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Site Transfer and a Support-Bound H–CO Complex on Ni/TiO$_2$

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Temperature-programmed reaction and desorption and isotope labeling are used to identify two forms of adsorbed CO, one on Ni metal and the other adsorbed as a H–CO complex on the support of a Ni/TiO$_2$ catalyst. The complex, which appears to be a methoxy species, forms by an activated process in which CH$_3$O or H and CO spill over onto the TiO$_2$ surface. The rate of spillover is much slower than the rate of CO hydrogenation on Ni/TiO$_2$ at 385 K. The rate of spillover is also much slower than that observed for the same process on Ni/Al$_2$O$_3$ catalysts. Because CO on Ni hydrogenates to CH$_4$ faster than the H–CO complex, CH$_4$ forms in two distinct peaks on Ni/TiO$_2$ during TPR of adsorbed CO, and isotope labeling shows that CO adsorbed on these two sites do not interact significantly. Evidence is also presented to show that reverse transfer of the complex from the TiO$_2$ to the Ni surface readily occurs between 425–455 K in the absence of gas-phase H$_2$.

INTRODUCTION

During temperature-programmed reaction (TPR) of adsorbed CO in flowing H$_2$, two distinct CH$_4$ peaks have been observed on Ni/Al$_2$O$_3$ catalysts (*1–6*). By combining isotope labeling and interrupted TPR, Glugla *et al.* (*6*) showed that CO adsorbed on the Ni surface at 300 K and CO spilled over onto the Al$_2$O$_3$ support in the presence of H$_2$ and at elevated temperatures. The CO was concluded to be on the Al$_2$O$_3$ surface as a CH$_3$O species (*7*), which may have been the species that spilled over. The CH$_3$O species was hydrogenated at a slower rate than the CO adsorbed on Ni, and thus two CH$_4$ peaks were observed during TPR. A CH$_3$O species was recently observed on a Pt/Al$_2$O$_3$ catalyst by infrared spectroscopy and the CH$_3$O was concluded to be on the Al$_2$O$_3$ surface (*8*). The CH$_3$O hydrogenated at a different rate than the CO adsorbed on Pt and thus two CH$_4$ peaks were also observed on the Pt/Al$_2$O$_3$ catalyst.

Though Ni/Al$_2$O$_3$ catalysts exhibit two distinct CH$_4$ peaks during TPR, for a wide range of Ni loadings (*3, 5*), the spillover process to form CH$_3$O was not observed on Ni/SiO$_2$ catalysts; only one CH$_4$ peak was seen during TPR on Ni/SiO$_2$ (*1, 3*). The present study shows that a Ni/TiO$_2$ catalyst also exhibits two CH$_4$ peaks during TPR of adsorbed CO. In analogy to Al$_2$O$_3$-supported catalysts, this observation has been attributed to CO adsorbed on Ni and a CH$_3$O species adsorbed on TiO$_2$. We have also shown that the rate of formation of a CH$_3$O species on the TiO$_2$ support of Ni/TiO$_2$ is much slower than on Ni/Al$_2$O$_3$ catalysts. Temperature-programmed reaction and desorption (TPR, TPD) combined with isotope labeling and isothermal studies are also used to study the transfer between sites. Both forward and the reverse spillover processes are observed and they are activated.

EXPERIMENTAL METHODS

Temperature-programmed reaction and desorption were carried out at ambient pressure using the same apparatus and procedure as those used for Ni/Al$_2$O$_3$ catalysts (*6, 7*). Products desorbing from the catalyst surface were analyzed immediately downstream from the reactor by a computer-controlled quadrupole mass spectrometer, which had the capability of monitoring the signals from up to 20 mass peaks and the

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catalyst temperature simultaneously. The catalyst was reduced *in situ* in pure H_2 for 1 h at 725 K before the initial TPR. Prior to subsequent experiments, it was held in H_2 for either 15 or 30 min at 725 K. It was then cooled in H_2 to the desired adsorption temperature (300 or 385 K), and 10% CO/He was pulsed (0.5 cm^3/pulse) into the flowing H_2 carrier gas.

Following CO adsorption, TPR was carried out by heating the catalyst in flowing H_2 at approximately 1 K/s to 725 K while continuously monitoring mass signals at 15(CH_4), 18(H_2O), 28(CO), and 44(CO_2). For some experiments the primary fragmentation peak of methanol at mass 31 was also monitored, but no signal was observed. For TPD of H_2 and CO coadsorbed at 385 K, the carrier gas was switched to He at 300 K before subjecting the catalyst to a linear temperature ramp of 1 K/s. The mass signals at 2(H_2), 15(CH_4), 18(H_2O), 28(CO), 32, and 44(CO_2) were monitored. The mass 28 signal was corrected for CO_2 cracking. The sensitivity of the mass spectrometer to each mass signal was calibrated separately by injecting 0.5 cm^3 of pure gas.

The two distinct sites on the Ni/TiO_2 catalyst were isotopically labeled; the more active site with ^{13}CO and the less active site with ^{12}CO. This was done by adsorbing the ^{12}CO in flowing H_2 at 385 K for 1 h (1 pulse/30 s). This procedure allowed ^{12}CO to adsorb on both sites, and the catalyst was then heated to 485–490 K to remove the more reactive ^{12}CO. The catalyst was then cooled to 300 K in H_2 and six pulses of ^{13}CO were injected into the H_2 carrier. Subsequently either a TPR or a TPD was performed. During TPR the mass signals at 15($^{12}CH_4$), 17($^{13}CH_4$), 18(H_2O), 28(^{12}CO), 29(^{13}CO), 32, 44($^{12}CO_2$), and 45($^{13}CO_2$) were monitored. The mass 17 signal was corrected for cracking of H_2O; however, this correction was small in the temperature range of interest since most of the H_2O readsorbs and then desorbs at higher temperatures. During TPD, the mass peaks at 2(H_2), 15(CH_4), 18(H_2O), 28(^{12}CO), 29(^{13}CO), and 44($^{12}CO_2$), and 45($^{13}CO_2$) were monitored. The mass 28 and 29 signals were corrected for $^{12}CO_2$ and $^{13}CO_2$ cracking, respectively.

Additional experiments were performed to study the transfer of adsorbed CO between the Ni surface and the support. To study transfer from Ni to TiO_2, CO was adsorbed for 1 h (120 pulses) in flowing H_2 at 385 K and the catalyst was then held in flowing He (140 standard cm^3/min) for various times at 350 K. Following this, a TPR was performed while monitoring mass signals 15(CH_4), 18(H_2O), 28(CO), and 44(CO_2). Transfer from TiO_2 to Ni was studied by adsorbing CO in H_2 at 385 K for either 45 min (90 pulses) or 1 h (120 pulses). The catalyst was then heated in flowing H_2 to 485–500 K to remove the CO adsorbed on Ni. Next the catalyst was cooled in H_2 to 300 K, the flow switched to He, and the catalyst heated to 425–455 K, where it was held for 5 min in most experiments. Finally, the catalyst was cooled to 300 K in He, and a TPR was performed in flowing H_2. Mass peaks at 15(CH_4), 18(H_2O), 28(CO), and 44(CO_2) were monitored. A sequence of experiments also combined the elements of the reverse and forward transfer processes.

The 5% Ni/TiO_2 catalysts was prepared by impregnation of Degussa P-25 titania to incipient wetness with an aqueous solution of nickel nitrate. The impregnated support was dried under vacuum at 400 K and then directly reduced in H_2 without calcination. During reduction the catalyst was heated at 1.5 K/min to 503 K, held at 503 K for 2 h, then heated to 723 K at 1.5 K/min and held in H_2 at 723 K for 12 h. The Ni content was measured by a gravimetric technique. The surface area of the TiO_2 support is 50 m^2/g (*9*).

RESULTS

Temperature-Programmed Reaction

As observed previously for Ni/TiO_2 catalysts (*1*, *9*), most of the CH_4 formed in a single peak during TPR of CO adsorbed at

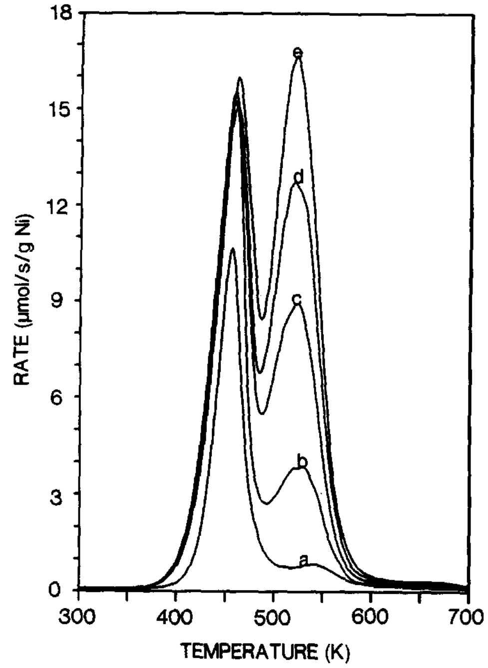

FIG. 1. Methane spectra from TPR of CO adsorbed in H_2 on a 5% Ni/TiO_2 catalyst. Adsorption temperature, number of CO pulses: (a) 300 K, 40; (b) 375 K, 40; (c) 385 K, 120; (d) 385 K, 240; (e) 385 K, 360.

300 K; only a small amount of CH_4 formed in a high-temperature peak (Fig. 1a). This behavior is distinctly different from that of Ni/Al_2O_3 catalysts of comparable metal-loading (*1–6*). When the adsorption temperature was raised to 375 K, however, two distinct peaks were seen on Ni/TiO_2 (Fig. 1b), and the amount of CH_4 in the high-temperature peak slowly increased with CO exposure at 385 K (Table 1 and Figs. 1c–1e). The low-temperature CH_4 peak was at 455 ± 3 K and the high-temperature peak was at 524 K, except for the TPR following adsorption at 300 K; neither peak shifted its peak maximum as the coverage increased. The rate of occupation of the site that formed the high-temperature CH_4 peak remained constant between 1 and 3 h of CO exposure. This result indicates that the high-temperature site was not saturated even after 3 h (360 pulses) of CO exposure. Longer exposure times were not attempted, however, in order to minimize Ni removal as nickel carbonyl. For CO adsorption at 300 K, unreacted CO was not detected during TPR, but for CO adsorption at 385 K, 200–300 μmol CO/g Ni desorbed. Most of this CO desorbed in a peak at 428 ± 2 K, but a small amount of CO adsorbed near 520 K, which is nearly coincident with CO desorption peak temperature obtained in a TPD experiment following 385 K adsorption.

To verify that the two CH_4 peaks in Fig. 1 are the result of two independent processes, ^{12}CO was adsorbed first (120 pulses at 385 K) and an interrupted TPR was used to remove the ^{12}CO as $^{12}CH_4$ in the peak at 455 K. The surface was then saturated at 300 K with ^{13}CO by pulsing ^{13}CO over the catalyst. The subsequent TPR (Fig. 2) showed that $^{12}CH_4$ and $^{13}CH_4$ formed in distinct peaks. The $^{12}CH_4$ was mostly in the peak at 524 K and the $^{13}CH_4$ was almost entirely in the peak at 455 K.

Figure 3 shows a series of TPR experiments performed to study the transfer of adsorbed CO between the two sites. Figure 3b is a TPR following 120 pulses of CO in H_2 at 385 K. The same CO adsorption was carried out for Figs. 3c and 3d, but the catalyst was then held in He at 350 K for 30 and 60 min, respectively, before the TPR was carried out. When the catalyst was held in He, the high-temperature CH_4 peak increased, the low-temperature CH_4 peak decreased slightly, and the total amount of

TABLE 1

TPR of CO Adsorbed in H_2 on 5% Ni/TiO_2

Adsorption temperature (K)	Number of CO pulses	Amount (μmol/g Ni)		CH_4 peak temperature (K)
		CH_4 peak	Unreacted CO	
300	40	425	<1	440,544
375	40	855	220	459,524
385	120	1165	255	455,524
385	240	1400	290	455,524
385	360	1600	290	455,524

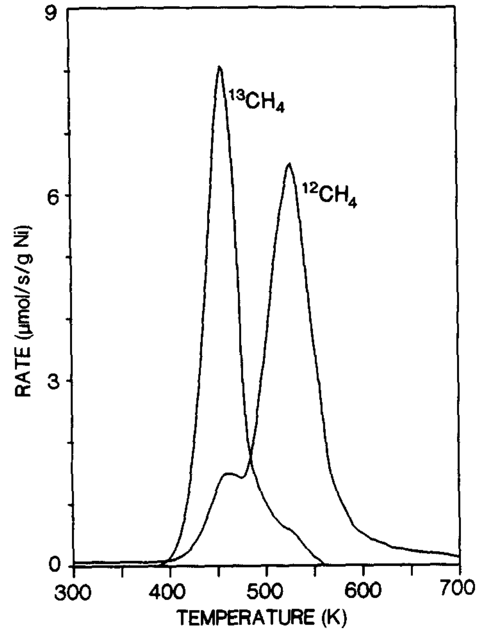

FIG. 2. Methane ($^{12}CH_4$ and $^{13}CH_4$) spectra for interrupted TPR on a 5% Ni/TiO$_2$ catalyst. The ^{12}CO (120 pulses) was adsorbed at 385 K in H$_2$, the catalyst was heated to 490 K to remove some ^{12}CO (as $^{12}CH_4$), and ^{13}CO was adsorbed at 300 K in H$_2$. The catalyst was then heated in H$_2$ to obtain the resulting TPR spectra.

CH$_4$ also increased. For 30 min in He, the amount of CH$_4$ increased by 118 to 1250 µmol/g Ni (Fig. 3c). This increase in CH$_4$ was accompanied by an almost equivalent decrease in the amount of unreacted CO (from 257 to 103 µmol/g Ni). The longer exposure (Fig. 3d) further increased the amount of high-temperature CH$_4$ and decreased the amount of low-temperature CH$_4$. However, the changes in the total CH$_4$ and CO amounts (relative to Fig. 3c) were small. The total CH$_4$ amount was 1270 µmol/g Ni and the total unreacted CO was 75 µmol/g Ni. Some CO may have desorbed during the 60 min in He at 350 K.

Exposure to He did not alter the peak temperatures. As shown in Fig. 3a, CO adsorption in He at 300 K yielded the same peak locations, although the high-temperature peak is quite small. The high-temperature peak is smaller when CO is adsorbed in He at 300 K (Fig. 3a) than when CO is adsorbed in H$_2$ at 300 K (Fig. 1a).

On Ni/Al$_2$O$_3$ (*6*) and Pd/Al$_2$O$_3$ (*10*) the conversion of CO from a support-bound complex to a metal-bonded species occurs in He. Figures 4a–4d show that this process occurs at a measurable rate on Ni/TiO$_2$ in the range 425–455 K. For each of these curves, CO was adsorbed in H$_2$ at 385 K (90 pulses), and an interrupted TPR was carried out to hydrogenate the CO adsorbed on Ni (i.e., to remove the CO that yields the low-temperature CH$_4$ peak). The catalyst was then cooled to 300 K. A subsequent TPR yielded Fig. 4a, in which all the CH$_4$ forms in the high-temperature peak. Figures 4b–4d are TPR spectra that were obtained by holding the catalyst in He at 425 K (5 min), 445 K (5 min), and 455 K (15 min), respectively, after the interrupted TPR. Holding the catalyst in He results in the appearance of a low-temperature CH$_4$ peak, but the peak temperature is 10–20 K lower than the peak temperature for the

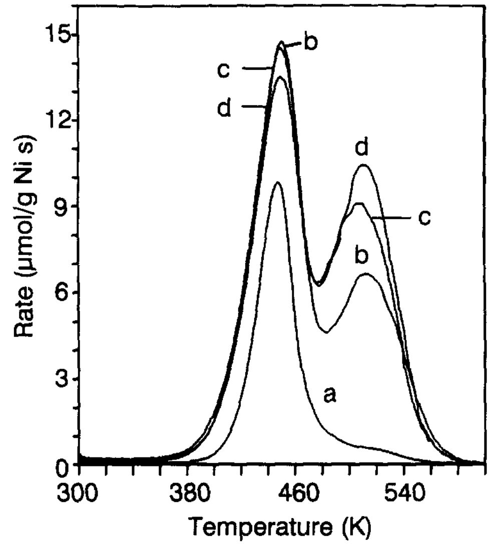

FIG. 3. Methane spectra from TPR of CO adsorbed on a 5% Ni/TiO$_2$ catalyst. Adsorption temperature, ambient gas, number of CO pulses: (a) 300, He, 40; (b) 385, H$_2$, 120; (c) 385, H$_2$, 120; (d) 385, H$_2$, 120. For curves c and d, the catalyst was held in He at 350 K for 30 and 60 min, respectively, before the TPR.

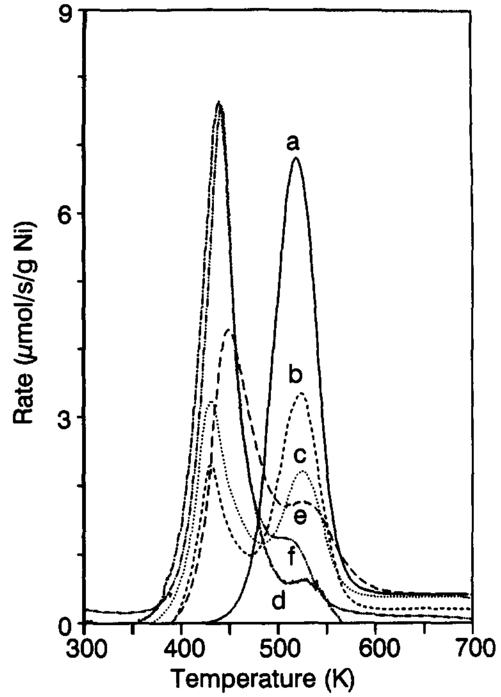

FIG. 4. Methane spectra from interrupted TPR on a 5% Ni/TiO_2 catalyst. Carbon monoxide was adsorbed at 385 K in flowing H_2. The catalyst was then heated in H_2 to react off some of the adsorbed CO that formed the low-temperature CH_4 peak. Subsequently, a complete TPR was performed to obtain curve a. Curves b–f were obtained by heating the catalyst in He before performing the TPR experiment. Number of CO pulses, interrupt temperature, He exposure: (a) 90, 485 K, 0 min; (b) 90, 490 K, 5 min at 425 K; (c) 90, 500 K, 5 min at 445 K; (d) 120, 485 K, 15 min at 455 K; (e) 90, 490 K, 5 min at 455 K, followed by 30 min at 350 K; (f) 90, 490 K, 5 min at 455 K, followed by 60 min at 350 K.

low-temperature peak in Fig. 1. The fraction of CO converted from a support-bound complex to a Ni-bound species is clearly a function of the temperature at which the catalyst is held in He, and this process appears to be essentially complete after 15 min in He at 455 K. The total amount of CH_4 formed is virtually unaffected by being held in He (Table 2), and no unreacted CO was detected desorbing from the catalyst surface.

Figures 4e and 4f show the CH_4 spectra obtained after an interrupted TPR to 490 K, 5 min in He at 455 K followed by 30 min (Fig. 4e) and 60 min (Fig. 4f) in He at 350 K. This treatment in He at 350 K causes the reappearance of the high-temperature CH_4 peak. It is important to note that more CH_4 was formed in the high-temperature peak after 30 min in He at 350 K (Fig. 4e) than for 60 min in He at the same temperature (Fig. 4f). This is probably because the catalyst was heated in H_2 from 300 to 455 K after interrupted TPR and then the flow was switched to He for Fig. 4e, but for Fig. 4f the flow was switched to He at 300 K. This may have resulted in a larger reservoir of surface H, which aided the formation of a support-bound H–CO complex.

Temperature-Programmed Desorption

Temperature-programmed desorption was carried out for CO adsorbed in He at 300 K and CO and H_2 coadsorption at 385 K. Figure 5 shows the spectrum for 300 K adsorption; CO desorbs in multiple peaks up to 725 K, when heating was stopped. Almost as much CO_2 formed as CO, and the CO_2 was in a peak at 545 K (Table 3).

Product spectra from TPD of CO and H_2

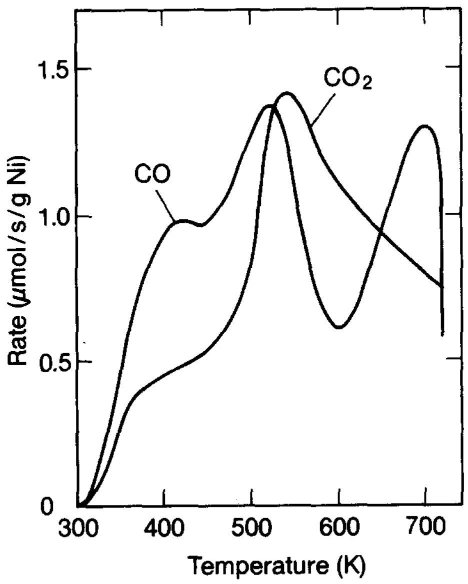

FIG. 5. Temperature-programmed desorption spectra for CO adsorbed in He at 300 K (40 pulses) on a 5% Ni/TiO_2 catalyst.

TABLE 2

Methane Formed from Interrupted TPR of CO Adsorbed at 385 K on 5% Ni/TiO_2

Number of pulses	Interrupt temperature (K)	Hold in He		Methane	
		Time (min)	Temperature (K)	Peak temperature (K)	Amount (μmol/g Ni)
90	485	0	—	519	381
90	490	5	425	429,524	308
90	500	5	445	431,524	315
120	485	15	455	444,524	463
90	490	5	455	450,524	397
		30	350		
90	490	5	455	433,524	389
		60	350		

coadsorbed at 385 K are shown in Fig. 6 for CO exposure of 120 pulses. Four times as much CO desorbed than desorbed when CO was adsorbed at 300 K, but no CH_4 was seen. The H_2 and CO desorb simultaneously in a large peak at 500 K. For a lower CO coverage (60 pulses of CO) the desorption features of H_2 and CO were similar to those obtained for the higher coverage. The H_2 peak temperatures were identical (500 K) and the CO peak was at a slightly higher temperature (516 K). The amounts of desorbing H_2 and CO doubled when the exposure was doubled (Table 3). However, unlike the 5.1% Ni/Al_2O_3 catalyst (7), significant H_2 desorption is evident in the 550–700 K range, and this desorption is not accompanied by simultaneous CO desorption. This high-temperature H_2 desorption appears to be associated with the CO_2 desorption. The amounts of the desorbing gases are listed in Table 3.

The H/CO ratio, as determined from the

TABLE 3

TPD for CO and H_2 Coadsorbed on 5% Ni/TiO_2

Adsorption temperature (K)	Number of pulses	Total amount desorbed (μmol/g Ni)		
		H_2	CO	CO_2
300[a]	40	—	232	208
385	60	991	426	121
385	120	1620	820	270

[a] Adsorption done in flowing He.

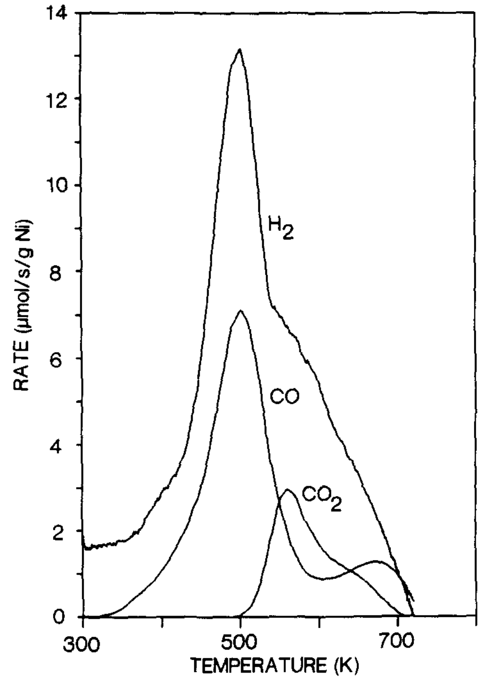

FIG. 6. Temperature-programmed desorption spectra for CO (120 pulses) and H_2 coadsorbed on a 5% Ni/TiO_2 catalyst at 385 K.

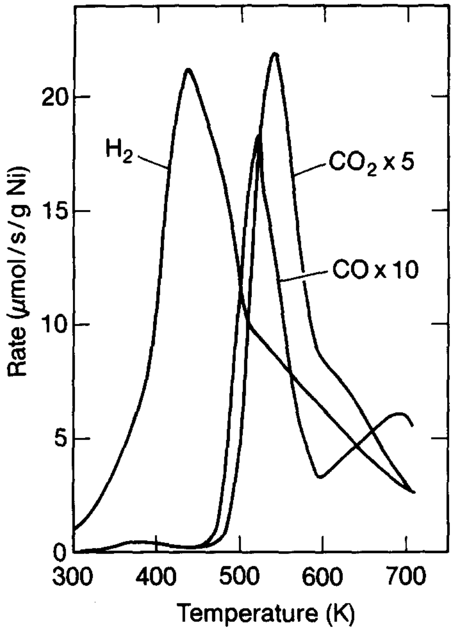

FIG. 7. Temperature-programmed desorption spectra for H_2, CO, and CO_2. The CO was adsorbed in H_2 flow on a 5% Ni/TiO_2 catalyst at 385 K (120 pulses). The catalyst was then heated in H_2 to 485 K to react off some of the adsorbed CO as CH_4. Following cooling to 300 K in flowing H_2, a TPD was performed.

amplitudes of the peaks at 500 K, is 3.5 for the higher CO exposure and 3.6 for the lower CO exposure. Since additional H_2 desorbed above 550 K and since this desorption was not accompanied by simultaneous CO desorption, the H/CO ratio obtained from the amounts desorbed was 4 for the higher CO coverage and 4.7 for the lower CO exposure. However, this H_2 desorption was accompanied by CO_2 desorption and the ratio of $H/(CO + CO_2)$ was 2.9 for the higher exposure and 3.6 for the lower exposure.

Temperature-programmed desorption was performed following an interrupted TPR to 485 K in order to correlate the adsorbed states of CO to the surface processes that yield two distinct CH_4 peaks. As shown in Fig. 7, H_2 desorbed in a broad peak with a maximum at 442 K and CO desorbed in a narrower peak centered at 523 K. The spectra in Fig. 7 are quite different from those obtained for adsorption at 385 K without interrupted TPR (Fig. 6). Nearly twice as much H_2 desorbed in the TPD following interrupted TPR, and the H_2 desorbed at a lower temperature (Table 4). Since much of the CO was removed as CH_4 during the interrupted TPR, the amount of CO desorbing was one-fourth of that following CO adsorption 385 K (Table 4 and Fig. 6); however, the peak temperature for CO desorption (523 K) was the same. The amount of CO and CO_2 (Fig. 7) is in reasonable agreement with the amount of $^{12}CH_4$ formed in the interrupted TPR experiment (Fig. 2).

In a separate experiment, TPD was carried out with isotope labeling, using the same procedure as that for the TPR in Fig. 2. An interrupted TPR to 485 K was carried out after ^{12}CO adsorption at 385 K for 1 h. After the catalyst was cooled, ^{13}CO was ad-

TABLE 4

TPD for CO and H_2 Coadsorbed on 5% Ni/TiO_2 after an Interrupted TPR

Adsorption temperature (K)	Number of pulses	Interrupt temperature (K)	Total amount desorbed (μmol/g Ni)			
			H_2	^{12}CO	^{13}CO	CO_2
385	120	485	3287	206	—	485
385	120	485	2287	456	766[a]	248
385	90	490	1946	160	—	230

[a] Six pulses of ^{13}CO adsorbed in flowing H_2 at 300 K.

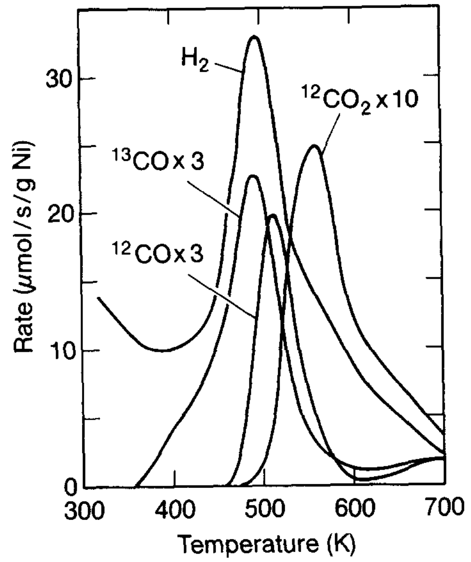

FIG. 8. Desorption spectra of H_2, ^{12}CO, ^{13}CO, and $^{12}CO_2$ from interrupted TPD on a 5% Ni/TiO_2 catalyst. The CO was adsorbed in H_2 flow on a 5% Ni/TiO_2 catalyst at 385 K (120 pulses). The catalyst was then heated in H_2 to 485 K to react off some of the adsorbed ^{12}CO as $^{12}CH_4$. It was then cooled to 300 K in flowing H_2 and ^{13}CO was adsorbed (six pulses). Following this, a TPD was performed.

sorbed at 300 K. The resulting TPD is shown in Fig. 8. The ^{12}CO desorption was similar to that in Fig. 7, centered in a peak at 513 K. The ^{13}CO desorbed in a peak located at 488 K, and the H_2 desorbed in a peak at 495 K.

Temperature-programmed desorption was also performed after the following steps: CO adsorption in H_2 at 385 K (90 pulses), interrupted TPR to 490 K, and exposure to He at 455 K for 5 min. A comparison to the spectra in Fig. 7, where the catalyst was not exposed to He at 455 K following interrupted TPR, shows that the desorption of CO_2 is similar and the peak locations and the amounts for CO desorption are comparable. However, after He treatment more CO desorbs in the peak located at 675 K. The peak maximum for H_2 desorption also increased significantly (60 K). This indicates that holding the catalyst in He at 455 K decreased the surface concentration of weakly bound H_2 (Table 4) and may have slightly altered the adsorbed state of CO.

DISCUSSION

The TPR experiments show that two distinct reaction sites for CO hydrogenation are present on Ni/TiO_2 catalysts. In analogy with TPR on a 5.1% Ni/Al_2O_3 catalyst (*6*), the CH_4 peak at 453 ± 2 K is attributed to CO adsorbed on Ni metal and the CH_4 peak at 520 ± 5 K to a H–CO complex on the TiO_2 support. On Ni/TiO_2 at 300 K, most of the CO adsorbs on the Ni metal, as was seen for a 5% Ni/Al_2O_3 catalyst (*6*). During TPR on Ni/Al_2O_3, a significant amount of the CO originally on the Ni moved to the Al_2O_3 surface. A high-temperature CH_4 peak, which was as large as the low-temperature peak, was thus seen on the Ni/Al_2O_3 catalyst. Both the Ni and Al_2O_3 sites were saturated on a 5.1% Ni/Al_2O_3 catalyst by 80 pulses of CO (1 pulse/30 s) in flowing H_2 at 385 K. In contrast, for adsorption at 300 K on Ni/TiO_2, only a small high-temperature peak was seen during TPR, apparently because the rate of transfer to a TiO_2 surface is much slower than that to an Al_2O_3 surface. That is, the CO hydrogenation rate is much faster than the spillover rate for Ni/TiO_2 and thus the CO is hydrogenated on the Ni before it has time to spill over onto the TiO_2. For both Ni/Al_2O_3 and Ni/TiO_2 catalysts, the transfer process was activated and thus occurred much more rapidly at 385 K than at 300 K. However, even for long CO exposures at 385 K, the TiO_2 surface was not saturated and the constant rate of increase in the amount of high-temperature CH_4 (Table 1 and Figure 1) indicates that the TiO_2 surface may be far from saturation coverage. We obtained a H–CO complex coverage of 1.2 μmol/m^2 of TiO_2 after 3 h of CO adsorption in H_2 (360 pulses). The monolayer concentration of methanol on TiO_2 has been estimated to be 6 μmol/m^2 of TiO_2 (*11–13*). If the H–CO complex on TiO_2 is a CH_3O species (see below), then a comparison to the CH_3OH coverage on TiO_2 is appropriate and establishes that our concentration of the support-bound complex reported in this study is consistent with the values reported in the literature for direct adsorption measurements.

The TPR experiments employing isotopes show clearly that CO on the Ni and on the TiO_2 do not intermix significantly (Fig. 2). This result verifies that the two sites are physically distinct and also shows that the transfer process is much slower than that seen on Ni/Al_2O_3 since almost no $^{13}CH_4$ formed in the high-temperature methane peak. Temperature-programmed desorption employing isotope labeling (Fig. 8) provides additional evidence for the presence of two distinct and physically exclusive adsorption sites for CO. The ^{13}CO, which is adsorbed on Ni, desorbs more readily than the ^{12}CO, which is on the TiO_2 in a H–CO complex. Moreover, as observed on Ni/Al_2O_3 (*7*), the ^{12}CO on the TiO_2 appears to affect ^{13}CO desorption from Ni, since the ^{13}CO desorption in Fig. 8 is quite different from the ^{12}CO desorption in Fig. 5. The desorption features of ^{12}CO in the two experiments are expected to be similar since both the gases were adsorbed on Ni at 300 K.

The TPD experiments for two initial coverages of coadsorbed H_2 and CO demonstrate that H_2 and CO form a complex when they adsorb at elevated temperatures on Ni/TiO_2. The simultaneous desorption of CO and H_2 (Fig. 6), in peak locations that are not present when CO (Fig. 5) or H_2 (*9*) is adsorbed alone, and the increased amounts of H_2 and CO adsorption indicate the presence of a complex. The formation of the complex is an activated process. The H/CO ratio for the simultaneous desorption at 500 K is 3.5 (estimated from the peak amplitudes).

We attempted to measure the stoichiometry of the H–CO complex more accurately by reacting CO off the Ni surface in an interrupted TPR and leaving the complex on the TiO_2. As shown in Fig. 7, the CO remaining on the surface subsequently desorbed during TPD. However, sites vacated by CO during the interrupted TPR were occupied by H_2 and thus the H_2 signal was quite large in Fig. 7 and an accurate measure of the stoichiometry could not be obtained. Adsorption of ^{13}CO on the Ni (Fig. 8) displaced some of the H_2, but we could not determine which H_2 was associated with the H–CO complex on TiO_2 and which was on the Ni surface. Also, activated adsorption of H_2 on TiO_2 has been reported (*14–17*), and thus some of the H_2 that desorbs during TPD may be H_2 on TiO_2 that is not associated with the complex. In contrast, on Ni/Al_2O_3 catalysts, saturation coverages of the H–CO complex could be obtained after relatively short exposure times and a TPD following an interrupted TPR yielded a H/CO ratio of 3 (*18*). Thus, because all the H–CO ratios from TPD of CO and H_2 coadsorbed at 385 K on Ni/TiO_2 are at least 3 and in analogy to the TPR data on Ni/Al_2O_3 (*6*) and Ru/Al_2O_3 catalysts (*19*), we conclude that a CH_3O is probably present on the TiO_2 surface of Ni/TiO_2 catalysts. Indeed, Dwyer (*20*) reported the formation of a CH_3O species on Pt/TiO_2 and Palazov *et al.* (*10*) reported CH_3O formation on Pd/Al_2O_3 in IR studies. Moreover, Robbins and Maruchi-Soos (*8*) showed in IR and TPR studies that CH_3O forms on a Pt/Al_2O_3 catalyst and that the CH_3O was hydrogenated at a different rate from CO adsorbed on Pt. They (*8*) concluded the CH_3O was on the Al_2O_3 surface.

Because the stoichiometry of the H–CO complex could not be measured accurately in our TPD studies, the possibility that a formate species is also present or is the dominant species on the Al_2O_3 cannot be ruled out. Several IR studies (*10, 21–24*) have observed formate on Al_2O_3 surfaces of Al_2O_3 supported metal catalysts. In general, however, formate was formed at low H/CO ratios and decomposition of formate in TPD is expected to yield CO_2 and H_2 instead of CO and H_2 (*25*).

The CH_3O complex is concluded to be on the TiO_2 support and not on the Ni metal by analogy to Ni/Al_2O_3 catalysts (*6, 7*). In addition, a CH_3O species on Ni(111) decomposes at 300 K (*26*), but is stable to 673 K on TiO_2 (*27*). An approximate measure of the rate of formation of the complex was obtained by dividing the amount of CO adsorbed (determined from a TPD experiment) by the time of adsorption. For a 5.1% Ni/Al_2O_3 catalyst this rate is 0.19 μmol/s g Al_2O_3 (*6*), whereas for the 5% Ni/TiO_2 catalyst this rate is 0.012 μmol/s g TiO_2. It should be emphasized that these are not true rates and they depend on the pulsing sequence, but serve as an approximate measure for comparing catalysts. Thus the rate of CH_3O formation is more than 10 times faster on Al_2O_3 than on TiO_2. This result shows that CH_3O formation depends on the support, as would be expected if CH_3O is adsorbed on the TiO_2 support and the rate of transfer from the metal to the support is influenced by the support.

The high-temperature CH_4 peak observed during TPR is concluded to result from hydrogenation of a TiO_2-bound methoxy complex (or its decomposition products) because formation of the complex observed in the TPD experiments and occupation of the high-temperature CH_4 peak seen in TPR are both activated processes. The increased quantities of CH_4 and unreacted CO in TPR are similar to the increased amounts of CO and H_2 in TPD (Tables 1 and 3). The peak temperature for CH_3O decomposition in TPD is 20 K lower than the peak temperature for CH_4 formation from CH_3O in TPR. If the CH_3O transfers back to Ni in order to decompose and be hydrogenated, then this reverse spillover must be slower when H_2 is present. Isotope experiments on Ni/Al_2O_3 indicate that the reverse spillover from Al_2O_3 is indeed inhibited by H_2 (*6*). In a separate study (*28*) we have also shown that reducing the partial pressure of H_2 in the gas phase during TPR increases the rate of hydrogenation of the CH_3O complex. Thus, one possibility is that formation of the high-temperature CH_4 peak is limited by reverse spillover and decomposition of the CH_3O species. Another possibility is that CH_3O is hydrogenated directly on the TiO_2 support; isotope studies indicate that this may occur on Pt/TiO_2 catalysts (*29*).

Direct evidence that CO transfers from Ni to TiO_2 was obtained by holding the catalyst in He at 350 K (Fig. 3). On Ni/Al_2O_3 catalysts (*6, 18*) transfer occurred rapidly (relative to Ni/TiO_2) by holding the catalysts in H_2 at 385 K. However, for Ni/TiO_2, attempts to effect the transfer in H_2 were not successful because the hydrogenation rate of CO on Ni is fast relative to the transfer rate and thus CO reacted to CH_4 before a significant amount transferred to TiO_2. The growth of the high-temperature CH_4 peak with time in He at 350 K (Fig. 3) shows clearly that CO transfers from Ni to the TiO_2 surface. Transfer to TiO_2 occurs through an activated process and a possible precursor to formation of a CH_3O species on TiO_2 could be formation of carbonyl hydride species, with Ni having one CO ligand and one or two hydrogen ligands. This species has been observed by infrared spectroscopy on Pd/Al_2O_3 (*10*) and Rh/Al_2O_3 (*30*).

The reverse transfer of the methoxy from TiO_2 to Ni appears to occur rapidly between 425–455 K (Fig. 4). A prerequisite for this transfer process is that vacant sites are available on the Ni surface. This is in agreement with the results obtained on a 5.1% Ni/Al_2O_3 catalyst (*6*). Temperature-programmed desorption of the adsorbed species that result after heating in He at 425–455 K indicates that carbon and oxygen are both present on the surface. However, the CH_4 peak temperatures after transfer from TiO_2 to Ni are lower than those observed for CO adsorption at 300 K. Such a decrease in peak temperature is expected if some of the CO dissociates and deposits carbon on the surface (*31*). The temperatures used for reverse transfer are sufficiently high that CO may have dissociated.

This study demonstrates that formation of a H–CO complex may be a general phenomena since the same type of spillover complex has been detected on both Al_2O_3 and TiO_2 surfaces. Because the TiO_2 surface was not saturated, a measurement of total sites was not possible. A measure of saturation coverage might help identify the nature of the sites. Fourier transform infrared studies for CH_3OH adsorption on δ-Al_2O_3 indicated that the number of sites associated with CH_3O adsorption correlates with the density of coordinately unsaturated Al^{3+} cations (*32, 33*). Methanol decomposition on ZnO and TiO_2 powders (*27*) have been directly related to desorption kinetics of a CH_3O species adsorbed on surface Zn and Ti cations. Studies by Rethwisch and Dumesic (*34*) also suggest that surface cations may act as centers for associative adsorption of an oxygenate intermediate in the water–gas shift reaction. On TiO_2, surface reduction of Ti^{4+} to Ti^{3+} is facile and proceeds readily in H_2 at 775 K (*35–37*), and thus Ti^{3+} sites should be available for CH_3O adsorption.

CONCLUSIONS

Two reaction sites for CO hydrogenation to CH_4 are present on a 5% Ni/TiO_2 catalyst. One site is CO adsorbed on Ni metal and the other is a H–CO species (most likely CH_3O) on the TiO_2 support. Evidence is presented that shows CO adsorbs on Ni and spills over onto the TiO_2 support in an activated process. The behavior of surface species in TPR and TPD experiments is similar to that on Ni/Al_2O_3 catalysts, but the CO transfer rate from Ni to the support is more than 10 times faster for an Al_2O_3 support. Isotope labeling shows that CO on the two sites do not interact significantly during TPR. On Ni/TiO_2, the hydrogenation rate of CO is much faster than the rate of spillover, but the two rates are comparable on Ni/Al_2O_3 catalysts at 385 K. The reverse transfer of CO from TiO_2 to Ni occurs readily between 425–455 K in the absence of gas-phase H_2.

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