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Temperature-Programmed Methanation on Pd/La_2O_3 and Pd/SiO_2 Catalysts

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Temperature-programmed reaction and desorption (TPR, TPD) spectra are compared for Pd/La_2O_3 and Pd/SiO_2 catalysts for CO methanation and CO and H_2 coadsorption. A methoxy (CH_3O) species readily forms on the La_2O_3 surface of Pd/La_2O_3 by spillover, and this CH_3O hydrogenates to CH_4 at a higher rate than CO adsorbed on Pd. Carbon also deposits on the catalyst surface during TPR, and then hydrogenates at a slower rate than CH_3O. In contrast, CH_3O does not form on Pd/SiO_2 from CO and H_2, and correspondingly Pd/SiO_2 has a lower methanation activity than Pd/La_2O_3. Isotope labeling, interrupted reaction, activated adsorption, high-temperature TPD/TPR, and CH_3OH adsorption are used to study the surface processes on Pd/La_2O_3. The high methanation activity of Pd/La_2O_3 catalysts during steady-state methanation may be related to the formation and hydrogenation of CH_3O.

INTRODUCTION

Rieck and Bell (*1*) reported that Pd/La_2O_3 catalysts exhibit much higher methanation activities than Pd/SiO_2 catalysts, and they attributed this difference to the observation that La_2O_3, by forming small islands on the Pd particles, created sites where CO readily dissociated into carbon and oxygen. These higher methanation activities were reported both at steady state (*2, 3*) and during temperature-programmed reaction (TPR), where adsorbed CO was reacted in flowing H_2 as the temperature was ramped (*1*).

Similarly, Pd/Al_2O_3 catalysts have significantly higher turnover frequencies (TOF) than Pd/SiO_2 at steady state (*4–6*) and during TPR (*7*). For example, at 548 K, the TOF for Pd/Al_2O_3 was 35 times that of Pd/SiO_2 (*4*). Hsiao and Falconer (*7*) concluded that the higher methanation activity could be due to a CH_3O species, which rapidly formed on the Al_2O_3 support (*8*) and was then hydrogenated to CH_4 at a faster rate than CO adsorbed on Pd. On a Pt/Al_2O_3 catalyst, CH_3O was detected by IR and was hydrogenated faster than CO adsorbed on Pt (*9*).

The present experiments were carried out to determine if Pd/La_2O_3 exhibited the same behavior as Pd/Al_2O_3 and if therefore an alternative explanation for the higher activity of Pd/La_2O_3 is that CH_3O forms on the support and is then hydrogenated to CH_4. For comparison, a Pd/SiO_2 catalyst, which is less active for methanation, was also used. These catalysts were prepared using the procedures reported by Rieck and Bell (*1*), and we carried out similar TPR experiments. We coadsorbed CO and H_2 on the catalysts at elevated temperatures (but below the temperature where the methanation rate was significant) to determine if a CH_3O species formed on the support and to measure the hydrogenation rates of such species. Since Pd catalysts selectively form CH_3OH at high pressures (*10*), CH_3O is expected to form on our catalyst, and we carried out CO adsorption at 2.6 atm to increase the rate of CH_3O formation. Interrupted TPR, in which reaction was stopped at a preset temperature and the catalyst sample was then rapidly cooled, was combined with

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isotope labeling to determine if the CH_3O species were on Pd or La_2O_3. Temperature-programmed desorption (TPD) following CO and H_2 coadsorption was used to determine whether a CH_xO_y species was present on the catalysts, and TPR and TPD of CH_3OH, $(CH_3)_2O$ (dimethyl ether), and HCOOH helped identify the type of species present.

Methoxy species appear to form on Pd/La_2O_3, and this catalyst exhibited TPR and TPD spectra similar to those reported for Pd/Al_2O_3 (*7*). In contrast, Pd/SiO_2 did not form a detectable CH_3O species from coadsorbed CO and H_2. Thus, an alternate explanation to more rapid CO dissociation on Pd/La_2O_3 for the higher activity of the Pd/La_2O_3 catalysts may be that CH_3O forms on La_2O_3 and is then hydrogenated faster than CO adsorbed on Pd.

EXPERIMENTAL METHODS

Temperature-programmed desorption (TPD) and reaction (TPR) experiments were carried out in an apparatus that has been described previously (*11, 12*). A quartz frit, mounted in a 1-cm OD, quartz downflow reactor, supported 100 mg of catalyst. Quartz wool was placed both between the catalyst and the quartz frit, and on top of the catalyst. The reactor was placed in an electric furnace with a 0.5-mm OD, chromel-alumel shielded thermocouple centered in the catalyst bed. A temperature programmer used feedback from this thermocouple to raise the catalyst temperature from 300 K to a maximum of 1173 K at a constant rate of 1 K/s.

Immediately downstream from the reactor, the effluent gas was analyzed continuously by a UTI quadrupole mass spectrometer. A sampling valve interfaced the atmospheric-pressure gas stream to the ultrahigh-vacuum system, which contained the mass spectrometer and was pumped by a turbomolecular pump. A computer allowed simultaneous observation of multiple masses and the thermocouple signal. Known volumes of pure gas or liquid were injected into the carrier gas, downstream of the reactor, to calibrate the mass spectrometer.

At the beginning of each series of experiments, the reduced catalyst was pretreated for 2 h at 773 K in ambient pressure H_2 flow. For TPD and TPR experiments the catalyst was cooled in He or H_2 to 300 or 385 K, and CO, $(CH_3)_2O$, or CH_3OH were adsorbed. TPD were then carried out by raising the catalyst temperature at 1 K/s in He flow (110 standard cm^3/min, sccm) at ambient pressure (0.8 atm), to a final temperature of 773 K. At the end of each TPD experiment, the catalyst was either cooled to 300 K in He and TPR was run to hydrogenate species that remained on the surface, or the carrier gas was switched to H_2 and the catalyst was held at 773 K for 5–15 min before being cooled to 300 K. After CO, $(CH_3)_2O$, HCOOH, or CH_3OH adsorption, TPR was carried out by raising the catalyst temperature at 1 K/s from 300 to 773 K in H_2 flow (110 cm^3/min) at ambient pressure. For a few experiments, TPR or TPD was carried out to 1070 or 1173 K to detect strongly bound or less reactive species; ^{13}CO was adsorbed for these experiments to distinguish ^{13}CO products from contaminants that were not removed by reduction at 773 K. No additional experiments were carried out on a catalyst after it has been heated to 1170 or 1173 K. Several interrupted TPR experiments were conducted in which the catalyst with adsorbed CO was heated in H_2 flow at 1 K/s to either 450 or 625 K and cooled to 300 K prior to TPD or TPR. Then, ^{13}CO was adsorbed at 300 K to exchange any ^{12}CO that remained on Pd and to distinguish adsorbed ^{13}CO on Pd from carbon deposits.

Carbon monoxide and $(CH_3)_2O$ were adsorbed on the catalyst by using a pulse valve, which injected 0.15 cm^3 (STP) samples of either 10% CO/90% He, ^{13}CO, or $(CH_3)_2O$ into the carrier gas twice a minute. Adsorption times in these experiments ranged from 2 min (4 pulses) to 60 min (120 pulses). Pulsing was done in either He or H_2 flow, at either 300 or 385 K, and at either ambient pressure (0.8 atm) or 2.6 atm. Methanol and formic acid were adsorbed by evaporating the liquid from the tip of a liquid syringe. A back pressure regulator controlled the system pressure above ambient.

For the TPD experiments, masses 2 (H_2), 15 (CH_4), 18 (H_2O), 28 (CO), 31 (CH_3OH), 44 (CO_2), and 46 (CH_3OCH_3) were monitored. Methane was monitored at mass 15 to avoid CO, CO_2, and H_2O cracking fractions at mass 16. Mass 31 is the largest cracking fragment of CH_3OH. The mass 28 signal was corrected for CO_2 cracking, and masses 2, 15, 28 and 31 signals were corrected for $(CH_3)_2O$ cracking. In the TPR experiments the same masses were monitored as during TPD, except for mass 2 (H_2). When TPD or TPR involving ^{13}CO were conducted, masses 15, 17 ($^{13}CH_4$), 28, 29 (^{13}CO), 31, 44, 45 ($^{13}CO_2$), and 46 were monitored. To obtain $^{13}CH_4$ spectra, mass 17 signals were corrected for H_2O cracking. To obtain $^{12}CH_4$ spectra, mass 15 signals were also corrected for $^{13}CH_4$ cracking.

The procedures used to prepare the Pd/SiO_2 and Pd/La_2O_3 catalysts were adapted from those of Rieck and Bell (*1*). The Pd/SiO_2 catalyst was prepared by impregnation to incipient wetness of 60–80 mesh Davison silica gel (Grade 62) with a HCl solution of $PdCl_2$ (Alfa Products). The Pd/La_2O_3 catalyst was prepared by ion exchange of the HCl solution of $PdCl_2$ with a suspension of La_2O_3 (99.99%, Aldrich Chemical Co.) in water and separation of the ion-exchanged La_2O_3 by filtration. Both catalysts were air-dried overnight, calcined in air at 623 K for 2 h, reduced in H_2 at 573 K for 3 h, and finally passivated with 2% O_2 in N_2 at room temperature. The catalysts were pretreated in H_2 at 773 K for 2 h before TPR or TPD experiments. The Pd/SiO_2 catalyst had a weight loading of 7.9% Pd, and the Pd/La_2O_3 catalyst a weight loading of 5.3% Pd, as measured by inductively coupled plasma.

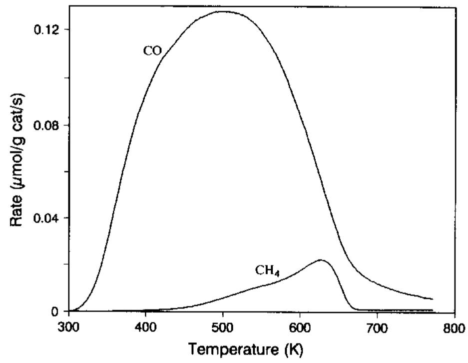

FIG. 1. TPR spectra on 7.9% Pd/SiO_2. Carbon monoxide was adsorbed at 300 K in He flow for 15 min.

The dispersions for these catalysts were estimated from the amounts of CH_4 and CO observed during TPR. Rieck and Bell (*1*) observed that percentages exposed calculated from TPR agreed with those determined from H_2–O_2 titrations. For our 7.9% Pd/SiO_2 catalyst the percentage exposed was 4.6%, and for the 5.3% Pd/La_2O_3 catalyst the percentage exposed was 0.8%. This low number for Pd/La_2O_3 is probably a result of the partial reduction of La_2O_3 and migration of LaO_x species onto the Pd (*13, 14*).

RESULTS

Palladium/Silica

As reported for steady-state methanation (*4–6*), Pd/SiO_2 is not a good methanation catalyst during TPR. The TPR spectra shown in Fig. 1 show that most of the CO that adsorbed at 300 K desorbed without reacting; less than 8% of the CO was hydrogenated to CH_4 (Table 1). The CH_4 formed in a peak at 630 K, but it also had a broad, low-temperature shoulder; the CH_4 spectrum is similar to that reported by Rieck and Bell for a 9% Pd/SiO_2 catalyst (*1*). However, for their catalyst, which had a dispersion of 18%, 42% of the adsorbed CO was hydrogenated to CH_4. Our 7.9% Pd/SiO_2, which was prepared by the same procedure, had a lower dispersion of 4.6%, and only 8% of the adsorbed CO was hydrogenated.

To determine if CH_3O formed on Pd/SiO_2, CO was exposed to the catalyst at 385 K in H_2 flow. These are the same

TABLE 1

Product Amounts during TPR on Pd/SiO$_2$ and Pd/La$_2$O$_3$ Catalysts

Catalyst support	Adsorption temperature (K)	Adsorbing gas (exposure time)	Amount of products (μmol/g catalyst)	
			CH$_4$	CO
SiO$_2$	300	He (15 min)	2.6	32
SiO$_2$	385	H$_2$ (30 min)	2.7	28
La$_2$O$_3$	300	He (15 min)	4.0	0
La$_2$O$_3$	385	H$_2$ (11 min)	18	0.6
La$_2$O$_3$	385	H$_2$ (30 min)	35	3.6
La$_2$O$_3$	385	H$_2$[a] (60 min)	38	22

[a] 2.6 atm H$_2$.

conditions that readily form CH$_3$O on Pd/Al$_2$O$_3$ (*7*). However, the subsequent CH$_4$ and CO TPR spectra were the same as those in Fig. 1, except that less CO desorbed below 385 K, the adsorption temperature. Similarly, TPD experiments following CO and H$_2$ exposure at 385 K showed no indication of CH$_3$O formation. Essentially the same CO TPD spectrum was obtained for CO adsorbed at 300 K in He and at 385 K in H$_2$, except that less CO desorbed below 385 K in the latter case. No indications of activated adsorption were obtained, and essentially no H$_2$ desorbed following coadsorption at 385 K. Apparently, CH$_3$O does not form at a significant rate on Pd/SiO$_2$ from CO and H$_2$ at 385 K, or if it forms, it is not stable on Pd/SiO$_2$ under these conditions.

The TPD spectrum for CO adsorbed at 300 K was similar to the CO TPR spectrum in Fig. 1; CO desorbed from 300 to 773 K, and no CO$_2$ was detected. Following TPD, the sample was cooled to 300 K and TPR was used to determine if surface carbon was present. The CH$_4$ detected during TPR corresponded to less than 2% of the amount of CO that desorbed during TPD. Thus, the amount of CO disproportionation or dissociation was quite small. Rieck and Bell (*1*) observed a similar broad CO desorption peak from a 9% Pd/SiO$_2$ catalyst, but 17% of the CO desorbed as CO$_2$ on their catalyst, and they observed CO and CO$_2$ desorption up to 900 K.

Palladium/Lanthana

Temperature-programmed reaction. The Pd/La$_2$O$_3$ catalyst showed higher methanation activity than Pd/SiO$_2$ during TPR. Essentially all the CO that adsorbed at 300 K was hydrogenated to CH$_4$; neither CO nor CO$_2$ was detected during TPR. The CH$_4$ peak temperature was 595 K, and CH$_4$ also formed in a high-temperature shoulder up to 775 K (Fig. 2). This CH$_4$ spectrum is similar

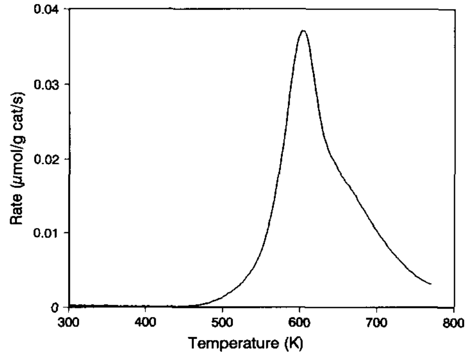

FIG. 2. Methane TPR spectra on 5.3% Pd/La$_2$O$_3$. Carbon monoxide was adsorbed at 300 K in He flow for 15 min.

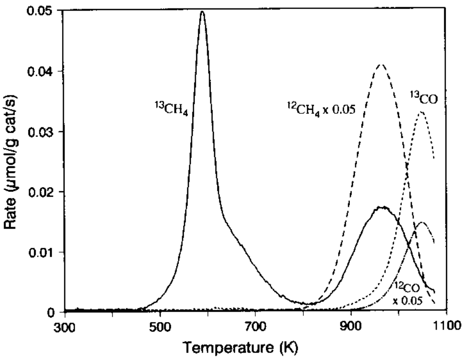

FIG. 3. High-temperature TPR spectra carried out to 1070 K on 5.3% Pd/La_2O_3. ^{13}CO was adsorbed at 300 K for 15 min in He flow.

to that reported by Rieck and Bell (*1*). They observed a single CH_4 peak with a small high-temperature shoulder, and 94% of adsorbed CO was hydrogenated to CH_4 on their 1.9% Pd/La_2O_3 catalyst. Because their catalyst was reduced at 573 K and ours was reduced to 773 K, their dispersion was higher (16%) and the CH_4 peak temperature was 70 K lower. However, the overall behavior is similar for these two Pd/La_2O_3 catalysts and quite different from that of Pd/SiO_2.

A similar TPR experiment was carried out to 1070 K, following ^{13}CO adsorption at 300 K, to determine if some CO remained on the surface until high temperature. After this experiment, the catalyst was not used in subsequent experiments. The resulting $^{13}CH_4$ spectrum below 800 K was the same as Fig. 2 and corresponded to 4 μmol/g catalyst, but half the adsorbed ^{13}CO left the surface above 800 K as $^{13}CH_4$ (2.4 μmol/g catalyst) and ^{13}CO (2.7 μmol/g catalyst). The ^{13}CO desorption was not complete by 1070 K. Because ^{13}CO was adsorbed, the $^{13}CH_4$ and ^{13}CO signals above 800 K are from adsorbed ^{13}CO and not from a carbon-containing species that remained on the surface after reduction at 773 K. Much larger quantities of $^{12}CH_4$ (100 μmol/g catalyst) and ^{12}CO (22 μmol/g catalyst) were observed, as shown in Fig. 3. Water (130 μmol/g catalyst) started to desorb at 800 K and had a maximum at 1030 K, but it is not shown in Fig. 3 for clarity. The $^{12}CH_4$ and ^{12}CO species resulted both from carbon-containing species that were not removed during reduction at 773 K and that remained from the previous TPR experiments with ^{12}CO. Carbonate species have been observed on La_2O_3 and these species decompose in the same temperature range that ^{12}CO desorbed (*15*). When this same experiment was carried out on a fresh catalyst (no previous TPR experiments), the $^{12}CH_4$ and ^{12}CO signals were half the size of those in Fig. 3. The signals in Fig. 3 were corrected for the naturally occurring ^{13}C in ^{12}C, and the $^{13}CH_4$ signal was also corrected for H_2O cracking at mass 17.

When CO was adsorbed at 385 K in H_2 flow for 30 min, the amount of CH_4 produced during the subsequent TPR increased by almost a factor of 10 over that observed for CO adsorption at 300 K, and some unreacted CO desorbed, as shown in Fig. 4. The CH_4 spectrum is quite similar in shape to that in Fig. 2, but the peak temperature is approximately 20 K lower. The amount of CH_4 did not increase much with adsorption times longer than 30 min at 385 K. However, the amount of unreacted CO increased with adsorption time and with higher H_2 adsorption pressure, and saturation was not

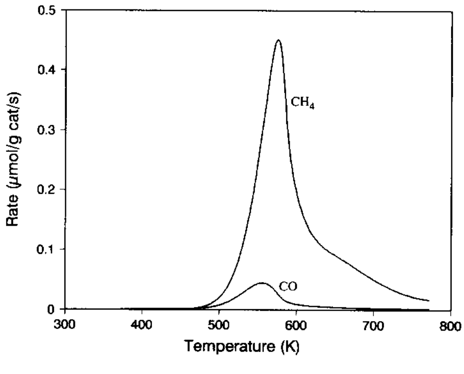

FIG. 4. TPR spectra on 5.3% Pd/La_2O_3 following CO adsorption at 385 K in ambient pressure H_2 flow for 30 min.

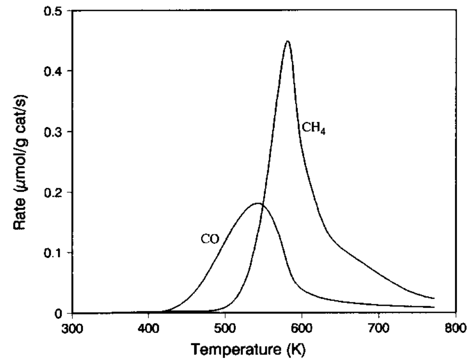

FIG. 5. TPR spectra for CH_3OH adsorption on 5.3% Pd/La_2O_3. The CH_3OH (1 μl) was adsorbed at 300 K in He flow.

reached for 60 min exposure in 2.6 atm H_2 flow at 385 K (Table 1). At these conditions, almost 40% of the CO desorbed unreacted. As the amount of unreacted CO increased, the CO peak temperature decreased from 570 to 538 K.

Temperature-programmed reaction of adsorbed CH_3OH yielded CH_4 and unreacted CO spectra (Fig. 5) that were almost identical to those obtained following CO adsorption for 60 min at 385 K in 2.6 atm H_2. The amounts of CH_4 and CO (35 and 19 μmol/g catalyst, respectively) for CH_3OH adsorption were almost the same as those from CO adsorption at 385 K in H_2 flow (38 and 22 μmol/g catalyst). When dimethyl ether (DME) was adsorbed at 300 K, the subsequent TPR yielded mostly DME, in a broad desorption peak centered at 425 K. A small amount of CH_4 formed (1.7 μmol/g catalyst), and an even smaller amount of CO desorbed. Temperature-programmed reaction of adsorbed HCOOH was quite different from that for CH_3OH or coadsorbed CO and H_2. For 1 μl HCOOH exposure at 300 K, almost no HCOOH desorbed, but CO_2 (20 μmol/g catalyst) formed in a peak at 465 K, CO (43 μmol/g catalyst) desorbed from 425 to 775 K with a maximum near 510 K, and CH_4 (86 μmol/g catalyst) formed in two peaks at 615 and 685 K.

Temperature-programmed desorption. When CO and H_2 were coadsorbed at 300 K on Pd/La_2O_3, almost exclusively H_2 desorbed by 775 K; less than 0.5 μmol CO/g catalyst desorbed. Since more than eight times as much CH_4 was detected by 775 K during TPR, much of the adsorbed CO remained on the surface during TPD to 775 K.

Following CO and H_2 coadsorption at 385 K (ambient pressure), much more CO and H_2 desorbed, and a small amount of CO_2 was also observed, above 650 K (Fig. 6). The CO desorbed in two peaks, and the larger peak (at 510 K) was accompanied by simultaneous H_2 desorption. However, H_2 also desorbed from 300 to 700 K. Larger coverages were obtained by coadsorption in 2.6 atm H_2 flow, and most of the increase in CO and H_2 desorption was centered at 500 K (Fig. 7).

The H/CO ratios for Figs. 6 and 7 were 12 and 9.5, respectively. These ratios are too large to correspond to decomposition of any reasonable CH_xO_y species, unless a significant fraction of the CO products remains on the surface. The TPD spectra obtained following CH_3OH adsorption at 300 K (Fig. 8) were quite similar to those in Fig. 7. Hydrogen and CO desorbed simultaneously at 490 K, and the H/CO ratio was 8.2. The CO_2 signal for CH_3OH adsorption was quite small. The total coverage in Fig. 8 was higher than that in Fig. 7. The similari-

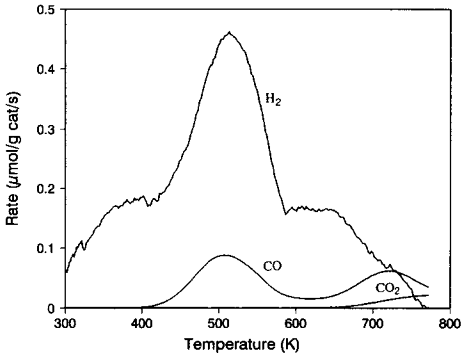

FIG. 6. TPD spectra for CO and H_2 coadsorbed on 5.3% Pd/La_2O_3 at 385 K. The CO was adsorbed for 30 min in ambient pressure H_2 flow.

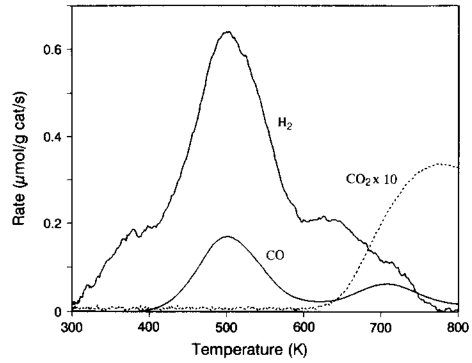

FIG. 7. TPD spectra for CO and H_2 coadsorbed on 5.3% Pd/La_2O_3 at 385 K. The CO was adsorbed for 30 min in H_2 flow at 2.6 atm.

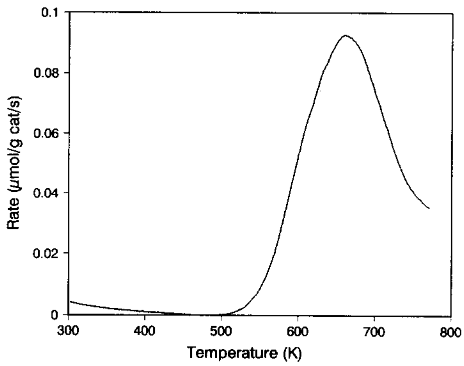

FIG. 9. TPR spectra carried out after the TPD spectra in Fig. 8.

ties in Figs. 7 and 8 suggests that CH_3O forms from H_2 and CO coadsorption at 385 K. The H_2 shoulder below 400 K in Fig. 7 was absent when CH_3OH was adsorbed in He and is likely due to adsorbed hydrogen.

To verify that CO and H_2 did not coadsorb at 385 K to form a formate, TPD was carried out following HCOOH adsorption at 300 K. The resulting spectra were quite different from those obtained for adsorbed CH_3OH or coadsorbed CO and H_2. The prominent carbon-containing species that desorbed was CO_2 (62 μmol/g catalyst) and only 21 μmol CO/g catalyst were observed. The CO_2 desorbed with a peak at 460 K but desorption continued to 773 K. The CO maxima were 470 and 615 K, while H_2 (160 μmol/g catalyst) desorbed in a peak at 480 K.

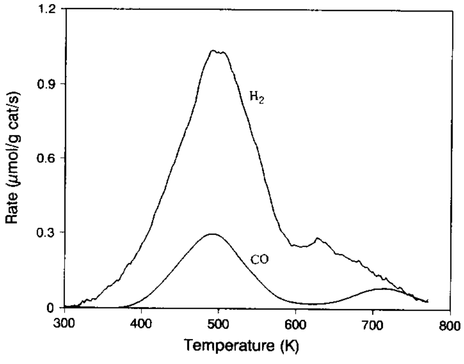

FIG. 8. TPD spectra for CH_3OH adsorbed on 5.3% Pd/La_2O_3. The CH_3OH (1 μl) was adsorbed at 300 K in He flow.

Immediately after the TPD experiments to 773 K, the catalyst was cooled to 300 K, the flow switched to H_2, and TPR carried out to 773 K. Following TPD of CH_3OH, a significant amount of CH_4 (13 μmol/g catalyst) formed from hydrogenation of carbon-containing species that remained (Fig. 9). Similar CH_4 spectra (10 μmol CH_4/g catalyst) were obtained for TPR following TPD of coadsorbed CO and H_2. If the surface species remaining after TPD is assumed to be carbon (and not CH_x), then when the amounts of CH_4 formed during these TPR experiments were taken into account, the H/C ratios (combined amounts for TPD and TPR) was 6.2 for CH_3OH adsorption and 4.4 for CO and H_2 coadsorption. For CH_3OH adsorption, the amount of carbon-containing products from TPD plus the subsequent TPR was identical to the amount from the TPR experiment described earlier. Thus, the TPD of adsorbed CH_3OH to 773 K did not create inactive carbon species that could not be hydrogenated by 773 K.

For TPD following DME adsorption at 300 K, mostly DME desorbed, with a peak temperature of 425 K; a small amount of CH_4 formed. Neither CO nor H_2 was detected, but some carbon was deposited and

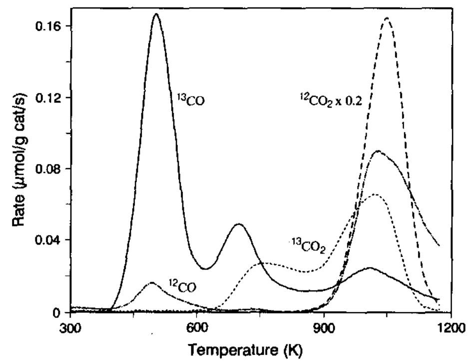

FIG. 10. High-temperature TPD spectra on 5.3% Pd/La$_2$O$_3$. ^{13}CO was adsorbed at 385 K for 30 min in 2.6 atm H$_2$ flow.

a TPR carried out after the TPD showed a CH$_4$ peak at 680 K.

The TPR experiments presented in Fig. 3, which had a final temperature of 1073 K, showed that some CO on Pd/La$_2$O$_3$ did not desorb or react until 1000 K. This ability of Pd/La$_2$O$_3$ to strongly bond CO may be responsible for the large H/CO ratios observed during TPD to 773 K. On Ni/Al$_2$O$_3$ catalysts, for example, the H/CO ratio following CH$_3$OH adsorption is 3.6 (*16*). Thus, TPD was carried out to 1170 K following ^{13}CO and H$_2$ coadsorption at 385 K in 2.6 atm H$_2$. Because the catalyst was only reduced at 773 K, ^{13}CO was used so that products from the adsorbed ^{13}CO could be distinguished from contaminants that were not removed by reduction at 773 K.

Figure 10 shows that 40% of adsorbed ^{13}CO desorbed as ^{13}CO and ^{13}CO$_2$ above 773 K. Most of the ^{13}CO$_2$ formed above 773 K. Even larger amounts of ^{12}CO and ^{12}CO$_2$ formed from contaminants and from two previous TPD and TPR experiments on this sample. The H$_2$ and ^{13}CO spectra below 773 K in Fig. 10 are identical to those in Fig. 7, and the H$_2$ spectrum is not presented for clarity.

Temperature-programmed reaction: Isotope studies. In an attempt to distinguish adsorption sites, ^{12}CO was adsorbed at 385 K in H$_2$ flow for 30 min; this was assumed to form ^{12}CH$_3$O on La$_2$O$_3$ and ^{12}CO on the Pd. Then, the catalyst at 300 K was exposed to ^{13}CO in He flow in order to exchange ^{12}CO on Pd with ^{13}CO. The resulting TPR (Fig. 11) yielded ^{12}CH$_4$ and ^{13}CH$_4$ in approximately a 10 : 1 ratio. The ^{12}CH$_3$O on the support did not exchange with gas-phase ^{13}CO; this is the same result observed for Ni/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ (*7, 8, 17*). The ^{13}CH$_4$ signal in Fig. 11 is almost identical in shape to ^{12}CH$_4$, but is one-tenth the size. Thus, two distinct methanation processes, due to hydrogenation of CO on Pd and hydrogenation of CH$_3$O on La$_2$O$_3$, could not be distinguished. The unreacted ^{12}CO and ^{13}CO also desorbed simultaneously, but the ^{12}CO/^{13}CO ratio was only 3.3. That is, below 773 K only 67% of the ^{13}CO was hydrogenated to ^{13}CH$_4$; for ^{13}CO adsorbed at 300 K in the absence of ^{12}CH$_3$O, more than 95% of the ^{13}C was hydrogenated. The total amount of ^{13}C products was identical for both experiments. When ^{12}CO was adsorbed for 60 min in 2.6 atm H$_2$ to create a higher coverage of ^{12}CH$_3$O before ^{13}CO adsorption at 300 K, only 31% of the ^{13}CO was hydrogenated to ^{13}CH$_4$ during TPR to 773 K. Thus, adsorbed ^{12}CH$_3$O on La$_2$O$_3$ decreased the amount of ^{13}CO (originally on Pd) that was hydrogenated.

Interrupted temperature-programmed re-

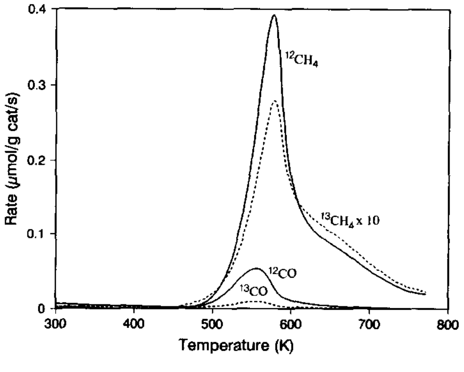

FIG. 11. TPR spectra on 5.3% Pd/La$_2$O$_3$ following ^{12}CO adsorption at 385 K in ambient pressure H$_2$ flow for 30 min and ^{13}CO adsorption at 300 K in He flow for 15 min.

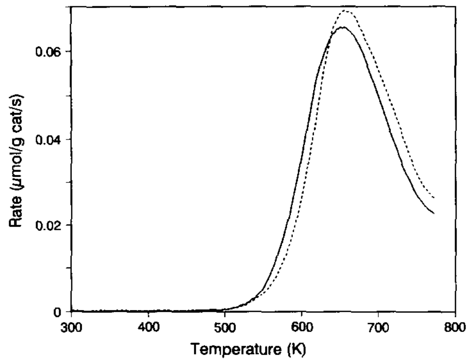

FIG. 12. Solid line: $^{12}CH_4$ spectra for a TPR that followed an interrupted TPR to 625 K. The ^{12}CO was adsorbed on 5.3% Pd/La_2O_3 at 385 K in H_2 flow for 30 min. Dashed line: $^{12}CH_4$ spectra for the same procedure as the solid curve, but ^{13}CO was exposed to the catalyst at 300 K prior to the final TPR.

action. The TPR spectrum for CH_4 in Fig. 2 clearly shows a high-temperature shoulder that may indicate two reaction processes to form CH_4. Indeed, when CO and H_2 were adsorbed at 385 K, the high-temperature shoulder did not grow as rapidly as the main CH_4 peak (Fig. 4). To study this, CO was adsorbed in H_2 flow at 385 K (30 min), TPR was started but was interrupted at 625 K, and the catalyst was rapidly cooled to 300 K. The subsequent TPR spectrum for CH_4 is shown in Fig. 12 (solid line). Methane formed in a broad peak with a maxima near 650 K.

When this procedure was repeated, but ^{13}CO was adsorbed in He flow at 300 K prior to the final TPR, the resulting $^{12}CH_4$ spectrum (Fig. 12, dashed line) was unchanged and the same amount of $^{12}CH_4$ formed (9.2 µmol/g catalyst). The amount of $^{13}CH_4$ was the same as that observed for ^{13}CO adsorption on a fresh surface. The precursor that produced the $^{12}CH_4$ peak did not exchange with gas-phase ^{13}CO. Thus, the adsorbed species that was hydrogenated to CH_4 in the high-temperature shoulder of Fig. 4 is not CO adsorbed on Pd because that readily exchanges with gas phase CO.

The CH_4 peaks in Fig. 12 are almost identical to the CH_4 peak obtained during TPR carried out immediately after a TPD to 773 K, for either CO and H_2 or CH_3OH adsorption (Fig. 9). Thus, the CH_4 in Fig. 12 did not result from hydrogenation of CO that desorbs by 773 K. This was also verified by carrying out a TPD to 773 K *after* an interrupted TPR to 625 K. No H_2, CO, CO_2, or CH_4 formed during this TPD, and a subsequent TPR was similar to those in Fig. 12, though the peak temperature was 20 K higher.

The same interrupted TPR experiment was also carried out following CO adsorption in He at 300 K. Though the amount of CH_4 was smaller, qualitatively the same results were obtained. After the interrupted TPR, 1.4 µmol CH_4/g catalyst formed during the subsequent TPR and its peak temperature was 665 K.

DISCUSSION

Palladium/Silica

Both TPR and TPD experiments on Pd/SiO_2 indicate that CH_3O does not form at a significant rate from CO and H_2 coadsorption at 385 K. These results are consistent with previous IR studies (*18*), which also did not detect any CH_3O formation on Pd/SiO_2. Methoxy is not expected to be stable on Pd under our conditions since CH_3OH decomposes at 220 K on Pd(111) to form CO and H_2 (*19*). Similarly, on Pt(110) (2 × 1), CH_3OH desorbs or decomposes by 275 K (*20*). These results also indicate that for CH_3O to be present at elevated temperatures on Pd/La_2O_3, the CH_3O must be on the La_2O_3.

Coincident with the lack of CH_3O formation, most of the CO adsorbed on Pd/SiO_2 desorbed during TPR; less than 10% was hydrogenated to CH_4. On a higher dispersion Pd/SiO_2 catalyst, Rieck and Bell (*1*) observed that 42% of the adsorbed CO was hydrogenated to CH_4 during TPR, but the CH_4 peak temperature was essentially the same as we observed. During TPD of adsorbed CO, they also observed more CO_2 from CO dissociation, which has been observed to increase with dispersion on Pd by

Doering *et al.* (*21, 22*) and Ichikawa *et al.* (*23*) but not by Rieck and Bell (*1*).

Palladium/Lanthana

As shown by a comparison of Figs. 1 and 2, Pd/La_2O_3 is much more active than Pd/SiO_2; as described below, Pd/La_2O_3 is quite similar to Pd/Al_2O_3 (*7*). Thus, the high methanation activity of Pd/La_2O_3, both for TPR and during steady state, may be a result of CH_3O formation and its subsequent hydrogenation. A spillover process results in CH_3O adsorbed on the La_2O_3. In the following discussion, the reasons for these conclusions are presented and more detailed comparisons are made to Pd/Al_2O_3.

Identification of CH_3O. Previous TPD studies on Ni/Al_2O_3 (*24, 25*) and Pd/Al_2O_3 (*7*) indicated that CH_3O formed on the Al_2O_3 support because H_2 and CO desorbed simultaneously and the H/CO ratio was close to 3. In addition, IR spectroscopy detected CH_3O on Pd/Al_2O_3 (*18*). The many similarities in both TPR and TPD for Pd/Al_2O_3 and Pd/La_2O_3 suggest that CH_3O also forms on Pd/La_2O_3. As shown in Figs. 6 and 7, H_2 and CO desorb simultaneously near 500 K, and as the exposure increased the peaks near 500 K increased. Though the H/CO ratio is much larger than 3, almost the identical behavior was observed for CH_3OH adsorption on Pd/La_2O_3 (Fig. 8). The desorption spectra are almost identical for Figs. 7 and 8. The large H/CO ratios are attributed to the fact that CO and CO_2 from CH_3O decomposition remain on the surface to high temperatures. As shown in Fig. 10, almost all the CO_2 and a significant amount of CO desorb above 800 K. Also, some H_2 is from adsorbed hydrogen, which desorbs in a broad desorption band from 300 to 700 K when adsorbed alone.

The similarity of TPR spectra for CH_3OH adsorption and for CO and H_2 coadsorption at 385 K also shows that CH_3O forms on Pd/La_2O_3. The peak shapes, peak temperatures, and the CH_4 amounts are almost identical for Figs. 4 and 5. Moreover, higher CO and H_2 exposures increased the amount of unreacted CO observed during TPR and yielded larger CO amounts, similar to those observed for CH_3OH adsorption. In addition, the TPR and TPD spectra for coadsorbed CO and H_2 are quite different from those observed for adsorbed HCOOH and $(CH_3)_2O$, two species that could form from CO and H_2.

The CH_3O species is assumed to be on the La_2O_3 support because so much more CO adsorbed in the presence of H_2. The CO that adsorbs in He only adsorbs on Pd. No additional CO adsorbed in H_2 flow at 385 K on Pd/SiO_2, but it did adsorb on Pd/Al_2O_3 and Pd/La_2O_3, so the adsorption site appears to be on the support. In addition, on Ni/Al_2O_3–Al_2O_3 mixtures (*26*), adsorbed CH_3O was shown directly to be on the support.

Methoxy formation and hydrogenation. Both La_2O_3 and Al_2O_3 supports increase the steady-state methanation activity of Pd. The large number of similarities in both TPR and TPD for Pd/Al_2O_3 and Pd/La_2O_3 strongly suggest that the same process is involved. That is, CO and H_2 adsorb on Pd and then spill over onto La_2O_3 to form CH_3O. The TPR experiment following CO and H_2 coadsorption at 385 K (Fig. 4) thus corresponds to CH_3O hydrogenation. Note that the CH_4 spectrum in Fig. 4 is similar in shape to that in Fig. 2, but the peak temperature is lower for Fig. 4. That is, CH_3O formed on La_2O_3 is hydrogenated to CH_4 as fast or faster than the CO originally adsorbed on Pd, and significantly faster than CO on Pd/SiO_2. Methoxy does not form on Pd/SiO_2 and thus Pd/SiO_2 is much less active for methanation.

A number of similarities between Pd/La_2O_3 and Pd/Al_2O_3 (*7*) support CH_3O formation and hydrogenation as a methanation pathway on Pd/La_2O_3:

- When $^{12}CH_3O$ was formed on the support and ^{13}CO was adsorbed on Pd, both types of carbon-containing species reacted at the same rate. The $^{12}CH_4$ and $^{13}CH_4$ spectra in Fig. 11 are almost identical in shape.

This is expected if the ^{13}CO spilled over to form $^{13}CH_3O$ before hydrogenation. This process was shown directly to occur on Pd/Al_2O_4 (*8*).

- When $^{12}CH_3O$ was on the support, a smaller fraction of the ^{13}CO adsorbed on Pd was hydrogenated to $^{13}CH_4$.
- More CH_3O formed when the H_2 pressure was increased.

Role of lanthana. The La_2O_3 support thus creates additional reaction sites that are more active than those on Pd metal. Rieck and Bell (*1*) observed that the activation energy for methanation on Pd/La_2O_3 was higher than that for Pd/SiO_2 and they concluded that LaO_x created a large number of active sites to compensate. Lanthana decreased CO adsorption on the metal surface for Pd (*1*) and Rh (*27*), apparently by covering the metal with LaO_x islands. Riech and Bell (*1*) concluded that these islands promoted CO dissociation. The resulting carbon was then hydrogenated to CH_4. Carbon formed by CO adsorption in 10% H_2 flow at 498 K hydrogenated faster than adsorbed CO, and they concluded that higher methanation activity of Pd/La_2O_3 was due to enhanced CO dissociation.

Vannice and co-workers (*2, 28*) observed that the heat of adsorption of CO was not affected by the support and concluded that oxygen vacancies at the Pd/La_2O_3 interface enhanced methanation by facilitating CO bond rupture. They pointed out that H-assisted bond rupture and direct involvement of the support to facilitate bond rupture may be parts of the reaction mechanism. They concluded that the CO bond is activated via electron transfer between CO and a site on the support.

Our results, though consistent with these observations, indicate that the enhanced dissociation may be due to formation of CH_3O, which is more readily hydrogenated to CH_4. Thus, its C–O bond is easier to break than that in CO. Much of the CH_3O adsorbed on La_2O_3 could contribute to steady-state methanation. The hydrogenation step could occur by H spillover from the Pd metal or by hydrogenation at the $Pd–La_2O_3$ interface.

Unreactive surface species. The TPR and TPD experiments in Figs. 3 and 10 indicate that large amounts of carbon-containing species remain on the surface following catalyst preparation and pretreatment. These species only react to CH_4 or desorb as CO and CO_2 above 900 K, in quantities 5–20 times larger than the amount of ^{13}CO that adsorbed. Similarly, half the ^{13}CO adsorbed at 300 K appeared as ^{13}CO or $^{13}CH_4$ above 800 K during TPR. These high-temperature peaks are not likely to contribute to steady-state methanation. The carbon-containing species remaining on the surface to 800 K may be carbonate species adsorbed on La_2O_3 (*15*). The fact that repeat TPR experiments carried out to 773 K showed no diminution in the amount of CH_4 produced, despite leaving carbon-containing species on the surface, indicates that these species do not occupy CH_3O adsorption sites on La_2O_3.

This high-temperature behavior of Pd/La_2O_3 is quite different from that of Pd/Al_2O_3. When ^{13}CO was adsorbed at 300 K on Pd/Al_2O_3, essentially no ^{13}CO and $^{13}CH_4$ were observed above 700 K (*16*). Moreover, the ^{12}C impurities were insignficant; only H_2O desorbed from Pd/Al_2O_3 in significant amounts above 800 K.

Another significant difference between Pd/La_2O_3 and Pd/Al_2O_3 is that Pd/Al_2O_3 did not exhibit a high-temperature CH_4 tail during TPR similar to that in Fig. 2. The interrupted TPR experiments showed that the species responsible for the CH_4 peak around 650 K was not CO on Pd, since it did not exchange with gas-phase CO (Fig. 12). The same species was also present on the Pd/La_2O_3 surface following TPD to 773 K for both CO + H_2 and CH_3OH adsorption (Fig. 9), and it corresponds to a strongly bound species that does not desorb by 773 K. Since this species remained on the surface after TPD but was hydrogenated during TPR, the amount of CO desorbed during TPD was less than the amount of CH_4 observed during TPR. However, additional inactive species formed during TPD because the amount of CO + CH_4 observed during TPR to 773 K (38 μmol/g catalyst) was larger than the amount of CO + CO_2 observed during TPD plus CH_4 during a subsequent TPR (total of 26 μmol/g catalyst). These inactive species may be carbonate adsorbed on La_2O_3.

CONCLUSIONS

- A methoxy species forms in an activated step on the support of Pd/La_2O_3 upon exposure to CO and H_2. Methoxy does not form on Pd/SiO_2 under the same conditions.
- Methoxy hydrogenates faster than CO on Pd, and this may be the reason Pd/La_2O_3 is more active for methanation than Pd/SiO_2. The La_2O_3 surface creates additional reaction sites where CH_3O adsorbs.
- Carbon monoxide strongly adsorbs on Pd/La_2O_3, and perhaps forms carbonates, which desorb above 1000 K.
- A species of carbon, less active for methanation than CH_3O, forms on Pd/La_2O_3.
- Carbon-containing contaminants, which may be carbonates, are not removed from the La_2O_3 support of Pd/La_2O_3 at 773 K.

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