JOURNAL OF CATALYSIS 113, 444–452 (1988)

Detection of Activated Adsorption Sites and a CO–H Surface Complex on Ru/Al_2O_3

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Received February 1, 1988; revised May 4, 1988

Temperature-programmed reaction and desorption (TPR, TPD), in combination with isotope labeling of CO, identified the existence of two distinct reaction sites for CO hydrogenation on Ru/Al_2O_3 catalysts. These sites are similar to those previously reported on Ni/Al_2O_3 catalysts. Carbon monoxide adsorbs on Ru crystallites at 300 K; at higher temperatures, in an activated process that requires H_2, CO transfers to the Al_2O_3 to form a CO–H complex, with the stoichiometry of a methoxy species. This transfer process is significantly slower than that on Ni/Al_2O_3. The decomposition of the CO–H complex limits the rate of CH_4 formation for the second peak seen in TPR. The first peak is due to hydrogenation of the CO absorbed on Ru. The similarities to Ni/Al_2O_3 catalysts imply that an aluminate is not required for multiple reaction sites on Ni/Al_2O_3. © 1988 Academic Press, Inc.

INTRODUCTION

Previous work in this laboratory has clearly shown that two distinct reaction sites are present for CO hydrogenation to methane on Ni/Al_2O_3 catalysts (*1–4*). These sites were identified with temperature-programmed reaction (TPR), (*1, 2*), and isotope labeling was used to separate the sites on the surface (*3*). One site was attributed to the presence of a reduced Ni phase, and the other to an oxygen-containing phase (*1, 2*). Huang *et al.* (*5*) concluded that this oxide phase is a surface aluminate, since they detected the presence of nickel aluminate with XPS.

One objective of the present study on Ru/Al_2O_3 was to determine if an aluminate was needed for multiple sites in CO hydrogenation. Consequently, Ru was used because it does not form a bulk aluminate but has a methanation activity comparable to that of Ni. Another objective was to determine if multiple sites are a more general phenomena on supported catalysts. Previous TPR studies did not observe multiple sites on Ru/Al_2O_3, but occupation of the oxide-containing phase on Ni/Al_2O_3 is activated (*1, 3*), and thus appropriate conditions may not have been used previously for Ru/Al_2O_3.

Since multiple reaction sites are present on Ni/Al_2O_3 but not on Ni/SiO_2 (*1, 6, 7*), an Al_2O_3 support was used for the Ru. Temperature-programmed reaction was used with isotope labeling and mass spectrometric detection to separate reaction sites. The effects of reduction temperature, adsorption temperature, and interrupted reaction were determined. Reaction was interrupted during heating, after some of the adsorbed CO had reacted, as an aid in labeling sites with different isotopes. Temperature-programmed desorption (TPD) following coadsorption of CO and H_2 provided insight into the bonding of the adsorbed CO. Previous TPD studies on Ni/Al_2O_3 by Glugla *et al.* (*4*) showed that the oxide site contained coadsorbed CO and H in a complex with the stoichiometry of a methoxy species.

The TPD and TPR experiments on Ru/Al_2O_3 show that two reaction sites are present, but adsorption on one site is activated, and thus it was not occupied in previous TPR experiments. Moreover, the sites have similar activities and thus are difficult to detect without isotope labeling.

0021-9517/88 $3.00

As observed on Ni/Al_2O_3, a CO–H complex with the stoichiometry of a methoxy species was also seen on Ru/Al_2O_3. The presence of these sites on Ru/Al_2O_3 and the ratio of adsorbed CO to total Ru atoms indicate that $NiAl_2O_4$ is probably not responsible for the oxide-phase sites on Ni/Al_2O_3 catalysts. Instead, the sites associated with an oxide are probably on the Al_2O_3 support.

EXPERIMENTAL METHODS

Catalyst Preparation

A 1% Ru/Al_2O_3 catalyst was prepared by impregnation of 60–80 mesh Al_2O_3 (Kaiser A-201) to incipient wetness with an aqueous solution of $RuCl_3 \cdot 1.7H_2O$. The catalyst was dried under vacuum at 410 K, heated in H_2 flow to 373 K at 1.5 K/min, and then held at 373 K for 1 h. The temperature was then increased to 523 K at 1.5 K/min and held in H_2 at 523 K for 1 h. Finally, the catalyst was heated to 623 K, at 1.5 K/min, and held there for 1 h. The catalyst was then cooled to room temperature and passivated in a 1% air in He mixture. The metal loading was determined by atomic absorption.

Temperature-Programmed Reaction and Desorption

Apparatus. The temperature-programmed reaction and desorption experiments were carried out in a tubular, quartz reactor that contained a quartz frit on which the catalyst sample (100 mg) was placed. A Chromel–Alumel thermocouple, positioned in the catalyst bed, was used to monitor the temperature and provide feedback to the proportional-derivative temperature programmer. The reactor effluent was analyzed immediately downstream by a computer-controlled UTI quadrupole mass spectrometer, which could monitor the signal from up to 20 mass peaks. The catalyst temperature was simultaneously recorded by the computer. Further details regarding the experimental apparatus, the purification of gases, and computer interfacing are given elsewhere (*1, 8–10*).

Temperature-programmed reaction. The catalyst was reduced in pure H_2 (98 standard cm^3/min) for 1 h at 550, 775, or 925 K prior to each TPR. It was then cooled in H_2 to either 300 or 385 K and held there while the adsorbate gas, 10% CO in He, was pulsed into the flowing H_2. For adsorption at 385 K, 2 pulses/min (0.5 ml/pulse) of CO were injected over the catalyst bed for 50 min. This procedure was used because the surface appeared to saturate after 2 pulses, but after a 1-min wait was able to adsorb additional CO. This process was referred to as pumping (*3*). At 300 K, 2 pulses/min of CO were injected for 11 min. These adsorption procedures (*3*) ensured saturation coverages of CO at these temperatures, as determined by measuring the effluent CO from the reactor during pulsing. Following CO adsorption, the catalyst was heated in flowing H_2 at approximately 1 K/s to either 775 or 925 K (depending on the reduction temperature chosen for the next TPR) while continuously monitoring *m/e* signals at 15 (CH_4), 28 (CO), 31, 32, 33, 44, 45, and 46 (hydrocarbons) with the mass spectrometer. In one experiment CO was adsorbed in pure He at 385 K, and the catalyst was cooled in He to 300 K before heating in H_2.

Temperature-programmed desorption. A procedure similar to TPR was followed for TPD except that subsequent to CO adsorption in H_2, the carrier gas was switched to He at 300 K. The catalyst was held in He for 10 min and then heated to 775 K at 1 K/s. Desorption and reaction products for *m/e* signals at 2 (H_2), 15 (CH_4), 28 (CO), 44 (CO_2), 31, 32, 33, 45, and 46 (hydrocarbons) were monitored. This experiment is not a standard TPD, but is TPD of coadsorbed CO and H_2.

Isotope labeling. Interrupted TPR was used in an attempt to occupy one surface site with ^{12}CO and the other with ^{13}CO, as done on Ni/Al_2O_3 (*3*). After reducing the catalyst for 1 h at 773 K, ^{12}CO was adsorbed in H_2 at 385 K (2 pulses/min for 50 min) to saturate all surface sites. The catalyst was then cooled to 300 K in H_2. In order to ensure saturation of the catalyst surface, 10 more pulses of ^{12}CO were injected into the flowing H_2 stream. The subsequent TPR was interrupted at different temperatures, after some $^{12}CH_4$ had formed, in order to vary the coverage of adsorbed ^{12}CO. The catalyst was then cooled to 300 K in H_2, and 10 pulses of ^{13}CO were injected into the H_2 stream. Following this a complete TPR was performed and the *m*/*e* signals at 15 ($^{12}CH_4$), 17 ($^{13}CH_4$), 28 (^{12}CO), and 29 (^{13}CO) were continuously monitored.

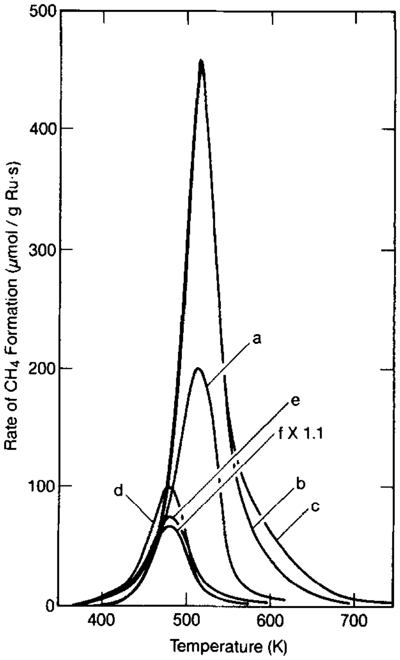

FIG. 1. Methane spectra for TPR of adsorbed CO on 1% Ru/Al_2O_3. Reduction temperature, adsorption temperature, gas present during CO adsorption: (a) 550 K, 385 K, H_2; (b) 775 K, 385 K, H_2; (c) 925 K, 385 K, H_2; (d) 775 K, 300 K, H_2; (e) 925 K, 300 K, H_2; (f) 775 K, 385 K, He.

RESULTS

Temperature-Programmed Reaction

The CH_4 produced from TPR of adsorbed CO are shown in Fig. 1 for three reduction temperatures and two adsorption temperatures (300 and 385 K). The CO was adsorbed in H_2 flow, except for curve f, where CO was adsorbed in He and then the gas was switched to H_2 for TPR.

Regardless of the temperature at which the catalyst was reduced, CO adsorption at 300 K yielded a single CH_4 peak at 478 K, with a half-width from 51 to 56 K. The molar ratio of CH_4 to total Ru was 0.6 (Table 1). Approximately 1% of the CO desorbed without reacting, and the resulting CO spectra did not have any distinct features (Figs. 2d and 2e). A methanation activation energy of 84 kJ/mol was estimated from half-width measurements for a first-order process.

The CH_4 and unreacted CO spectra ob-

TABLE 1

TPR of Adsorbed CO from 1% Ru/Al_2O_3

Reduction temperature (K)	CO Adsorption temperature[a] (K)	CH_4 peak temperature (K)	Half-width (K)	CH_4 produced		Unreacted CO $\left(\frac{\mu mol}{g\ cat}\right)$
				$\left(\frac{\mu mol}{g\ cat}\right)$	$\left(\frac{mol\ CH_4}{mol\ Ru}\right)$	
550	385	515	46	128	1.3	11
775	385	515	49	272	2.8	24
925	385	515	49	285	2.9	23
775	300	478	51	61	0.6	0.7
925	300	478	56	55	0.6	0.5
775	385 (He)	478	51	48	0.5	—

[a] CO adsorbed in H_2, except as indicated.

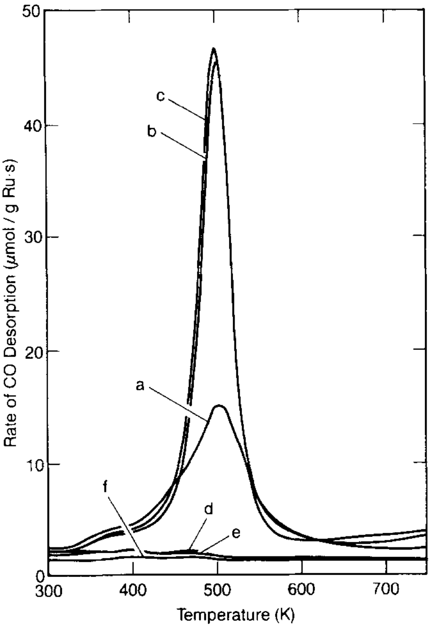

FIG. 2. Desorption of unreacted CO during TPR on 1% Ru/Al_2O_3. Conditions are the same as those in Fig. 1.

tained from TPR by adsoring CO in He at 385 K (Figs. 1f and 2f) had the same features as those for CO adsorption in H_2 at 300 K. As was seen for Ni/Al_2O_3 catalysts (*1*, *10*), less CH_4 formed when CO was adsorbed in He instead of H_2.

When CO was adsorbed in H_2 at 385 K instead of at 300 K, however, the CH_4 spectra were quite different (Fig. 1), and much more CO adsorbed at 385 K. That is, CO adsorption is activated in the presence of H_2. The amount of CH_4 increased four- to fivefold (depending on reduction temperature), and the peak shifted to a higher maximum temperature (515 K). The Ru may not have been completely reduced at 550 K, since significantly more CH_4 formed as the reduction temperature was increased to 775 K. A chlorine impurity from the catalyst precursor may be responsible for this difference, however (*11*). Additional reduction at 925 K had little effect. The molar ratio of CH_4 to total Ru was 1.3 when the catalyst was reduced at 550 K, and 2.8 and 2.9 for reduction at 775 and 925 K, respectively (Table 1). In addition to the large increase in the amount of adsorbed CO for adsorption at 385 K, the fraction of unreacted CO increased, and 8% of the CO desorbed without reacting. The CO formed in a peak near 500 K (Fig. 2). A small mass 45 signal was also seen with a peak above 500 K, but no signals were detected at masses 31, 32, 33, and 46.

Temperature-Programmed Desorption

When CO and H_2 were coadsorbed at 300 K by injecting CO into flowing H_2, the CO appeared to displace most of the H_2 from the surface so that the resulting TPD (heating in He) for the coadsorbed species yielded mostly CO (Fig. 3). Small amounts of H_2 and CO_2 were also seen, but no CH_4 or higher hydrocarbons were detected. The CO desorbed in a broad temperature range from 300 to 770 K, with a peak maximum at

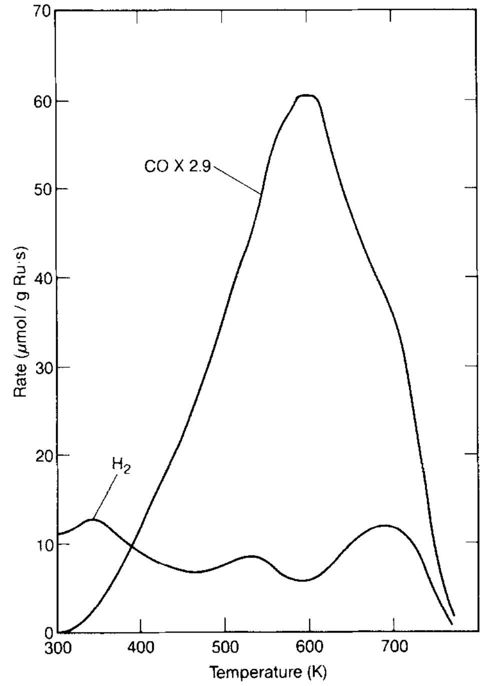

FIG. 3. TPD spectra for CO and H_2 coadsorbed on 1% Ru/Al_2O_3. Pulses of CO were injected over the catalyst in H_2 flow *at 300 K* until saturation. The catalyst was reduced at 775 K.

TABLE 2

TPD of CO Adsorbed in the Presence of H_2 on 1% Ru/Al_2O_3[a]

CO adsorption temperature (K)	H_2 desorbed		CO desorbed	
	$\left(\frac{\mu mol}{g\ cat}\right)$	$\left(\frac{mol\ H}{mol\ Ru}\right)$	$\left(\frac{\mu mol}{g\ cat}\right)$	$\left(\frac{mol\ CO}{mol\ Ru}\right)$
385	400	8.2	260	2.6
300	15	0.3	48	0.5

[a] Catalyst reduced at 775 K.

600 K and a small shoulder at 700 K. The molar ratio of CO plus H to total Ru was 0.8 (Table 2).

As observed in the TPR experiments, adsorption at 385 K was dramatically different from adsorption at 300 K. Much more CO adsorbed, and the amount of adsorbed H_2 increased even more (Table 2). The CO and H_2 desorbed together in narrower peaks (than seen for 300 K adsorption) with peak temperatures near 518 K. The ratio of H to CO was 3.2. The molar ratio of total CO plus H to total Ru was 11. In addition, small amounts of CH_4 and CO_2 desorbed (Fig. 4), but no signals were seen at masses 31, 32, 33, 45, and 46.

Interrupted Reaction and Isotope Labeling

On Ni/Al_2O_3 catalysts, two distinct reaction sites were observed during TPR (*1*), and the amount of the less-reactive site increased significantly when the CO adsorption temperature was increased to 385 K (*3*). For Ru/Al_2O_3, the TPR spectra show similar increases in the amount desorbed but two distinct sites are not seen. Thus, two sites may also be present on Ru/Al_2O_3, but their activities may be similar so that the two TPR peaks overlap. To confirm this, interrupted TPR and isotope labeling were used. The objective was to occupy the less-active site with ^{12}CO and the more-active site with ^{13}CO.

The catalyst surface was first saturated with ^{12}CO by adsorption at 385 K. Some ^{12}CO was then removed as $^{12}CH_4$ by heating to varying temperatures (445, 465, 480 K) in H_2, and ^{13}CO was adsorbed at 300 K on the vacated sites. As shown in Fig. 5, the resulting TPR yielded two distinct peaks, with $^{13}CH_4$ forming in a peak at 499 ± 1 K and $^{12}CH_4$ forming in a peak at 517 ± 1 K. Note that for CO adsorbed only at 300 K, CH_4 formed in a peak at 478 K (Fig. 1); for ^{13}CO adsorbed after saturation with ^{12}CO at 385 K and interrupted TPR, $^{13}CH_4$ formed at 499 K. For the three interruption temperatures used, similar results were obtained (Fig. 5, Table 3). For higher interruption temperatures, less $^{12}CH_4$ formed in the

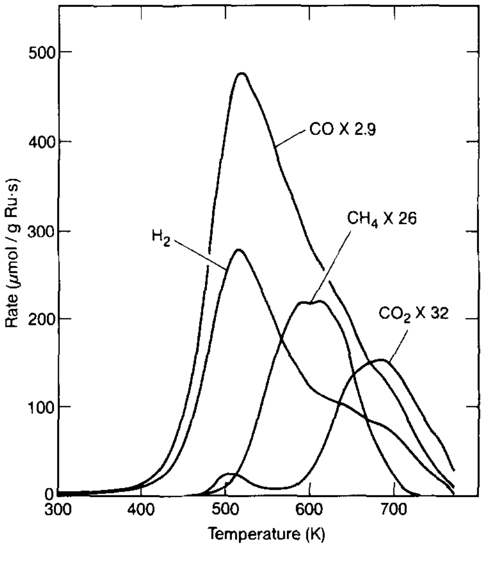

FIG. 4. TPD spectra for CO and H_2 coadsorbed on 1% Ru/Al_2O_3. Pulses of CO were injected over the catalyst in H_2 flow *at 385 K* until saturation. The catalyst was reduced at 775 K.

TABLE 3

Interrupted TPR for Ru/Al_2O_3[a]

Interruption temperature (K)	$^{12}CH_4$ produced		$^{12}CH_4$ peak temperature (K)	$^{13}CH_4$ produced		$^{13}CH_4$ peak temperature (K)
	$\left(\frac{\mu mol}{g\ cat}\right)$	$\left(\frac{mol\ ^{12}CH_4}{mol\ Ru}\right)$		$\left(\frac{\mu mol}{g\ cat}\right)$	$\left(\frac{mol\ ^{13}CH_4}{mol\ Ru}\right)$	
445	285	2.9	517	27	0.27	500
465	260	2.6	517	32	0.33	498
480	230	2.3	516	33	0.34	498

[a] Catalyst reduced at 775 K, ^{12}CO adsorbed at 385 K, and ^{13}CO adsorbed at 300 K.

subsequent TPR. This decrease in $^{12}CH_4$ was not accompanied by a corresponding increase in $^{13}CH_4$ because ^{13}CO was adsorbed at 300 K and the rate of transfer to the activated adsorption site was slow.

DISCUSSION

The adsorption and hydrogenation of CO on a Ru/Al_2O_3 catalyst are quite similar to the same processes on Ni/Al_2O_3 catalysts. Carbon monoxide adsorbs on and saturates the Ru metal at 300 K. The CO on Ru transfers to the Al_2O_3 or the Ru–Al_2O_3 interface at 385 K. This transfer requires H_2 and a species with the stoichiometry of a methoxy (CH_3O) forms at the interface. The two peaks in TPR are then due to CO from the Ru and CO from the adsorbed CH_3O. On Ni/Al_2O_3 the transfer between Ni metal and the support or interface was studied in detail with isotopes by Glugla *et al.* (*3, 4*), and CO transferred during the TPR heating. Although CO also transferred between sites on Ru/Al_2O_3, the transfer was slower and thus did not occur during the TPR heating. The presence of two sites was not reported previously for methanation on Ru/Al_2O_3, both because the rate of transfer between sites is slower on Ru/Al_2O_3 than on Ni/Al_2O_3 and because the TPR peaks overlap on Ru/Al_2O_3 but are separate on Ni/Al_2O_3. During TPD, the methoxy decomposes to form H_2 and CO. During TPR, the methoxy decomposition limits the rate of methanation. A justification and an explanation for these steps are presented below.

Adsorption and Reaction on Ru Metal

At 300 K, CO adsorbs to saturation coverage on the Ru crystallites and the amount of CO adsorption corresponds to a dispersion of at least 60% for reduction at 775 K. This dispersion assumes linear adsorption

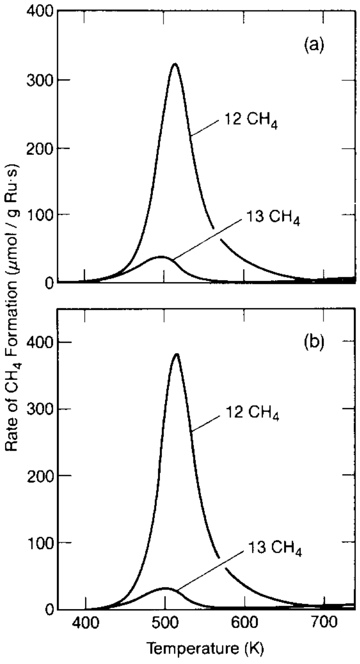

FIG. 5. Methane spectra for TPR on 1% Ru/Al_2O_3. ^{12}CO was adsorbed at 385 K in H_2 to saturation. The catalyst was then heated in H_2 to (a) 445 K and (b) 465 K, and cooled. At 300 K, ^{13}CO was adsorbed in H_2 to saturation, and the TPR was carried out.

of CO and thus the dispersion may be slightly higher. Approximately the same amount of CO adsorbed at 300 K in H_2 as in He flow (Tables 1 and 2) even though some H_2 also adsorbed. At 385 K in He flow, the same amount of CO adsorbed as at 300 K in He or H_2; that is, the adsorption of CO alone on Ru/Al_2O_3 is not activated. Whether adsorbed in H_2 or He at 300 K, CO reacts during TPR to form CH_4 with a peak temperature of 478 K. The activation energy of 84 kJ/mol estimated from the peak width is in reasonable agreement with the value of 90.4 kJ/mol obtained for a 1% Ru/Al_2O_3 catalyst in a differential reactor (*12*).

Methanation by TPR has been reported previously for Ru on SiO_2 and Al_2O_3 with similar results, although the peak temperature appears to depend on the dispersion and the support. The methanation activity declines as dispersion increases (*13, 14*), so the peak temperature is expected to depend on dispersion. Low and Bell (*15*) observed a single CH_4 peak at 420 K for CO adsorption at 303 K on a 5% Ru/Al_2O_3 catalyst, and they found that the peak temperature was independent of adsorption temperature for adsorption in He. Similarly, McCarty and Wise (*16*) observed a CH_4 peak at 470 K for CO adsorption in He at 307 K, and Zagli and Falconer (*17*) reported a single CH_4 peak at 459 K on a 0.8% Ru/SiO_2 catalyst. In these studies, only a single CH_4 peak was observed because adsorption was done in He. As discussed below, in the presence of H_2 and at elevated temperatures, more than one site can be occupied.

Formation of a Surface Complex

The TPD spectra for CO and H_2 coadsorbed at 385 K indicate that CO and H_2 interact on the Ru/Al_2O_3 surface; the CO and H_2 desorbed at the same temperature (Fig. 4), in desorption peaks that were not seen for adsorption of CO and H_2 separately. Apparently formation of CO and H_2 during TPD was limited by decomposition of a surface complex. Since the increase in the amount of CO adsorption at higher temperatures occurred only in the presence of H_2, and since H_2 adsorption also increased, the CO and H must interact on the surface. The H/CO stoichiometry of 3 suggests that a surface methoxy (CH_3O) was present following adsorption at 385 K.

Infrared studies for Ru (*18*), Ni (*19, 20*), Rh (*21*), and Pd (*22*) on Al_2O_3, following exposure to H_2/CO mixture, all detected a surface formate. The formate formed in a slow process at elevated temperatures, and these studies concluded that the formate was on the Al_2O_3 support. At a high H_2/CO ratio (300/1), however, a methoxy species was detected on Pd/Al_2O_3 (*22*). Since we pulsed CO in a pure H_2 stream, formation of a methoxy instead of a formate seems consistent with the IR data. Some formate or dimethyl ether may also be present on the surface since we detected a small TPR signal at mass 45.

A surface methoxy species is also consistent with other studies. Methanol decomposition on Pt, Pd, and Ni is initiated by loss of hydroxyl hydrogen (*23*), and methanol decomposes to CO and H_2. Methanol is the principal oxygenated product on Ru/Al_2O_3, and its formation is believed to proceed through an adsorbed methoxy species. On Ni(111), Shustorovich and Bell (*24*) calculated that formation of a CH_3O surface complex has a lower activation energy than cleavage of the CO bond, and hence should be favored at a low temperature.

In agreement with the IR studies, our results indicate that the CH_3O is on the Al_2O_3. The amount of H_2 and CO adsorbed corresponds to more than three methoxy groups for each surface Ru atom and thus the CH_3O must be on the Al_2O_3. For this low Ru loading, however, only a small fraction of the Al_2O_3 surface is occupied; presumably this is the Al_2O_3 at the Ru–Al_2O_3 interface.

As the reduction temperature increased from 550 to 775 K, more CH_3O adsorbed on the surface (Fig. 1). Since the higher reduction temperature increased the amount of reduced Ru, but did not change the Al_2O_3 surface area, the amount of CH_3O appears to be limited by the amount of reduced Ru. This result is consistent if CH_3O is adsorbed at the Ru–Al_2O_3 interface. A further increase in reduction temperature to 925 K did not increase the amount of CH_3O. Apparently, the Ru reduced completely by 775 K, and thus the higher temperature had essentially no effect. Since chloride from catalyst preparation is removed only by reduction above 900 K(11), some of these changes may be due to removal of chloride.

Multiple Reaction Sites

The CH_4 peak seen during TPR following CO adsorption at 300 K was due to hydrogenation of CO adsorbed on the Ru metal. The CH_4 from TPR following CO adsorption in H_2 at 385 K consisted of two peaks, each of which could be labeled with a different isotope of carbon (Fig. 5). These peaks could not be separated, however, without isotope labeling. The distinct nature of these peaks was confirmed since their peak temperatures did not change as the interruption temperature was changed (Table 3).

Since the temperature at which CH_3O decomposed (in TPD) was essentially the same as the temperature at which CH_4 formed in TPR (517 K), we conclude that methanation of CH_3O was limited by CH_3O decomposition. The CH_4 peak at 517 K is thus due to hydrogenation of CH_3O. As soon as the CH_3O decomposed, the resulting CO was hydrogenated to CH_4. Not all the CO was hydrogenated, and thus CO was observed in the TPR experiment at the same temperature that CH_4 formed (Fig. 2). The CH_3O, if at the interface, may have to move back to the metal to decompose and be hydrogenated, as proposed for Ni/Al_2O_3 (*10, 19*).

The agreement between the TPD and the TPR results verifies that neither of the CH_4 peaks is due to a reactive carbon species on the surface. Also, carbon is more reactive than CO on Ru (*15, 25*); carbon reacts at 385 K to form CH_4.

For ^{12}CO adsorbed at 300 K, the $^{12}CH_4$ peak in TPR had a peak temperature of 478 K. In contrast, when ^{13}CO was adsorbed after the surface was saturated with ^{12}CO at 385 K and some ^{12}CO was removed by reaction, $^{13}CH_4$ formed with a peak temperature of 499 K, more than 20 K higher. A similar increase was seen for Ni/Al_2O_3 catalysts (*3*). This decrease in methanation rate on Ru metal may indicate that the CH_3O species affects reaction on the metal.

Comparison to Ni/Al_2O_3 Catalysts

Both the TPD and the TPR results reported here are similar to those reported recently for Ni/Al_2O_3 catalysts (*3, 4*). On Ni/Al_2O_3, however, two sites were seen in a standard TPR (300 K adsorption) because CO, which adsorbed on the Ni metal, transferred to the Al_2O_3 during the TPR. Also, the activities of the two peaks were sufficiently different that distinct peaks could be seen without isotope labeling. For a slow heating rate (0.07 K/s), all the CO transferred from the Ni to the support, and only the high-temperature CH_4 peak was observed in TPR. That is, on Ni/Al_2O_3 catalysts, the rate of transfer is similar to the rate of methanation on Ni metal. On Ru/Al_2O_3, however, the rate of transfer is slower, and essentially no transfer occurs during a TPR for a heating rate of 1 K/s. The activation energy for transfer may be higher on Ru/Al_2O_3. Thus the rate of transfer is not limited by the Al_2O_3 support, but by transfer at the interface or by formation of the CH_3O on the metal. The rate of transfer may thus be a measure of the interaction between the metal and the support.

The transfer from the metal to Al_2O_3 occurred slowly at 385 K. Thus, the Ru or Ni could be saturated at 385 K after a number of CO pulses. After a 1-min delay, however, more CO adsorbed because some had transferred to the Al_2O_3. The pumping procedure (2 pulses/min) was thus used to saturate the catalysts at 385 K. Carbon monoxide adsorbed only on Ru and Ni and not on the Al_2O_3 at 300 K.

Huang *et al.* (*5*) concluded that one of the two sites on Ni/Al_2O_3 was due to nickel aluminate because they observed the aluminate with XPS. Although one study suggested that a surface Ru aluminate could form (*26*), Ru does not form a bulk aluminate, and there is no direct evidence for a surface aluminate. Thus an aluminate is not necessary for formation of the high-temperature site (referred to as the B site on Ni/Al_2O_3). The fact that an aluminate is present on Ni/Al_2O_3 is not sufficient justification for concluding that the high-temperature site can be attributed to the surface aluminate.

CONCLUSIONS

Isotope labeling has shown that, similar to Ni/Al_2O_3 catalysts, two distinct reaction sites (CO and Ru and a CO–H complex on Al_2O_3) are present for CO hydrogenation on Ru/Al_2O_3 catalysts. Thus, the presence of an aluminate on Ni/Al_2O_3 is probably not required for two reaction sites to be present. On Ru/Al_2O_3, filling the less-active site is an activated process that requires H_2. A CO–H species with a methoxy stoichiometry adsorbs on the Al_2O_3, probably at the $Ru–Al_2O_3$ interface. This methoxy is responsible for the second site seen in TPR, and decomposition of the methoxy appears to limit the rate of CH_4 formation during TPR. Carbon monoxide adsorbs only on Ru, and the methoxy apparently forms on Ru, and then transfers to the Al_2O_3, or forms at the interface. This transfer process is much slower on Ru/Al_2O_3 than on Ni/Al_2O_3.

ACKNOWLEDGMENTS

We gratefully acknowledge support by the National Science Foundation, Grant CBT-8616494. We greatly appreciate the assistance of Professor Paul G. Glugla and Dr. Keith M. Bailey in the initial experiments. We also thank Kevin M. Larson for preparing the Ru/Al_2O_3 catalyst and Professor Bruce E. Koel for the initial suggestion regarding use of Ru/Al_2O_3 catalyst in this study.

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