Activated Formation of a H–CO Complex on Ni/Al$_2$O$_3$ Catalysts

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Temperature-programmed desorption (TPD) of coadsorbed H$_2$ and CO was used to detect the presence of a H–CO complex on a Ni/Al$_2$O$_3$ catalyst, and isotope labeling was used to separate adsorbed species that were present on separate sites. The surface complex was shown to be present on the Al$_2$O$_3$ support and to have the stoichiometry of methoxy (H/CO = 3). The complex formed through an activated process carried out at 385 K. Much more CO and H$_2$ adsorbed at 385 K than at 300 K. Both CO and H$_2$ adsorbed on the Ni, after which they transferred to the Al$_2$O$_3$; activated adsorption of H$_2$ appeared to limit the transfer. At high coverage, a new CO desorption state was detected on the Ni surface. During TPD following CO and H$_2$ adsorption at 385 K, decomposition of the complex limited formation of CO and H$_2$. During temperature-programmed reaction (TPR), the two CH$_4$ peaks previously reported (Glugla *et al.* 1988) are shown to result from two forms of adsorbed CO: on the Ni surface and on the Al$_2$O$_3$ as a complex. Hydrogenation of the complex is limited by its decomposition, which is slower than CO hydrogenation on Ni. Good agreement is shown between TPD and TPR. © 1989 Academic Press, Inc.

INTRODUCTION

The temperature-programmed reaction (TPR) in H$_2$ flow of adsorbed CO to form CH$_4$ on a Ni/Al$_2$O$_3$ catalyst shows two reaction sites (Fig. 1). In a recent study (*1*), we used isotope labeling and TPR to separate the two reaction sites by sequentially adsorbing ^{12}CO and ^{13}CO and then reacting these adsorbed species by heating the catalyst in H$_2$. In a series of experiments in which heating was interrupted and adsorption temperatures were varied, communication between the two sites (called A and B in earlier studies (*2–5*)) was observed. The A site was identified as reduced Ni metal (*1, 2, 6*), and the B site was attributed to adsorption on the Al$_2$O$_3$ support (*1*). Carbon monoxide was found to adsorb only on the Ni at 300 K. The Al$_2$O$_3$ site was only occupied in the presence of H$_2$; CO transferred from the Ni through an activated process. These experiments showed that the time scale for this transfer was similar to the

time scale for methanation of Ni. Thus, in the standard TPR experiments reported previously by us and others (*2–5, 7, 8*), methanation competed with transfer of CO to the Al$_2$O$_3$, and the Al$_2$O$_3$ was not saturated. For example, for the 5.1% Ni/Al$_2$O$_3$ used in the present study, a standard TPR corresponded to less than 20% of saturation (*1*). Also, previous temperature-programmed desorption (TPD) studies were not carried out for CO and H$_2$ coadsorbed on the surface, and thus they did not reflect the same state of the catalyst as the previous TPR studies. That is, the two sites in TPR could not be related to the desorption observed in TPD since only Ni sites were occupied for a standard TPD.

Two aspects of the previous study (*1*) motivated the direction of the present study:

1. The transfer of CO from Ni to the Al$_2$O$_3$ appeared to require surface hydrogen.

2. The reverse process, in which CO on Al$_2$O$_3$ transferred to Ni, was almost completely inhibited by H$_2$, but occurred readily if H$_2$ was desorbed at 460 K.

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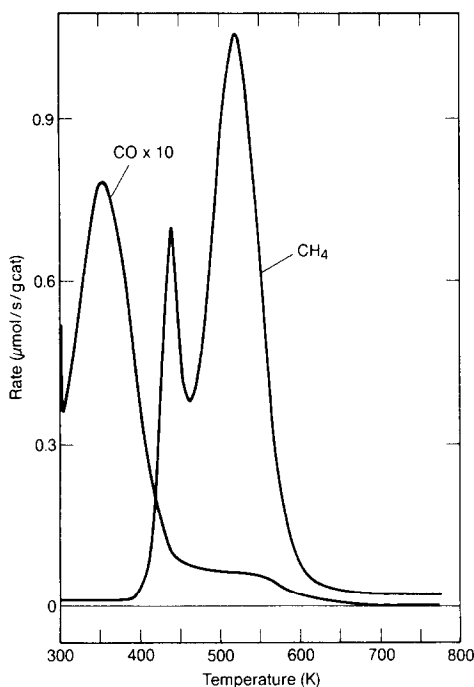[2] Currently with BASF, Wyandotte, MI.

FIG. 1. Methane and unreacted CO observed during temperature-programmed reaction (TPR) of CO adsorbed at 300 K after the 5.1% Ni/Al$_2$O$_3$ catalyst was cooled from 775 K in H$_2$. The catalyst was heated in pure H$_2$ flow.

The objectives of the present paper are to determine the form of the CO that is adsorbed on the Al$_2$O$_3$ and to relate adsorption and reaction sites and thus determine whether saturated TPR and saturated TPD studies agree.

To study the bonding of the adsorbed CO and the rate-determining steps for site transfer and methanation at the B site, coadsorption of H$_2$ and CO was studied. Pumping experiments (adsorption on Ni and transfer to Al$_2$O$_3$ (1)) were also carried out, and isotopes were used in an attempt to label the Ni and Al$_2$O$_3$ sites separately. The pumping was done by adsorption of CO at an elevated temperature in H$_2$. The CO and H$_2$ were then desorbed in a He stream using TPD. The combination of isotopes with TPD after pumping shows that CO exists in different forms on the two sites; a H–CO complex is present on the

Al$_2$O$_3$ site. Also, the saturated TPD and TPR are in good agreement with each other.

EXPERIMENTAL

The TPD system was similar to that described previously (9). A 100-mg catalyst sample was located on a quartz frit in a 1-cm OD quartz downflow reactor. An electric furnace was used to heat the catalyst. The heating rate was 0.7 K/s for most experiments. A constant rate of heating was maintained through feedback control monitored by a small thermocouple located in the catalyst bed. The system was operated near ambient pressure, and the gas residence time in the bed was less than 0.07 s. The effluent from the reactor was analyzed immediately downstream with a quadrupole mass spectrometer. A computer system allowed simultaneous detection of multiple mass peaks.

Carbon monoxide (^{12}CO or ^{13}CO) was adsorbed by injecting 0.5 ml pulses, with a pulse valve, into a H$_2$ or He carrier gas that continually flowed through the catalyst. Most adsorptions were done in H$_2$ so that both CO and H$_2$ adsorbed. These experiments are referred to as TPD since the final heating was done in a He gas stream. Adsorption was done at 300 or 385 K by repeated injections. In most experiments, pulses were continued until no additional adsorption was detected. A 10% CO in He (UHP, Matheson) gas was used for ^{12}CO adsorption. The ^{13}CO was from Monsanto Research Corporation and was specified as 99.25% carbon monoxide, of which 99.6% was labeled with ^{13}C. The H$_2$ and He carrier gases were UHP grade (Matheson) and were further purified catalytically and with molecular sieves at liquid nitrogen temperatures.

A 5.1% Ni/Al$_2$O$_3$ catalyst was prepared with nickel nitrate on Kaiser A-201 γ-alumina by impregnation to incipient wetness, as described previously (1). The impurities in the alumina, as specified by the supplier, were Na$_2$O (0.35%), FeO (0.02%), and SiO$_2$

(0.02%). Similar results have been obtained for other aluminas. The nickel nitrate was directly reduced in H_2 for 12 h without calcining. The Ni loading was measured by atomic absorption.

TPD was carried out by adsorbing CO (either one or both isotopes) on the surface in a H_2 stream and then heating the catalyst in He while detecting ^{12}CO, ^{13}CO, $^{12}CH_4$ (mass 15), $^{13}CH_4$ (mass 17), $^{12}CO_2$, $^{13}CO_2$, and H_2 with the mass spectrometer. The cracking fractions at masses 28 and 29, from $^{12}CO_2$ and $^{13}CO_2$ respectively, were subtracted from the appropriate signals in order to measure the CO signals. The cracking fractions of $^{13}CH_4$ at mass 15 was subtracted from the mass 15 signal to obtain the $^{12}CH_4$ signal. The water product, from methanation, adsorbed on the Al_2O_3 and desorbed at sufficiently high temperature (for the small amounts formed) that no cracking fraction correction was needed at mass 17. In most experiments masses 29, 30, 45, 46, and 47 were also observed in an attempt to determine if hydrocarbons were forming that might account for some observations.

The adsorption temperature and the adsorbate gas (^{12}CO or ^{13}CO) were varied. Interrupted TPR, in which some carbon monoxide was removed from the surface by hydrogenation, was used to deplete reaction sites. The details of each experiment will be described in the Results section to avoid duplication. Calibrations were done with high-purity CO, H_2, CO_2, and CH_4. Prior to each experiment, the catalyst was reduced in H_2 at 785 K for 2 h.

RESULTS

Standard TPD. To obtain a standard TPD of adsorbed CO, the catalyst was reduced in H_2 at 785 K for 2 h, the carrier gas was switched to He, and the catalyst was cooled in He. Carbon monoxide was adsorbed in He flow by pulsing a 10% CO in He mixture over the catalyst to saturation at 300 K. Saturation was determined by recording the CO effluent signal with the mass spectrometer. The first few pulses
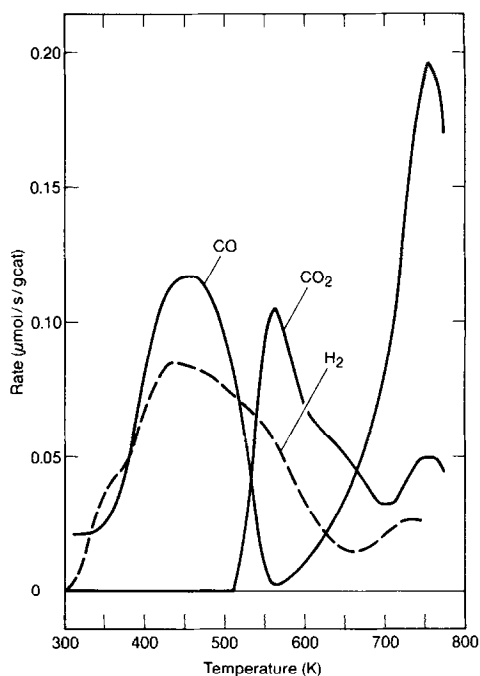

FIG. 2. Solid lines: CO and CO_2 spectra for TPD of CO adsorbed at 300 K in He on 5.1% Ni/Al_2O_3 (no H_2 exposure). Dashed line: TPD spectrum of H_2 that was adsorbed while cooling in H_2 from 775 K (no CO exposure).

produced a small signal because most of the injected CO adsorbed. Once the catalyst was saturated, the pulses became larger and each pulse produced the same signal. Typically, 12 pulses (2.2 μmol CO/pulse) were needed to produce saturation.

The TPD was carried out by heating the catalyst at a constant rate of 0.7 K/s to 775 K in He. As shown in Fig. 2 (solid lines), both CO (21 μmol/g cat) and CO_2 (14.5 μmol/g cat) formed, as has been observed previously (6). As a variant to this experiment, the catalyst was cooled in He carrier gas, but the pulsing was done in H_2 carrier gas at 300 K. The TPD heating was carried out in He. The resulting CO and CO_2 desorption spectra were the same as those in Fig. 2. In this second test a small amount of H_2 desorbed (5 μmol/g cat) in a broad featureless peak with a maximum at ~415 K. Note that the total of CO and CO_2 was less
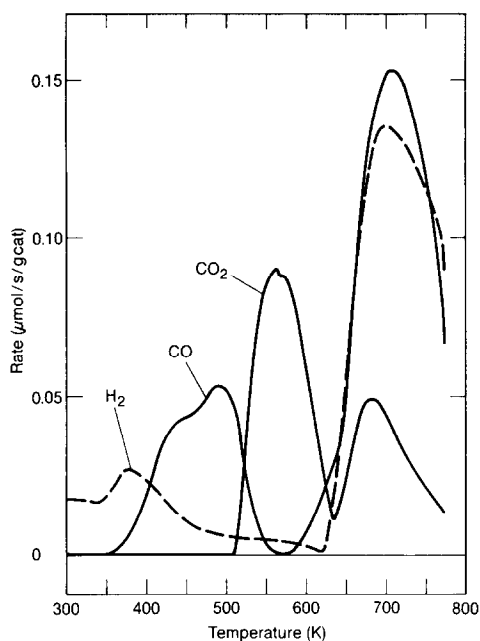
FIG. 3. Carbon monoxide, CO_2 and H_2 spectra for TPD of coadsorbed CO and H_2 on 5.1% Ni/Al_2O_3. The CO was adsorbed after the catalyst was cooled to 300 K in H_2. Less than 1 μmol CH_4/g cat was seen.

then the amount of CH_4 seen in a standard TPR (60 μmol/g cat) because of CO disproportionation and because desorption was not complete when heating was stopped.

For comparison, H_2 was adsorbed (without CO) by cooling the catalyst from 785 K in a H_2 carrier. A small amount of H_2 absorbed (15 μmol/g cat), and it desorbed in a broad peak (Fig. 2, dashed curve). The amount of adsorption was quite sensitive to experimental conditions, as was reported by Huang et al. (10). However, the main aspect of this experiment was that H_2 desorbed in a broad peak that was much smaller than the H_2 peak in the pumped coadsorption experiments described below.

TPD of CO after cooling in H_2. Cooling the reduced catalyst in H_2 to 300 K and then absorbing CO in H_2 produced TPD spectra that were quite different from those shown in Fig. 2. After saturating the catalyst with CO in a H_2 carrier gas, the carrier gas was switched to He before heating was initi-

ated. Carbon monoxide, CO_2, and H_2 desorbed from the surface (Fig. 3), but very little CH_4 was detected (<1 μmol/g cat). The CO (20 μmol/g cat) was somewhat similar to that in Fig. 2, but the high-temperature CO shifted to lower temperature. The H_2 desorption (16 μmol/g cat) was dramatically different. Instead of the broad featureless peak in Fig. 2, two distinct peaks were observed. Furthermore, the high-temperature peaks of CO and H_2 were similar in size and shape.

As a variant to this experiment, the cooling was done in H_2, but the pulsing was done in He. This produced the same results as shown on Fig. 3. As mentioned, cooling in He but carrying out the adsorption in H_2 at 300 K matched Fig. 2 and not Fig. 3. Also, cooling in H_2 but pulsing in He at 385 K instead of 300 K produced the same result as in Fig. 3.

TPD after CO pumping in H_2. In our previous study (1), we found that the amount of methane from CO hydrogenation during TPR could be increased a factor of 4 by pulsing the CO in H_2 at 385 K. However, a special pulsing technique (referred to as pumping) was required to achieve saturation. This technique consisted of delivering only two pulses per minute of CO (10% CO in He) at 385 K for 40 min. For Fig. 4, the same pumping procedure was used, but the carrier gas was switched to He prior to heating.

Much larger quantities of CO (390 μmol/g cat) and H_2 (590 μmol/g cat) adsorbed during pumping than during adsorption at 300 K. This is nearly 20 times the total amount of CO and H_2 observed in the standard TPD. As shown in Fig. 4, the CO and H_2 desorbed simultaneously with a peak temperature of 520 K, which is close to the temperature of the B peak (517 K) in the TPR in Fig. 1 (1). As shown in Table 1 for a series of repeated experiments at various partial saturations, the H/CO stoichiometry for this simultaneous desorption was 2.9 ± 0.4.
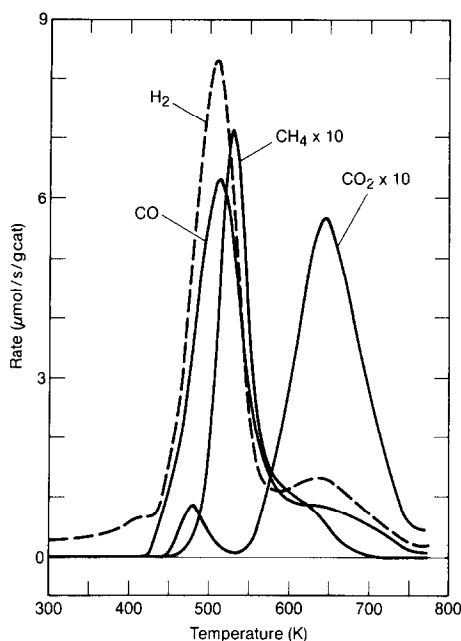
At the high-temperature end of the simul-

FIG. 4. Desorption and reaction products for pumped TPD of coadsorbed CO and H_2 on 5.1% Ni/ Al_2O_3. Eighty pulses of CO (2.2 μmol/pulse, 2 pulses/ min) were administered at 385 K in H_2. The catalyst was then cooled to 300 K and the desorption was carried out in He flow.

taneous formation of CO and H_2, a small amount (25 μmol/g cat) of CH_4 formed with a peak temperature of 540 K; a shoulder was also present at 610 K (Fig. 4). At 650

TABLE 1

Desorption Amounts for TPD of CO and H_2

TPD conditions	Amounts (μmol/g cat)				H/CO ratio
	H_2	CO	CO_2	CH_4	
CO alone	—	21	14.5	—	—
H_2 alone	15	—	—	—	—
CO and H_2 coadsorbed at 300 K (cooled in H_2)	16	20	14.5	<1	2^a
CO pumped in H_2 at 385 K (saturated)					
#1	590	440	45	25	2.7
#2	540	410	47	26	2.6
#3	650	390	45	25	3.3
CO pumped in H_2 at 385 K (partially saturated)					
#1	320	230	31	15	2.8
#2	510	290	32	14	3.5
#3	380	280	30	15	2.7

^{a} High-temperature peaks only.

K, small simultaneous peaks were seen for CO, H_2, and CO_2 (Fig. 4). Approximately 45 μmol/g cat of CO_2 formed. Several mass peaks that correspond to hydrocarbon fragments were also observed, in much smaller amounts, with peaks at 520 and 650 K, as shown in Fig. 5. Since the molecule or molecules desorbing were not known, and since these amounts were small (almost three orders of magnitude smaller than the H_2 desorption), they are plotted using the calibration for CH_4 for illustration purposes. While measurable amounts of hydrocarbons at masses 29, 30, 45, and 46 desorbed, the amount desorbing at mass 47 was not above the noise level of the mass spectrometer. Thus the signals at masses 29, 30, 45, and 46 were not artifacts of the high mass spectrometer sensitivity. The mass 29 signal was almost identical to the mass 30 signal and is not plotted for clarity.
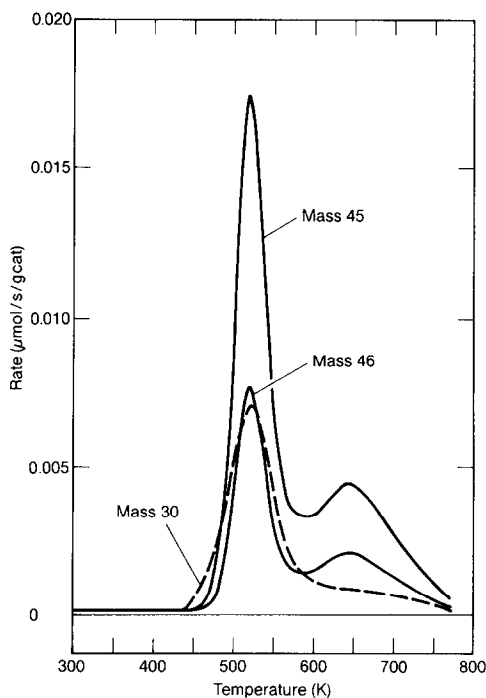

FIG. 5. Hydrocarbon products observed during pumped TPD of coadsorbed CO and H_2 (same conditions as Fig. 4). Note the small amplitude of these signals relative to Fig. 4. The methane calibration was used for all signals since the compounds producing these signals were not identified.
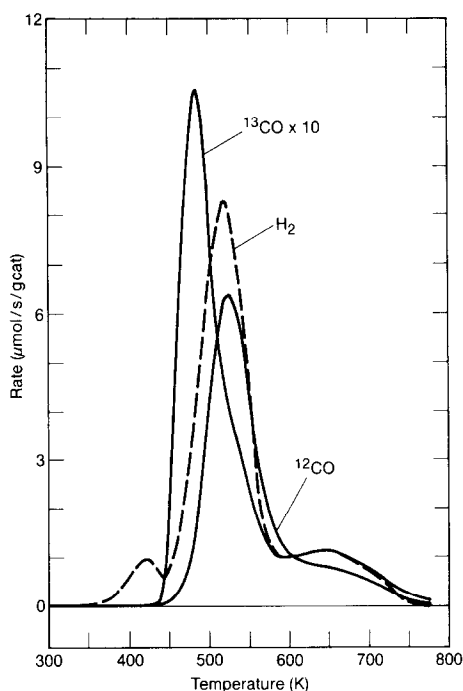
FIG. 6. Isotopic CO and H_2 desorption spectra for pumped TPD of coadsorbed CO and H_2 on 5.1% Ni/ Al_2O_3. The ^{12}CO was adsorbed to saturation at 385 K in H_2 flow. The catalyst was then heated to 460 K in H_2 to react off peak A, cooled to 385 K, and exposed to ^{13}CO until saturation. The catalyst was then cooled to 300 K and heated in He.

Isotope labeling after pumping and interrupted TPR. In our previous study (*1*), the A and B peaks in TPR both grew with pumping and the peaks overlapped at saturation. We demonstrated that two distinct sites were present using isotopes of CO. The catalyst was saturated with ^{12}CO at 385 K, and heated in H_2 to 460 K, which is the minimum between the two TPR peaks (Fig. 1). This cleans the A site by forming CH_4. The reaction was interrupted by cooling before much of the high-temperature TPR peak (the B peak) had reacted. When the catalyst was cooled and reheated in H_2, no A peak was seen and the B peak was unaffected. That is, CO was not on the A sites. Subsequent pulsing of ^{13}CO at 300 or 385 K occupied the A peak without transfer of ^{12}CO from the B peak, and the two peaks

were labeled with different isotopes for the subsequent TPR (*1*).

We attempted in the present experiments to use the same interrupted TPR procedure to distribute ^{13}CO and ^{12}CO isotopes on the A and B sites, respectively, but then desorb the carbon monoxide in He so as to relate the adsorption sites to the reaction sites. As shown in Fig. 6, ^{13}CO appeared in a peak at 485 K, and the ^{12}CO appeared in a separate peak at 530 K. Hydrogen desorbed in a peak that mimicked the sum of the two CO peaks. The total amount of H_2 and CO was the same as in Fig. 4; 50 μm of of $^{13}CO/g$ cat desorbed and 340 μmol of $^{12}CO/g$ cat desorbed. These values are accurate to ±15%. The H/CO ratio is approximately 3.

Note that the amount of ^{13}CO is comparable to the amount of $^{13}CH_4$ seen in the A peak in TPR. Moreover, when this experiment was repeated, for less than saturated coverage of the ^{12}CO, i.e., fewer pulses at 385 K, the size of the ^{12}CO peak decreased, but the ^{13}CO peak remained the same and at the same location (Fig. 7). That is, the two peaks are distinct. The H/CO ratio is again approximately 3 for the partially saturated TPD.

In addition to the CO and H_2, CH_4 and CO_2 were seen for both types of isotopes, as shown in Fig. 8. The two CH_4 isotopes formed at the same temperatures and in about a 5/1 ratio favoring $^{12}CH_4$. This is smaller than the ratio of the CO isotopes. The $^{12}CO_2$ and $^{13}CO_2$ each formed in a peak at 650 K. The $^{12}CO_2$ peak was 10 times the size of the $^{13}CO_2$ peak.

DISCUSSION

The TPD of coadsorbed CO and H_2 shows that CO and H_2 are adsorbed together on the surface; they simultaneously desorb from states that are not present for individual adsorptions of H_2 or CO. The surface species has the stoichiometry of a methoxy, and the rate of formation of CO and H_2 is limited by the rate of decomposition of this adsorbed methoxy. The rate of methanation of the methoxy during TPR is
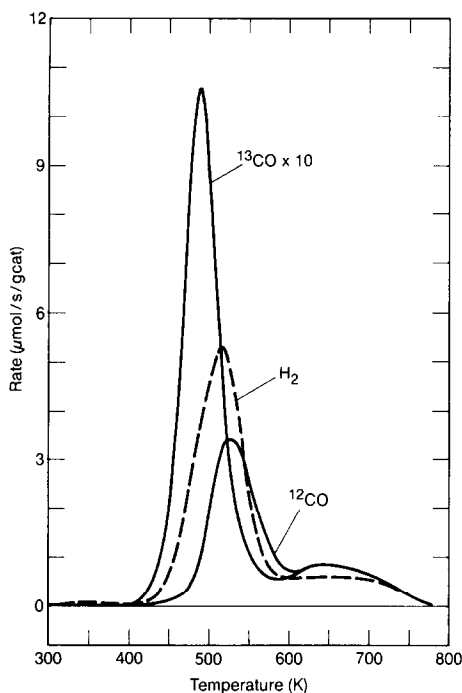
FIG. 7. Carbon monoxide and H_2 desorption spectra for pumped TPD of coadsorbed CO and H_2 on 5.1% Ni/Al_2O_3. In contrast to Fig. 6, the ^{12}CO was *not* adsorbed to saturation. Only 30 pulses of CO were administered at 385 K in H_2 flow. The catalyst was then heated to 460 K in H_2 to react off peak A, cooled to 300 K, and exposed to ^{13}CO until saturation. The ^{13}CO was not pulsed at 385 K since it would readily transfer to the B site at that temperature. Final heating was carried out in He.

also limited by its rate of decomposition, and thus two distinct CH_4 peaks are seen in TPR. We will describe below the reasons for these conclusions and discuss the relation between adsorption and reaction sites.

Surface complexes. When CO and H_2 were adsorbed at 385 K, much more of each gas adsorbed than for individual adsorptions of these gases. Figure 4 clearly shows a coordination between the adsorbed CO and hydrogen on the Ni/Al_2O_3 catalysts; CO desorption mimics the H_2 desorption. Though the H_2 and CO desorption spectra are similar, they are not identical. Other minor sites fill when exposed to H_2 and CO at 300 K, but these sites are dwarfed by the

major sites that fill at 385 K (compare Figs. 2 and 3 to Fig. 4).

When CO and H_2 were adsorbed separately (Fig. 2), the desorption peaks were not coordinated. When CO and H_2 were coadsorbed (Figs. 3 and 4), a striking coordination was seen in the TPD spectra. The high-temperature H_2 and CO peaks in Fig. 3 are nearly identical in shape and position. Similarly, the much larger CO and H_2 peaks at 520 K in Fig. 4 are nearly identical. Furthermore, the H_2 desorption changed from a broad featureless peak in Fig. 2 to sharp, clearly identifiable peaks in Figs. 3 and 4. Presumably, H_2 is desorbing from reduced Ni in Fig. 2. One must conclude that the sharp desorptions seen in Figs. 3 and 4 are not simple desorptions from reduced Ni. The enhanced adsorption is the result of an interaction of CO and H on the surface.

If this interaction is assumed to be due to the formation of a surface intermediate, the H/CO stoichiometry of 3 indicates that a methoxy (CH_3O) species may be present on
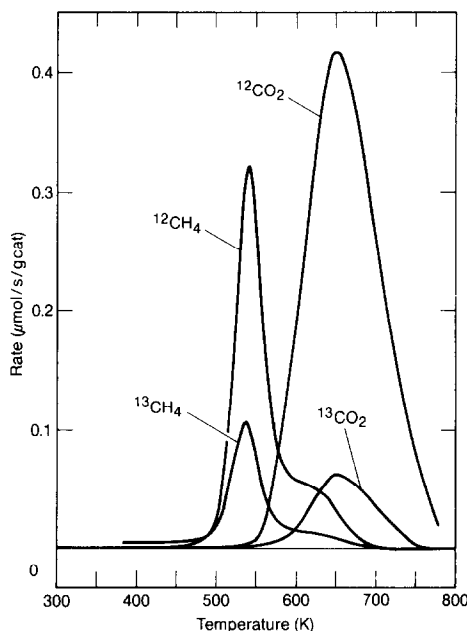

FIG. 8. Carbon dioxide ($^{12}CO_2$, $^{13}CO_2$) and methane ($^{12}CH_4$, $^{13}CH_4$) spectra for pumped TPD of coadsorbed ^{12}CO, ^{13}CO, and H_2. Conditions are the same as those in Fig. 6.

the surface. For the six experiments listed in Table 1 for adsorption at 385 K, the H/CO stoichiometry was 3, independent of coverage. This stoichiometry would be expected to change with coverage unless a surface complex formed. Thus, the constant stoichiometry, the simultaneous desorption of CO and H_2, and the greatly enhanced adsorption provide strong evidence that a surface complex is present. The small amounts of hydrocarbons seen (Fig. 5) are consistent with a methoxy or a formate, but their concentrations are sufficiently low that they could also be Fischer–Tropsch synthesis products. As described below, both methoxy and formate have been observed on support surfaces by IR, but the stoichiometry observed from TPD experiments shows that much more H_2 is present than is consistent with a formate. Moreover, when we adsorbed formic acid on Ni/Al_2O_3 catalysts, the desorption spectra were quite different from those reported here, and CO_2 was the dominant carbon-containing product. Thus, our results are more consistent with a methoxy than a formate.

Location of the surface complex. The methoxy is assumed to be present on the Al_2O_3 surface. There are several reasons for this conclusion. A surface Ni atom is covered by H_2 or CO in the standard TPD. During the pumped experiments (saturation by periodic exposure to CO in H_2 flow at 385 K) 20 times more total gas adsorbed than during coadsorption of CO and H_2 at 300 K. The complex can access sites that are not accessible to either H_2 or CO alone. Also, methoxy has been reported to be unstable on Ni at room temperature (*11, 12*) and thus is not likely to be present on the Ni at 520 K. Infrared studies on Ni/Al_2O_3 (*7, 8*) and on Al_2O_3-supported transition metals (*13–15*) found that a surface formate formed upon exposure to H_2/CO mixtures at elevated temperatures. These studies all concluded that the formate was present on the Al_2O_3. In one study on Pd/Al_2O_3 (*15*), a surface methoxy was detected by IR when

the surface was exposed to a gas stream with a high ratio of H_2 to CO. Our conditions correspond to a high H_2/CO ratio, and thus it is reasonable for a methoxy to form on our alumina support. A surface methoxy has also been detected by IR for CO and H_2 on Pt/TiO_2 catalysts (*16*).

Formation of the surface complex. Pumping did not occur at 300 K; 385 K was required to achieve large amounts of CO and H_2 on the surface. That is, methoxy formation is an activated process. For adsorption at 300 K, no coordination was observed between the CO and H_2 peaks below 650 K (Fig. 3). This indicates that a new species formed on the surface during exposure at higher temperatures. A methoxy did not form at 300 K; CO adsorption was the same in the presence of either H_2 or He at 300 K after cooling in He from 775 K.

Cooling in H_2, however, yielded quite different spectra; the high-temperature CO and H_2 peaks were coordinated (Fig. 3). However, the H/CO ratio of approximately 2 for the high-temperature peaks was close to the stoichiometry of formic acid instead of methoxy. The CO spectra in Fig. 3 is similar to that in Fig. 2, but shifted to lower temperatures. These results demonstrate two points. First, the H_2 that adsorbs during cooling is different from H_2 adsorbed at 300 K; we have also shown directly that H_2 adsorption on Ni/Al_2O_3 is activated (*6*). Second, the complex that forms at 385 K is different from the complex that forms at 300 K. We believe that methoxy formation at 385 K is limited by activated H_2 adsorption at 385 K.

Reactions of coadsorbed species. Figure 4 shows that CH_4 formed during a pumped TPD, but the CH_4 peak temperature is higher than those for the CO and H_2 peaks. Less than 5% of the CO reacted to CH_4. Methane also forms at higher temperatures than during a TPR; a similar shift was seen when TPR was run in 10% H_2 in He instead of 100% H_2 (*6*). Since Al_2O_3 is not a hydrogenation catalyst, and since methoxy is unstable on Ni, we believe that the methoxy

moves to the Ni to decompose. Since the CO and H_2 peaks in pumped TPD are at the same location as the second CH_4 peak in TPR, it appears that, once the CH_3O decomposes, hydrogenation is fast in excess H_2. For the pumped TPD, not much H_2 is available to form CH_4, and thus the CH_4 amount is small and the rate is slower than during TPR.

Relation of desorption and reaction sites. In our previous study (1), we found that CO adsorbed on the Ni metal at 300 K and moved to the Al_2O_3 support during heating in H_2. Thus, during a standard TPR (Fig. 1), CH_4 formed in two distinct peaks; the CO on the Ni hydrogenated first and then the methoxy on the support reacted. Isotope labeling showed that CO on the Al_2O_3 moved back to the Ni during heating in He (1). Therefore, for a standard TPD in which CO was pulsed in He at 300 K, the CO was not on the Al_2O_3. For TPR, the Al_2O_3 site could only be saturated at 385 K in H_2. This same procedure was used to occupy the Al_2O_3 for TPD (Figs. 4–8). The increased amount of desorption following adsorption at 385 K was from the Al_2O_3. A comparison of Figs. 1 and 4 shows that the methoxy complex decomposes to form CO and H_2 at about the same temperature that the high-temperature methane peak forms in TPR of adsorbed CO. The high-temperature CH_4 peak in TPR thus appears to be limited by either transport or decomposition of the methoxy.

Isotope labeling for pumped TPD (Fig. 6) shows a clear separation of CO desorption into distinct peaks. Interrupted TPR was used to fill the Al_2O_3 sites with ^{12}CO, and the Ni sites were then filled with ^{13}CO. Both adsorptions were done in excess H_2. The ^{13}CO had a maximum at 490 K, and the ^{12}CO maximum was at 530 K. We believe that the peak at 490 K corresponds to the low-temperature TPR peak, which is from Ni, and the peak at 530 K corresponds to the high-temperature TPR peak, which is from the Al_2O_3. The amount of CO that desorbed from the low-temperature peak is

similar to the amount of CH_4 formed from Ni during a TPR, and the amount of CO that desorbed from the high-temperature peak in the TPD is similar to the amount of CH_4 formed from Al_2O_3. Figure 6 shows that the two sites, observable in TPR, cannot be separated in TPD (Fig. 4) unless isotope labeling is used.

Note that the isotopes did not mix in either the saturated or partially saturated TPD (Figs. 6 and 7). A TPR for an unsaturated surface showed that CO transported from the Ni to the Al_2O_3. In all of these experiments, the Ni site, the low-temperature site, is initially saturated. This is demonstrated by the fact that the ^{13}CO peak size is not a function of saturation. The Al_2O_3 site is not full, however. Activated H_2 adsorption is needed to access the Al_2O_3 site. For TPD, the activated H_2 desorbs and is not available to transfer CO from Ni to Al_2O_3. Since H_2 is not available, mixing of the type seen in TPR is not expected in the TPD.

The pumped TPD indicates that at higher coverage, CO exists in coordination with H_2 on the Al_2O_3 sites. The ^{13}CO desorption in Fig. 6 is totally different from CO desorption from the Ni in a standard TPD (Fig. 2). This may be because the methoxy on the Al_2O_3 modifies desorption from the Ni; i.e., a supply of methoxy is waiting to fill the Ni site as it is emptied by desorption. This difference in CO bonding is also reflected in a shift of the low-temperature CH_4 peak from 443 K on an unpumped surface to 465 K on a pumped surface (1).

CONCLUSIONS

(1) A H–CO complex with a 3 : 1 stoichiometry, which is suggestive of a methoxy species, forms on a Ni/Al_2O_3 catalyst through an activated process. Much more CO and H_2 adsorb at 385 K than at 300 K.

(2) The methoxy is present on the Al_2O_3. Both CO and H_2 adsorb on the Ni and transfer to the Al_2O_3; activated H_2 appears necessary for this transfer.

(3) During temperature-programmed reaction in flowing H_2, the rate of methanation of the methoxy is limited by the rate of CH_3O decomposition. Since this decomposition rate is slower than CO hydrogenation on Ni, two peaks are seen in TPR. During temperature-programmed desorption in flowing He, the rates of CO and H_2 formation are limited by CH_3O decomposition.

(4) At high coverage of CH_3O, a new CO desorption state appears on the Ni surface.

(5) The use of isotopes is effective in separating sites and demonstrating agreement between TPR and TPD of coadsorbed CO and H_2.

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