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Hydrogen Exchange with Adsorbed Methanol and Methoxy on Nickel/Alumina

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Hydrogen isotope exchange with adsorbed CH_3OH and coadsorbed CO + H_2 (which form CH_3O) was studied on a Ni/Al_2O_3 catalyst by temperature-programmed reaction and desorption (TPR, TPD). Since both CH_3OH and CH_3O are adsorbed on the Al_2O_3 support, but H_2 adsorbs and dissociates on the Ni surface, H atom spillover onto the Al_2O_3 surface is an important step in the exchange process. Hydroxyl hydrogens in CH_3OH exchange orders of magnitude more rapidly than methyl hydrogens, and both types of exchange are faster than CH_3OH hydrogenation to CH_4. Thus, TPR allows these processes to be separated in time, and exchange during TPR also allows different adsorbed species to be distinguished. Coadsorbed CO + H_2 exhibit two exchange processes, one of which is different from those observed for adsorbed CH_3OH. These differences demonstrate that CH_3OH and CO + H_2 do not form identical species on Al_2O_3. Coadsorption of CO + H_2 forms H on Al_2O_3 in addition to CH_3O, and this H results in an H_2 TPD peak in addition to H_2 that forms from CH_3O decomposition. Exchange is inhibited significantly by CO adsorbed on Ni, apparently because CO blocks H_2 adsorption sites.

INTRODUCTION

Temperature-programmed reaction and desorption (TPR, TPD) have shown that two types of CO hydrogenation processes take place on Ni/Al_2O_3 catalysts (1–3). During TPR, when the catalyst temperature is ramped in H_2 flow following CO adsorption on the Ni surface, two distinct CH_4 peaks are observed; these CH_4 peaks correspond to the two processes. Some of the CO on Ni hydrogenates to form a low-temperature CH_4 peak, and the rest of the CO spills over onto Al_2O_3 as a CH_3O species (1, 4). Hydrogenation of the CH_3O results in a CH_4 peak at higher temperature. The CH_3O species can be formed at higher coverages by coadsorption of CO and H_2 at 385 K. Similarly, CH_3OH, which adsorbs directly on the Al_2O_3 surface and forms a CH_3O species (5, 6), hydrogenates during TPR to form a CH_4 peak at the same location as the high-temperature CH_4 peak from coadsorbed CO + H_2. Methanol also decomposes during TPD to form CO and H_2 in a spectrum that is similar to that for CO and H_2 coadsorbed at 385 K (7).

The similarity of CH_3OH and CH_3O TPR and TPD spectra prompted a more detailed comparison of the two types of adsorbed species. Exchange between adsorbed species and gas-phase hydrogen during TPR is shown to be an effective method of distinguishing adsorbed CH_3O and CH_3OH. The H_2 (or D_2) dissociates on the Ni surface before exchanging with CH_3OH (or CH_3O) adsorbed on the Al_2O_3 surface. Since the exchange involves spillover, these exchange experiments also provide a method to determine the rate of spillover. The hydroxyl hydrogens in CH_3OH exchange faster than the methyl hydrogens, and exchange is faster than hydrogenation to CH_4. Two distinct exchange processes were also observed for CH_3O formed from coadsorbed CO + H_2: one exchange was for methyl hydrogens, but the faster exchange did not correspond to hydroxyl exchange. That is, identical species are not formed on Al_2O_3 from CH_3OH and CO + H_2.

Another way to characterize the species formed from coadsorbed CO + H_2 is to study the low-temperature H_2 desorption peak (~450 K) observed during TPD. This H_2 desorption peak is distinct from the H_2 desorption observed due to CH_3O decomposition, and it is only observed if interrupted TPR is carried out prior to TPD. The low-temperature H_2 peak was not observed for TPD of adsorbed CH_3OH, however. Thus, a series of experiments was carried out in which CH_3O was formed on the Al_2O_3 surface of Ni/Al_2O_3 and interrupted TPR was carried out to various temperatures. Subsequently, TPD or TPR was carried out to study the desorption and reaction properties of the remaining species. Similar to the exchange experiments, the TPD experiments also show that CO + H_2 do not coadsorb to form CH_3OH, but form adsorbed H in addition to CH_3O.

EXPERIMENTAL METHODS

TPD and TPR experiments were carried out on a 5.1% Ni/Al_2O_3 catalyst and on Al_2O_3. Methanol was adsorbed

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at 300 or 385 K, and CO + H_2 (or D_2) were coadsorbed at 385 K. For TPR, the catalyst temperature was raised at 1 K/s in H_2, D_2, H_2/Ar, or D_2/Ar flow. For TPD, the catalyst temperature was raised at 1 K/s in Ar or He flow. The flow and detection system has been described previously (3, 8). Briefly a 100-mg sample of reduced and passivated Ni/Al_2O_3 catalyst or a 100-mg sample of Al_2O_3 was placed in a 1-cm OD tubular quartz downflow reactor, which was heated by a temperature-programmed electric furnace. A 0.5-mm OD, chromel-alumel thermocouple, placed in the center of the catalyst bed, measured catalyst temperature and provided feedback to the temperature programmer. Species leaving the catalyst surface were detected immediately downstream of the reactor by a computer-controlled UTI quadrupole mass spectrometer. The computer system recorded the catalyst temperature and the amplitudes of a number of mass peaks simultaneously.

Both the Ni/Al_2O_3 catalyst and the Al_2O_3 were pretreated at 773 K in H_2 flow for 2 h at the start of each day of experiments. Methanol (1–3 μl liquid) was adsorbed at 300 or 385 K by allowing liquid CH_3OH to evaporate into the carrier gas upstream of the catalyst. When CH_3OH was adsorbed on Al_2O_3, TPR was carried out in a 7% D_2/93% Ar mixture. For Ni/Al_2O_3, TPR was carried out in 100% D_2, 5% H_2/95% Ar, 3% D_2/97% Ar, 10% D_2/90% Ar, or 100% H_2. For deuterated methanol (CH_3OD), TPR was carried out in 100% D_2, 10% D_2/90% Ar, and 100% H_2. In one experiment, ^{13}CO was adsorbed after CH_3OH adsorption on Ni/Al_2O_3. Carbon monoxide and H_2 (or D_2) were coadsorbed at 385 K by injecting CO pulses into the H_2 (or D_2) carrier gas. When ^{12}CO was used, 150 μL (STP) pulses of a 10% CO/He mixture were used. When ^{13}CO was used, 50 μl (STP) pulses of pure ^{13}CO were used.

Temperature-programmed desorption (TPD) was carried out *after* interrupted TPR. For these experiments, CH_3OH or CO + H_2 (or D_2) was adsorbed on the catalyst as described above. The catalyst temperature was raised in H_2 or D_2 to temperatures from 440 to 500 K and the catalyst was then cooled at approximately 10 K/s. Next, TPD was carried out in He or Ar flow. For some experiments the catalyst was exposed to D_2 or ^{13}CO at 300 K prior to TPD. This was done to displace H_2 from Ni.

During TPR and TPD, the mass spectrometer signals for CO, CO_2, CH_4, H_2, D_2, and HD were monitored. The mass 28 signal was corrected for cracking of CO_2 to form CO in the mass spectrometer. Argon was used instead of He when D_2 at mass 4 was monitored. Because methane and water crack in the mass spectrometer, masses 15–20 were used to detect the various CH_xD_{4-x} products. These masses do not yield unique product identification, but the main emphasis in this paper is on the H_2, HD, and D_2 signals, and previous studies have reported on the rate of CH_4 formation during TPR (1, 9). Masses 31 (CH_3OH) and 46 ($(CH_3)_2O$) were also monitored.

The 5.1% Ni/Al_2O_3 catalyst was prepared by impregnation of Kaiser A-201 alumina with nickel nitrate. The impregnated Al_2O_3 was dried in vacuum and then directly reduced in H_2 using procedures described previously (3). The final reduction temperature was 775 K. The weight loading was measured by atomic absorption.

RESULTS

Methanol Hydrogenation and Exchange

Methanol adsorbed on alumina. Following CH_3OH adsorption at 300 K on Kaiser A-201 Al_2O_3, TPR was carried out in 7% D_2/93% Ar flow. The presence of gas-phase D_2 or H_2 does not affect the rate of CH_3OH decomposition, which occurs mostly above 700 K (7), where H_2 and CO form during TPD. A significant amount of D_2 was only consumed above 550 K, and two minima were observed in the D_2 signal near 660 and 750 K.

Methanol adsorbed on nickel/alumina. A TPR in 100% D_2 flow, following CH_3OH adsorption on Ni/Al_2O_3 at 385 K in H_2 flow, formed CD_4 as the dominant methane product. The single CD_4 peak near 540 K was essentially the same as the CH_4 peak obtained for TPR in H_2 flow, when CH_3OH was adsorbed at either 300 or 385 K (9, 10). In addition to CD_4, partially deuterated methane (CD_3H and CD_2H_2) signals were observed, but they were approximately 15 and 10% of the CD_4 signal amplitude, respectively. The CDH_3 and CH_4 signals were even smaller, but all methane peaks have similar shapes and peak temperatures. Because of the various cracking fractions and the presence of both CD_4 and D_2O at mass 20, accurate determination of the amounts of the various methane products was difficult. The main interest here, however, is not on the methane peaks, since they have been studied extensively by TPR in H_2 flow (9, 10).

Instead, the emphasis is on the various hydrogen peaks, and thus TPR was carried out in either 3% D_2/97% Ar or 10% D_2/90 Ar flow so that changes in the D_2 signals could be more easily measured. The use of Ar as an inert gas allowed the D_2 signal at mass 4 to be detected, but the doubly ionized Ar signal at mass 20 prevented detection of the CD_4 parent peak. Thus, methane formation was monitored by masses 18 and 16. As shown in Fig. 1 for TPR in 3% D_2 flow, CD_4, as monitored by mass 18, formed in a single peak at 550 K. The high-temperature tail for mass 18 represents cracking of D_2O, as was verified by TPR in H_2 flow. The mass 16 signal in Fig. 1 is due to cracking of several deuterated methane products. In contrast to TPR in 100% D_2, in 3% D_2 a significant fraction of the CH_3OH decomposed to form CO, which desorbed instead of being hydrogenated to CD_4.

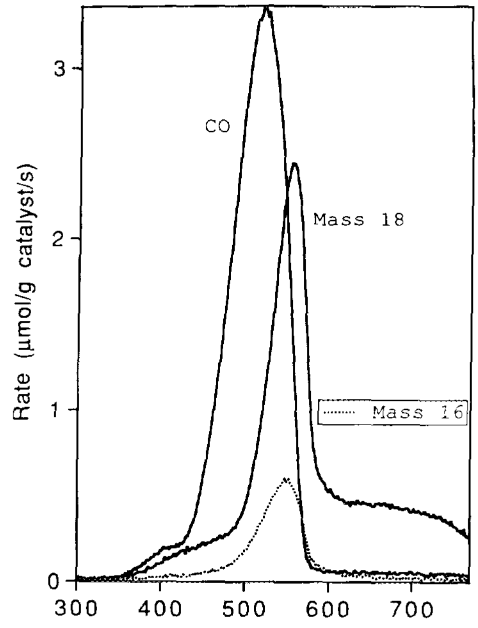

FIG. 1. TPR spectra in 3% D_2/97% Ar flow for 3 µl CH_3OH adsorbed on 5.1% Ni/Al_2O_3 at 300 K in H_2 flow. The CO, mass 18 (CD_4 cracking, H_2O), and mass 16 (CH_4, CD_4 cracking) signals are shown.

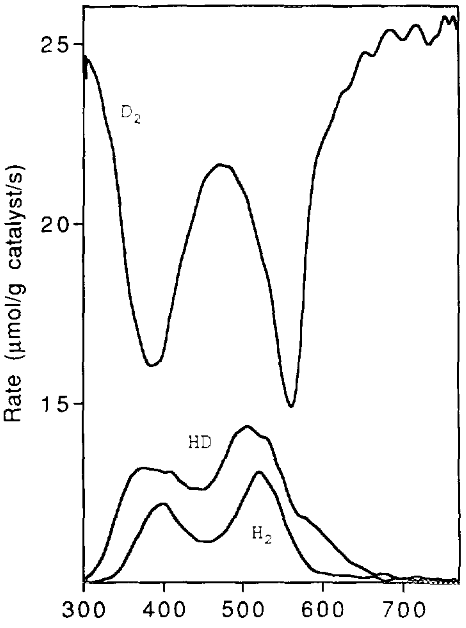

FIG. 2. TPR spectra in 3% D_2/97% Ar flow for 3 µl CH_3OH adsorbed on 5.1% Ni/Al_2O_3 at 300 K in H_2 flow. The D_2, HD, and H_2 signals are shown.

As shown in Fig. 2, H_2 and HD desorbed in two distinct peaks from Ni/Al_2O_3 when TPR of adsorbed CH_3OH was carried out in 3% D_2 flow. The H_2 and HD peaks near 400 K were accompanied by significant D_2 consumption, which was attributed to exchange with adsorbed CH_3OH, as will be discussed later. The D_2 consumption peak near 580 K approximately coincided with the formation of CD_4 (Fig. 1). The amount of D_2 consumed appeared larger than the amount needed to form HD, CD_4, and D_2O, but accurate measurements were complicated by calibrations. The HD calibration was taken as an average of the H_2 and D_2 calibrations, and as D_2 was consumed all calibrations changed so that the H_2, HD, and D_2 signals are only qualitative measurements of the surface processes. When 10% D_2 was used during TPR and less CH_3OH was adsorbed, the fraction of the D_2 flow consumed was smaller and mass balances were better.

Deuterated methanol adsorbed on nickel/alumina. The use of isotopically labeled methanol (CH_3OD) allows us to determine if the methyl and hydroxyl hydrogens exhibit different behavior during TPR. When TPR of adsorbed CH_3OD was carried out in H_2 flow, D_2 and HD peaks were observed near 365 K, but neither HD nor D_2 desorbed above 400 K. When TPR of adsorbed CH_3OD was carried out in 100% D_2 flow, neither H_2 nor HD formed *below* 400 K, and as shown in Fig. 3, HD and H_2 formed in peaks centered at 510 K. For the high concentration of D_2 in the gas phase, mostly HD formed and the methane product was mostly CD_4.

Coadsorbed methanol and carbon monoxide on nickel/alumina. When CH_3OH and ^{13}CO were coadsorbed on

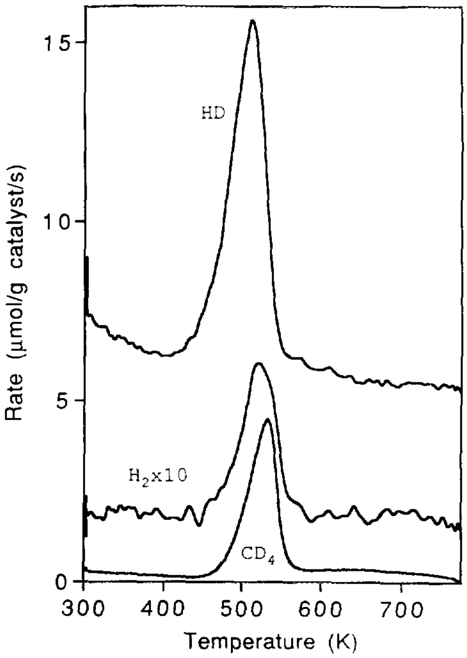

FIG. 3. TPR spectra in D_2 flow of H_2, HD, and CD_4 for adsorption of 1 µl CH_3OD on 5.1% Ni/Al_2O_3 at 300 K in H_2 flow.

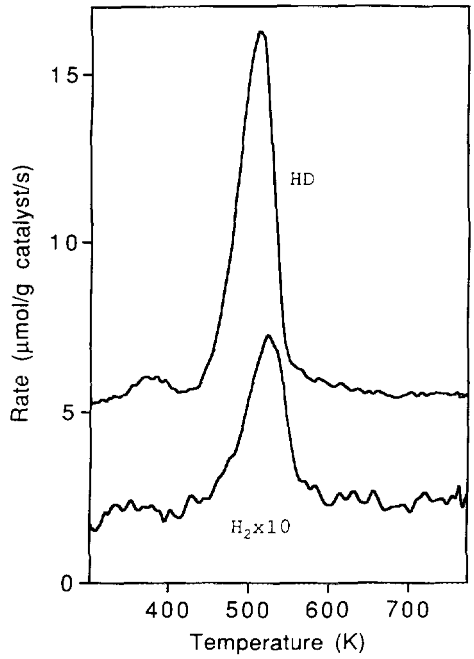

FIG. 4. TPR spectra of H_2 and HD from TPR in D_2 flow over 5.1% Ni/Al_2O_3. Approximately 1 μl $^{12}CH_3OH$ was adsorbed at 300 K and then ^{13}CO was adsorbed at 300 K in D_2 flow.

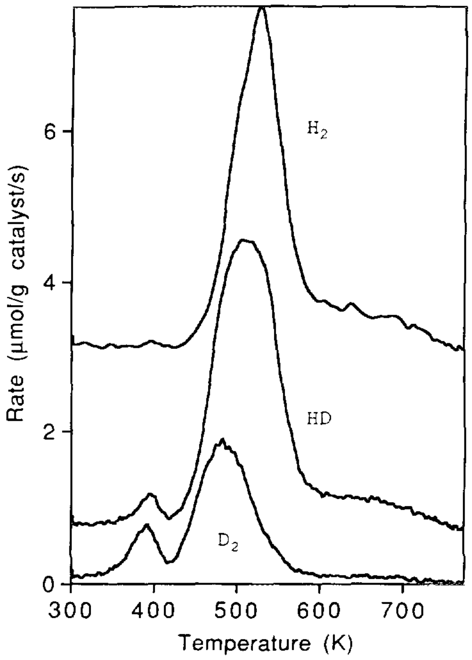

FIG. 6. TPD spectra of H_2, HD, and D_2. After CH_3OH was adsorbed on 5.1% Ni/Al_2O_3 at 300 K in H_2 flow, a TPR experiment in D_2 flow was interrupted at 445 K and the sample rapidly cooled prior to the TPD in Ar flow.

Ni/Al_2O_3 at 300 K (CH_3OH adsorbed first), HD and H_2 formed in essentially one peak during TPR in 100% D_2 flow. As shown in Fig. 4, the peak maximum was at approximately 510 K and most of the dihydrogen was HD. The $^{12}CD_4$ signal (Fig. 5) was the same as that observed when CH_3OH was adsorbed alone. The $^{13}CD_4$ (Fig. 5) formed in two distinct peaks, due to hydrogenation of ^{13}CO adsorbed on Ni (lower-temperature peak) and spillover to form $^{13}CH_3O$, which was then hydrogenated to $^{13}CH_4$ (1). The high-temperature $^{13}CD_4$ peak is similar in shape and location to the $^{12}CD_4$ peak. As shown in Fig. 5, only a small amount of ^{13}CO desorbed, unreacted, in two distinct peaks, and ^{12}CO formed one peak.

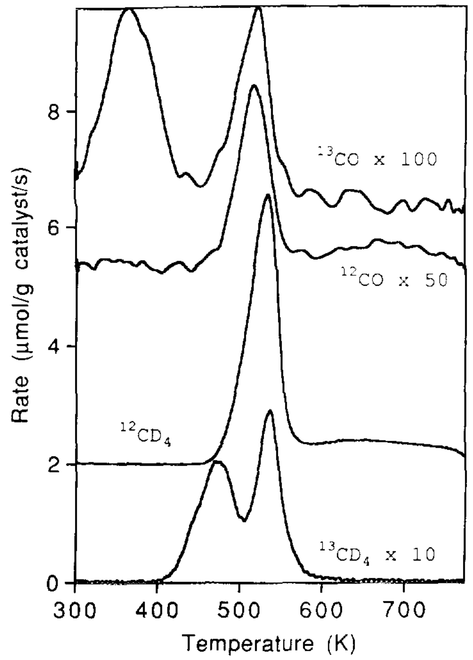

FIG. 5. TPR spectra of ^{12}CO, ^{13}CO, $^{12}CD_4$, and $^{13}CD_4$ for same experiment as in Fig. 4.

Interrupted TPR and TPD on nickel/alumina. An interrupted TPR was carried out on Ni/Al_2O_3 by adsorbing CH_3OH at 300 K and then raising the catalyst temperature in D_2 flow only to 445 K before cooling the catalyst. This temperature corresponds to that where the first D_2 consumption peak (Fig. 2) was essentially complete. A TPD spectrum was then obtained, by raising the catalyst temperature in Ar flow, to determine what species remained on the surface. As shown in Fig. 6, H_2, HD, and D_2 desorbed during the TPD. Carbon monoxide formed in a peak near the H_2 peak (7), but for clarity it is not included. The D_2, HD, and H_2 peaks have maximum at 480, 520, and 526 K, respectively. In addition, HD and D_2 exhibited small peaks below 400 K.

Interrupted TPR of adsorbed CH_3OH was carried out in H_2 flow to a higher temperature (480 K) before cooling, and the subsequent TPD in He flow is shown in Fig. 7. As reported previously for a normal TPD following CH_3OH

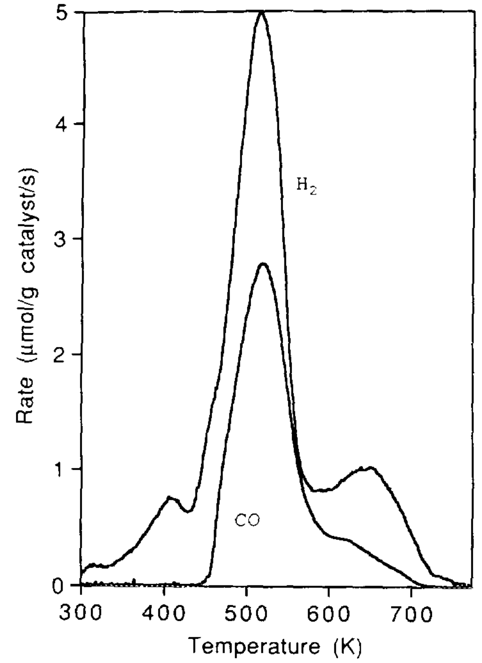

FIG. 7. H_2 and CO TPD spectra on 5.1% Ni/Al_2O_3 following CH_3OH (1 µl) adsorption at 300 K, and interrupted TPR in H_2 flow to 480 K.

adsorption (7), CO and H_2 desorbed simultaneously, with a large peak near 500 K and a smaller peak near 650 K. As the result of the interrupted TPR, a small H_2 peak was also observed at 410 K. When the interrupted TPR procedure to 480 K was repeated but CO was adsorbed in H_2 flow at 300 K prior to TPD, the H_2 peak at 410 K was absent.

CO and H_2 (D_2) Coadsorption on Nickel/Alumina

When CO and D_2 were coadsorbed at 385 K on Ni/Al_2O_3, CD_3O formed on the Al_2O_3 support by a spillover process (1, 11). During TPR in 100% H_2, the methane produced was 98% CH_4, and even for TPR in 5% H_2/95% Ar, 95% of the methane was CH_4. The remainder was CH_3D. As shown in Fig. 8, CH_4 formed in two distinct peaks due to hydrogenation of CO on Ni (low-temperature peak) and hydrogenation of methoxy on Al_2O_3 (high-temperature peak) (1). Both HD and D_2 formed during TPR in two distinct peaks (450 and 510 K) as shown in Fig. 8. The HD signal was 10 times the D_2 signal, but the peak shapes were identical.

Interrupted TPR and TPD. The following procedure was used to study adsorbed CH_3O and Ni/Al_2O_3:

(1) CO + H_2 coadsorption at 385 K for 30 min
(2) Interrupted TPR in 100% H_2
(3) Rapid cooling to 300 K
(4) TPD in He flow

The coadsorption step formed CH_3O on Al_2O_3 and also resulted in CO adsorbed on the Ni surface (12). The interrupted TPR removed some CO from the Ni surface, either by forming gaseous CH_4 or by spillover to form additional CH_3O on the Al_2O_3 surface. Figures 9 and 10 show the H_2 and CO desorption obtained during the TPD experiments for interruption temperatures between 300 and 500 K. In addition, CO_2 and CH_4 formed, and in each case their total amount was less than 25% of the amount of CO that desorbed. Methane formed in a peak between 543 and 550 K, and CO_2 formed on a peak near 670 K, with a smaller peak at 520 K.

Hydrogen desorbed in three distinct peaks (Fig. 9), and the low-temperature peak was not observed in the absence of an interrupted TPR. As shown in Table 1 and Fig. 9, the peak temperature and the amount of the low-temperature peak increased as the interruption temperature increased. The peak temperatures of the other two peaks remained relatively constant. The H_2 peaks at 525 and 600 K result from decomposition of CH_3O (11, 12) and thus are accompanied by CO formation (Fig. 10). As the interruption temperature was increased, the onset temperature for CO desorption increased. The peak temperatures for CO desorption remained almost constant.

Similar results were obtained when CD_3O was formed by coadsorption of CO and D_2 at 385 K. Figure 11 shows the TPD spectra obtained when interrupted TPR in D_2 flow was carried out to 480 K before the TPD. Three D_2 desorption peaks were observed that were similar to the

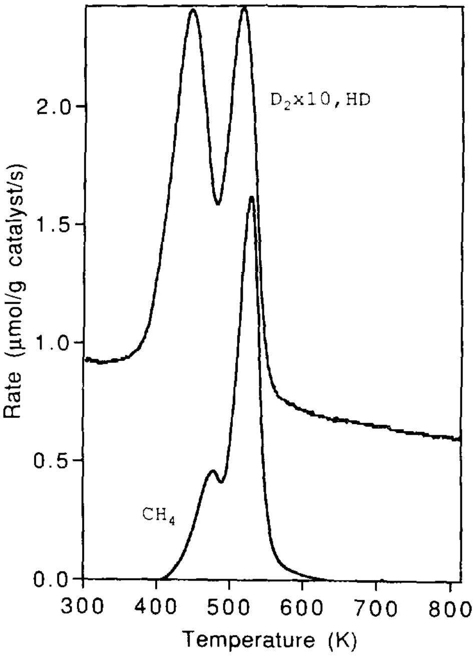

FIG. 8. TPR spectra in 100% H_2 flow for CO and D_2 coadsorbed at 385 K for 20 min. Only the HD, D_2, and CH_4 signals are shown.

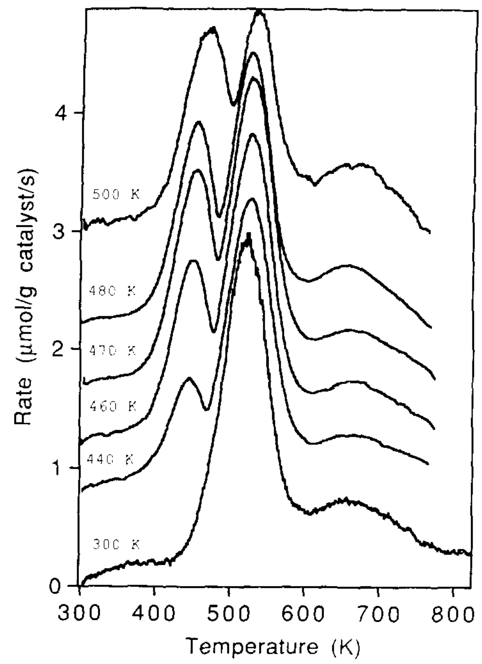

FIG. 9. H_2 TPD spectra on 5.1% Ni/Al_2O_3 for CO adsorbed at 385 K for 30 min in H_2 flow. An interrupted TPR in H_2 was carried out to the indicated temperature prior to TPD.

H_2 peaks in Fig. 9. A small amount of HD formed, apparently due to H_2 and HD impurities in the D_2.

In a separate experiment, CO and H_2 was coadsorbed at 385 K, but interrupted TPR was carried out in D_2 flow, and only to 400 K. As expected from the spectra in Fig. 8, not much HD or H_2 formed during the TPR to 400 K. A subsequent TPD showed no low temperature H_2 or HD peak and only a small amount of HD formed, near 500 K.

TABLE 1

Amounts Desorbed during TPD after Interrupted TPR in H_2

Interruption temperature (K)	Amounts desorbed (μmol/g catalyst) Total H_2	H_2 low-temperature peak	CO	CH_4	CO_2
500	326	132	108	6	22
480	337	112	132	5	20
470	376	124	164	11	16
460	380	108	173	12	20
440	335	68	170	13	15
300 (No Interrupt)	296	0	171	13	15

Note. H_2 + CO were coadsorbed at 385 K.

Displacement from the nickel surface. To study the low temperature H_2 peak in Fig. 9, the following procedure was used:

(1) CO and H_2 coadsorption at 385 K for 30 min
(2) Interrupted TPR in H_2 to 480 K
(3) Rapid cooling to 300 K

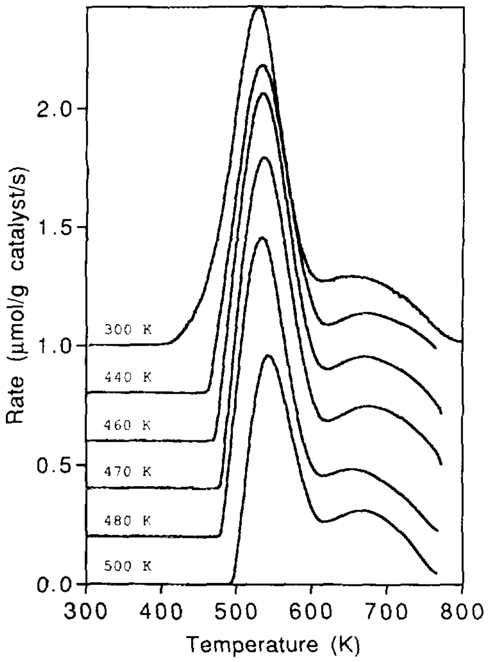

FIG. 10. CO TPD spectra for the same conditions as Fig. 9.

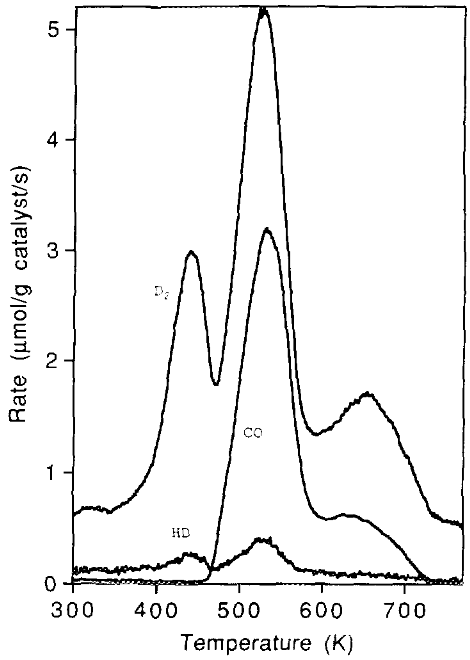

FIG. 11. TPD spectra for D_2, CO, and HD for CO and D_2 coadsorbed at 385 K for 30 min on 5.1% Ni/Al_2O_3. Prior to TPD, interrupted TPR was carried out to 480 K in D_2 flow.

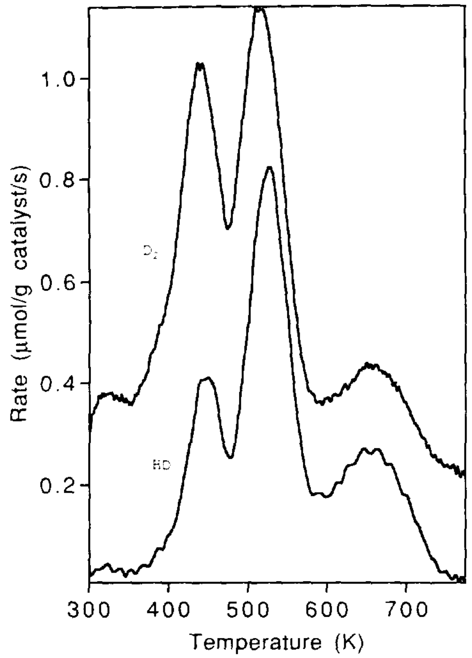

FIG. 12. D_2 and HD spectra for TPD when CO and H_2 were coadsorbed at 385 K for 30 min on 5.1% Ni/Al_2O_3. Prior to TPD, interrupted TPR was carried out to 480 K in D_2 flow.

(4) D_2 flow at 300 K
(5) TPD in He flow

The D_2 exposure was used in order to exchange any hydrogen adsorbed on Ni with deuterium. However, the H_2 TPD spectrum was the same as that in Fig. 9 for an interruption temperature of 480 K. A total of 19 μmol HD/g catalyst also desorbed below 500 K.

In a similar experiment, step 4 was replaced by ^{13}CO exposure at 300 K. As reported previously (11,12) for ^{13}CO adsorption after $^{12}CH_3O$ formation, ^{13}CO desorbed in a peak at 475 K. However, in contrast to Fig. 9, the low-temperature H_2 peak was absent and the total amount of H_2 desorption was lower by 13 μmol/g catalyst. The H_2 peak at 525 K was larger and broader than in Fig. 9.

Interrupted TPR, exchange, and TPD. The following procedure was used to study the interaction between CH_3O and D_2:

(1) CO and H_2 coadsorption at 385 K for 30 min
(2) Interrupted TPR in D_2 flow to 480 K
(3) Rapid cooling to 300 K
(4) TPD in He flow

During the interrupted TPR, 26% of the original CH_3O was hydrogenated to methane. As shown in Fig. 12, both D_2 (140 μmol/g catalyst) and HD (100 μmol/g catalyst) desorbed in three peaks during TPD. The amount of H_2 that desorbed was insignificant. Approximately 73% of the total hydrogen atoms (H + D) leaving the surface was deuterium.

DISCUSSION

Hydrogen Exchange with Methanol

Two distinct HD and H_2 peaks are observed during TPR in D_2 flow of adsorbed CH_3OH on Ni/Al_2O_3. These peaks are attributed to exchange between D_2 and CH_3OH for the following reasons:

- As HD and D_2 form, D_2 is consumed (Fig. 2) and no other deuterium-containing products are observed until CD_4 forms.
- During TPD, CH_3OH does not start to decompose on Ni/Al_2O_3 to form H_2 and CO at a significant rate until 450 K (7). During TPR, CH_3OH decomposition is inhibited. Thus, the HD and H_2 signals below 450 K cannot be due to CH_3OH decomposition.
- TPD experiments carried out after interrupted TPR in D_2 flow show that D_2 and HD form at approximately the same temperatures as H_2 and CO (Fig. 6). Since previous TPD studies of CH_3OH (7), without interrupted TPR, show that CH_3OH decomposes to form H_2 and CO simultaneously, Fig. 6 indicates that D is incorporated into adsorbed CH_3OH during interrupted TPR. These experiments provide a direct measure of the composition of the resulting adsorbed species after exchange. The HD and D_2 products are the result of decomposition of $CH_xD_{3-x}OH$ and $CH_xD_{3-x}OD$.

Exchange between gas-phase D_2 and adsorbed CH_3OH apparently occurs by a hydrogen spillover process. Methanol is adsorbed on the Al_2O_3 surface (7, 9) and D_2 adsorbs dissociatively on the Ni surface. Direct exchange between gas-phase D_2 and adsorbed CH_3OH is concluded to be much slower because:

- For CH_3OH adsorbed on Al_2O_3 without Ni, a significant amount of D_2 was only consumed above 550 K. In contrast, D_2 consumption starts at 300 K for CH_3OH adsorbed on Ni/Al_2O_3.
- Exchange between D_2 and CH_3OH is much slower on Ni/Al_2O_3 when CO is adsorbed on the Ni surface (Fig. 4). Adsorbed CO inhibits D_2 adsorption on Ni and thus inhibits exchange. As a result, the low-temperature HD and H_2 exchange peaks are absent. Since the experiment with coadsorbed CH_3OH and ^{13}CO was carried out in 100% D_2, ^{13}CO is very effective at inhibiting exchange. The low-temperature exchange occurs even in 3% D_2 when CO is not coadsorbed with CH_3OH. At higher temperatures CO is removed by hydrogenation and thus exchange takes place.

Most likely the D atoms on Ni spill over and diffuse to adsorbed CH_3OH and exchange occurs on the Al_2O_3 surface. Hydrogen spillover has been reported to be fast even at room temperature by Ioannides and Verykios (13). They observed that exposure of a Ru/Al_2O_3 catalyst that had benzene adsorbed on the Al_2O_3 support formed cyclohexane at 298 K. Spillover hydrogen reacted with benzene to hydrogenate it at 298 K. It is possible, however, that adsorbed CH_3OH diffuses to the Ni/Al_2O_3 interface to exchange. This diffusion may be more important as the temperature increases, since CH_3OH decomposes on Ni/Al_2O_3 by diffusing along the Al_2O_3 surface to the Ni/Al_2O_3 interface (7).

For TPR in D_2 flow, two HD and H_2 peaks are observed for adsorbed CH_3OH (Fig. 2) but only the high-temperature peaks are observed for adsorbed CH_3OD (Fig. 3). These experiments show that the low-temperature peaks (near 400 K) are due to exchange of the hydroxyl hydrogens since exchange between D_2 and the deuterated-labeled hydrogens in CH_3OD will not create HD or H_2 peaks. Similarly, for TPR in H_2 flow for adsorbed CH_3OD, only the low-temperature peaks are observed, and neither HD nor D_2 desorbed above 400 K. Therefore, the exchange peaks near 525 K are due to exchange of the methyl hydrogens. Therefore, hydroxyl hydrogen in methanol exchange much faster than methyl hydrogens, and hydrogen spillover is sufficiently fast so that the hydroxyl hydrogens exchange by 400 K.

The rate of hydrogen exchange with the methyl groups in adsorbed methanol appears to be faster than the rate of methanol hydrogenation to form methane. Only a small amount of methane forms during interrupted TPR in H_2 flow to 445 K, for example, but a subsequent TPD (Fig. 6) shows that approximately 40% of the desorbing hydrogen is labeled with deuterium in the form of either HD or D_2.

Our findings are consistent with those reported by Guczi *et al.* (14, 15). They observed that D_2 exchanges with CH_3OH much faster on Pt/Al_2O_3 than on Al_2O_3 or on Pt black. They concluded that Pt is required to dissociate D_2 and also that Pt cleaves the CH bond in CH_3O when it is adsorbed on an adjacent Al^+ site. That is, they concluded that methoxide species are held on Lewis sites of Al_2O_3 and the CH_3 group can interact with the Pt. They stated that the majority of multiple exchanges take place at a metal–support perimeter. Unlike the studies of Guczi *et al.*, we did not have gas-phase CH_3OH present during exchange, and thus we have shown that CH_3OH adsorbed on Al_2O_3 exchanges with H_2 adsorbed on the Ni. Thus, even CH_3OH that is not near the Ni–Al_2O_3 perimeter exchanges. The metal–support perimeter is important for this exchange, but we cannot determine whether exchange takes place at the perimeter or H diffuses onto the Al_2O_3 surface.

Guczi *et al.* observed that OH groups in CH_3OH exchange 2–3 orders of magnitude faster than CH_3 groups on their Pt/Al_2O_3 catalysts. We also see large differences in exchange rates on Ni/Al_2O_3. The peak temperatures of HD and H_2 peaks were used to *estimate* activation energies for OH exchange (108 kJ/mol) and CH_3 exchange (144 kJ/mol). These energies were obtained by assuming a preexponential factor of $10^{13}\ s^{-1}$ and exchange rates were then calculated from these energies. The ratio of rates of OH to CH_3 exchange is 6×10^4 at 400 K and 6×10^3 at 500 K. These differences in exchange rates are similar to those reported by Guczi *et al.*, who also reported that CH_3 exchange has a higher activation energy. In order for exchange to occur rapidly, spillover must be rapid, and thus these exchange experiments provide a lower limit on the rate of spillover of H atoms from nickel to alumina.

Coadsorbed H_2 and CO

Similar processes take place during TPR for coadsorbed CO and H_2 (D_2) as for adsorbed CH_3OH. As shown previously (1, 7, 11), CO and H_2, when coadsorbed at 385 K on Ni/Al_2O_3, form CH_3O on the Al_2O_3 support. During TPR in 100% H_2, the D atoms in coadsorbed CO + D_2 exchange with gas-phase H_2 to form HD and D_2 in two distinct peaks (Fig. 8). As shown in Fig. 9 for TPD without interrupted TPR (300 K interruption temperature) CH_3O formed from CO and H_2 does not start decomposing until 450 K, whereas exchange starts below 400 K (Fig. 8). The exchange peaks are not at the same temperature for CH_3OH as for coadsorbed CO and D_2. The low-temperatures peak in Fig. 8 is at a significantly higher temperature than the low-temperature peak in Fig. 2. This difference is not due to the presence of CO adsorbed on Ni when CO and H_2 are coadsorbed. The same TPR spectra as Fig. 8 were obtained when the catalyst was held in D_2 for 30 min, after CO + D_2 adsorption, in order to remove CO from Ni. The differences in the hydrogen-exchange spectra during TPR indicate that adsorbed CH_3OH and coadsorbed CO + H_2 do not form identical surface species on Al_2O_3. In addition to the different exchange properties, a low-temperature H_2 desorption peak is seen during TPD of coadsorbed CO + H_2 (Fig. 9), but is not seen during TPD of adsorbed CH_3OH. This H_2 desorption will be discussed in the next section.

As seen for adsorbed CH_3OH, exchange with CH_3O is faster than hydrogenation to methane. When an interrupted TPR in D_2 flow is carried out to 480 K, after CO and H_2 are coadsorbed at 385 K, 73% of the hydrogen that desorbs during TPD (Fig. 12) is deuterated. Since only 26% of the original CH_3O is removed during TPR, exchange is faster than hydrogenation during interrupted TPR. The TPD experiment is an effective means to determine how much deuterium is incorporated into the adsorbed species. Note that more of the H in Fig. 12 is in the high-temperature peak, as expected since the species responsible for the low-temperature peak exchanges more rapidly.

Hydrogen Desorption

The low-temperature exchange peak observed during TPR following CO + D_2 coadsorption (Fig. 8) occurs at a similar temperature to the low-temperature H_2 TPD peak that was seen for TPD after interrupted TPR in H_2 flow (Fig. 9). The low-temperature H_2 peak in Fig. 9 is not due to desorption of H_2 that is adsorbed on Ni because the amount is significantly larger than what adsorbs on the Ni surface. Also, exposing the catalyst to D_2 at 300 K after interrupted TPR did not cause the species responsible for the low-temperature TPD peak to exchange, whereas H_2 adsorbed on Ni readily exchanges with gas-phase D_2 at 300 K. Thus, the species responsible for the low-temperature H_2 exchange peak is not H on Ni. Moreover, since this H_2 peak is at a lower temperature than methyl hydrogens of adsorbed CH_3OH exchange, this hydrogen is not part of adsorbed CH_3O. A small HD peak (15 μmol/g catalyst) was seen below 500 K and this peak is attributed to desorption from the Ni surface. Since 26 μmol CO/g catalyst adsorbs on the Ni surface of this catalyst, the amount of HD desorbing from Ni is reasonable.

Figure 8 shows that two CH_4 peaks are present during TPR of coadsorbed CO + H_2 (or D_2), and as has been shown previously (1), the CH_4 peak at 480 K is due to hydrogenation of CO adsorbed on Ni. During CO + H_2 coadsorption at 385 K, and during the subsequent cooling, some CO remains on the Ni surface. As can be seen from Fig. 8, interrupted TPR to 440 K and higher removes some of this CO from Ni by forming CH_4. In addition, some of this CO is converted to CH_3O, which remains on the Al_2O_3 surface. Thus, the TPD spectra in Fig. 9 at successively higher temperatures correspond to lower CO coverages on Ni. When ^{13}CO is adsorbed after interrupted TPR, the low-temperature H_2 desorption peak is absent, and more H_2 desorbs at higher temperature instead. The total amount of H_2 desorption decreases by 13 μmol/g catalyst when ^{13}CO is adsorbed; this amount corresponds approximately to the amount of Ni surface atoms.

In contrast, CH_3OH adsorption does not form CO on Ni, as evidenced by the lack of a low-temperature CH_4 peak during TPR. Instead, CH_3OH adsorbs only on the Al_2O_3 surface (9). Despite the absence of CO on Ni, a low-temperature H_2 peak is not observed during TPD of CH_3OH, even when the same interrupted TPR procedure is used prior to TPD. Thus, the low-temperature H_2 TPD peak in Fig. 9 indicates that CH_3OH and CO + H_2 do not form identical species on the Al_2O_3 surface.

The low-temperature H_2 TPD peak is concluded to be desorption of H_2 that is coadsorbed on the Al_2O_3 surface with CH_3O. Since this low-temperature H_2 peak is not accompanied by simultaneous desorption of CO, formation of this H_2 is not limited by decomposition of CH_3O. In contrast, the H_2 peak at 525 K is accompanied by simultaneous desorption of CO and thus represents CH_3O decomposition. Apparently H_2 in the low-temperature peak desorbs by first undergoing reverse spillover. Carbon monoxide adsorbed on the Ni surface inhibits reverse spillover, and thus in the presence of adsorbed CO, this H_2 desorbs at the same temperature that CH_3O decomposes. The higher pressure of H_2 during the interrupted TPR apparently inhibits this reverse spillover since many of the interrupt temperatures are above the peak temperatures of the low-temperature H_2 peaks observed during TPD.

CONCLUSIONS

Both methyl and hydroxyl hydrogens of CH_3OH adsorbed on the Al_2O_3 support of Ni/Al_2O_3 exchange with hydrogen atoms adsorbed on the Ni. Hydroxyl hydrogens exchange several orders of magnitude more rapidly than methyl hydrogens, and both types of exchange are faster than the rate that CH_3OH hydrogenates to CH_4. Temperature-programmed reaction allows the exchange steps and the reaction to be separated in time. Exchange takes place by spillover of H from the Ni surface and these experiments provide a lower limit on the rate of spillover of H atoms on Ni/Al_2O_3. Carbon monoxide adsorbed on Ni significantly inhibits exchange of the hydroxyl hydrogens. Methoxy formed from coadsorption of CO and H_2 at 385 K also exhibits two distinct exchange processes, but CH_3OH and coadsorbed CO + H_2 do not form identical species on the Al_2O_3 surface. An additional H_2 desorption peak observed when CO + H_2 are coadsorbed on Ni/Al_2O_3 results from H adsorbed on the Al_2O_3 surface.

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REFERENCES

1. Glugla, P. G., Bailey, K. M., and Falconer, J. L., *J. Phys. Chem.* **92,** 4474 (1988).
2. Sen, B., and Falconer, J. L., *J. Catal.* **117,** 404 (1989).
3. Kester, K. B., and Falconer, J. L., *J. Catal.* **89,** 380 (1984).
4. Sen, B., Falconer, J. L., Mao, T.-F., Yu, M., and Flesner, R. L., *J. Catal.* **126,** 465 (1990).
5. Matsushima, T., and White, J. M., *J. Catal.* **44,** 183 (1976).
6. Rossi, P. F., Busca, G., and Lorenzelli, V., *Z. Phys. Chem. NF* **149,** 99 (1986).
7. Chen, B., and Falconer, J. L., *J. Catal.* **144,** 214 (1993).
8. Falconer, J. L., and Schwarz, J. A., *Catal. Rev. Sci. Eng.* **25,** 141 (1983).

9. Chen, B., and Falconer, J. L., *J. Catal.* **147,** 72 (1994).
10. Chen, B., Falconer, J. L., and Chang, L., *J. Catal.* **127,** 732 (1991).
11. Glugla, P. G., Bailey, K. M., and Falconer, J. L., *J. Catal.* **115,** 24 (1989).
12. Flesner, R. L., and Falconer, J. L., *J. Catal.* **133,** 515 (1992).
13. Ioannides, T., and Verykios, X. E., *J. Catal.* **143,** 175 (1993).
14. Guczi, L., Hoffer, T., and Tetenyi, P., *Chem. Eng. Commun.* **83,** 75 (1989).
15. Hoffer, T., and Guczi, L., *J. Mol. Catal.* **70,** 85 (1991).