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Formation and Decomposition of Methoxy Species on a Ni/Al_2O_3 Catalyst

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Temperature-programmed reaction and desorption (TPR, TPD) were combined with isotope exchange to study the forward and reverse spillover of CO on a 5.1% Ni/Al_2O_3 catalyst. Carbon monoxide adsorbs nondissociatively on Ni at 300 K, but a fraction of adsorbed CO dissociates at 425 K. Carbon monoxide on Ni, in the presence of H_2 at elevated temperature, spills over to form CH_3O on Al_2O_3. This CH_3O can undergo reverse spillover to form both CO and carbon on Ni. For low CH_3O coverages, mostly carbon forms, but at higher CH_3O coverages, mostly CO forms on Ni. The reverse spillover is faster at higher temperatures, for longer times, and for higher CH_3O coverages. The rate of reverse spillover is comparable to the rate of CH_3O hydrogenation, and reverse spillover may be the limiting step in CH_3O hydrogenation. The rate of carbon hydrogenation on Ni is significantly inhibited by the presence of CO adsorbed on Ni, perhaps because H_2 adsorption sites are blocked.

INTRODUCTION

Previous studies have used temperature-programmed reaction (TPR) combined with isotope labeling to show that two distinct methanation sites are present on Ni/Al_2O_3 catalysts (*1–5*). In these studies, carbon monoxide was adsorbed on the catalyst, and the rate of CH_4 formation was measured as the catalyst temperature was raised in ambient pressure H_2. The more active site was identified as CO adsorbed on reduced Ni, and the less active site was concluded to be a methoxy (CH_3O) species adsorbed on the Al_2O_3 support (*5–7*). Studies with physical mixtures of Al_2O_3 and supported Ni catalysts showed directly that CH_3O was on the support (*7*). A combination of TPR and IR spectroscopy showed that similar processes occur on Pt/Al_2O_3, and IR verified that CH_3O was adsorbed on one of the sites (*8*). On Ni/Al_2O_3 catalysts, CO only adsorbed on the Ni surface at 300 K in He flow. At higher temperatures in H_2 flow, CO transferred from Ni to the Al_2O_3 surface in a spillover process (*5, 7*). This spillover thus took place during TPR experiments. At the same temperatures in He flow, CO remained unchanged on the Ni surface (*5*). In a few experiments the reverse spillover of CH_3O from Al_2O_3 to Ni was observed (*1, 5*). The objectives of the present study were to measure the rate of the reverse spillover process and identify the species formed on Ni following reverse spillover.

Isothermal treatments in He at various temperatures and for various times were used to transfer CH_3O from the Al_2O_3 surface. Three species were present on a 5.1% Ni/Al_2O_3 catalyst after these treatments, and they were distinguished by their kinetic properties:

- Methoxy on the Al_2O_3 surface hydrogenates during TPR between approximately 475 and 650 K, with a maximum rate near 540 K.

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- Carbon monoxide on Ni hydrogenates between 400 and 475 K, with a maximum rate near 450 K. Carbon monoxide also readily exchanges with gas phase CO at 300 K (*9, 10*).
- Carbon on Ni hydrogenates between 300 and 500 K, with a maximum rate near 435 K, and carbon does *not* exchange with gas phase CO at 300 K. However, the presence of coadsorbed CO decreases the rate of carbon hydrogenation.

Carbon that forms from CO dissociation can hydrogenate over a wide temperature range because it can be present in several forms on a Ni/Al_2O_3 catalyst (*11*). The most active form has been concluded to be isolated chemisorbed carbon atoms (*11*) or a surface carbide (*12*). These species hydrogenate to CH_4 during TPR with peak temperatures of 447 K (*11*) to 475 K (*12*). At low coverage, these chemisorbed carbon atoms are even more reactive, and they hydrogenate starting at 300–325 K (*11*). The carbon formed in our experiments appears to be composed almost completely of these active forms, since it hydrogenates at low temperatures. A CH_x species is also possible, however, when hydrogen is present (*13, 14*).

In a few experiments, CH_3OH was directly adsorbed on the catalyst and the same type of reverse spillover that took place for CO and H_2 coadsorption was observed. This study demonstrates that the combination of TPR and isotope exchange can be effective for determining the form and concentration of adsorbed species on supported catalysts. By the proper choice of experimental conditions, adsorbed species can be moved from the Ni to the Al_2O_3 surface and then back to the Ni surface.

EXPERIMENTAL METHODS

The TPD/TPR apparatus was described previously (*14*). A 100-mg catalyst sample was located on a quartz frit in a 1-cm o.d. quartz downflow reactor. The tip of a shielded thermocouple was placed in the catalyst bed to measure temperature. The catalyst was heated at 1 K/s from 300 to 775 K in ambient pressure H_2 (TPR) or He (TPD). Effluent from the reactor was analyzed immediately downstream by a UTI quadrupole mass spectrometer, which was interfaced to a computer system so that several mass peaks could be analyzed simultaneously.

To carry out TPR experiments, CO was adsorbed in He flow at 300 or 425 K by injecting 0.15 cm^3 (STP) pulses of a 10% CO/90% He mixture into the He carrier gas upstream of the catalyst. A pulse was injected every 30 s for 15 min. In some TPR and TPD experiments, CO was adsorbed at 385 K in H_2 flow using the same procedure. After adsorption, various treatments were used before most TPR and TPD experiments were carried out, although TPR experiments were carried out directly after adsorption in some cases. These treatments include:

- Interrupted TPR. The catalyst temperature was raised to 460 K in H_2 flow at a heating rate of 1 K/s. This procedure removed CO that was adsorbed on Ni by transferring it to the support, by hydrogenating it to CH_4, and be desorbing some as CO.
- Isothermal treatment in H_2. The catalyst was held at 400 K in H_2 in order to transfer CO from Ni to Al_2O_3. Some CO was also hydrogenated to CH_4.
- Isothermal treatment in He. After interrupted TPR, the catalyst was held in He at various temperatures (300–550 K) for 5–60 min in order to effect reverse spillover.

After one or more of these treatments, the catalyst was cooled to 300 K and TPR was carried out by heating the catalyst in ambient pressure H_2 at a rate of 1K/s. Though the catalyst temperature was raised to 775 K, most of the TPR data to be presented will only show the CH_4 signal up to 700 K, since an insignificant amount of CH_4 formed above 700 K. The main product in all cases was CH_4, which was detected at mass 15 to avoid the cracking fraction of CO at mass 16. When CO was adsorbed at 300 K, approximately 10% of the CO desorbed unreacted during TPR. For CO and H_2 coadsorption at 385 K for 10 min, only 1% of the CO desorbed, the rest reacted to CH_4. When isothermal treatments in He were carried out immediately before TPR, no unreacted CO was observed during TPR. Thus, only the CH_4 signal is presented in the figures. For TPD experiments following one or more of the above treatments, the catalyst temperature was raised in ambient pressure He at 1 K/s, starting at 300 K. The mass signals for CO, CO_2, H_2, and CH_4 were monitored during TPD. The mass 28 signal was corrected for CO_2 cracking. The mass 15 signal was used to detect CH_4 and avoid cracking from CO and CO_2 at mass 16. The mass spectrometer was calibrated by injecting 1 cm^3 pulses of each gas into the flowing gas downstream from the reactor, and calibrated rates are plotted in all TPD and TPR spectra.

For some experiments, ^{13}CO was adsorbed instead of ^{12}CO, using the same procedure described above, but 100% ^{13}CO was used instead of the 10% ^{12}CO/90% He mixture. Similar treatments were used before carrying out TPR. In addition, after some treatments following ^{13}CO adsorption, the catalyst was exposed to ^{12}CO pulses at 300 K for 15 min in order to exchange gas phase ^{12}CO with ^{13}CO adsorbed on Ni. During the subsequent TPR, both $^{13}CH_4$ (mass 17) and $^{12}CH_4$ (mass 15) signals were monitored.

For one series of experiments, CH_3OH was adsorbed in He flow at 300 K. A 0.1-μl sample of liquid CH_3OH was evaporated from the tip of a needle upstream of the catalyst so that only gas phase CH_3OH contacted the catalyst. A TPR experiment was then carried out in ambient pressure H_2, or the catalyst was held in He at 425 K before TPR.

The 5.1% Ni/Al_2O_3 catalyst was prepared by impregnation of Kaiser A-201 alumina to incipient wetness with nickel nitrate (*1*). The impregnated Al_2O_3 was dried for 24 h, reduced in H_2 at 503 K for 2 h and at 775 K for 12 h, and then passivated at 300 K in a 2% O_2/He mixture. The Ni weight loading was determined by atomic absorption. The passivated catalyst was pretreated for 2 h in H_2 at 775 K before the first TPR on a given day. For subsequent TPR experiments on the same day, the catalyst was held in H_2 for 15 min at 775 K. This treatment was used to remove H_2O from the Al_2O_3 surface. During TPR, the H_2O product adsorbed on the Al_2O_3.

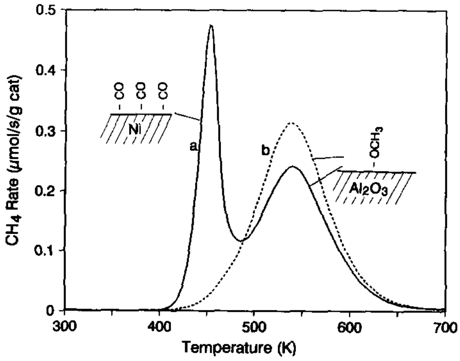

FIG. 1. Methane TPR spectra following (a) CO adsorption at 300 K in He for 15 min, (b) CO adsorption at 300 K in He for 15 min, and isothermal treatment in H_2 at 400 K for 20 min.

RESULTS AND DISCUSSION

Transfer in Hydrogen

As mentioned in the introduction, CH_4 forms in two distinct peaks on 5.1% Ni/Al_2O_3 when CO is adsorbed in He flow at 300 K and the catalyst temperature is then raised at 1 K/s in ambient pressure H_2 (TPR) (Fig. 1a). The narrow peak at 450 K has been shown to result from hydrogenation of CO adsorbed on Ni (*5*). During the TPR experiment, more than half the CO originally on the Ni transfers to the Al_2O_3 support to form a H–CO complex, which appears to be a CH_3O species. Only 10% of the CO desorbs without reacting, and the peak temperature for CO desorption was below 400 K. The broader CH_4 peak, centered at 540 K in Fig. 1a, results from hydrogenation of the CH_3O species (*6*). A representation of the species that are hydrogenated to CH_4 is given in Fig. 1 and many of the other figures.

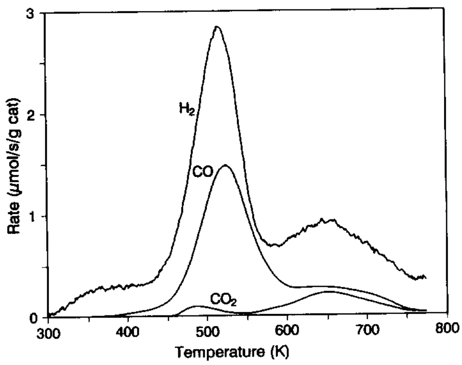

FIG. 2. TPD spectra following CO adsorption at 385 K in H_2 for 10 min and interrupted TPR to 460 K.

When CO was adsorbed in He flow at 300 K, and the catalyst was then held in H_2 flow for 20 min at 400 K prior to TPR, a CH_4 peak was not observed at 450 K. Instead, the CH_4 peak at 540 K increased by 30%, as shown in Fig. 1b. Thus, at 400 K in H_2 flow, CO on Ni transfers to the Al_2O_3 surface to form CH_3O. Figure 1a corresponds to 37 μmol CH_4/g catalyst, but only 30 μmol CH_4/g catalysts were formed during TPR for Fig. 1b, because some CO was removed as CH_4 and unreacted CO at 400 K and below. This CH_4 and CO were detected by the mass spectrometer. The slow heating rate used as the catalyst approached 400 K meant that CH_4 formed at 400 K and below; for a heating rate of 1 K/s (Fig. 1a), CH_4 only formed at a significant rate above 400 K.

Temperature-Programmed Desorption

To further justify that a CH_3O species was formed on the Al_2O_3 surface, TPD was carried out after a 10-min exposure to CO in H_2 flow at 385 K and an interrupted TPR to 460 K. As shown in Fig. 2, H_2 and CO formed simultaneously. Since the interrupted TPR to 460 K removed CO from Ni, the H_2, CO, and CO_2 that desorbed during TPD should be mostly from the CH_3O species if a large amount of H_2 did not adsorb on the Ni surface. Indeed the H/(CO + $2CO_2$) ratio is 2.8 for the peak near 525 K. The high-temperature peaks have a H/(CO + $2CO_2$) ratio of 1.5.

Isotope Exchange

On single crystal Ni, gas phase CO rapidly exchanges with adsorbed CO at 200 K (*10*). Isotope labeling was used to verify that similar exchange takes place on our 5.1% Ni/Al_2O_3 catalyst. At 300 K in He flow, ^{13}CO was adsorbed, and the catalyst was then exposed to ^{12}CO for 15 min. The subsequent TPR spectra consisted almost exclusively of $^{12}CH_4$ and ^{12}CO; the $^{12}CH_4$ spectrum was the same as that in Fig. 1a. At 300 K in He, all the ^{13}CO was adsorbed on the Ni surface, and thus the exchange on Ni appears to be rapid at 300 K.

Methoxy species on Al_2O_3 do not undergo similar exchange with gas phase CO. Methoxy ($^{13}CH_3O$) was formed on Al_2O_3 by coadsorption of ^{13}CO and H_2 at 385 K. Subsequent exposure to ^{12}CO at 300 K did not displace the $^{13}CH_3O$ but only displaced the ^{13}CO that was on Ni. The difference in exchange rates between CO on Ni and CH_3O on Al_2O_3 is used in subsequent experiments to determine how much CO is present on Ni.

Adsorption at 425 K

Because the objective of this paper is to study the transfer of adsorbed species at elevated temperatures, CO was also adsorbed at 425 K in He to determine how elevated temperature affected CO dissociation and the subsequent TPR. As shown in Fig. 3, when CO was adsorbed in He flow at 425 K instead of at 300 K, the CH_4 spectrum obtained during the subsequent TPR was similar to that in Fig. 1a. However, several differences were observed that were attributed to hydrogenation of carbon, which formed from CO dissociation at 425 K. Because carbon hydrogenates faster than CO on Ni (*11*, *16*), CH_4 started to form at 375 K in Fig. 3 instead of above 400 K (Fig. 1a). The CH_4 peak at 450 K was also broader (35 K halfwidth instead of 25 K) because it consisted of two overlapping peaks due to

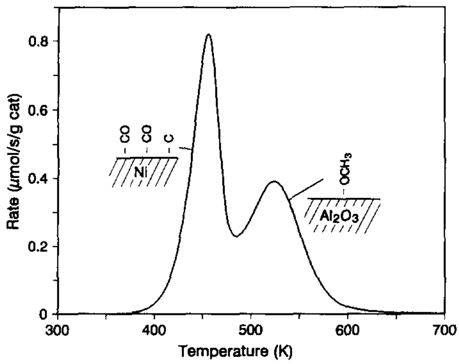

FIG. 3. Methane TPR spectra following CO adsorption at 425 K in He for 15 min.

carbon hydrogenation and CO hydrogenation. More total CH_4 (59 μmol/g catalyst) also formed at a result of adsorption at 425 K.

To verify that the changes that resulted from CO adsorption at 425 K were due to carbon formation, the following sequence was carried out:

(1) ^{13}CO was adsorbed at 425 K in He flow to form ^{13}C and ^{13}CO on Ni.

(2) The catalyst was then exposed to ^{12}CO pulses at 300 K in He flow for 15 min to exchange the adsorbed ^{13}CO with ^{12}CO.

(3) Both $^{12}CH_4$ and $^{13}CH_4$ signals were observed during the subsequent TPR.

During TPR (Fig. 4a), 14 μmol $^{13}CH_4$/g catalyst formed; i.e., approximately 25% of the ^{13}CO that adsorbed at 425 K did not exchange with ^{12}CO at 300 K. Almost all the $^{13}CH_4$ formed in a peak at 450 K, with a halfwidth of 37 K, as shown in Fig. 4a. The ^{12}CO that exchanged with ^{13}CO formed $^{12}CH_4$ in a spectrum that was essentially identical to that in Fig. 1a. The $^{13}CH_4$ spectrum in Fig. 4a does not correspond to hydrogenation of ^{13}CO adsorbed on Ni because:

- Experiments described in the previous section showed that ^{13}CO on Ni exchanges essentially completely with gas phase ^{12}CO.
- The TPR results in Fig. 1a show that CO adsorbed on Ni will spillover to Al_2O_3 during TPR to form CH_4 in a peak at 540 K. Not much ^{13} CH_4 formed at 540 K in Fig. 4a and thus the amount of $^{13}CH_3O$ formed by ^{13}CO spillover during TPR was small.

Thus the $^{13}CH_4$ signal in Fig. 4a is not due to ^{13}CO hydrogenation, but is due to ^{13}C hydrogenation.

When the same adsorption procedure (steps 1 and 2 above) was followed by an isothermal treatment in H_2 at 400 K for 20 min, only 4.8 μmol $^{13}CH_4$ signal was unchanged. The $^{12}CH_4$ signal observed during the TPR for Fig. 4b was the same as that for Fig. 1b. The spectrum in Fig. 4b also indicates that some ^{13}C formed when ^{13}CO was adsorbed at 425 K in He, since ^{13}CO would transfer to Al_2O_3 at 400 K in H_2 to form $^{13}CH_3O$. Carbon does not transfer, but it hydrogenates to methane at 400 K in H_2.

Isothermal Treatment in He (300 K Adsorption)

To study the transfer of CH_3O from Al_2O_3 to Ni, CO was adsorbed at 300 K in He flow, and an interrupted TPR to 460 K was used to remove CO from the Ni surface both by forming CH_4 and by transferring CO to the support to form CH_3O. After the sample was

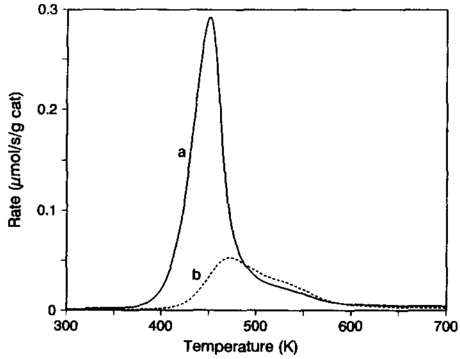

FIG. 4. The $^{13}CH_4$ TPR spectra following (a) ^{13}CO adsorption at 425 K in He for 15 min and ^{12}CO adsorption at 300 K in He for 15 min, (b) ^{13}CO adsorption at 425 K in He for 15 min and ^{12}CO adsorption at 300 K in He for 15 min, and isothermal treatment in H_2 at 400 K for 20 min.

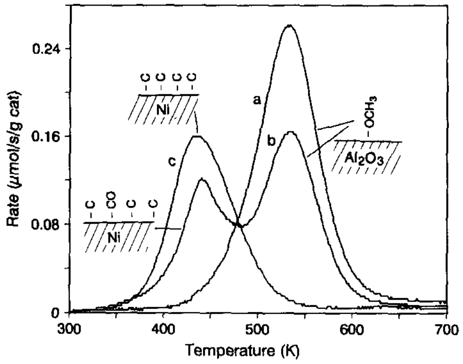

FIG. 5. Methane TPR spectra following CO adsorption at 300 K in He for 15 min, an interrupted TPR to 460 K, and then a 30-min isothermal treatment in He at (a) 300 K, (b) 425 K, (c) 550 K.

rapidly cooled to 300 K, the carrier gas flow was switched to He, and the catalyst was then held in He flow at various temperatures (300–500 K) for various times (0–60 min). A TPR experiment was then carried out. Figure 5 shows the CH_4 signals obtained, after 30 min in He at 300 K (Fig. 5a), 425 K (Fig. 5b), and 550 K (Fig. 5c). The CH_4 signal in Fig. 5a is essentially identical to the high-temperature CH_4 peak in Fig. 1a. This CH_4 formed from hydrogenation of CH_3O, which formed when CO transferred from Ni to Al_2O_3 during the interrupted TPR. Thirty min in He at 300 K had no effect on the hydrogenation behavior of the adsorbed CH_3O species.

When the catalyst was treated in He flow at 425 and 550 K, the high-temperature CH_4 peak observed during TPR decreased and a broad low-temperature CH_4 peak appeared (Figs. 5b,c). The amount of CH_4 formed in Fig. 5b (20 μmol/g catalyst) was approximately the same as the amount of CH_4 formed during TPR in Fig. 5a. However, the CH_4 started forming near 325 K in Fig. 5b, and the peak at 440 K had a halfwidth of 50 K. When the catalyst was held in He flow at 550 K prior to TPR, only 13 μmol CH_4/g catalyst was observed, and all the CH_4 formed in a peak at 440 K with a 78 K halfwidth (Fig. 5c). The CH_4 also started to form at 325 K. These low-temperature CH_4 peaks, which are much broader than those obtained for CO adsorption at 300 or 425 K, are attributed to hydrogenation of carbon that formed during the 30 min in He. The peaks are broader than the low-temperature CH_4 peak in Fig. 3 (for CO adsorption at 425 K) and CH_4 starts forming at a lower temperature, because not much CO was coadsorbed with the carbon on the Ni surface at the start of the TPR experiments in Fig. 5. As shown later, coadsorbed CO significantly affects the rate of carbon hydrogenation.

The above procedure (interrupted TPR to 460 K, hold in He, cool to 300 K, and TPR) was used to obtain a series of TPR spectra (Fig. 6) in which the time in He at 425 K was varied. With longer times in He, the amplitude of the low-temperature peak increased and that of the high-temperature peak decreased. That is, the amount of CH_3O decreased and the amount of carbon and CO on Ni increased. The total amount of CH_4 formed is essentially the same (22.8 ± 0.6 μmol CH_4/g catalyst) for each curve in Fig. 6. The amount of CH_4 formed in the low-temperature peak did not increase between 30 and 60 min in He.

In Figs. 5b, 5c and 6b–6e, CH_4 started

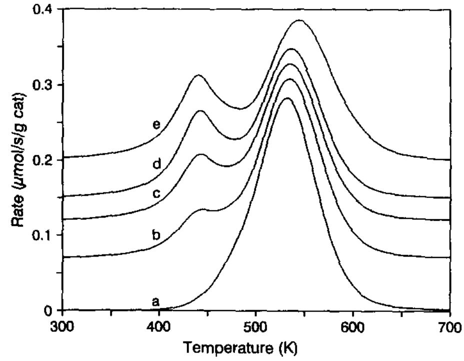

FIG. 6. Methane TPR spectra following CO adsorption at 300 K in He for 15 min, an interrupted TPR to 460 K, and then an isothermal treatment in He at 425 K for (a) 0 min, (b) 5 min, (c) 15 min, (d) 30 min, (e) 60 min.

forming just above 300 K. This high hydrogenation activity is indicative of active carbon on the Ni surface (*11*). To determine if some CO was also present on Ni, the above procedure was used, but the catalyst was held in H_2 flow at 400 K before carrying out the TPR experiment. This treatment in H_2 was shown earlier to transfer CO from Ni to form CH_3O on the Al_2O_3 surface. For the experiment in which a 30-min treatment in He at 425 K was used, the 30-min treatment at 400 K in H_2 removed the species that formed the low-temperature CH_4 peak, and the high-temperature peak was larger than that in Fig. 5b. That is, the treatment in H_2 at 400 K formed additional CH_3O on the Al_3O_3. A 40-min treatment in He at 425 K appeared to form mostly carbon on Ni because no additional CH_3O formed during the 400 K treatment in H_2.

When the treatment in He was carried out at 550 K for 30 min, a subsequent 30-min treatment in H_2 at 400 K removed most of the absorbed species; only 2 μmol CH_4/g catalyst formed during TPR. The CH_4 peak temperature was 480 K and no high-temperature peak was present. The species formed on Ni following treatment at 550 K, or at 425 K for longer times, appears to be almost exclusively carbon and thus it cannot transfer in H_2 flow to reform CH_3O.

Isothermal Treatment in He and Isotope Exchange

The displacement of adsorbed CO by gas phase CO was used to help identify the species present on Ni following the isothermal treatments in He. To do so, ^{13}CO was adsorbed at 300 K, and an interrupted TPR was used to remove ^{13}CO from Ni. The catalyst was held in He at 425 K for 30 min to effect reverse transfer, and then exposed to ^{12}CO pulses for 15 min at 300 K. The subsequent TPR is shown in Fig. 7. This procedure is similar to that used in the previous section, but an additional step (^{12}CO exposure at 300 K before TPR) was added to displace any ^{13}CO that was present on the Ni surface after the treatment in He. The ^{13}CO does not displace carbon present on Ni nor does it displace $^{13}CH_3O$ on the Al_2O_3.

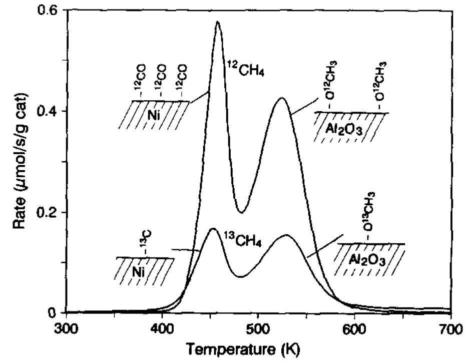

FIG. 7. Methane TPR spectra following ^{13}CO adsorption at 300 K in He for 15 min, an interrupted TPR to 460 K, an isothermal treatment in He at 425 K for 30 min, and then ^{12}CO adsorption at 300 K in He for 15 min.

Both $^{13}CH_4$ (17 μmol/g catalyst) and $^{12}CH_4$ (43 μmol/g catalyst) were observed during TPR (Fig. 7). The amount of ^{13}CO was insignificant; the small amount of ^{12}CO was the same as that observed for Fig. 1a. The $^{13}CH_4$ signal consists of two peaks. The high-temperature $^{13}CH_4$ peak results from ^{13}CO that transferred to the support during the interrupted TPR and was not removed from the support during the treatment in He. This experiment gives an accurate measure of how much ^{13}CO did not transfer from Al_2O_3 to Ni during the treatment in He. Note that the amount of $^{13}CH_4$ in the high-temperature peak in Fig. 7 is almost the same as that in 540 K peak in Fig. 5b; not much ^{13}CO was on the Ni surface after the treatment in He. Also, the amount of $^{13}CH_4$ (17 μmol/g catalyst) is close to the amount of $^{12}CH_4$ in Fig. 5b (20 μmol/g catalyst). That is, not much ^{13}CO was displaced by ^{12}CO. However, the amplitude of the $^{13}CH_4$ peak at 450 K in Fig. 7 is greater than that in Fig. 5b. The $^{13}CH_4$ did not start to form until 375 K in Fig. 7, and its peak temperature was 10 K higher than that in Fig. 5b. The low-temperature $^{13}CH_4$ peak is due to hydrogenation of ^{13}C, which does not exchange significantly with

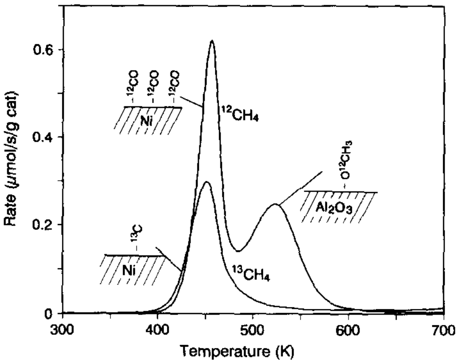

FIG. 8. Methane TPR spectra following ^{13}CO adsorption at 300 K in He for 15 min, an interrupted TPR to 460 K, an isothermal treatment in He at 550 K for 30 min, and then ^{12}CO adsorption at 300 K in He for 15 min.

gas phase ^{12}CO. The presence of ^{12}CO on Ni, however, clearly affects the rate of hydrogenation of the ^{13}C species on Ni.

The $^{12}CH_4$ signal in Fig. 7, though similar to that in Fig. 1a, has a larger high-temperature peak. When Ni/Al_2O_3 catalysts are cooled in H_2 flow from 775 K and CO is then adsorbed at 300 K in He flow, the high-temperature CH_4 peak is significantly larger than when the catalyst is cooled in He flow from 775 K (*1*, *3*, *5*). Activated adsorption of H_2 appears to be responsible for the additional adsorption and CH_3O formation. Hydrogen that remained absorbed after the interrupted TPR apparently was responsible for the larger $^{12}CH_4$ peak at high temperature in Fig. 7. The presence of the high-temperature $^{12}CH_4$ peak also shows that carbon on the Ni surface did not inhibit spillover to form CH_3O.

In another experiment the same procedure was used (^{13}CO adsorption at 300 K, interrupted TPR, isothermal treatment in He, ^{12}CO exposure at 300 K) except that the catalyst was held in He for 30 min at 550 K instead of 425 K. Only one $^{13}CH_4$ peak was seen during TPR (Fig. 8). The amount of $^{13}CH_4$ in Fig. 8 was the same as that in Fig. 5c; ^{12}CO did not displace any ^{13}CO from Ni, apparently because only carbon remained on the surface after treatment at 550 K in He. However, the methanation rates of the ^{13}C species were quite different for the two experiments. In Fig. 8 (relative to Fig. 5c), $^{13}CH_4$ formed in a peak that was twice as high in amplitude, had a halfwidth of 34 K (instead of 78 K in Fig. 5c), and had a 10 K higher peak temperature. Also, $^{13}CH_4$ only started forming above 375 K (instead of at 300 K). This result shows that the ^{12}CO adsorbed on Ni significantly affects the rate of ^{13}C hydrogenation.

The $^{12}CH_4$ signal in Fig. 8 was similar to that in Fig. 1a, rather than that in Fig. 7. Though hydrogen remained on the Ni surface following an interrupted TPR and an isothermal treatment in He at 425 K, the treatment at 550 K desorbed most of the hydrogen that remained after the interrupted TPR. This was verified by TPD experiments. Thus, the $^{12}CH_4$ signal was the same as that observed when CO was adsorbed after the catalyst was cooled in He (Fig. 1a).

Isothermal Treatment in He (385 K Adsorption)

Higher $^{13}CH_3O$ coverages on Al_2O_3 were obtained by ^{13}CO adsorption at 385 K in H_2 flow, as shown by the $^{13}CH_4$ TPR spectrum in Fig. 9a. Interrupted TPR to 460 K effec-

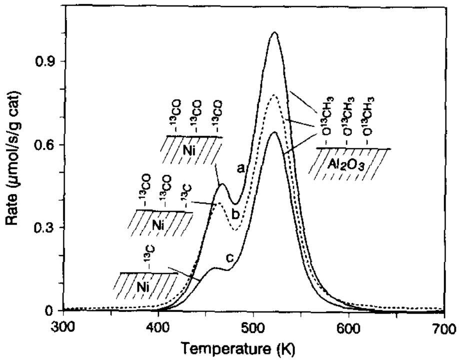

FIG. 9. The $^{13}CH_4$ TPR spectra following: (a) ^{13}CO adsorption at 385 K in H_2 flow for 10 min; (b) step (a) plus an interrupted TPR to 460 K followed by a 10-min isothermal treatment in He at 425 K; (c) step (b) followed by ^{12}CO exposure at 300 K in He for 15 min.

tively removed the ^{13}CO adsorbed on Ni, so that a subsequent TPR consisted of only the high-temperature $^{13}CH_4$ peak. Ten min in He at 425 K (after an interrupted TPR) recreated the low-temperature $^{13}CH_4$ peak (Fig. 9b). This rate of reverse transfer from Al_2O_3 to Ni is much faster than that observed when CO was adsorbed at 300 K. The low-temperature $^{13}CH_4$ started forming at a lower temperature in Fig. 9b because carbon was formed at 425 K in He. The high-temperature $^{13}CH_4$ signal in Fig. 9b is smaller than that in Fig. 9a because of the CH_3O species that transferred from Al_2O_3 to Ni at 425 K in He. This reverse spillover was sufficiently rapid that 5 min at 425 K in He yielded the same result at 10 min, and 2 min at 425 K in He was sufficient time to reform a low-temperature peak that was 85% the size of that obtained for 10 min in He.

The isothermal treatment in He transferred ^{13}CO from Al_2O_3 back to Ni, but the TPR experiment used to measure the amount of $^{13}CH_4$ that formed from each adsorption site also transferred some of the ^{13}CO from Ni back to Al_2O_3. To determine how much ^{13}CO was present on the Ni surface at the start of the TPR experiment in Fig. 9b, the catalyst was exposed to ^{12}CO pulses for 15 min at 300 K after interrupted TPR and the isothermal treatment in He. The ^{12}CO displaced ^{13}CO that was adsorbed on the Ni surface, but it did not displace carbon or the $^{13}CH_3O$. The amount of $^{13}CH_4$ formed during the subsequent TPR (Fig. 9c) was reduced to 39 μmol $^{13}CH_4$/g catalyst from the 57 μmol $^{13}CH_4$/g catalyst observed in Fig. 9b. That is, 18 μmol ^{13}CO/g catalyst transferred from Al_2O_3 to Ni at 425 K and then exchanged with gas phase ^{12}CO at 300 K. Both the low- and high-temperature $^{13}CH_4$ peaks are smaller in Fig. 9c than in 9b, but the low-temperature peak preferentially decreased. The decrease in the size of the high-temperature $^{13}CH_4$ peak demonstrates that *during* TPR for Fig. 9b, some ^{13}CO transferred to the Al_2O_3. Before the TPR of Fig. 9c, this ^{13}CO was removed from the Ni by exchange and thus was not available to transfer to Al_2O_3 during TPR. Note that in Fig. 9c the low-temperature $^{13}CH_4$, which is due mostly to ^{13}C hydrogenation, did not start forming at as low a temperature as in Fig. 9b. This is another indication that the presence of coadsorbed ^{12}CO on Ni decreased the rate of carbon hydrogenation. The $^{12}CH_4$ spectrum that was observed at the same time as Fig. 9c was similar to the $^{12}CH_4$ spectrum in Fig. 7. This was expected because ^{12}CO was adsorbed on Ni at 300 K after an interrupted TPR, which are the same conditions that resulted in the $^{12}CH_4$ spectrum in Fig. 7. The amount of ^{13}CO that desorbed was insignificant, and the ^{12}CO desorption was the same as that observed for Fig. 1a.

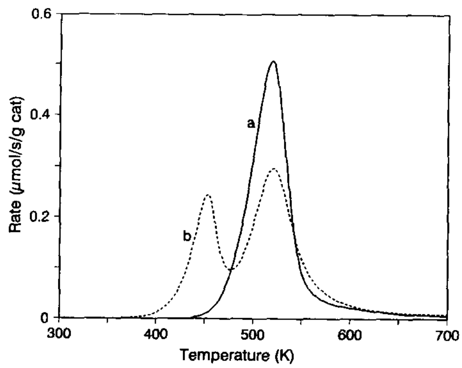

FIG. 10. Methane TPR spectra following (a) CH_3OH adsorption at 300 K in He flow, (b) CH_3OH adsorption at 300 K in He flow and isothermal treatment in He at 425 K for 30 min.

Methanol Adsorption

Methanol adsorption on the Ni/Al_2O_3 catalyst may be another means to create a CH_3O species on the Al_2O_3 surface, and thus a TPR experiment was carried out following CH_3OH adsorption at 300 K in He. Only one CH_4 peak, with a peak temperature of 520 K (Fig. 10a), was observed. This experiment does not correspond to saturation coverage of CH_3OH. Instead, the exposure was chosen to yield a coverage (26 μmol CH_4/g catalyst) similar to that obtained during TPR following CO adsorption at 300 K. When the catalyst was held in He at 425 K for 30 min, after CH_3OH adsorption at 300 K, two CH_4 peaks were seen during TPR (Fig. 10b). The CH_4 peak at 520 K decreased and a CH_4 peak at 450 K was observed. The total amount of CH_4 was the same as that for Fig. 10a. No CH_3OH desorption was detected for either experiment. At 300 K, CH_3OH adsorbed on Al_2O_3, and at 425 K in He, some CH_3OH or CH_3O transferred to Ni to create CO and H_2.

The similarity between these results and those obtained following CO and H_2 coadsorption indicate that the same processes are occurring in both cases. At low coverage, CH_3OH appears to adsorb mainly on the Al_2O_3 surface at 300 K. Some CH_3OH may also have decomposed on Ni at 300 K and the CO then transferred to Al_2O_3 during TPR. The reverse transfer from Al_2O_3 to Ni is quantitative; not much is lost to the gas phase. The TPR spectra in Fig. 10 are also further justification that CO and H_2 form CH_3O on Al_2O_3.

Spillover from Al_2O_3 to Ni

The TPR experiments demonstrate that CO adsorbs on Ni and transfers to form CH_3O on Al_2O_3 at elevated temperatures and in the presence of H_2. The CH_3O species can then transfer back to the Ni surface to form CO and C. A CH_3O species is not expected to form on Ni as a result of reverse spillover because CH_3O is unstable on Ni (*17–24*) and decomposes to form CO and H_2 (*22–24*). Following the reverse transfer experiments at 425 K (presented in Fig. 9), 17 μmol CO/g catalyst (the difference in amounts for Fig. 9b and 9c) and 5 μmol C/g catalyst (Fig. 9c) were present on the surface. For lower CH_3O coverages (Fig. 5), mostly carbon was present following reverse transfer at 425 K, and only carbon appeared to be present on Ni following reverse transfer at 550 K. When CO was adsorbed at 425 K in He, the majority of the CO did not dissociate. For the isothermal treatments in He, however, the CO had a longer time to dissociate and the presence of adsorbed H from CH_3O dissociations may have accelerated dissociations (*25*). As described above, carbon was identified as a species that reacted to form CH_4 at a slightly faster rate than CO, but did not exchange with gas phase CO.

Rate of Reverse Spillover

The reverse spillover of CH_3O from Al_2O_3 to Ni is faster at:

- Higher coverages of CH_3O. Two min at 425 K in He transferred 19 μmol CO/g catalyst when a high CH_3O coverage was created by CO and H_2 coadsorption at 385 K. Only ~4 μmol CO/g catalyst transferred in 5 min at 425 K in He when CO was originally absorbed at 300 K and interrupted TPR created a low coverage of CH_3O. Thus, the rate of transfer during the first 2 min was much higher for the higher CH_3O coverage.
- Higher temperatures. For 30 min in He at 300 K, no reverse spillover took place. At 425 K, almost half the CH_3O transferred back to Ni (for CO adsorption at 300 K). At 550 K in He, all the CH_3O was removed in 30 min, though a significant amount went into the gas phase because of the higher temperature.
- Longer transfer times at 425 K, as shown in Fig. 6. These data also indicate that an equilibrium appears to exist at 425 K, and the rate slowed down even though more than half the original CH_3O was still present.

The rate of reverse spillover was estimated from the results obtained for high CH_3O coverages. In only 2 min at 425 K, approximately 19 μmol CH_3O/g transferred. Although some of this CH_3O transferred as the catalyst temperature was raised to 425 K, an estimate of an average rate of 0.16 μmol CH_3O/g/s was obtained by assuming all the transfer occurred in the 2 min at 425 K. Since the reverse transfer appears to reach an equilibrium at 425 K, and almost as much CO transferred to Ni in 2 min as 10 min, this estimate is a lower limit for the initial rate at 425 K. Note that this rate is the same order of magnitude as the rate of CH_3O hy-

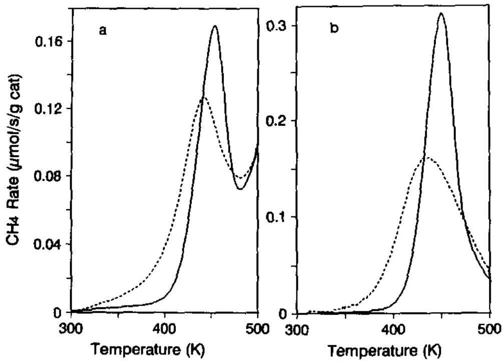

FIG. 11. Methane TPR spectra for carbon hydrogenation in the presence (solid lines) and absence (dashed lines) of coadsorbed CO. The carbon was formed on Ni by isothermal treatments in He for 30 min (following interrupted TPR) at: (a) 425 K, (b) 550 K.

drogenation at higher temperatures (0.65 μmol CH_4/g/s at 500 K from Fig. 9c). For an activation energy of 35 kJ/mol for the reverse transfer process, the same rates would be obtained. Thus, the reverse transfer may be the step that limited CH_3O hydrogenation or CH_3O decomposition.

The rate of reverse spillover may be controlled by the H_2 coverage on Ni, since the isothermal treatments in He desorb H_2. Following treatment at 425 K in He, H_2 desorption starts just above this temperature in TPD. This desorption may free up Ni sites for CH_3O reverse spillover and decomposition. At 550 K, where most of the H_2 desorbs in 30 min in He flow, all the CH_3O can transfer back to Ni.

Rate of Carbon Hydrogenation

When CH_3O underwent reverse spillover, active carbon formed on Ni, and this carbon was hydrogenated to CH_4 in a broad peak, starting near 300 K. However, when additional ^{12}CO was adsorbed after reverse spillover of $^{13}CH_3O$, the rate of carbon hydrogenation was significantly slower below 425 K. The resulting $^{13}CH_4$ peak was narrower and had a higher amplitude and a higher peak temperature than in the absence of coadsorbed ^{12}CO. Figure 11 compares the data in Figs. 5b and 7 (reverse transfer at 425 K) and in Figs. 5c and 8 (reverse transfer at 550 K). Note that for each transfer temperature, the amount of CH_4 in the low-temperature peak is similar but the CH_4 curves are quite different. The CO coadsorbed with carbon significantly inhibits carbon hydrogenation, perhaps by blocking H_2 adsorption sites.

CONCLUSIONS

Carbon monoxide adsorbs nondissociatively on Ni/Al_2O_3 at 300 K, but CO dissociates at 425 K and above to form surface carbon. Carbon hydrogenates faster than CO on Ni, but the presence of coadsorbed CO significantly inhibits the rate of carbon hydrogenation. In the presence of H_2 and at elevated temperatures, CO on Ni spills over onto Al_2O_3 to form CH_3O. Reverse spillover of CH_3O from Al_2O_3 to Ni occurs readily at 425 K and above, and both CO and carbon result from CH_3O decomposition. Reverse spillover is faster at higher CH_3O coverages, higher temperatures, and for longer times, though an equilibrium appears to be reached at 425 K. The rate of reverse spillover is comparable to the hydrogenation rate of CH_3O during TPR, and thus reverse spillover may limit the rate of CH_3O decomposition or hydrogenation. The combination of temperature-programmed reaction and isotope exchange is shown to be an effective means to identify adsorbed species on supported catalysts.

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