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# Spillover Sites on a 19% $Ni/Al_2O_3$ Catalyst

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Two distinct methanation sites are clearly identified on a 19% $Ni/Al_2O_3$ catalyst by temperature-programmed reaction (TPR) employing isotope labeling. The two sites, which are present after reduction at 975 K, are due to CO adsorption on Ni crystallites and CO and H spillover onto the $Al_2O_3$ support. The concentration of sites on the support is 250 $\mu$mol/g $Al_2O_3$ ($5 \times 10^{13}$ molecules/$cm^2$), which is the same value measured for a 5.1% $Ni/Al_2O_3$ catalyst and for a 1.0% $Ru/Al_2O_3$ catalyst. Temperature-programmed desorption suggests that the CO and H on the $Al_2O_3$ are in the form of a H–CO complex. The formation of this complex is an activated process, which is related to the activated adsorption of $H_2$. The $H_2$ that adsorbs between 300 and 385 K is responsible for this spillover process onto the $Al_2O_3$. Isotope labeling and TPR were used to verify that a H–CO complex does not form on $Ni/SiO_2$ catalysts. Carbon monoxide adsorption on $Ni/SiO_2$ was not activated and only one methanation site was seen.

## INTRODUCTION

On $Ni/Al_2O_3$ catalysts, two sites for CO methanation have been observed (*1–3*) by the presence of two $CH_4$ peaks during temperature-programmed reaction (TPR). Glugla *et al.* (*3, 4*) attributed the two distinct peaks on a 5.1% $Ni/Al_2O_3$ catalyst to CO adsorbed on Ni metal and CO adsorbed, as a H–CO complex, on the $Al_2O_3$ support. Carbon monoxide was found to adsorb first on the Ni and then spillover onto the $Al_2O_3$ in an activated process that required $H_2$. That is, both CO and H spilled over onto the $Al_2O_3$. The resulting complex had the stoichiometry of a $CH_3O$ species. Recent studies on a physical mixture of $Al_2O_3$ and a 19% $Ni/Al_2O_3$ catalyst provided direct evidence that the H–CO complex was on the $Al_2O_3$ surface (*5*).

Though the methanation activities of the two sites on 5.1% $Ni/Al_2O_3$ were quite different (*3*), on a 19% $Ni/Al_2O_3$ catalyst the two $CH_4$ peaks overlapped significantly, and their presence was only detected by observing the difference in TPR spectra for adsorption in He and adsorption in $H_2$ (*6*). Indeed, in an earlier study on a 15% $Ni/Al_2O_3$ catalyst (*2*), only one broad $CH_4$ peak appeared to be present.

Some of the objectives of the present study were to show directly with isotope labeling that two distinct $CH_4$ peaks are present on a high Ni loading catalyst, to determine how the spillover rate depends on Ni loading, and to determine if the same type of H–CO complex forms as seen on 5.1% $Ni/Al_2O_3$. A 19% $Ni/Al_2O_3$ catalyst is more reduced than a 5.1% $Ni/Al_2O_3$ catalyst, and thus the role of unreduced Ni can be clarified. Moreover, reduction was carried out at 975 K to obtain almost complete reduction. Previous studies have attributed one of the $CH_4$ peaks in TPR to CO adsorbed on isolated Ni (*1*) or on nickel aluminate (*7*). If the complexes are on the $Al_2O_3$, then the concentration of H–CO complexes at saturation should be proportional to the $Al_2O_3$ surface area and not the Ni surface area; a comparison of the 19% $Ni/Al_2O_3$ catalyst to the 5.1% $Ni/Al_2O_3$ catalyst should allow this to be determined. In addition, the role of $H_2$ in the spillover process was studied on the 19% $Ni/Al_2O_3$ catalyst.

The two $CH_4$ peaks on 19% $Ni/Al_2O_3$ overlap because their activities are similar, and thus the TPR spectra for 19% $Ni/Al_2O_3$ were similar to those seen for $Ni/SiO_2$ catalysts. Therefore, we examined two $Ni/SiO_2$

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catalysts (that differ in metal loading) by TPR employing isotope labeling to determine if the same spillover process occurred on $Ni/SiO_2$, but was not detected because of overlapping peaks. In addition to TPR with isotope labeling, temperature-programmed desorption (TPD) of coadsorbed CO and $H_2$ was also performed on the $Ni/SiO_2$ catalysts to determine if a H–CO complex was present. The results presented here show that two sites are present on the 19% $Ni/Al_2O_3$ catalyst but only one site is present on $Ni/SiO_2$ catalysts. The CO spillover process is shown to occur onto $Al_2O_3$ but not onto $SiO_2$ surfaces.

## EXPERIMENTAL

TPR of adsorbed CO in flowing $H_2$ was used to study a 19% $Ni/Al_2O_3$ catalyst and two $Ni/SiO_2$ catalysts. Carbon isotopes of CO allowed individual reaction sites to be characterized. TPD was used in which CO and $H_2$ were coadsorbed on the catalyst at elevated temperatures.

### *Temperature-Programmed Reaction*

A detailed description of the experimental apparatus is given elsewhere (*8*, *9*). The passivated catalyst (100 mg) was reduced in pure $H_2$ (98 standard $cm^3$/min) for 2 h at 775 K prior to the initial TPR. For subsequent experiments the catalyst was held in flowing $H_2$ at 775 K for either 15 min or 1 h. It was then cooled in $H_2$ and held at either 300 or 385 K while 10% CO/He was pulsed over the catalyst. A uniform pulsing procedure (one 0.5-$cm^3$ pulse every 30 s) was followed for all experiments. The number of pulses was varied to examine the effect of initial CO surface coverage on the $CH_4$ peak temperature and to confirm that the catalyst was saturated. Following CO adsorption, the catalyst was subjected to a linear temperature ramp (1 K/s) under flowing $H_2$ to 775 K while continuously monitoring mass signals at 15 ($CH_4$), 18, 28, and 44 with the mass spectrometer. The mass 28 signal was corrected for $CO_2$ cracking. For a few experiments, the 19% $Ni/Al_2O_3$ catalyst was also reduced for 2 h at 975 K to ensure complete reduction of the Ni. However, unless indicated otherwise, data to be reported were obtained on catalysts reduced only at 775 K.

### *Temperature-Programmed Desorption*

For TPD, the reduction procedure was the same as that for TPR. After reduction in $H_2$ at 775 K, however, the carrier gas was switched to He and the catalyst held in He for 5 min before cooling. The catalyst was then cooled in He to a given temperature, the carrier gas was switched back to $H_2$, and cooling was continued in $H_2$. The adsorbate gas, 10% CO/He, was then pulsed into the carrier gas (either $H_2$ or He flow) for 1 h (1 pulse/30 s) at 385 or 300 K. The catalyst was then cooled to 300 K (if at 385 K), the carrier gas was switched to He (if not already in He), and the catalyst was held in He at 300 K for 10–30 min. The TPD experiment was carried out for the coadsorbed CO and $H_2$ by heating the catalyst to 775 K in He at 1 K/s. Desorption and reaction products for mass signals at 2, 15, 18, 28, and 44 were monitored. Note that in all cases, the reactor was rapidly cooled by flowing compressed air over the outside of the reactor.

### *Isotope Labeling with Interrupted TPR*

By adsorbing $^{12}CO$ on one site and $^{13}CO$ on the other, Glugla *et al.* (*3*) separated the two distinct methanation sites during TPR on a 5.1% $Ni/Al_2O_3$ catalyst. A similar procedure was used here for TPR on the 19% $Ni/Al_2O_3$ catalyst. At 385 K, $^{12}CO$ was adsorbed to saturation coverage in $H_2$ flow, and 10 more pulses of $^{12}CO$ were injected at 300 K. Following this, a fraction of the adsorbed $^{12}CO$ was reacted off by heating the catalyst in $H_2$ at 1 K/s. Heating was stopped while $CH_4$ was still forming, and the catalyst was cooled to 300 K in $H_2$. This will be referred to as interrupted TPR. The interruption temperature was varied. At 300 K, 20 pulses (1 pulse/30 s) of $^{13}CO$ were then injected into the He carrier gas in order to adsorb $^{13}CO$ on the sites from which $^{12}CO$ had been removed. A complete TPR was then carried out to 775 K, at a heating rate of 1 K/s, while continuously monitoring the mass signals at 15 ($^{12}CH_4$), 17 ($^{13}CH_4$), 28 ($^{12}CO$), and 29 ($^{13}CO$). Similar procedures, in which the interruption temperature and the number of pulses of $^{13}CO$ were varied, were used for the $Ni/SiO_2$ catalysts.

For a few experiments, isotope exchange was used instead of interrupted TPR to replace $^{12}CO$ by $^{13}CO$. The same adsorption procedure was used for $^{12}CO$, but instead of interrupted reaction to remove $^{12}CO$ from one of the sites, $^{13}CO$ was pulsed over the saturated catalyst at 300 K and the $^{12}CO$ on one of the sites was displaced by $^{13}CO$. The experiments on $Ni/SiO_2$ demonstrate that $^{13}CO$ displaces $^{12}CO$ from Ni at 300 K.

### *Catalyst Preparation*

A 19% $Ni/Al_2O_3$ catalyst was prepared by impregnation of 60- to 80-mesh $Al_2O_3$ (Kaiser A-201) to incipient wetness with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ using procedures described previously (*1*). After being air-dried at 300 K for 24 h, the catalyst was reduced in $H_2$ at 503 K for 2 h and at 775 K for 12 h, and then passivated at 300 K with 2% $O_2$ in He. The A-201 $Al_2O_3$ was specified by the manufacturer to have a BET surface area of 315 $m^2/g$ and impurities of $Na_2O$ (0.35%), FeO (0.02%), and $SiO_2$ (0.02%). Two $Ni/SiO_2$ catalysts (5% and 9.2 wt% Ni) were prepared by the same procedure. The passivated catalysts were treated for an additional 2 h at 775 K ($Ni/SiO_2$, $Ni/Al_2O_3$) or 975 K ($Ni/Al_2O_3$) in the TPR apparatus. The Ni weight loadings were determined by atomic absorption.

## RESULTS

### *Nickel/Alumina Catalyst*

*Temperature-programmed reaction.* The hydrogenation of adsorbed CO on the 19% $Ni/Al_2O_3$ catalyst was studied as a function of adsorption temperature and CO exposure. Since most of the adsorbed CO reacted to form $CH_4$ during heating in $H_2$, only the $CH_4$ and unreacted CO spectra will be discussed. At 300 K in $H_2$ flow, the surface was essentially saturated with CO after 76 pulses; an increase to 272 pulses only increased the amount of $CH_4$ by 15% (Table 1). The amount of unreacted CO also increased by 15%. The amount of $CO_2$ formed was negligible. The $CH_4$ formed in what will be shown to be two overlapping peaks, with a overall peak maximum at 492 K (Fig. 1). For adsorption at 300 K, most of the unreacted CO desorbed before the methanation rate was significant. As shown in Fig. 2, the unreacted CO desorbed in peaks at 368 and 450 K. As exposure increased, the peak at 450 K increased and that at 368 K decreased. This CO desorption is different from that observed on low loading $Ni/Al_2O_3$ (*1*), for which only one CO peak was seen (395 ± 3 K).

More CO adsorbed at 385 than at 300 K

TABLE 1

TPR of CO Adsorbed on 19% $Ni/Al_2O_3$

| Adsorption temperature (K) | Number of pulses | $CH_4$ peak temperature (K) | $CH_4$ amount (μmol/g Ni) | Unreacted CO (μmol/g Ni) |
|---|---|---|---|---|
| 300 | 76 | 492[a] | 1370 | 70 |
| 300 | 272 | 492[a] | 1610 | 90 |
| 385 | 120 | 494 | 2340 | 330 |
| 385 | 240 | 500 | 1990 | 450 |
| 385,300 | 120,120 | 500 | 1980 | 330 |

[a] Low-temperature shoulder seen.

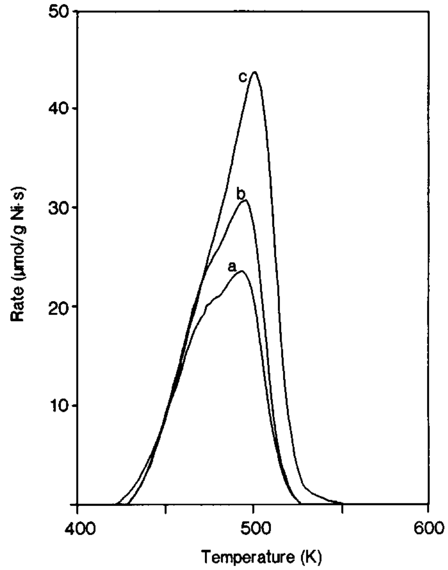

FIG. 1. Methane TPR spectra for CO adsorbed in $H_2$ on 19% $Ni/Al_2O_3$: (a) 76 pulses of CO at 300 K; (b) 272 pulses at 300 K; (c) 240 pulses at 385 K.

(Fig. 1), but after this long exposure (240 pulses at 385 K), the amount of CO adsorbed for subsequent TPR experiments decreased. Apparently some Ni was removed as nickel carbonyl at these conditions (*10*). Subsequently, the amount of $CH_4$ formed was the same (within 1%) for preadsorption of 120 or 240 pulses; the surface is apparently saturated after 120 pulses of CO at 385 K. Twenty percent more $CH_4$ formed for adsorption at 385 than at 300 K, and the overall peak maximum increased by 8 K to 500 K (Table 1). As the adsorption temperature increased from 300 to 385 K, much more unreacted CO desorbed (Fig. 2). For adsorption at 385 K, approximately 16% of the CO desorbed unreacted, but less than 1% of the CO desorbed as $CO_2$.

To investigate whether incomplete reduction of the Ni is responsible for the additional adsorption at 385 K and for the two peaks in TPR, the 19% $Ni/Al_2O_3$ catalyst was reduced for an additional 2 h at 975 K. For CO adsorption at 300 K, two distinct $CH_4$ peaks were still observed during TPR, but the total amount of $CH_4$ produced had decreased significantly. Figure 3a shows the TPR spectra for CO adsorption at 300 K in He instead of $H_2$. The amount of $CH_4$ (340 μmol/g Ni) was less than half the amount of $CH_4$ seen for CO adsorption in He following reduction at 775 K (*5*). Less CO adsorbs in He than in $H_2$ (*1*, *6*), but reduction at 975 K significantly reduced the amount of CO that adsorbs in He. The peak temperature of the low-temperature peak was 462 K and it did not change with reduction temperature. The peak temperature of the higher peak was 536 K for reduction at 975 K. The higher temperature peak was below 500 K for reduction at 775 K.

Much more CO adsorbed at 385 K than at 300 K for the catalyst reduced at 975 K, and two overlapping peaks (Fig. 3b) formed that were similar to those reported for reduction at 775 K. The total amount of $CH_4$ was smaller, however, than for the catalyst reduced only at 775 K.

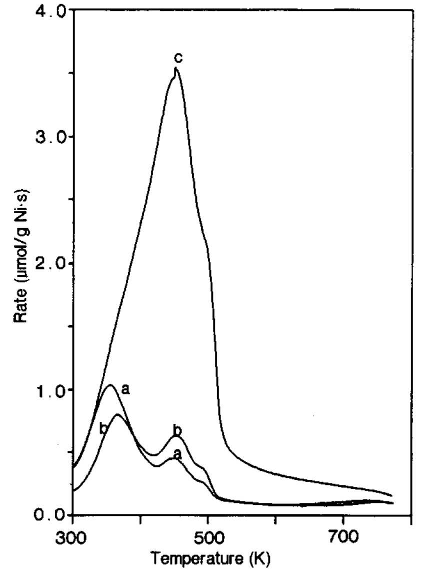

FIG. 2. Unreacted CO observed during TPR for CO adsorbed in $H_2$ on 19% $Ni/Al_2O_3$: (a) 76 pulses of CO at 300 K; (b) 272 pulses at 300 K; (c) 240 pulses at 385 K.

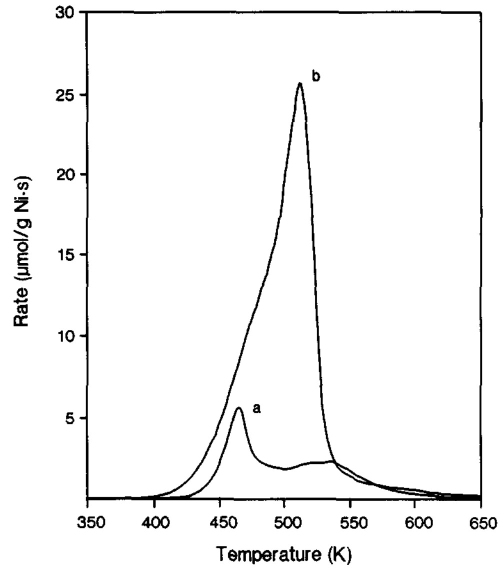

FIG. 3. Methane TPR spectra for CO adsorbed on 19% Ni/$Al_2O_3$ after reduction at 975 K for 2 h: (a) CO adsorbed in He at 300 K; (b) CO adsorbed in $H_2$ at 385 K.

*Interrupted reaction and isotopic labeling.* The $CH_4$ product in Fig. 1 was shown to consist of two distinct $CH_4$ peaks by labeling the site responsible for the high-temperature peak with $^{12}CO$ and that responsible for the low-temperature peak with $^{13}CO$. To accomplish this labeling, $^{12}CO$ was adsorbed at 385 K in $H_2$, and the catalyst was then heated in $H_2$ to remove some $^{12}CO$ as $^{12}CH_4$. Thus, heating was stopped (interrupted TPR) after a fraction of the $^{12}CO$ had reacted. The catalyst was then cooled to 300 K and exposed to $^{13}CO$ to fill the empty sites created by the interrupted TPR. The subsequent TPR (Fig. 4) exhibited two peaks: $^{13}CH_4$ at 470 ± 2 K and $^{12}CH_4$ at 487 ± 4 K. The total amount of methane formed ($^{13}CH_4$ + $^{12}CH_4$) was the same as that seen for TPR following $^{12}CO$ adsorption at 385 K. These experiments were carried out at three interruption temperatures with similar results. Two distinct peaks were obtained in each case. The amounts in the $^{12}CH_4$ and $^{13}CH_4$ peaks depended on interruption temperature because $^{12}CH_4$ was present in both the low- and high-temperature peaks, as is evident from Fig. 4. The mass 17 signal above 500 K in Fig. 4 was due mostly to cracking of the $H_2O$ product. Water readsorbs on $Al_2O_3$ and then desorbs over a wide temperature range starting above 500 K.

As a result of similar experiments on Ni/$SiO_2$ catalysts (described below), a modified form of the isotopic labeling experiment was carried out for the 19% Ni/$Al_2O_3$ catalyst sample that was reduced at 975 K. As before, $^{12}CO$ was adsorbed to saturation at 385 K in $H_2$, and the catalyst was then cooled to 300 K. Instead of carrying out an interrupted TPR, however, the catalyst was then exposed to $^{13}CO$ at 300 K. Much of the $^{12}CO$ that was located on the Ni readily exchanged with $^{13}CO$ at 300 K, so that the resulting TPR yielded two peaks, as shown in Fig. 5. The two $CH_4$ peaks are resolved better than those in Fig.

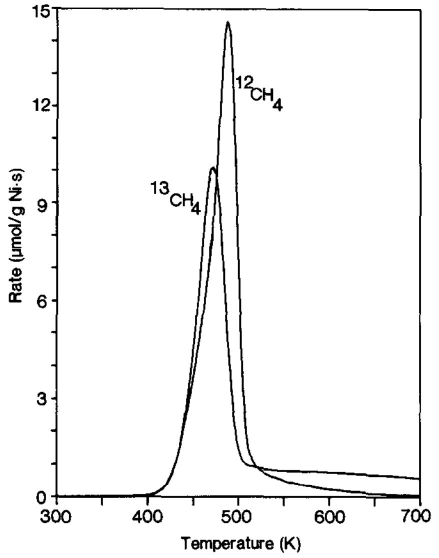

FIG. 4. Methane ($^{12}CH_4$ and $^{13}CH_4$) TPR spectra from 19% Ni/$Al_2O_3$. The $^{12}CO$ was adsorbed in $H_2$ at 385 K and the catalyst was then heated to 485 K to remove some $^{12}CO$. The catalyst was cooled in $H_2$ and $^{13}CO$ was adsorbed at 300 K. Note that the mass 17 signal above 500 K is mostly due to cracking of the $H_2O$ product.

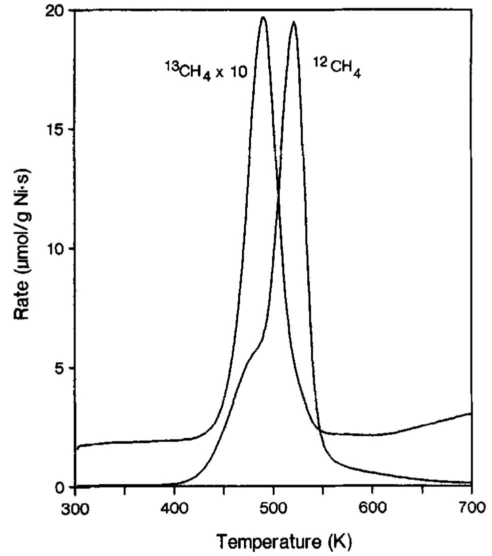

FIG. 5. Methane ($^{12}$CH$_4$ and $^{13}$CH$_4$) TPR spectra from 19% Ni/Al$_2$O$_3$ after reduction at 975 K for 2 h. The $^{12}$CO was adsorbed at 385 K and the catalyst was then exposed to $^{13}$CO at 300 K. The $^{13}$CH$_4$ curve is displaced vertically.

4 because the higher reduction temperature results in a bigger difference in the methanation activities of the two sites. As shown by the shoulder on the $^{12}$CH$_4$ peak, not all the $^{12}$CO on the Ni exchanged at 300 K during the short exposure to $^{13}$CO.

*Temperature-programmed desorption.* Glugla *et al.* (*4*) detected a H–CO complex on a 5.1% Ni/Al$_2$O$_3$ catalyst following CO adsorption in H$_2$ at 385 K. In those experiments, the catalyst was cooled from 775 K in H$_2$ before adsorbing CO. The presence of a similar H–CO complex was detected in the present experiments, and the bonding of the surface hydrogen needed to form the complex was studied by varying the maximum temperature at which the catalyst was exposed to H$_2$ before adsorbing CO. To do this, the catalyst was reduced in H$_2$ at 775 K, the carrier gas switched to He before cooling, and the carrier gas then switched back to H$_2$ at either 548 or 300 K. In one experiment the catalyst was cooled in H$_2$ from 775 K, using the same procedure as Glugla *et al.* (*4*). For each of these experiments, CO was adsorbed in H$_2$ at 385 K.

For CO and H$_2$ coadsorbed at 385 K, large amounts of CO and H$_2$ (Table 2) desorbed together in a narrow, well-defined peak at 500 K. A significant amount of CO$_2$ formed (much more than seen for the 5.1% Ni/Al$_2$O$_3$ catalyst (*4*)) and a small amount of CH$_4$ was also seen. Figure 6 shows the TPD spectra obtained when the catalyst was cooled from 550 K in H$_2$ before CO was adsorbed. The total H/CO ratio is 3.8. Similar results were obtained when the carrier gas flow was switched to H$_2$ at 300 K and CO was then adsorbed at 385 K in H$_2$; the total H/CO ratio in the peak at 500 K was 3.6.

When the catalyst was cooled in H$_2$ from

TABLE 2

TPD for CO and H$_2$ Adsorbed on 19% Ni/Al$_2$O$_3$

| Temperature (K) for H$_2$ switch[a] | Adsorption temperature (K) | Total amount desorbed (μmol/g Ni) | | |
|---|---|---|---|---|
| | | H$_2$ | CO | CO$_2$ |
| 775 | 385 | 2670 | 1360 | 590 |
| 550 | 385 | 2360 | 1240 | 570 |
| 300 | 385 | 2370 | 1305 | 560 |
| 775 | 300 | — | 400 | 370 |
| 385 | 300 | — | 330 | 370 |
| 300 | 300 | — | 260 | 330 |
| Not switched | 300 (He) | — | 190 | 330 |

[a] After reduction in H$_2$, the catalyst was cooled in He to this temperature and flow was then switched back to H$_2$.

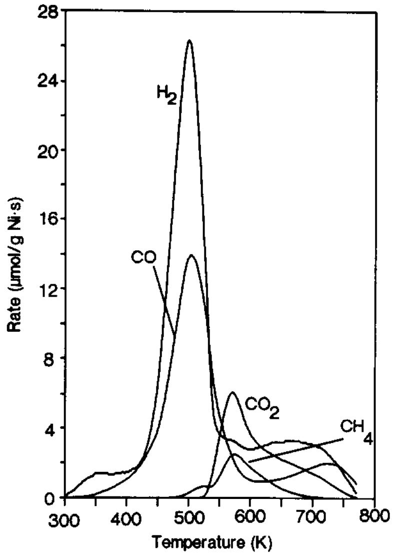

FIG. 6. Temperature-programmed desorption spectra of CO, $H_2$, $CO_2$, and $CH_4$ for CO and $H_2$ coadsorbed on 19% Ni/$Al_2O_3$. Following reduction, the catalyst was cooled in He from 775 to 550 K and in $H_2$ from 550 to 300 K, and the CO was adsorbed in $H_2$ at 385 K.

775 K before CO was adsorbed, an additional $H_2$ desorption peak was seen at 425 K (Fig. 7). This state was not present on a 5.1% Ni/$Al_2O_3$ catalyst (*4*). This additional $H_2$ adsorption state apparently affected CO desorption, which did not begin until 450 K; for cooling from 550 K (Fig. 6), CO desorption began at 350 K. The H/CO ratio for the peaks at 500 K in Fig. 7 could not be measured because of the overlapping $H_2$ peaks. An estimate of 3.4 was obtained from the ratio of peak amplitudes, but this estimate assumes the curve shapes are identical.

Similar TPD results were obtained for the 19% Ni/$Al_2O_3$ catalyst that was reduced at 975 K. The amount of CO that adsorbed in He was less than half of that seen for the catalyst reduced at 775 K, but adsorption at 385 K in $H_2$ dramatically increased the amounts of adsorbed CO and $H_2$. The simultaneous desorption of CO and $H_2$ with H/CO ratios near 3 was also seen, and the peaks were at higher temperatures (521 ± 3 K) than for the catalyst reduced at 775 K.

Temperature-programmed desorption of coadsorbed CO and $H_2$ was also performed, on the 19% Ni/$Al_2O_3$ catalyst reduced at 775 K, for CO adsorbed in the presence of $H_2$ at 300 K for three conditions: (a) cooling in $H_2$ from 775 to 300 K; (b) cooling in $H_2$ from 385 to 300 K; and, (c) exposing the catalyst to $H_2$ only at 300 K. As the temperature at which the catalyst was exposed to $H_2$ increased, the amount of CO that desorbed increased (Table 2). For CO adsorption in He at 300 K, half as much CO desorbed as that seen for CO adsorption at 300 K after cooling in $H_2$ from 775 K (Table 2). Simultaneous CO and $H_2$ desorptions were not observed for CO adsorbed in He. When CO was adsorbed in $H_2$ at 300 K, after cooling in He to 300 K, the desorption spectrum was almost identical to that obtained for CO adsorption in He. Only $H_2$ preadsorbed at 385 K or higher was able to enhance CO adsorption.

### *Nickel/Silica Catalysts*

Similar TPD and TPR experiments were carried out on 5 and 9.2% Ni/$SiO_2$ cata-

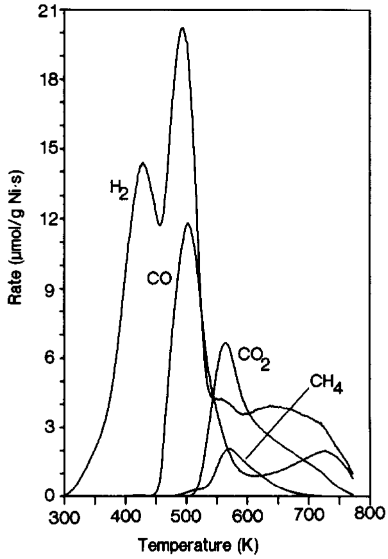

FIG. 7. Temperature-programmed desorption spectra of CO, $H_2$, $CO_2$, and $CH_4$ for CO and $H_2$ coadsorbed on 19% Ni/$Al_2O_3$. The catalyst was cooled in $H_2$ following reduction at 775 K, and the CO was adsorbed in $H_2$ at 385 K.

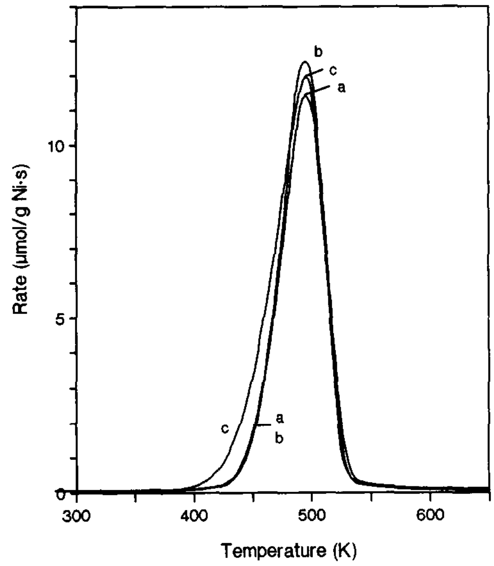

FIG. 8. Methane TPR spectra for CO adsorbed in $H_2$ on 5% Ni/SiO$_2$: (a) 20 pulses of CO at 300 K; (b) 100 pulses of CO at 300 K; (c) 100 pulses of CO at 385 K.

lysts. Data will be presented for the 5% Ni/SiO$_2$ catalyst, but similar results were obtained for the 9.2% Ni/SiO$_2$ catalyst. As shown in Fig. 8, in contrast to the Ni/Al$_2$O$_3$ catalysts, the amount of CH$_4$ that formed during TPR did not increase as CO was adsorbed at a higher temperature. The only difference seen was a slight increase in the CH$_4$ signal amplitude between 400 and 450 K.

Isotopes were used to determine if the TPR spectra in Fig. 8 consisted of two overlapping CH$_4$ peaks. The catalyst was first saturated with $^{12}$CO (40 pulses) in H$_2$ flow at 385 K. Interrupted TPR was then carried out, for interruption temperatures from 393 to 493 K, and $^{13}$CO (7 pulses) was adsorbed in H$_2$ at 300 K. The resulting TPR (shown in Fig. 9 for an interruption temperature of 403 K) was similar. Mostly $^{13}$CH$_4$ formed because $^{12}$CO on Ni readily exchanged with $^{13}$CO in the gas phase. The peak temperatures for $^{12}$CH$_4$ and $^{13}$CH$_4$ were the same; two CH$_4$ peaks were not present.

Temperature-programmed desorption of coadsorbed H$_2$ and CO on both Ni/SiO$_2$ catalysts was also carried out for adsorptions at 300 and 385 K. The amounts of adsorbed CO and H$_2$ did not change with adsorption temperature, and the TPD spectra of each were essentially identical to those obtained for individual adsorptions. The CO and H$_2$ did not desorb in simultaneous peaks, and much more CO than H$_2$ was present on the surface. A large amount of CO$_2$ also desorbed. On the 5% Ni/SiO$_2$ catalyst, 200 µmol of CO/g Ni and 265 µmol of CO$_2$/g Ni desorbed.

## DISCUSSION

Methane formed in a broad peak during TPR of adsorbed CO on the 19% Ni/Al$_2$O$_3$ catalyst, but isotope labeling shows clearly that two distinct peaks are present (Figs. 4 and 5). For lower Ni loadings, the two peaks have sufficiently different activities that they can be distinguished without isotopes (*1–3*), but isotopes verified that the two sites were distinct and also allowed the

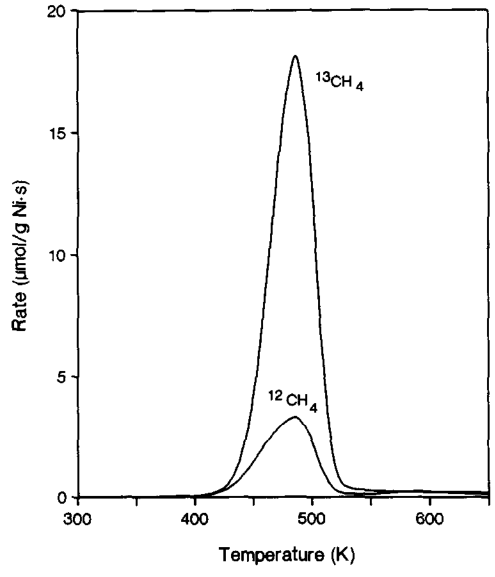

FIG. 9. Methane ($^{12}$CH$_4$ and $^{13}$CH$_4$) spectra from 5% Ni/SiO$_2$. The $^{12}$CO (40 pulses) was adsorbed in H$_2$ flow at 385 K prior to an interrupted TPR to 403 K. After cooling to 300 K, the catalyst was exposed to $^{13}$CO (7 pulses) in H$_2$ at 300 K before a subsequent TPR.

transfer between sites to be studied (*3*). As discussed previously, the two $CH_4$ peaks appear to be due to CO adsorbed on Ni crystallites (the low-temperature peak) and to CO adsorbed on the $Al_2O_3$ support (the high-temperature peak). For a 19% Ni/$Al_2O_3$ catalyst reduced at 975 K, almost all of the Ni is reduced (*11, 12*), but the high-temperature $CH_4$ peak is present, and thus unreduced Ni is not needed for the two $CH_4$ peaks to exist.

On a 5.1% Ni/$Al_2O_3$ catalyst, CO appeared to adsorb only on Ni in He flow at 300 K, and then spillover to the $Al_2O_3$ support during TPR. This transfer required $H_2$ and was activated. At 385 K in $H_2$, all the CO on the Ni could be transferred to the $Al_2O_3$ catalyst reduced at 975 K, almost all of the Ni is reduced (*11, 12*), but the high-temperature $CH_4$ peak is present, and thus unreduced Ni is not needed for the two $CH_4$ peaks to exist.

Similar processes appear to occur on the 19% Ni/$Al_2O_3$ catalyst since both the TPR and the TPD (of coadsorbed CO and $H_2$) are qualitatively similar to those on the 5.1% Ni/$Al_2O_3$ catalyst. However, the relative amounts of each site differ. The CO on the $Al_2O_3$ sites is hydrogenated more rapidly on the 19% Ni/$Al_2O_3$ catalyst, but the methanation activities of CO on Ni sites appear to be similar on the two catalysts.

On the Ni/$SiO_2$ catalysts, isotope studies indicated that two distinct sites for CO adsorption are not present. The $^{12}CH_4$ and $^{13}CH_4$ peaks were similar in shape and had the same peak temperature. Two aspects of these curves are of interest, however. For a wide range of interruption temperatures, the majority of the methane was $^{13}CH_4$, even though the surface was originally covered with $^{12}CO$. Apparently, $^{13}CO$ exchanges with (displaces) $^{12}CO$ on the Ni. A similar exchange was seen on 19% Ni/$Al_2O_3$ for the $^{12}CO$ that was on the Ni, but the $^{12}CO$ that had spilled over onto the $Al_2O_3$ support did not readily exchange. Thus, the TPR spectra in Fig. 5 were obtained by taking advantage of this difference in exchange rates; the $^{12}CO$ on the Ni was exchanged with $^{13}CO$ without affecting the $^{12}CO$ on the $Al_2O_3$ support. This difference in exchange rates is further verification that the CO on Ni/$Al_2O_3$ is adsorbed in two distinct chemical forms, only one of which exchanges readily with the gas phase at 300 K. This also indicates that the low-temperature $CH_4$ peak is from the Ni metal, since CO on Ni of Ni/$SiO_2$ exchanges readily.

The other aspect of interest for the Ni/$SiO_2$ catalysts is that the $^{12}CH_4$ signal had a slightly higher rate than the $^{13}CH_4$ signal at low temperatures. This occurred even though the $^{12}CH_4$ peak was smaller than the $^{13}CH_4$ peak (Fig. 9). The additional $^{12}CH_4$ that formed at low temperatures is most likely due to small amounts of active carbon that formed during the interrupted heating in $H_2$. Carbon reacts more rapidly with $H_2$ than does adsorbed CO (*13*). Carbon formation was not observed on Ni/$Al_2O_3$ under the same conditions, apparently because the CO spilled over onto the $Al_2O_3$ instead of reacting to form carbon.

### *Concentrations of Sites*

On 5.1% Ni/$Al_2O_3$, the amount of CO adsorbed at 385 K, in the presence of $H_2$, was 5 times that adsorbed at 300 K in $H_2$ and 7.7 times the amount adsorbed in He at 300 K (*3, 6*). In contrast, for the 19% Ni/$Al_2O_3$ catalyst, the amount of CO adsorbed at 385 K was only 1.4 times that for adsorption at 300 K in $H_2$ and 1.6 times that for adsorption at 300 K in He. This increase in adsorption at 385 K is due to adsorption on $Al_2O_3$ sites; at 300 K in He, CO only adsorbs on Ni sites. There are several reasons for concluding that CO spills over onto the $Al_2O_3$ at 385 K. The most direct evidence is TPR and TPD experiments carried out on a physical mixture of $Al_2O_3$ and 19% Ni/$Al_2O_3$ (*5*). In that study, the amount of CO that adsorbed at 385 K on the mixture, per gram of Ni, was much higher than the amount adsorbed on the catalyst alone. That is, CO adsorbed on the Ni and spilled over onto both the catalyst's $Al_2O_3$ support and the $Al_2O_3$ that was in physical contact with the catalyst.

The amounts of Ni and $Al_2O_3$ sites on the 19% $Ni/Al_2O_3$ catalyst were determined from the isotope labeling and interrupted TPR experiments. The amount of Ni sites was also calculated from CO adsorption in He; the total number of sites was determined from CO adsorption in $H_2$ at 385 K. For the 19% $Ni/Al_2O_3$ catalyst, excellent agreement was obtained by these methods. For 5.1% Ni, the agreement between the two methods was not as good, and the adsorption in He is considered more accurate. We estimate from previous studies (*11, 12*) that the 19% catalyst is probably completely reduced and the 5.1% catalyst is approximately 70% reduced. Thus, the number of Ni sites is similar per gram of reduced Ni (1121 $\mu$mol/g Ni for 5.1% $Ni/Al_2O_3$ and 1220 $\mu$mol/g Ni for 19% $Ni/Al_2O_3$).

On a per gram $Al_2O_3$ basis, the amount of $CH_4$ that came from the $Al_2O_3$ sites was approximately the same on the two catalysts (240 and 260 $\mu$mol/g $Al_2O_3$). For a surface area of 315 $m^2/g$, this corresponds to $5 \times 10^{13}$ molecules/$cm^2$. That is, the number of high-temperature $CH_4$ sites is independent of the Ni loading, as expected if the high-temperature $CH_4$ peak is from CO on $Al_2O_3$. When normalized per gram of reduced Ni, the number of $Al_2O_3$ sites on the 5.1% catalyst was five times that on the 19% catalyst. Since the Ni dispersions for these two catalysts are similar, these results are strong supporting evidence for identifying the high-temperature $CH_4$ as forming from CO on the $Al_2O_3$ in both cases. Reduction at 975 K significantly sintered the 19% $Ni/Al_2O_3$ catalyst, as shown by the decreased amount of CO that adsorbed in He. The difference between CO adsorption in He at 300 K and CO adsorption in $H_2$ at 385 K was the same (250 $\mu$mol/g $Al_2O_3$) for both reduction temperatures; thus, the number of $Al_2O_3$ sites was unchanged by reduction at 975 K. Similarly, for a 1% $Ru/Al_2O_3$ catalyst on which similar experiments were carried out (*14*), the number of high-temperature $CH_4$ sites was 245 $\mu$mol/g $Al_3O_3$. This is further support that the high-temperature $CH_4$ results from CO on the $Al_3O_3$. The same $Al_2O_3$ was used to prepare all three catalysts.

### *Surface Complex*

When CO and $H_2$ were coadsorbed at 385 K on a 5.1% $Ni/Al_2O_3$ catalyst, $H_2$ and CO desorbed simultaneously during TPD in a 3:1 ratio of H to CO. This simultaneous desorption was attributed to the decomposition of a H–CO surface complex that was on the $Al_2O_3$ surface (*4*). The complex appeared to have the stoichiometry of a methoxy species.

For the 19% $Ni/Al_2O_3$ catalyst, the TPD of $H_2$ and CO coadsorbed at 385 K was qualitatively similar to that for the 5.1% $Ni/Al_2O_3$ catalyst. The $H_2$ and CO desorbed simultaneously, with peaks centered at 500 K, but the H : CO ratio for the simultaneous peaks was larger than 3. The similarity in the $H_2$ and CO peak temperatures indicates the existence of a H–CO surface complex. In contrast to the 5.1% $Ni/Al_2O_3$ catalyst, much more $CO_2$ formed on the 19% $Ni/Al_2O_3$ catalyst. The $CO_2$/CO ratio for the 5.1% $Ni/Al_2O_3$ catalyst was 0.10–0.15, but this ratio was 0.40–0.45 for the 19% $Ni/Al_2O_3$ catalyst. Moreover, for the 19% $Ni/Al_2O_3$ catalyst, a much larger fraction of the CO is on the Ni sites than for the 5.1% $Ni/Al_2O_3$ catalyst. Also, determination of how much $H_2$ is associated with CO on Ni was not made. Thus, identification of the stoichiometry of the complex on the 19% $Ni/Al_2O_3$ catalyst is not possible without additional studies, but analogy to the 5.1% $Ni/Al_2O_3$ indicates that the complex may be a $CH_3O$ species.

When CO was adsorbed at 300 K in $H_2$ (following cooling in He), the complex did not form, and thus much less CO adsorbed. The activated adsorption of $H_2$ that was necessary for complex formation occurred between 300 and 385 K. Weatherbee and

Bartholomew (*15*) reported that more $H_2$ adsorbed on a 14% Ni/$Al_2O_3$ catalyst at 373 K than at 323 K. When our catalyst was cooled from 775 K, a new state, due to additional activated adsorption of $H_2$, was also seen (Fig. 7). This desorption was not accompanied by simultaneous desorption of CO, however, and apparently this $H_2$ was not adsorbed as part of a complex.

A H–CO complex did not form on the two Ni/$SiO_2$ catalysts at 300 or 385 K; no indication of coordination between CO and $H_2$ desorption was seen. Thus, a H–CO complex does not form by spillover of CO onto $SiO_2$ under these conditions. The rate of complex formation on a Ni/$TiO_2$ catalyst (*16*) was less than one tenth of the rate on Ni/$Al_2O_3$; either the rate on Ni/$SiO_2$ is even lower or a complex does not form on the $SiO_2$ surface.

### *Transfer between Sites*

The difference in the amounts adsorbed in He and in $H_2$ at 300 K indicates how much CO transfers to the $Al_2O_3$ surface at 300 K, due to the presence of activated $H_2$ adsorption. For the 19% catalyst, 35 μmol CO/g $Al_2O_3$ transferred; for the 5.1% catalyst, half this amount transferred. However, since almost four times as much CO adsorbs (per g $Al_2O_3$) on the 19% Ni/$Al_2O_3$ at 300 K, a smaller fraction of the adsorbed CO transfers to the support of the 19% Ni/$Al_2O_3$ catalyst. For both catalysts this is a small fraction of the total amount of CO that can transfer onto the $Al_2O_3$ (250 μmol/g $Al_2O_3$). Thus, the rates of transfer appear comparable for different Ni loadings and transfer is probably limited by the amount of activated $H_2$ adsorbed during cooling.

During TPR, the formation of $CH_4$ from the CO adsorbed on $Al_2O_3$ appears limited by the rate of decomposition of the H–CO complex, since the peak temperatures for the high-temperature $CH_4$ peak and for the simultaneous $H_2$ and CO desorption in TPD are similar for each Ni/$Al_2O_3$ catalyst. Since the complex decomposes faster on the 19% Ni/$Al_2O_3$ than on the 5.1% Ni/$Al_2O_3$ catalyst, the decomposition rate does not appear to be limited by the $Al_2O_3$, but by the Ni concentration. This result implies that the complex decomposes on the Ni and perhaps its decomposition is limited by surface diffusion to the Ni. Indeed, for a 0.7% Ni/$Al_2O_3$ catalyst, the peak temperature for the high-temperature $CH_4$ peak was much higher, 680 K (*6*). For reduction at 975 K, the $CH_4$ peak from the complex formed at higher temperature; catalyst sintering reduced the Ni surface area and thus the catalyst behaved like a lower loading catalyst.

## CONCLUSIONS

Isotope labeling combined with temperature-programmed reaction shows that two distinct sites for methanation are present on a 19% Ni/$Al_2O_3$ catalyst. Reduced Ni is the more active of the two sites. At elevated temperature in the presence of $H_2$, CO spills over onto the $Al_2O_3$ support. This adsorbed CO, which is present as a H–CO complex, is hydrogenated at a slower rate than is the CO on Ni. The complex decomposes at a faster rate as Ni loading is increased; the complex apparently decomposes on the Ni surface, and the decomposition rate may be limited by diffusion of the complex. The rate of formation of the complex appears limited by activated $H_2$ adsorption that takes place at 385 K or below. At saturation, the complex concentration is 250 μmol/g $Al_2O_3$ ($5 \times 10^{13}$ molecules/$cm^2$), independent of Ni loading; this confirms that the complex is on the $Al_2O_3$ surface. A complex does not form on Ni/$SiO_2$ catalysts at the same conditions that one forms on Ni/$Al_2O_3$ catalysts.

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