form on the SiO_2 surface under these conditions, and thus a high-temperature CH_4 peak does not form on Ni/SiO_2 (*18*).

Hydrogenation of CO Adsorbed on Ni

On Ni/SiO_2, the methanation rate during TPR is approximately first order in H_2 pressure below 0.8 atm (Fig. 2). The CH_4 formed in the low-temperature peaks on Ni/Al_2O_3 and Ni/TiO_2 exhibits a similar dependence on H_2 partial pressure (Fig. 4). This similarity in kinetic behavior is an additional indication that the low-temperature CH_4 peaks on Ni/Al_2O_3 and Ni/TiO_2 are due to hydrogenation of CO adsorbed on Ni. During steady-state methanation studies the formation of CH_4 is approximately first order in H_2 pressure at atmospheric pressure, and a weaker dependence on H_2 pressures is observed at pressures greater than 1 atm (*26*). Our results are in good agreement with the steady-state studies (*26*).

Since the methanation rate exhibits the same dependence on H_2 pressure during TPR and steady-state experiments, the kinetics of CH_4 formation appear to be similar for both conditions. The first-order dependence on H_2 pressure below 0.8 atm indicates that under reaction conditions the surface concentration of CO(ad) is much greater than H(ad). At H_2 pressures greater than 0.8 atm, H_2 is able to compete more effectively with CO for surface sites.

Hydrogenation of the H–CO Complex

The high-temperature CH_4 peak observed on Ni/Al_2O_3 and Ni/TiO_2 during TPR has been attributed to the hydrogenation of a support-bound H–CO complex as described previously (*16–18*). The formation of CH_4 from the H–CO complex exhibits a negative order dependence on H_2 partial pressure; i.e., the rate of the H–CO complex hydrogenation decreases with an increase in H_2 partial pressure. A possible explanation for the negative order in H_2 pressure is that the H–CO complex must transfer back to Ni to decompose and be hydrogenated, and H adsorbed on Ni inhibits this reverse spillover. The inhibiting influence of gas-phase H_2 on the transfer from the support to Ni metal has been demonstrated experimentally (*15, 19*). As the H_2 partial pressure is reduced, the H surface coverage on Ni is lowered, and the H–CO complex can transfer to Ni at a faster rate. Similarly, Palazov *et al.* (*30*) observed with IR that CO (present as a CH_3O species) moved from Al_2O_3 to Pd when H_2 was removed from the gas phase.

Thus, during TPR, H and CO coverages on Ni decrease as the temperature is raised and vacant sites are created on the Ni. The H–CO complex transfers to the Ni and decomposes, and the products are then hydrogenated. However, our TPR studies cannot rule out the possibility that hydrogenation occurs directly on the support, and adsorbed H blocks reaction sites on the support.

Hydrogen availability does not limit the rate of hydrogenation for the H_2 partial pressures used in this study, and the amount of CH_4 is the same for all pressures studied. However, if no H_2 is present in the gas phase (TPD carried out in He), not much CH_4 forms and the small amount that forms on Ni/Al_2O_3 has a higher peak temperature than that seen during TPR (*17, 18*). Although some H is present as a result of decomposition of the H–CO complex, the H surface coverage during TPD is not sufficient to produce CH_4 at a significant rate. Thus, at H_2 pressures lower than those used for our TPR studies (i.e., less than 0.2 atm), the rate of hydrogenation of the complex may be positive order in H_2.

On Ni/TiO_2, the simultaneous desorption of H_2 and CO during TPD occurs in a peak at approximately 500 K (*16*), which is close to the CH_4 peak temperature at the lowest H_2 pressure used during TPR. In atmospheric pressure H_2, the CH_4 peak temperature is 25 K higher, and the amount of CO desorbing at 500 K is not significant. This result also indicates that the reverse spillover from the support to the Ni is inhibited by H_2. The fastest rate of reverse spillover is expected in pure He, and the formation of CO and H_2 during TPD may then be limited by revese spillover if decomposition of the H–CO complex is rapid on the Ni.

Since almost no spillover occurs onto TiO_2 during TPR, the rate that the H–CO complex is hydrogenated on Ni/TiO_2 was measured independently of the spillover rate onto the TiO_2. On Ni/Al_2O_3, in contrast, spillover onto Al_2O_3 occurs during TPR. For TPR at low H_2 pressures, CH_4 forms from both sites in approximately equal amounts, but for TPR at 2 atm H_2 pressure, more than 80% of the CH_4 is from the high-temperature peak. Thus, the rate of spillover from Ni to Al_2O_3 increases as the H_2 pressure increases. Whether the rate of transfer from Ni to Al_2O_3 or the rate of formation of the complex changes with H_2 pressure cannot be determined.

This study shows that varying the reactant pressure in TPR experiments provides additional information about surface catalytic processes. For example, the two CH_4 peaks on Ni/Al_2O_3 catalysts can be more clearly separated in TPR above atmospheric pressure, and such studies at higher pressures might separate multiple peaks that overlap on other surfaces or for other reactions that exhibit multiple reaction sites.

CONCLUSIONS

During temperature-programmed reaction (CO hydrogenation), the rate of methanation of CO adsorbed on Ni metal supported on SiO_2, TiO_2, and Al_2O_3 is approximately first order in H_2 pressure in the range 0.1–0.8 atm and is zero order in H_2 at 0.8–2 atm. On Ni/TiO_2 and Ni/Al_2O_3, a H–CO complex (most likely CH_3O) forms on the support by spillover from Ni, and this complex is hydrogenated to CH_4 at a slower rate than CO on Ni during TPR. The hydrogenation rate of the complex is inhibited by H_2, perhaps because reverse spillover of the complex limits its hydrogenation rate. Hydrogen could inhibit this reverse spillover by occupying sites on the catalyst surface.

ACKNOWLEDGMENTS

We gratefully acknowledge support by the National Science Foundation, Grant CBT 86-16494. We appreciate Willy Grothe's assistance in making modifications to the TPR system.

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