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The Role of Spillover in Carbon Monoxide Hydrogenation over Alumina-Supported Platinum

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Temperature-programmed reaction and desorption (TPR, TPD) were used to study the formation and hydrogenation of CH_3O on a 7.7% Pt/Al_2O_3 catalyst. Methoxy forms in an activated spillover process following CO and H_2 adsorption on Pt, and adsorbed CH_3O has the same desorption and reaction properties as adsorbed CH_3OH. The CH_3O species hydrogenates faster to CH_4 than does CO adsorbed on Pt. Spillover is faster than hydrogenation at low temperatures, but the activation energy for spillover is smaller. Water significantly inhibits spillover by poisoning the adsorption sites on Al_2O_3. A physical mixture of Al_2O_3 and Pt/Al_2O_3 was used to show that CH_3O was adsorbed on Al_2O_3. At elevated temperature and in the absence of gas-phase H_2, CH_3O decomposition limits the formation of gas-phase CO and H_2. The processes of spillover and hydrogenation to CH_4 were studied by TPR in combination with isotope labeling, interrupted reaction, and H_2O preadsorption. The surface coverage, heating rate, and H_2 pressure during TPR were also varied.

INTRODUCTION

On Ni/Al_2O_3 catalysts, two types of methanation sites have been identified during temperature-programmed reaction (TPR) by the presence of two distinct CH_4 peaks (*1–3*). The lower temperature CH_4 peak was due to hydrogenation of CO on Ni and the higher temperature peak was the result of hydrogenation of CH_3O, which was adsorbed on Al_2O_3; the CO on Ni hydrogenated at a faster rate. The CH_3O formed by spillover from the Ni in an activated process that occurred during TPR. A similar spillover process was also observed on Pt/Al_2O_3 (*4*), but CH_3O hydrogenated at a faster rate than CO on Pt. On Pd/Al_2O_3, CH_3O also hydrogenated faster than CO on Pd, though two distinct CH_4 peaks were not observed (*5*).

Alumina-supported Pt and Pd catalysts exhibit higher methanation rates than the silica-supported or unsupported metals during steady-state measurements. For example, the site-time yield on Pt/Al_2O_3 has been reported to be 20–40 times higher than on Pt powder (*4, 6, 7*). These enhanced activities may be the result of CH_3O hydrogenation, and thus we have studied the spillover and methanation processes on Pt/Al_2O_3 in more detail in the present study. Robbins and Marucchi-Soos (*4*) showed clearly, with a combination of TPR and IR on a 12% Pt/Al_2O_3 catalyst, that CH_3O hydrogenated faster than CO. The peak temperature for CH_4 from CH_3O was 490 K and for CH_4 from CO on Pt was 613 K. They showed that CO adsorbed molecularly on Pt at 300 K, but converted to CH_3O, which was adsorbed on Al_2O_3, when their 12% Pt/Al_2O_3 catalyst was heated to 380 K in H_2. The relative amplitudes of the two distinct CH_4 peaks changed as H_2O adsorbed on the surface; the peak due to CH_3O hydrogenation decreased significantly in amplitude. They concluded that formation or stabilization of reactive CH_3O required a vacant Al cation on the surface, and these Al cations were formed when the surface was dehydroxylated at temperatures above 473–523 K. Using molecular orbital theory, Anderson and Jen (*8*) modeled CH_3O mobility on Al_2O_3 and found that

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CH_3O can move from one Al^{3+} site to another while H moves in parallel along O^{2} sites. They also calculated that CH_3O was more likely to hydrogenate to CH_4 than CH_3OH because recombination of CH_3O adsorbed on a Al^{3-} site with H is less endothermic for CH_4 formation than for CH_3OH formation.

On Pt/Al_2O_3, CO spillover removed CO from the Pt, but some CO remained on the Pt at elevated temperatures. Robbins and Marucchi-Soos (*4*) could not tell if the Al cation sites act as catalysts in the formation of CH_3O or simply as reservoirs for CH_3O species. Because H_2O forms during CO hydrogenation, and because H_2O inhibits CH_3O formation, the role of these sites during steady-state reaction was unclear. A correlation is seen, however, between steady-state kinetics and TPR. No methane formed during TPR of CO adsorbed on Pt powder (*4*), which also exhibits a lower steady-state methanation activity than Pt/Al_2O_3 (*6, 7*).

Temperature-programmed reaction and desorption experiments were carried out in the present study on a 7.7% Pt/Al_2O_3 catalyst. By using a mass spectrometer to detect all the reaction products and by using a number of variations on the standard TPR experiment (including isotope labeling), additional insight into the surface processes was obtained. The same process occurred as observed on 12% Pt/Al_2O_3 (*4*). Since reduction in H_2 was carried out at 773 K in the present study, only one CH_4 peak was observed during a standard TPR. On 12% Pt/Al_2O_3, two peaks were observed, but only for experiments preceded by lower temperature reduction (*4, 9*). Temperature-programmed desorption (TPD) helped verify the presence of CH_3O, and TPR on Al_2O_3–Pt/Al_2O_3 physical mixtures was used to show CH_3O was adsorbed on the support. Methanol was also adsorbed so a direct comparison could be made to CO and H_2 coadsorption.

By interrupting TPR after some CH_4 had formed, and rapidly cooling the catalyst, lower coverages were obtained and the two reaction sites were studied as H_2 pressure, heating rate, and the presence of coadsorbed species (H_2O, ^{13}CO) were varied. The rate of spillover was shown to be rapid and to have a lower activation energy than methanation. At atmospheric pressure and below, the spillover rate appears to be linear in H_2 pressure. Higher CH_3O coverages were also obtained by CO and H_2 adsorption at 385 K, and as the CH_3O coverage increased, the rate of CH_4 formation decreased. Though the *amount* of CH_4 formed increased, a large amount of CO also desorbed from the catalyst, and in a few cases dimethyl ether and methanol were observed.

EXPERIMENTAL METHODS

Temperature-programmed desorption (TPD) and reaction (TPR) experiments were carried out on a 7.7% Pt/Al_2O_3 catalyst in a flow and detection system that has been described previously (*10, 11*). Briefly, a 100-mg sample of reduced and passivated catalyst 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. The catalyst was pretreated at 773 K in H_2 flow for 2 h, and then the catalyst was cooled to 300 K in either H_2 or He. Carbon monoxide was adsorbed at 300 or 385 K by injecting 0.15 cm^3 (STP) pulses of a 10% CO/He mixture into H_2 or He carrier gas. Isotope experiments were carried out to label CH_3O on the support with one carbon isotope (e.g., $^{13}CH_3O$) and CO on the metal with another C isotope (e.g., ^{12}CO). When ^{13}CO was used for isotope labeling experiments, 0.05 cm^3 (STP) pulses of the pure gas were injected into the carrier gas stream.

To obtain TPR spectra, the catalyst was heated in 100% H_2, 100% D_2, or a H_2/He mixture after CO adsorption. The total pressure was approximately 0.8 atm except for two TPR experiments, where the pressure of the H_2 carrier gas was 2 atm. For TPR experiments the heating rate was set at 0.5, 1, or 2.5 K/s. Most TPR experiments were run at 1 K/s. To obtain TPD spectra of coadsorbed CO and H_2, the carrier gas was switched to He after CO adsorption in H_2 flow, and the catalyst temperature was then raised at 1 K/s in He. After TPD, TPR was carried out, without additional adsorption, to determine the amount of surface carbon that remained on the catalyst. Species leaving the catalyst surface were detected immediately downstream of the reactor by a computer-controlled, UTI quadrupole mass spectrometer. This system allowed the catalyst temperature and multiple mass peaks to be detected simultaneously. Mass signals for H_2, CO, CO_2, CH_4, CH_3OH, and $(CH_3)_2O$ were recorded, and calibrations were done by injecting known volumes of pure gases. The CO signal was corrected for cracking from CO_2. The mass to charge (*m/e*) signal recorded for CH_4 was 15, for CH_3OH, 31, and for $(CH_3)_2O$, 31 and 45.

For some experiments, interrupted TPR was used to remove some of the adsorbed CO and obtain less-than-saturation coverage. Immediately after reaching the interruption temperature while heating at 1 K/s, the catalyst was cooled at approximately 30 K/s in H_2. The interruption temperature was chosen such that some CO or CH_3O was left on the surface. A subsequent TPR or TPD to 775 K was carried out to study the reactivity and desorption properties of the remaining adsorbed species. Methanol was adsorbed to form CH_3O on the Al_2O_3 (*12*) by slowly evaporating 1 μl of liquid CH_3OH into H_2 flow at 300 K, and TPR and TPD were carried out for adsorbed CH_3OH. Water was adsorbed after CO adsorption by evaporating H_2O from the tip of a needle upstream of the catalyst, in a similar fashion to CH_3OH injection, to study the effect of H_2O adsorbed on Al_2O_3 on the spillover mechanism.

The 7.7% Pt/Al_2O_3 catalyst was prepared at Exxon by impregnation to incipient wetness of reforming grade Ketjen alumina with chloroplatinic acid in acetone/water. The impregnated Al_2O_3 was heated in H_2 to 523 K and held there for 1 h before cooling to room temperature, and then was heated to 673 K and held there for 10 h. The catalyst was pretreated at 775 K in pure H_2 for 2 h before the initial TPR and for 15 min between experiments. The CO/Pt ratio, as determined from TPR following CO adsorption at 300 K, was 0.22.

To show that CH_3O was adsorbed on Al_2O_3, a catalyst was made by crushing equal amounts of 7.7% Pt/Al_2O_3 and Kaiser A-201 Al_2O_3 in distilled water. The water was used to increase contact between particles (*3*). The catalyst–support mixture was then placed in a vacuum oven at approximately 330 to 350 K for 24 h, and it was pretreated for 2 h in H_2 at 773 K before TPR experiments were carried out.

RESULTS AND DISCUSSION

As described in the Introduction, CO and H_2 adsorb on Pt and then form CH_3O in an activated process. The CH_3O was concluded to be adsorbed on the Al_2O_3 surface at vacant Al cation sites (*4*). To aid in understanding the results, the overall reactions that are involved are listed here.

(1) Adsorption on Pt:

$$H_2(g) + 2\,Pt \leftrightarrow 2\,H\text{–}Pt$$
$$CO(g) + Pt \leftrightarrow CO\text{–}Pt.$$

(2) Methoxy formation and spillover. These two processes are referred to as spillover since they could not be distinguished with the experiments. Methoxy may form on Pt or at the $Pt\text{–}Al_2O_3$ interface, and then spillover onto Al_2O_3:

$$3\,H\text{–}Pt + CO\text{–}Pt + Al \leftrightarrow CH_3O\text{–}Al + 4\,Pt.$$

(3) Methanation of CO adsorbed on Pt:

$$CO\text{–}Pt + 6\,H\text{–}Pt \rightarrow CH_4(g) + H_2O(g) + 6\,Pt.$$

(4) Methoxy hydrogenation to CH_4, perhaps at the $Pt\text{–}Al_2O_3$ interface, though this cannot be determined from current results:

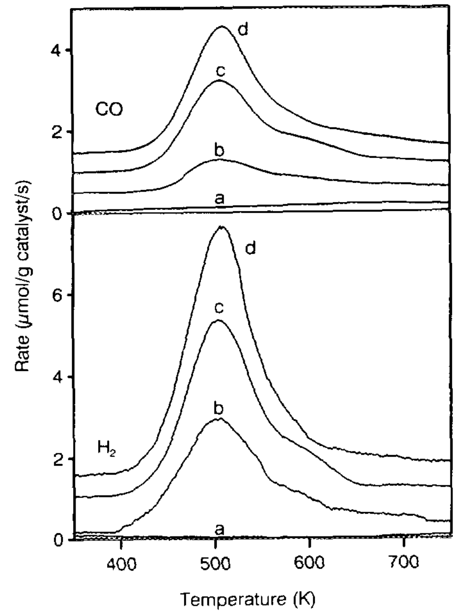

FIG. 1. Carbon monoxide and H_2 spectra from TPD of CO adsorbed in H_2 flow on a 7.7% Pt/Al_2O_3 catalyst at: (a) 300 K for 30 min; and 385 K for (b) 15, (c) 30, and (d) 60 min. The spectra are offset vertically.

$$CH_3O\text{-}Al + 6\ H\text{-}Pt \rightarrow CH_4(g) + H_2O(g) + 6\ Pt + Al.$$

Note that reactions (3) and (4) are not reversible and that the H_2O product readsorbs on the Al_2O_3 surface and desorbs at higher temperatures.

Methoxy Identification

To verify that CH_3O forms on our 7.7% Pt/Al_2O_3 catalyst as it did on 12% Pt/Al_2O_3 (*4*), TPD of coadsorbed CO and H_2 and of CH_3OH were compared. The simultaneous desorption of H_2 and CO, in an approximate 3 : 1 ratio, from Ni/Al_2O_3 (*2*, *13*), Ru/Al_2O_3 (*14*), and Pd/Al_2O_3 (*5*) have been used to conclude that CH_3O formed on the Al_2O_3 support of these catalysts upon exposure to CO and H_2 at 385 K. Figure 1 shows that similar TPD spectra were observed for 7.7% Pt/Al_2O_3; CO and H_2 desorbed simultaneously in a peak at 500 K when they were coadsorbed at 385 K. This simultaneous formation of CO and H_2 indicates that CH_3O decomposition limits the appearance of CO and H_2. Much smaller amounts of CH_4 and CO_2 also formed, as shown in Fig. 2.

The amount of CO and H_2 desorption increased with CO and H_2 exposure at 385 K, as shown in Fig. 1. An H : CO ratio of 2.9 to 3.7 was estimated by measuring the total desorption amounts of H_2 and CO for 30 min and 60 min CO exposure at 385 K. For comparison, methanol adsorption (1 μl liquid) at 300 K gave similar, but not identical, TPD spectra. The CO and H_2 desorbed simultaneously at 500 K with an H : CO ratio of 4.4 based on peak amplitudes at 500 K, and the CH_4 and CO_2 signals were similar to those in Fig. 2. No unreacted CH_3OH and no $(CH_3)_2O$ desorbed. The amount of CO (195 μmol/g catalyst) was similar to that in Fig. 1b. Since IR has shown that CH_3OH adsorbs on Al_2O_3 and forms CH_3O (*12*, *15*), these TPD results confirm that CH_3O forms from coadsorption of CO and H_2 on Pt/Al_2O_3. The formation of CH_3O from CO and

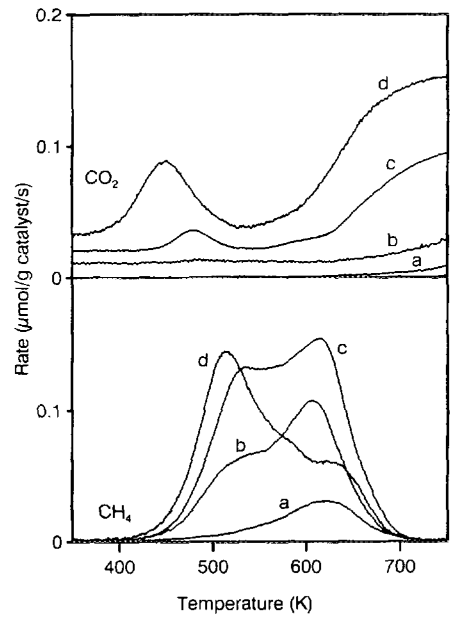

FIG. 2. Carbon dioxide and CH_4 spectra from TPD: same conditions as Fig. 1. The CO_2 spectra are offset vertically.

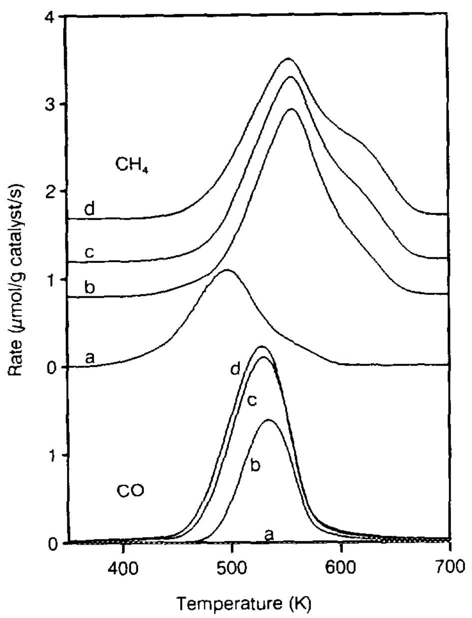

FIG. 3. Methane and CO spectra from TPR of CO adsorbed at : (a) 300 K for 30 min in He flow; and 385 K for (b) 30, (c) 60, and (d) 90 min in H_2 flow on a 7.7% Pt/Al_2O_3 catalyst. The CH_4 spectra are offset vertically.

H_2 adsorption was activated; when CO and H_2 were coadsorbed at 300 K instead of 385 K on 7.7% Pt/Al_2O_3, less CO and H_2 adsorbed and CO and H_2 did not desorb simultaneously during TPD.

The decomposition of CH_3O or CH_3OH during TPD occurs by reverse spillover and decomposition on the Pt or at the $Pt–Al_2O_3$ interface. Methanol adsorbed on Al_2O_3 decomposes at a much higher temperature when Pt is not present (*16*).

Carbon Monoxide and Methoxy Hydrogenation

When CO was adsorbed on 7.7% Pt/Al_2O_3 at 300 K in He flow, the subsequent TPR spectra in H_2 flow (Fig. 3a) showed that CH_4 started forming near 350 K, and the CH_4 peak temperature was 495 K. A small shoulder was present near 580 K. Similar TPR results were obtained by Robbins (*9*) for this catalyst, and the amount of CH_4 (88 μmol/g catalyst) was similar to that observed by Robbins (95 μmol/g catalyst). Carbon monoxide adsorption at 385 K in He flow or at 300 K in H_2 flow gave the same spectra as in Fig. 3a. For all three adsorption conditions, the unreacted CO was less than 1% of the CH_4 amount and no CO_2, CH_3OH, or $(CH_3)_2O$ was detected.

The rapid formation of CH_4 in Fig. 3a is attributed to spillover, which occurs during TPR, to form CH_3O on Al_2O_3 (*4, 5, 17, 18*). The methoxy is then hydrogenated to CH_4, though we cannot distinguish whether CH_3O is hydrogenated on Pt, Al_2O_3, or the $Pt–Al_2O_3$ interface. When CH_3O was formed on the catalyst prior to TPR by CO and H_2 coadsorption at 385 K, however, the CH_4 peak temperature increased to 560 K (Figs. 3b–3d), which indicated that CH_4 formation was slower. The amount of CH_4 doubled, and the amount of unreacted CO increased dramatically for adsorption at 385 K (Figs. 3b–3d). Since more than 150 μmol CO/g catalyst desorbed during TPR following 60 and 90 min of CO adsorption at 385 K in H_2 flow, and only 88 μmol CO/g catalyst adsorbed on Pt (as determined by CO adsorption at 300 K), a significant portion of the CO that desorbed during TPR came from CH_3O decomposition and not from CO adsorbed on Pt. In addition, CO_2 and $(CH_3)_2O$ formed, as shown in Fig. 4. The amount of $(CH_3)_2O$ increased faster than the increase in exposure, but even at 90 min exposure, the amount of $(CH_3)_2O$ was less than 5% of the CH_4 amount. No CH_3OH formed.

Figure 3 shows that as CH_3O coverage increased, the rate of hydrogenation decreased and CO started to desorb. Robbins and Marucchi-Soos (*4*) also observed a decrease in the rate of CH_4 formation when CO was adsorbed at 380 K instead of 300 K, but the peak temperature increase was only 40 K on their more highly loaded catalyst. The decreased rate of CH_4 formation may be due to CO on Pt inhibiting H_2 adsorption (*5, 9*). For high CH_3O coverages on Al_2O_3, CO cannot form CH_3O and spill over as rapidly and thus fewer vacant sites are created on Pt for H_2 adsorption. As a result, CO

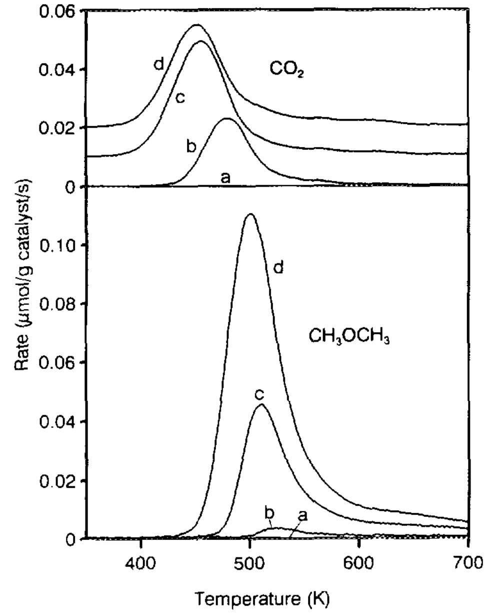

FIG. 4. Carbon dioxide and $(CH_3)_2O$ spectra from TPR: same conditions as Fig. 3. The CO_2 spectra are offset vertically.

desorbs during TPR instead of forming CH_3O, and the CH_3O on Al_2O_3 undergoes reverse spillover and decomposes instead of being hydrogenated.

To study this effect, CO and H_2 were coadsorbed at 385 K for 15 min and the catalyst was held on additional 15 min in H_2 at 385 K in an attempt to remove all the CO from Pt by forming CH_3O on Al_2O_3. The resulting TPR spectrum (Fig. 5b) had the same peak temperature (550 K) as for Figs. 3b–3d, in which the hold-in-hydrogen step was omitted, *but* CH_4 formation started near 350 K, as was observed when CO was adsorbed at 300 K (Fig. 5a). When the experiment for Fig. 5b was repeated, but CO was also adsorbed at 300 K before TPR in order to saturate the Pt surface, the initial rate of CH_4 formation decreased (Fig. 5c). Apparently, CO on Pt inhibited H_2 adsorption and thus CH_3O hydrogenation. High CH_3O coverages may also delay spillover since the CH_4 peak temperatures are the same for Figs. 5b and 5c, and they are significantly higher than Fig. 5a (CO adsorption at 300 K). The additional CO that was adsorbed on the Pt at 300 K for the experiment in Fig. 5c desorbed unreacted, in the same manner as shown in Fig. 3. The decrease in spillover due to the high CH_3O coverage allowed CO to desorb from the Pt surface, though some CH_3O may have also decomposed to CO and H_2.

Temperature-programmed reaction of CH_3OH adsorbed at 300 K was similar to that for CH_3O hydrogenation (Fig. 3b) but less CO desorbed (13 μmol CO/g catalyst, 230 μmol CH_4/g catalyst) possibly because not as much CO was adsorbed on the Pt surface. The CH_4 peak temperature was 562 K, the same as for CO and H_2 adsorption at 385 K. Neither CH_3OH nor $(CH_3)_2O$ formed for this coverage of adsorbed CH_3OH.

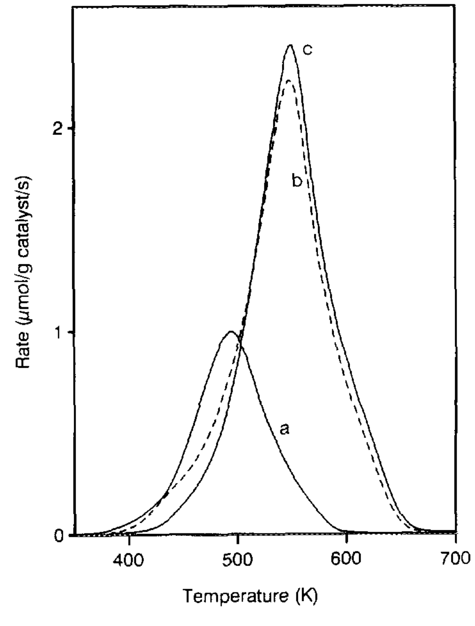

FIG. 5. Methane spectra from TPR of CO adsorbed in H_2 flow on a 7.7% Pt/Al_2O_3 catalyst at: (a) 300 K for 15 min, (b) 385 K for 15 min followed by holding the catalyst in H_2 flow at 385 K for 15 min, and (c) 385 K for 15 min followed by holding the catalyst in H_2 flow at 385 K for 15 min and then CO adsorption at 300 K for 15 min.

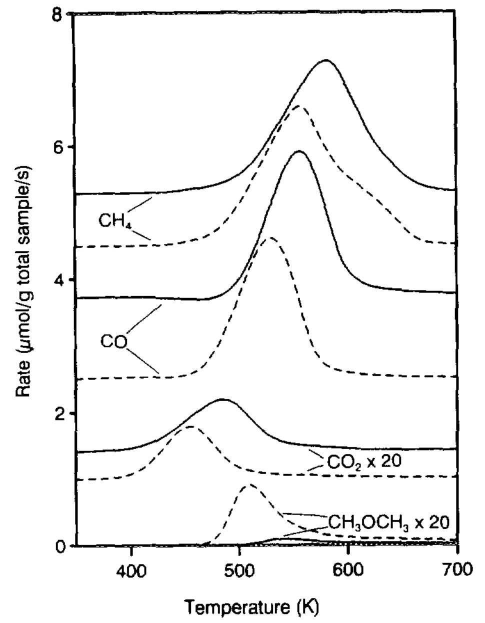

FIG. 6. Methane, CO, CO_2, and $(CH_3)_2O$ spectra from TPR of CO adsorbed at 385 K for 60 min in H_2 flow on a 1 : 1 mixture of 7.7% Pt/Al_2O_3 and Al_2O_3 (solid lines) and on a 7.7% Pt/Al_2O_3 catalyst (dashed lines). The spectra are offset vertically.

Methoxy Location

A physical mixture of Al_2O_3 and the Pt/Al_2O_3 catalyst was used to verify that CH_3O was on the support and to determine how the reaction rate was affected by increasing the available Al_2O_3 area. Similar experiments have been carried out on Al_2O_3–Ni/Al_2O_3 mixtures (*3*). For CO and H_2 coadsorption for 60 min at 385 K, the CH_4 and CO spectra (Fig. 6, solid lines) were similar in shape to those obtained on Pt/Al_2O_3 alone (Fig. 6, dashed lines), but the peak temperatures were both 26 K higher. Similar amounts of CH_4 and CO formed, *per gram material in the reactor*, even though only half as much Pt was in the mixture. For shorter exposures at 385 K less CH_4 and CO formed from the mixture, and for adsorption at 300 K, more than half as much CH_4 (59 μmol/g catalyst for the mixture, 88 μmol/g catalyst for Pt/Al_2O_3) formed per gram material in the reactor.

The amounts of CH_3O adsorbed on the catalyst and on the mixture were calculated by the difference in total products for 385 and 300 K adsorption, and they were normalized *per gram Al_2O_3*. For 30 min adsorption the CH_3O amounts for the catalyst and the mixture were 200 and 155 μmol CH_3O/g Al_2O_3, respectively. At higher exposure (60 min) the surfaces were closer to saturation and the amounts were almost equal (280 and 285 μmol CH_3O/g Al_2O_3). Though the exact same values are not expected since a different Al_2O_3 was used for the mixture than for catalyst preparation, these results show that the CH_3O was absorbed on the Al_2O_3 surface. When CO and H_2 were exposed to the Al_2O_3 alone at 385 K (*3*, *4*), essentially no adsorption was observed; adsorption from CO and H_2 on the Al_2O_3 surface of Pt/Al_2O_3 occurred by spillover from Pt.

An increase in peak temperature during TPR on the mixture was also observed for CH_3O hydrogenation on Al_2O_3–Ni/Al_2O_3 mixtures (*3*). Both formation and hydrogenation of CH_3O were slower when more Al_2O_3 was present; the added Al_2O_3 was not as close to Pt particles and thus the diffusion distance was increased. Consistent with this observation, the CH_4 peak temperature was 27 K lower on the 12% Pt/Al_2O_3 catalyst (*4*) than on our 7.7% Pt/Al_2O_3. Also, during adsorption, CH_3O formation was slower when less Pt was available (per gram material in the reactor) because the Pt area is the original location of CO and H_2 adsorption.

Isotope Labeling

On Ni/Al_2O_3 catalysts, the CH_3O (on Al_2O_3) and the CO (on Ni) were labeled with different carbon isotopes (*1*, *19*) so that the CH_4 formed from metal and support could be distinguished. These experiments on Ni/Al_2O_3 were accomplished by exchanging CO on the Ni with isotopically labeled CO; the CH_3O did not exchange at 300 K. To determine if the same labeling could be carried out for Pt/Al_2O_3 catalysts, ^{12}CO was adsorbed at 300 K (10 min) and ^{13}CO was then exposed to the catalyst at 300 K (30 min).

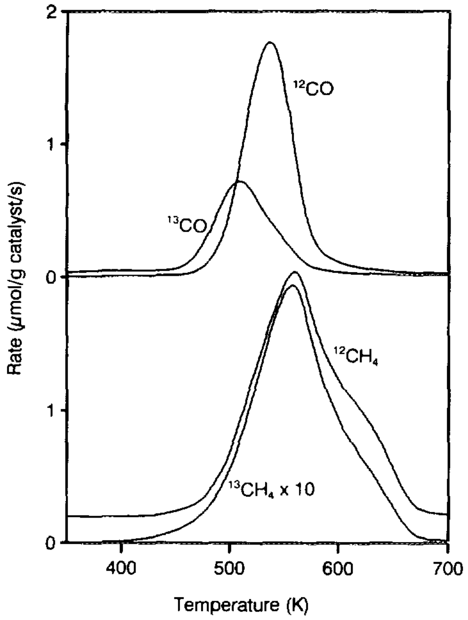

FIG. 7. TPR spectra of $^{12}CH_4$, $^{13}CH_4$, ^{12}CO, and ^{13}CO for ^{12}CO adsorbed at 385 K for 60 min in H_2 followed by ^{13}CO adsorption at 300 K for 30 min on a 7.7% Pt/Al_2O_3 catalyst.

The subsequent TPR showed that 90% of the ^{12}CO was displaced by ^{13}CO. On Ni/Al_2O_3, essentially all the CO on Ni exchanged in a shorter time. Ninety percent exchange was more than sufficient, however, for distinguishing adsorption sites.

Thus, ^{12}CO was adsorbed at 385 K in H_2 flow to form $^{12}CH_3O$, and then ^{13}CO was exposed to the catalyst at 300 K for 30 min to displace ^{12}CO on the Pt. The subsequent TPR spectra, in Fig. 7, show that the $^{12}CH_4$ (from $^{12}CH_3O$ hydrogenation) and $^{13}CH_4$ (from CO hydrogenation) have almost identical shapes. However, 62% of the $^{12}CH_3O$ was hydrogenated while only 23% of the ^{13}CO was hydrogenated. In contrast, when CO was adsorbed on Pt at 300 K and no CH_3O was present on the support, essentially all the CO was hydrogenated to CH_4 (Fig. 3). The amount of $^{12}CH_4$ in Fig. 7 was 10 times the amount of $^{13}CH_4$. Note also that ^{13}CO desorbed at a lower temperature than ^{12}CO. Similar observations were made for Pd/Al_2O_3 (*5*). At low CH_3O coverage, CO on Pt can spill over during TPR to form CH_3O, which is then hydrogenated. At high CH_3O coverages, fewer sites are available for spillover and thus CO desorption competes effectively with spillover. The total amount of ^{13}C products ($^{13}CH_4$, ^{13}CO, $^{13}CO_2$) was 85 μmol/g catalyst, and this is close to the value expected for 90% exchange of ^{12}CO from the Pt (79 μmol/g catalyst).

In Fig. 7, the ^{13}CO desorbed at lower temperature than ^{12}CO, but the $^{12}CH_4$ and $^{13}CH_4$ signals are nearly identical in shape and peak temperature. This indicates that both $^{12}CH_4$ and $^{13}CH_4$ formed by the same process, but the formation of ^{12}CO and ^{13}CO are limited by different processes. For example, ^{13}CO may desorb directly from the Pt, but $^{12}CH_3O$ decomposition at the metal or metal–support interface limits ^{12}CO formation. During TPR, some ^{13}CO spills over to the support, and the resulting $^{13}CH_3O$ forms $^{13}CH_4$ at nearly the same temperature that $^{12}CH_3O$ forms $^{12}CH_4$. Some of this $^{13}CH_3O$ may also decompose to form ^{13}CO and that is reflected in the ^{13}CO tail near 550 K.

Influence of Water Adsorption

On a 12% Pt/Al_2O_3 catalyst, two distinct CH_4 peaks, due to CH_3O and CO hydrogenation, were readily observed during TPR (*4*). Exposure to H_2O vapor at room temperature, followed by reduction at temperatures between 523 and 723 K prior to CO adsorption, changed the relative distribution of the two types of sites during TPR. The H_2O occupied sites on the Al_2O_3 surface, and for low reduction temperatures the CH_3O hydrogenation peak was almost eliminated (*4*). On our 7.7% Pt/Al_2O_3 catalyst (reduced at 773 K), instead of two distinct CH_4 peaks, essentially all the CO adsorbed at 300 K appears to be hydrogenated in the low-temperature peak, which is due to CH_3O hydrogenation. When a fresh 7.7% Pt/Al_2O_3 catalyst (which had been stored in air) was pretreated at 573 K instead of 773 K, however, results similar to those of Robbins and Marucchi-Soos (*4*) were obtained: two

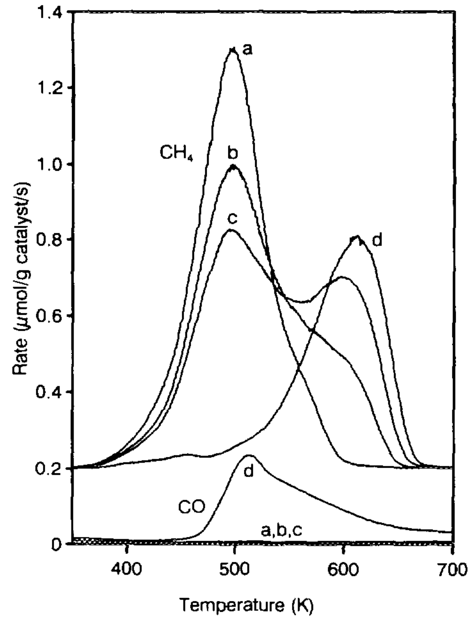

FIG. 8. Methane and CO spectra from TPR of CO adsorbed at 300 K for 30 min in H_2 flow followed by H_2O adsorption on a 7.7% Pt/Al_2O_3 catalyst. Water amounts: (a) 0, (b) 100, (c) 200, and (d) 540 μmol/(g catalyst).

distinct CH_4 peaks of approximately the same amplitude were observed. According to Robbins and Marucchi-Soos (*4*), at higher reduction temperatures, extensive dehydration of the Al_2O_3 occurs, and a sufficient number of Al cation support sites exist so that most of the CO on the metal can form CH_3O on the support by spillover. To verify this, H_2O was adsorbed to hydrate some of these support sites after CO adsorption at 300 K. As shown in Fig. 8, as the amount of adsorbed H_2O increased, less CH_4 formed at low temperature and a high-temperature CH_4 peak grew. For a high H_2O coverage, essentially all the CH_4 formed in the peak above 600 K (Fig. 8d). Carbon monoxide only desorbed when virtually no CH_4 formed in the low-temperature peak (at the highest H_2O exposure shown in Fig. 8d). The corresponding water desorption curves are shown in Fig. 9.

Since H_2O has a significant effect on the distribution of reaction sites, and since H_2O is formed as CH_3O is hydrogenated during TPR, water is expected to influence methanation during TPR. Interrupted TPR, in which some CO (as CH_3O) is hydrogenated to CH_4 before the heating is interrupted and the sample quickly cooled, yields a lower surface coverage of CO. This was used to study the effect of H_2O and to help distinguish the two distinct methanation processes. Figure 10 shows two distinct CH_4 peaks in TPR spectra obtained following interrupted TPR to 500, 520, or 540 K and rapid cooling to 300 K. The CO was initially adsorbed at 300 K. The amounts of CH_4 in the high-temperature peaks are small compared to the total CH_4 formed during the standard TPR (Fig. 10a).

Note in Fig. 10 that a significant fraction of the CH_4 forms below the interruption temperature. For example, even though interrupted TPR was carried out to 520 K, during the subsequent TPR (Fig. 10c) more than half the CH_4 formed below 520 K and the methanation rate became significant near 360 K. In other words, CH_4 starts form-

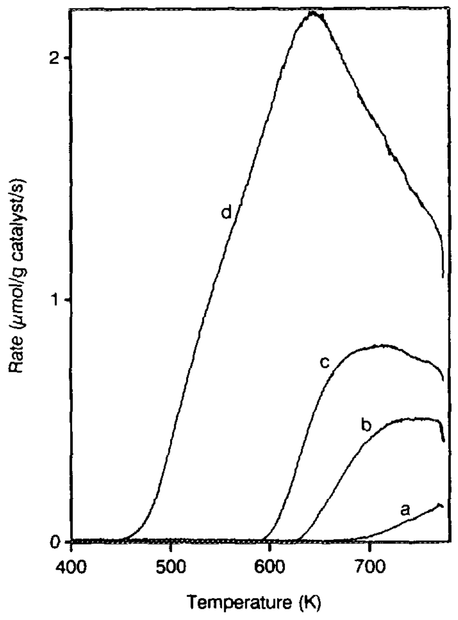

FIG. 9. Water spectra from TPR: same conditions as Fig. 8.

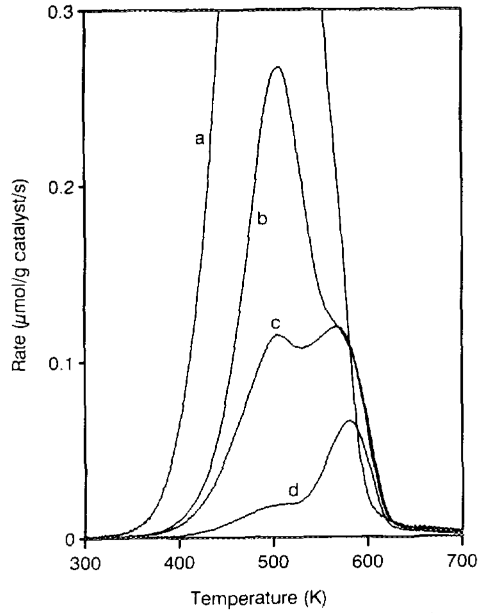

FIG. 10. Methane spectra from TPR of CO adsorbed at 300 K for 30 min in H_2 flow on a 7.7% Pt/Al_2O_3 catalyst. After CO adsorption, interrupted TPR was carried out at 1 K/s to: (a) 300 K, (b) 500 K, (c) 520 K and (d) 540 K.

ing at approximately 160 K lower temperature than was reached during the interrupted TPR. The portion of the CH_4 curve below the peak maximum in Fig. 10a was fit to a first-order TPD simulation by using an activation energy of 69 kJ/mol. The interrupted reaction experiments were then simulated by integrating to the interruption temperature and then restarting the numerical simulation at 300 K for the resulting lower surface coverage. The calculated spectra for the CH_4 signals up to 500 K were similar to those shown in Figs. 10b–10d. That is, the simulation indicates that it is reasonable for CH_4 to form at much lower temperature than the interruption temperature, and a significant fraction of the CH_4 is expected to form below the interruption temperature for a first-order process.

To verify that H_2O poisons support sites, interrupted TPR was carried out following CO and H_2 coadsorption at 385 K. This adsorption created a high CH_3O coverage on Al_2O_3, so interrupted TPR to 580 K was used to remove most of the CH_3O from the catalyst (and thus deposit more H_2O on the Al_2O_3 surface). During a subsequent TPR (Fig. 11a), two distinct CH_4 peaks of equal amplitude were observed, and less than 2 μmol/g catalyst of CO desorbed, similar to the results for 300 K adsorption followed by interrupted TPR (Fig. 10c). When H_2O (~1100 μmol/g catalyst) was adsorbed on the catalyst after cooling to 300 K following the interrupted TPR, essentially all the CH_4 formed in the high temperature peak during the subsequent TPR (Fig. 11b). This result shows that after the interrupted TPR, the CO remaining on the catalyst was adsorbed on the Pt; adsorbing H_2O to high coverage prevented CH_3O formation and thus almost all the CO was hydrogenated on the Pt surface. When H_2O was not adsorbed, CO spilled over to form CH_3O as the temperature increased, and the CH_3O was then hydrogenated at low temperatures.

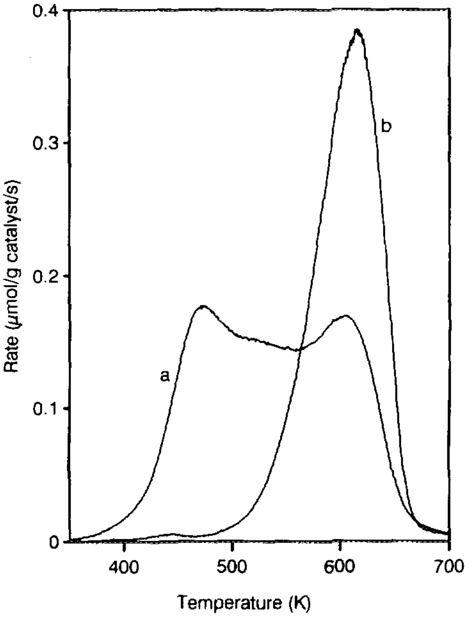

FIG. 11. Methane spectra from TPR of CO adsorbed at 385 K followed by interrupted TPR to 580 K and subsequent injection of H_2O onto a 7.7% Pt/Al_2O_3 catalyst. H_2O amounts are: (a) 0 and (b) 1080 μmol/(g catalyst).

The H_2O that was adsorbed for Fig. 11b started desorbing at 320 K and desorbed in two broad peaks up to 775 K. In contrast, H_2O for Fig. 11a did not start desorbing until 580 K (the interruption temperature) and was an order of magnitude smaller. Essentially all the H_2O observed for Fig. 11a resulted from hydrogenation and as H_2O coverages decrease on Al_2O_3, H_2O desorbs at higher temperatures.

Rate of Spillover before Hydrogenation

The spillover rate was compared to the rate of CH_4 formation by adsorbing ^{13}CO at 300 K and carrying out interrupted TPR to 420 K, a temperature at which less than 5% of the ^{13}CO had reacted to form $^{13}CH_4$. After the catalyst was rapidly cooled, the ^{13}CO remaining on Pt was displaced by ^{12}CO adsorption at 300 K. Any $^{13}CH_3O$ that formed on Al_2O_3 due to spillover would not exchange with ^{12}CO at 300 K (*19*), and thus the amount of $^{13}CH_4$ observed in a subsequent TPR is a measure of how much spillover occurred by 420 K. This procedure has been shown to be effective at estimating spillover rates on Pd/Al_2O_3 (*18*). The 36-μmol $^{13}CH_4$/g catalyst observed during TPR indicates that 46% of the ^{13}CO originally on Pt had spilled over by 420 K. Since only 5% of the original ^{13}CO reacted to form $^{13}CH_4$ during the interrupted TPR to 420 K, the spillover rate is faster than methanation below 420 K. The $^{12}CH_4$ signal (84 μmol/g catalyst) observed during TPR was the amount expected if most of the ^{13}CO remaining on Pt was displaced by ^{12}CO.

Spillover and Methanation

Dependence of hydrogen pressure. Interrupted TPR was used to determine how the rate of spillover depends on the H_2 partial pressure. As shown previously, interrupted TPR left sufficient H_2O on the support to inhibit methanation so that two distinct CH_4 peaks could be detected during a subsequent TPR. Thus, interrupted TPR was carried out to 580 K in ambient pressure H_2 after CO adsorption in H_2 flow at 385 K. Different H_2 partial pressures were then used during the subsequent TPR experiments to determine how much CH_4 formed in each peak. Figure 12 shows that the distribution between the two CH_4 peaks changed dramatically for a 10-fold variation in H_2 partial pressure. At 0.08 atm H_2, essentially all the CO was hydrogenated in the high-temperature peak; at 0.82 atm, more than half the CO had spilled over and was hydrogenated in the low-temperature peak. The amount of CH_4 was almost the same for each TPR. The amplitudes of the low-temperature CH_4 peaks are approximately proportional to the H_2 partial pressure. That is, the spillover rate appears proportional to the H_2 pressure.

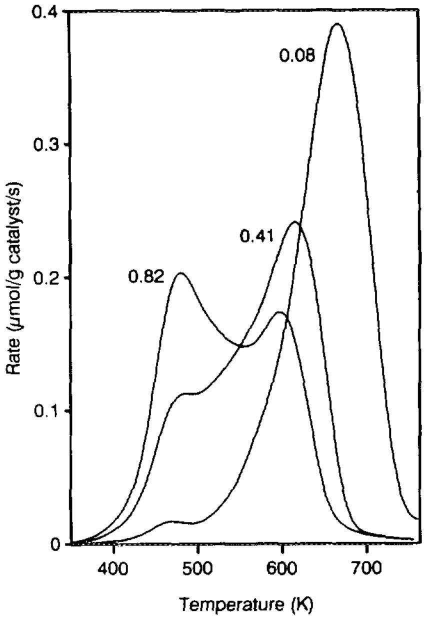

FIG. 12. Methane spectra from TPR of CO adsorbed at 385 K for 30 min in H_2 flow on a 7.7% Pt/Al_2O_3 catalyst. After CO adsorption, an interrupted TPR in ambient pressure H_2 to 580 K removed 90% of the adsorbed CO. The TPR experiments were then carried out with H_2 at the indicated partial pressure in atm.

The spectra in Fig. 12 show that the CH_3O hydrogenation rate under these conditions does not show a strong dependence on H_2 pressure since the peak temperature for the low temperature peak did not change as the

H_2 pressure changed. On Ni/Al_2O_3 and Ni/TiO_2 catalysts, CH_3O is hydrogenated slower than CO on Ni, and CH_3O hydrogenation is negative order in H_2 pressure (*20*). Thus, while the spillover rate increases with H_2 pressure, the hydrogenation rate of the CH_3O that forms does not. In contrast, the hydrogenation rate of CO on Pt increases as the H_2 pressure increases. The peak temperature for the high-temperature CH_4 peak decreased 60 K as the H_2 partial pressure increased a factor of ten. The same type dependence for CO hydrogenation on the Ni surfaces of Ni/SiO_2, Ni/Al_2O_3 and Ni/TiO_2 has been observed (*20*). The amount of CO that desorbed increased as the H_2 pressure decreased, although the amount (3.3 μmol/g catalyst) was small even for hydrogenation in 0.08 atm H_2. Results similar to those in Fig. 12 were obtained following interrupted TPR to 520 K for CO adsorbed at 300 K. For those experiments, the highest H_2 pressure used was 2 atm, and above 0.82 atm the increase in spillover was not proportional to H_2 pressure.

Variation in heating rate. On Ni/Al_2O_3 catalysts, varying the heating rate was an effective way to determine the relative activation energies of spillover and CO hydrogenation on Ni (*1*). When the heating rate was decreased, spillover was faster than CO hydrogenation on Ni, so that the CH_4 peak due to CH_3O hydrogenation increased and that due to CO hydrogenation decreased. That is, the lower heating rate favored the lower activation energy process (spillover) because more time was available for spillover.

Similar experiments on Pt/Al_2O_3 show that the same process occurs so that at lower heating rates the low-temperature peak increased because that peak is due to CH_3O hydrogenation. To carry out these experiments on Pt/Al_2O_3, interrupted TPR to 580 K, following CO and H_2 coadsorption at 385 K, was used so that two distinct CH_4 peaks could be distinguished. Subsequent TPR spectra, obtained at three heating rates, are shown in Fig. 13. Note that the total CH_4 amount (the area under the curve divided by the heating rate) is the same for the three spectra in Fig. 13. Peak amplitudes were used to estimate the relative amounts in each peak. At a heating rate of 2.5 K/s, approximately 35% of the CH_4 was from CH_3O hydrogenation, but at 0.5 K/s, 62% of the CH_4 was from CH_3O hydrogenation. Since the slower heating, which allows more time at lower temperatures, favors spillover, the activation energy for spillover is lower than that for CO hydrogenation on Pt.

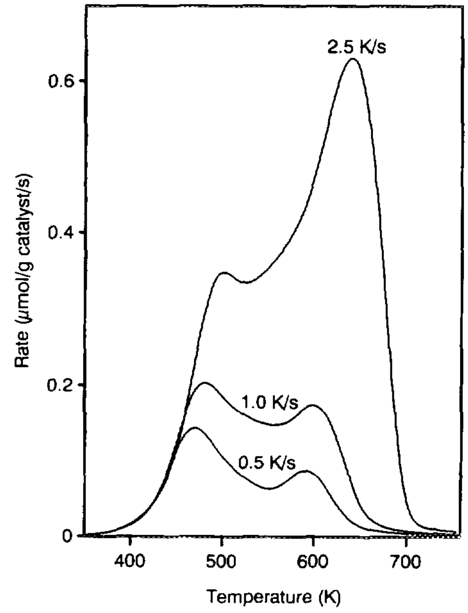

FIG. 13. Methane spectra from TPR at three heating rates on a 7.7% Pt/Al_2O_3 catalyst. Carbon monoxide was adsorbed at 385 K in H_2 flow and an interrupted TPR at 1 K/s was carried out to 580 K prior to the TPR.

An interesting result from Fig. 13 is that the initial rate of CH_4 formation is the same for all three heating rates. Such behavior is indicative of zero-order kinetics, since the CH_3O coverages are different for the three heating rates but the methanation rates are the same. An activation energy of 63 kJ/mol was calculated for this initial rise. This value is close to that reported by Vannice and Twu, 72 kJ/mol, for steady-state hydrogenation of CO on Pt/Al_2O_3 at 548 K (*6*). This initial zero-order behavior in CH_3O coveraged did not occur after interrupted TPR of CO initially adsorbed only on Pt (compare Figs. 10 and 13). The main difference is that for Fig. 13 a significant amount of H_2O formed, which poisoned some support sites. Therefore, the zero-order behavior in Fig. 13 may result because CH_3O hydrogenates on a limited number of sites. The initial rates may be the same at different heating rates or CH_3O coverages because the reaction sites are saturated; the initial reaction order is zero, and the initial rate only changes because the rate constant changes. In Fig. 10, H_2O has not poisoned a significant number of support sites, so the reaction sites are not the rate limiting factor. Instead, the reaction for the low-temperature peak was modeled using a first-order reaction assumption, and the model approximated the experimental data.

Hydrogen isotope effect. No kinetic isotope effect was observed when D_2 was replaced by H_2 during TPR following CO adsorption in He at 300 K. The difference in peak temperatures between CH_4 and CD_4 was less than 3 K. In these experiments, ^{13}CO was adsorbed when D_2 was used to avoid interference at mass 20 ($^{12}CD_4$, D_2O). When CO was adsorbed in H_2 flow at 385 K and an interrupted TPR to 580 K was used to obtain a lower coverage, two distinct methane peaks were observed during the subsequent TPR. When the TPR was carried out in H_2 flow, the 480 K peak was larger than the 600 K peak (Fig. 12, 0.82 atm), whereas when D_2 flow was used, the 600 K peak was larger (Fig. 14). Apparently, CH_3O formation and spillover is slower with D_2. Deuterium dissociation requires more energy than H_2 dissociation, and surface reactions where H_2 dissociation is important, either through equilibrium or by being a rate-determining step, will be slower for D_2 than for H_2 if all other factors are the same (*21*).

CONCLUSIONS

Methoxy forms on Pt/Al_2O_3 in an activated spillover process following CO and H_2 coadsorption on Pt. At elevated temperatures and in the absence of gas-phase H_2, CH_3O decomposes, and the formation of gas-phase CO and H_2 is limited by the rate of CH_3O decomposition. In the presence of gas-phase H_2, CH_3O hydrogenates to CH_4 faster than does CO adsorbed on Pt. At low CH_3O coverages, the rate of CH_3O formation and spillover is faster than the hydrogenation rate at low temperatures. The activation energy for spillover is also lower. The spillover rate is approximately first-order in H_2 pressure, but the CH_3O hydrogenation rate does not exhibit a strong dependence on H_2 pressure. At high CH_3O coverages, CH_3O decomposition and CO desorption from Pt compete with spillover and CH_3O hydrogenation. High CH_3O coverage appears to inhibit methanation. The CH_3O was shown to be adsorbed on Al_2O_3, and H_2O

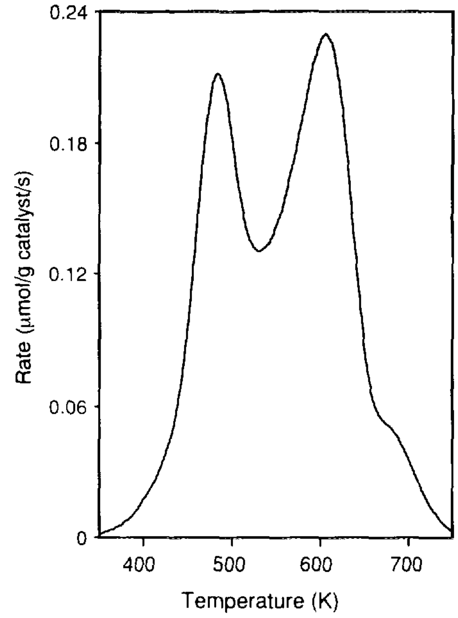

FIG. 14. CD_4 spectra from TPR of CO adsorbed at 385 K for 30 min in H_2 flow on a 7.7% Pt/Al_2O_3 catalyst. After CO adsorption, an interrupted TPR was carried out to 580 K in H_2 flow. The subsequent TPR was then carried out in D_2.

poisons the sites where CH_3O adsorbs, and thus decreases the spillover rate.

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