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Methanation Sites on a Pt/TiO$_2$ Catalyst

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The adsorption of H_2 and CO and the hydrogenation of CO were studied by temperature-programmed desorption and reaction (TPD, TPR) on a 1.8% Pt/TiO$_2$ catalyst. Two types of adsorbed CO were observed: CO is adsorbed on Pt and a H–CO complex is adsorbed on the TiO$_2$ support. The H–CO complex, which appears to be a methoxy (CH_3O) species, hydrogenates at a faster rate than does the CO on Pt. Isotope labeling indicates that the methoxy species may be directly hydrogenated to CH_4. The CO transfers rapidly from Pt to TiO$_2$ at methanation temperatures and below. The effects of H_2 pressure and adsorption temperature on the methanation rate during TPR are presented. The higher rate of hydrogenation of the CH_3O species adsorbed on the support (relative to CO adsorbed on Pt) may be related to the enhanced methanation activity of Pt/TiO$_2$ catalysts at steady state.

INTRODUCTION

The strong metal–support interaction (SMSI) reported for Pt/TiO$_2$ catalysts after high temperature reduction (*1*) has been attributed to migration of TiO$_x$ species onto the Pt surface (*2–5*). This migration of TiO$_x$ decreases the Pt surface area available for chemisorption. One of the interesting aspects of the SMSI is that Pt/TiO$_2$ catalysts have significantly higher activities for methanation than Pt on other supports, and Pt/TiO$_2$ catalysts are more active than Pt/SiO$_2$, even when the Pt/TiO$_2$ is reduced at low temperatures, where the SMSI effect is not expected to be important (*4, 6*). Moreover, Pt/Al$_2$O$_3$ is also significantly more active than Pt/SiO$_2$ for methanation (*6*). Dwyer *et al.* (*4*) stated it was likely that enhanced methanation rates on Pt/TiO$_2$ catalysts are not directly related to the SMSI effect.

Bracey and Burch (*7*) attributed the higher methanation activity on Pt/TiO$_2$ to special interfacial sites that were highly active for CO bond breaking. Vannice and Twu (*6*) also attributed the higher activity to special sites at the interface. Dwyer (*8*) proposed that a methoxy species was present on the TiO$_2$ surface and that this species was an intermediate for CH_3OH or CH_4 products. This proposal was based on IR and kinetic studies. When SiO$_2$, Al$_2$O$_3$, or TiO$_2$ were deposited onto Pt powder, the methanation activity increased significantly although the Pt surface area, as measured by ISS, decreased upon deposition of the oxides (*4, 8*). The oxides covered a significant fraction of the Pt surface. Moreover, the highest activity was observed when TiO$_2$ was deposited on Pt powder, although this surface had the smallest fraction of Pt exposed. For example, the deposition of TiO$_2$ equivalent to 10 monolayers onto Pt black increased the methanation activity by more than two orders of magnitude (the rate was normalized to the total surface area, not the Pt surface area) although ISS indicated only 5% of the surface was Pt. Infrared studies on supported Pt/TiO$_2$ showed the presence of CH_3O species, which were assigned to a Ti–O–CH$_3$ species. In addition, programmed heating in H_2, combined with IR, showed that the Pt–CO was the least reactive species. They proposed that a partially hydrogenated intermediate migrates from the Pt to the TiO$_2$ support, and the support acts as a large surface area reservoir for the intermediates, which are subsequently hydrogenated to

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CH_4. A recent study by Robbins and Marucchi-Soos (*9*) saw similar results on a Pt/Al_2O_3 catalyst. Two methanation sites were observed by temperature-programmed reaction (TPR), and one of the sites on Pt/Al_2O_3 was associated with a CH_3O species on Al_2O_3 (*9*). The CH_3O, detected by IR, was shown to be hydrogenated faster than CO on Pt.

The studies by Dwyer *et al.* (*4, 8*) prompted us to study the reactivity of Pt/TiO_2 by temperature-programmed reaction and desorption (TPR, TPD), since we had shown previously that TPR allows multiple reaction sites to be detected on supported Ni catalysts (*10–12*). By combining TPR with isotope labeling, we showed that two distinct sites were present on Ni/Al_2O_3 (*11*) and Ni/TiO_2 (*12*), and TPD experiments indicated that the stoichiometry of one of the adsorbed species was that of a methoxy species (*12, 13*). Temperature-programmed reaction experiments on mixtures of Ni/SiO_2 and Al_2O_3 showed that the methoxy was adsorbed on the Al_2O_3 support (*14*). The isotope experiments indicated that the methoxy formed by CO and H_2 adsorption on Ni and subsequent transfer to the support (*11*).

The methoxy species were hydrogenated at a slower rate on Ni/Al_2O_3 than the CO adsorbed on Ni, but Pt is a much poorer methanation catalyst than Ni and thus the methoxy may be more active on a Pt/TiO_2 catalyst, as it is on Pt/Al_2O_3 (*9*). The objectives of the present studies were to use TPR and TPD to:

- directly measure the reactivity of adsorbed species
- measure site concentrations
- verify the presence of a H–CO complex on TiO_2
- study transfer between sites
- determine if the H–CO species is directly hydrogenated on TiO_2
- compare Pt/TiO_2 to Ni/Al_2O_3 and Ni/TiO_2 catalysts

Thus, adsorption was carried out at both 300 and 385 K and isotope labeling (^{12}CO and ^{13}CO) was used in an attempt to separate reaction sites. A range of H_2 partial pressures were used during TPR in an effort to separate sites. On Ni/Al_2O_3 and Ni/TiO_2 catalysts, the hydrogenation rates of CO and of CH_3O have different orders in H_2 pressure (*15*). The reaction of H_2 with an adsorbed D–CO species was studied by adsorbing CO in D_2 flow and then carrying out TPR in H_2 flow. The reactivity of CH_3OH was also studied by adsorbing CH_3OH on the catalyst and on TiO_2 alone.

The catalyst was reduced for 2 h at 475 K, but in order to carry out TPR experiments, the catalyst must be heated to 775 K in H_2. Thus, to obtain reproducible results, all the TPR and TPD spectra presented were obtained after the catalyst was heated in H_2 at 1 K/s to 775 K.

Our studies show that a CH_3O species on the support of a Pt/TiO_2 catalyst is hydrogenated to CH_4 at a faster rate than the CO adsorbed on Pt. Moreover, CO transfer between the Pt and the TiO_2 is rapid in the presence of H_2 and is much faster than on Ni/Al_2O_3 and Ni/TiO_2 catalysts. Direct hydrogenation of the CH_3O species appears to take place on TiO_2. Since the reaction sites on the oxide are more active, they may play a role in steady-state hydrogenation of CO on Pt/TiO_2 catalysts.

EXPERIMENTAL METHODS

Temperature-programmed reaction of adsorbed CO in flowing H_2 and temperature-programmed desorption of coadsorbed CO and H_2 were used to study multiple reaction sites on a 1.8% Pt/TiO_2 catalyst. A detailed description of the experimental apparatus is given elsewhere (*16*). A 100-mg catalyst sample was heated in a quartz downflow reactor and the reactor effluent was continuously analyzed by a quadrupole mass spectrometer, which was interfaced to a computer system.

The procedures for TPR and TPD are similar to those described previously for Ni/Al_2O_3 catalysts (*11, 13*). The previously reduced Pt/TiO_2 catalyst was pretreated in H_2 flow for 2 h at 475 K and then heated at 1

K/s in H_2 flow to 775 K. The catalyst was then quickly cooled in H_2 flow for a TPR or TPD experiment. Carbon monoxide was adsorbed in H_2 flow at either 300 or 385 K by injecting pulses of CO into the H_2 flow with a computer-controlled pulse valve. For TPR, the catalyst was heated in ambient pressure H_2 at 1 K/s to 775 K while continuously monitoring mass signals for CH_4, CO, and CO_2. Methane was monitored at mass 15 to avoid the cracking fractions from CO and CO_2 at mass 16. For TPD, the catalyst was heated in He flow at 1 K/s to 775 K and mass peaks for H_2, CO, CO_2, and CH_4 were monitored. The mass 28 signals were corrected for CO_2 cracking. The H_2 or He flow rate was 100 cm^3/min. Calibrations for CH_4 and CO were carried out by injecting 1-cm^3 pulses of these gases into the carrier gases.

Several variations were used for the TPR experiments. In one series of experiments, CO was adsorbed following cooling in ambient pressure H_2, but the catalyst was heated in a H_2/He mixture at ambient pressure or in pure H_2 at 2 atm pressure. Separate calibrations of CH_4 and CO were carried out for each H_2/He mixture. The consumption of H_2 was also observed during TPR. In a few experiments the catalyst was cooled from 775 K in He instead of H_2 flow since this procedure affected the amount of H_2 adsorption on Ni/Al_2O_3 catalysts (*11*). In one set of experiments, CO was adsorbed at 385 K in ambient pressure D_2 flow after cooling the catalyst from 775 K in D_2 flow. The catalyst was then cooled to 300 K, the flow switched to H_2, and TPR carried out in ambient pressure H_2. Signals were monitored for masses 4 (D_2), 15 (CH_4), 17 (CDH_3), 18 (H_2O, CH_2H_2), 19 (HDO, CD_3H), and 20 (D_2O, CD_4). Note that because of cracking in the mass spectrometer, the products indicated for a given mass are not unique. For example, cracking of CD_4 will give a signal at mass 18 and cracking of CD_3H will give signals at masses 18 (CD_3^+) and 17 (CD_2H^+).

For both the TPR and TPD experiments, attempts were made to separate sites with isotopes by adsorbing ^{12}CO at 385 K in H_2 flow and then exposing the catalyst to ^{13}CO at 300 K in H_2 flow in order to exchange some of the ^{12}CO adsorbed on Pt with ^{13}CO. In other experiments, ^{12}CO was adsorbed at 385 K, and interrupted TPR was used to remove some of the ^{12}CO before adsorbing ^{13}CO.

Since a methoxy species appeared to be present on the TiO_2 support, we adsorbed CH_3OH on the catalyst at 385 K in H_2 flow and carried out TPR and TPD experiments. The CH_3OH was adsorbed by slowly injecting pulses of liquid methanol with a syringe and allowing the CH_3OH to evaporate into the H_2 stream that flowed over the catalyst.

A TiO_2 support without Pt was used to determine if CO and H_2 adsorb on TiO_2 in the absence of Pt. The TiO_2 was pretreated in the same manner as the catalyst, and TPD and TPR experiments were carried out following CO exposure at 385 K in H_2 flow. Methanol was also adsorbed on the TiO_2 at 385 K before TPD and TPR experiments were carried out.

The 1.8% Pt/TiO_2 catalyst was prepared by impregnating TiO_2 (Degussa P-25) to incipient wetness with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$. The sample was dried under vacuum at 380 K for 16 h, heated in H_2 flow to 475 K at 1.5 K/min, and held in H_2 flow at 475 K for 2 h. The sample was slowly exposed to a 2% O_2/N_2 mixture at room temperature before removal from the preparation apparatus. The Pt weight loading was determined by atomic absorption.

RESULTS

PLATINUM/TITANIA CATALYST

Temperature-Programmed Reaction of CO

When CO was adsorbed at 300 K in H_2 flow (after cooling in H_2 from 775 K) by injecting 2 pulses of CO per min for 30 min (saturation exposure at 300 K), the subsequent TPR showed that the Pt/TiO_2 catalyst was almost as active for methanation as a Ni/SiO_2 catalyst. A single, broad peak was observed with a peak temperature at 500 K

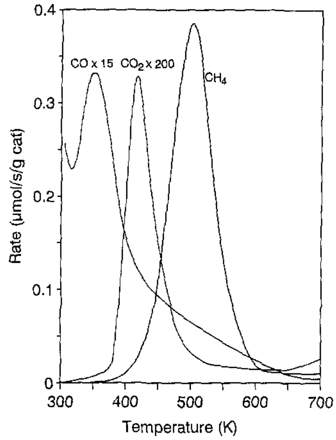

FIG. 1. TPR spectra for CO adsorbed at 300 K on 1.8% Pt/TiO_2 for 30 min in H_2 flow, following cooling in H_2 from 775 K.

(Fig. 1). The only other gas desorbing in significant quantities was unreacted CO. The CO desorbed in a peak at 350 K, but the amount was small; 97% of the adsorbed CO reacted to form CH_4 (36 μmol/g catalyst) during TPR. A small amount of CO_2 was also seen, with a peak at 420 K, but as shown by the scale factor in Fig. 1, this peak corresponds to less than 0.4% of the CH_4 amount. When CO was adsorbed in He flow at 300 K, following cooling in He from 775 K, the subsequent TPR spectra were almost identical to those in Fig. 1. Note that the TPR was carried out to 775 K, but the amount desorbing above 700 K was insignificant and thus the spectra are only shown to 700 K in Fig. 1.

For a few TPR experiments following CO adsorption at 300 K in H_2 flow, the heating rate was varied from 0.1 to 4 K/s. For a heating of 0.1 K/s, the CH_4 peak temperature was 460 K and no unreacted CO was detected. For a heating rate of 4 K/s, the peak temperature was 577 K and more CO desorbed than for a heating rate of 1 K/s. No separation of the CH_4 signal into two distant peaks was observed at either heating range.

As shown in Fig. 2, the TPR spectra following CO adsorption at 385 K in H_2 flow for 30 min were quite different from those seen for CO adsorption at 300 K:

- The amount of CH_4 (77 μmol CH_4/g catalyst) was more than twice that seen for CO adsorption at 300 K.
- The CH_4 peak temperature increased to 545 K.
- Much more unreacted CO desorbed (69 μmol/g catalyst); almost half the adsorbed CO desorbed without reacting.
- The unreacted CO desorbed in a peak at 525 K instead of at 350 K.
- The amount of CO_2 that formed was 18 times larger and the CO_2 peak was at 460 K.

Longer CO exposures times (60 min) increased the amount of unreacted CO, but the CH_4 signal was essentially unchanged. The CO signal had the same peak temperature, but its amplitude increased to 1.4 μmol/s/g catalyst, so that more than half the adsorbed CO desorbed instead of reacting. Adsorption for 120 and for 240 min yielded essentially the same spectra as that for 60 min.

Because the CH_4 signal in Fig. 2 appeared to have a large tail and because two distinct CH_4 peaks were observed on Ni/Al_2O_3, Ni/TiO_2, and Pt/Al_2O_3 catalysts, iso-

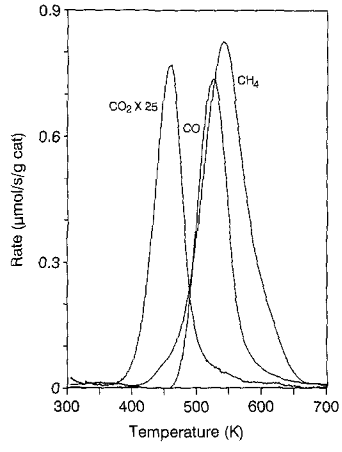

FIG. 2. TPR spectra for CO adsorbed at 385 K on 1.8% Pt/TiO_2 for 30 min in H_2 flow, following cooling in H_2 from 775 K.

topes were used in an attempt to determine if two CH_4 peaks (corresponding to two reaction sites) were present on Pt/TiO$_2$. On Ni/Al$_2$O$_3$ and Ni/TiO$_2$, one of the sites could be labeled with ^{12}CO and the other with ^{13}CO. Attempts to separately label sites on Pt/TiO$_2$ were made by first saturating the catalyst with ^{12}CO at 385 K, and then exposing it to ^{13}CO at 300 K. Unlike the results on Ni catalysts, the $^{12}CH_4$ and $^{13}CH_4$ peaks were almost identical in shape, and the unreacted ^{12}CO and ^{13}CO were almost identical in shape. Not a large amount of ^{12}CO was displaced by ^{13}CO at 300 K. When more ^{13}CO was adsorbed by using interrupted TPR to remove some of the adsorbed ^{12}CO and then adsorbing ^{13}CO, the ^{13}CO peak was at a lower temperature than the ^{12}CO peak, but the $^{12}CH_4$ and $^{13}CH_4$ signals were still identical in shape. Thus, if two distinct reaction sites were present on Pt/TiO$_2$, they could not be separately labeled with isotopes.

Hydrogen pressure variations. The rate of methanation during TPR on Ni/Al$_2$O$_3$ and Ni/TiO$_2$ catalysts is a function of the H_2 partial pressure, and the two reaction sites showed different dependences on the H_2 pressure when the H–CO species was not at saturation coverage (*15*). Thus, TPR experiments were run for a range of H_2 partial pressures on Pt/TiO$_2$ to determine if the CH_4 spectra obtained at ambient pressure (Fig. 2) were composed of two overlapping peaks. A series of experiments was carried out in which CO was adsorbed at 385 K for 30 min in ambient pressure H_2 flow, the catalyst was cooled to 300 K, the carrier gas was replaced by either a H_2/He mixture or H_2 at 2 atm pressure, and a TPR experiment was carried out. Carrying out TPR in 2 atm of H_2 changed the CH_4 spectra slightly from that at ambient pressure; the CH_4 peak narrowed slightly and shifted a few degrees to higher temperature. The most notable changes, however, were a 15-K shift in the unreacted CO peak to higher temperature, a narrowing of the CO peak, and a decrease in the amount of unreacted CO. The CO peak shifted so that the CO and CH_4 peaks were identical in shape and location. These changes were accompanied by an increase in the amount of CH_4 formed. For ambient pressure TPR, the CO and CH_4 peaks had almost the same amplitude (Fig. 2). For TPR under 2 atm H_2 pressure, the amplitude of the CO peak was only two-thirds that of the CH_4 peak.

Temperature-programmed reaction experiments carried out at H_2 partial pressures below ambient showed changes that were the opposite of those observed when 2 atm H_2 pressure was used. For 20% H_2/He:

- Less CH_4 formed than at ambient pressure.
- More unreacted CO desorbed.
- The CH_4 signal broadened significantly; the halfwidth increased from 75 to 132 K.
- Methane formation continued to 750 K; in ambient pressure H_2, CH_4 formation was complete by 600 K.

The broadening of the CH_4 signal occurred at high temperature, and the low temperature part of the CH_4 signal was unchanged in shape.

When TPR was carried out in a 3% H_2/He mixture, two distinct CH_4 peaks were observed. The low-temperature peak was centered at 535 K, the high-temperature peak was at 620 K, and CH_4 formed up to 740 K. Less than half as much CH_4 formed as that seen for TPR in 20% H_2/He, and thus much more unreacted CO was observed. The unreacted CO signal was also broader and shifted to lower temperature for TPR in 3% H_2. Note that for the rate of CH_4 formation measured, less than 3% of the H_2 flowing over the catalyst was reacting to form CH_4, and thus the H_2/He mixture was not significantly depleted of H_2 during the TPR experiment. Detection of the H_2 signal during TPR verified this. The H_2 signal was constant until 450 K and then *increased* as H_2 and CO formed simultaneously. Only above 550 K, as CH_4 continued to form, did the H_2 signal decrease below the 3% concentration that was entering the reactor.

Isotopes were used in an attempt to separate the two CH_4 peaks by adsorbing ^{12}CO at 385 K and then adsorbing ^{13}CO at 300 K. The objective was to label the site that formed one peak with ^{12}CO and the other site with ^{13}CO. As shown in Fig. 3, when TPR was carried out in 3% H_2, two distinct CH_4 peaks are seen, as described in the previous paragraph. The $^{13}CH_4$ signal was small (2.5% of the $^{12}CH_4$ signal) and noisy and thus is not shown. However, the $^{13}CH_4$ showed a preference for the high-temperature peak, but each of the peaks contained both $^{12}CH_4$ and $^{13}CH_4$. The unreacted CO peaks were distinctly different, however, and ^{13}CO desorbed with a peak at 30 K lower temperature than that of ^{12}CO (Fig. 3). The amount of ^{13}CO was less than a third of the ^{12}CO amount, and most of the ^{13}CO desorbed instead of being hydrogenated. These experiments indicate that two distinct reaction pathways are present on Pt/TiO_2, and in low H_2 pressure the pathways are partially separated.

Adsorption in deuterium. To gain insight into how CO adsorbed on Pt/TiO_2 is hydrogenated, CO was adsorbed at 385 K in D_2 flow, following cooling the catalyst in D_2 from 775 K. A subsequent TPR was carried out in ambient pressure H_2 flow. Figure 4 shows the resulting signals for D_2 and for masses 15, 18, 19, and 20. Signals were also observed at masses 16 and 17, but they are not presented for clarity. A significant amount of D_2 desorbed between 300 and 450 K, and this is probably due to exchange with gas phase H_2, since a H_2 desorption peak is not seen in this temperature range during TPD (described later). The H_2 signal was not monitored, however, because small changes in H_2 flow are difficult to detect when ambient pressure H_2 is used.

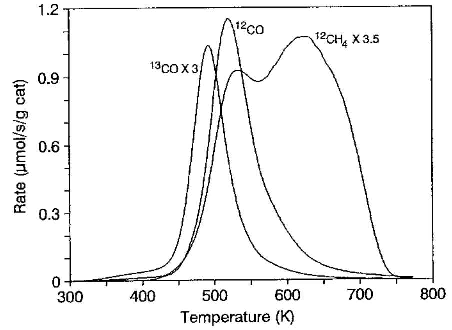

FIG. 3. TPR spectra for ^{12}CO adsorbed on 1.8% Pt/TiO_2 at 385 K for 30 min in H_2 flow, following cooling in H_2. The catalyst was then exposed to ^{13}CO for 10 min at 300 K and TPR was carried out in a 3% H_2/He mixture.

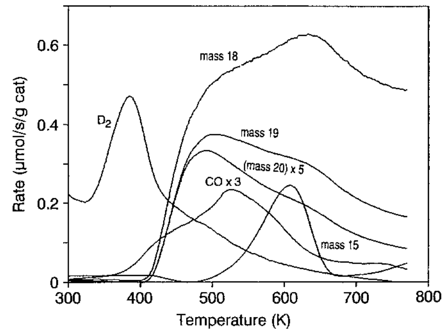

FIG. 4. TPR spectra for CO adsorbed on 1.8% Pt/TiO_2 at 385 K for 20 min in D_2 flow following cooling in D_2 from 775 K. After CO adsorption, the catalyst was cooled to 300 K, flow was switched to H_2, and TPR carried out in H_2. Signals for masses 4, 15, 18, 19, and 20 are presented. Signals were also seen at masses 16 and 17.

The main objective of this experiment was to determine whether deuterated methane products formed in significant quantities. Since the cracking fractions of each of the products make accurate determination of the amount of each deuterated methane product difficult, and because these amounts were not needed for our analysis, spectra in which all the signals have been corrected for cracking are not presented. However, a qualitative discussion of the contributions to the various mass signals will be presented.

Since CH_4 was not detected above 650 K when CO was adsorbed in H_2 at 385 K (Fig. 2), the signals above 650 K at masses 17–20 are not due to deuterated methane products. Instead, they are due to the water products (D_2O, HDO, H_2O) and the cracking fractions of water products. Immediately prior to the experiment the results of which are shown in Fig. 4, an identical TPR was carried out, but CO was adsorbed in H_2 instead of D_2. Thus, the water signal detected in that experiment at mass 18 (and its cracking fraction at mass 17) should correspond to the various water products in Fig. 4. Water started to form above 600 K and desorbed up to 775 K, where heating was stopped. The amount of water formed should be almost independent of whether CO was adsorbed in H_2 or D_2. However, because three water products can form (D_2O, HDO, and H_2O), and because each of these products also cracks in the mass spectrometer, determination of the amount of each product is difficult. The mass 20 signal above 650 is due to D_2O formation and the scale factor in Fig. 4 shows that the amount of D_2O is small. The mass 20 signal below 650 K corresponds mostly to CD_4. Similarly, the mass 18 and 19 signals at high temperatures were assumed to be due to H_2O and HDO formation, respectively. Some of the high-temperature mass 18 signal is also due to cracking of HDO. The signal at mass 18 from cracking of D_2O was small because the D_2O signal was small. Mass 17 (not shown) is expected to have contributions from cracking of both HDO and H_2O.

The large amplitudes of the mass 18 and 19 signals below 600 K indicate that CD_2H_2 and CD_3H are the predominant methane peaks. Since the CD_4 signal was small, the contribution to the mass 18 signal from the CD_3^+ cracking fragment of CD_4 is small. However, the contribution to the mass 18 signal from CD_3H cracking is significant, but not large enough to account for the mass 18 signal. Thus, the CD_2H_2 signal appears to be of the same magnitude as the CD_3H signal. The majority of mass 17 appears to be cracking. A CH_4 signal (measured at mass 15 to avoid cracking of CD_2H_2, water, CO, and CO_2 at mass 16) is seen, but only above 500 K. Because of the small amount of CDH_3, cracking of CDH_3 does not make a significant contribution to the mass 15 signal.

Thus, adsorption of CO in D_2 created a surface species that contains D. Subsequent hydrogenation retained much of this deuterium in the final methane products. Methane with all H atoms was only observed above 500 K.

It should be noted that the CO desorption signal in Fig. 4 is smaller in amplitude than that in Fig. 2. Moreover, CO desorbed over a wider temperature range when CO was adsorbed in D_2 than when CO was adsorbed in H_2. These diffferences were reproducible. They may be related to the difference in decomposition rates of CH_3O and CD_3O species, but a large isotope effect would not be expected.

Temperature-Programmed Desorption of Coadsorbed CO and H_2

When a TPD experiment instead of a TPR experiment was carried out following CO adsorption in H_2 flow at 385 K, the amount of hydrogen that is coadsorbed with the CO can be measured. Figure 5 shows that the TPD spectra for Pt/TiO$_2$ is similar to that observed for Ni/Al$_2$O$_3$ (*13*). Carbon monoxide and H_2 desorbed simultaneously, with peaks centered at 500 K. The peak shapes of H_2 and CO are almost iden-

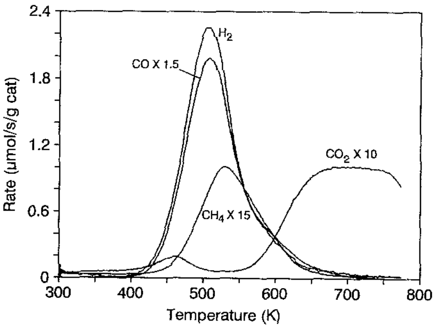

FIG. 5. TPD spectra for CO and H_2 coadsorbed on 1.8% Pt/TiO$_2$. The catalyst was exposed to CO pulses in H_2 flow at 385 K for 30 min. It was then cooled to 300 K and heated in He.

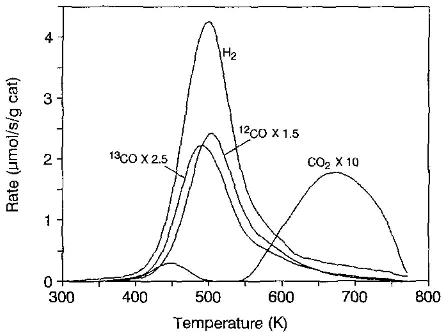

FIG. 6. TPD spectra for CO and H_2 coadsorbed on 1.8% Pt/TiO_2. The catalyst was exposed to ^{12}CO pulses in H_2 flow at 385 K for 30 min. It was then cooled to 300 K and exposed to ^{13}CO for 30 min, before being heated in He flow.

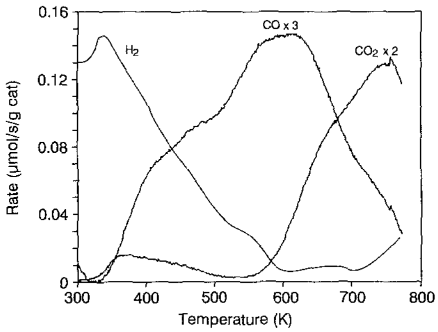

FIG. 7. TPD spectra for CO and H_2 coadsorbed at 300 K on 1.8% Pt/TiO_2. The catalyst was exposed to pulses of CO in H_2 flow for 30 min. The catalyst was cooled in H_2 from 775 K before adsorbing CO.

tical. The H/CO ratio appears slightly larger than 3 from the amplitudes of the curves. A small amount of CO_2 (10% of the CO) formed at higher temperature, and a small amount of CH_4 (less than 5% of the CO amount) formed in a peak at 520 K. The simultaneous formation of CO and H_2 indicates that a H–CO complex is present on the catalyst surface, and decomposition of the complex limits the rate of formation of CO and H_2.

Since the TPD experiments indicate that a complex may be present on the Pt/TiO_2 catalyst, as was seen on Ni/Al_2O_3, an attempt was made to use isotopes to label sites on the surface. At 385 K, ^{12}CO was adsorbed for 30 min in H_2 flow. After the catalyst was cooled to 300 K, ^{13}CO was adsorbed for 30 min in H_2. During the subsequent TPD, the smaller ^{13}CO signal had a 15 K lower peak temperature than the ^{12}CO signal (Fig. 6). The H_2 peak was similar in shape and location to the sum of the ^{12}CO and ^{13}CO peaks. The $^{12}CH_4$ and $^{13}CH_4$ peaks were identical in shape, but three times as much $^{12}CH_4$ formed as $^{13}CH_4$. For clarity, the $^{12}CH_4$ and $^{13}CH_4$ signals are not shown in Fig. 6; they were identical in shape to the CH_4 signal in Fig. 5.

When CO was adsorbed at 300 K on Pt/TiO_2 in H_2 flow, the resulting TPD spectra (Fig. 7) were quite different. The CO and H_2 did not desorb simultaneously, the CO and H_2 signals were significantly smaller, and CO desorbed over the entire temperature range. Table 1 shows the amounts desorbing for the two adsorption temperatures. Thus the H–CO complex that formed at 385 K in the H_2 flow did not appear to form at 300 K.

TABLE 1

TPD for CO and H_2 Coadsorbed on 1.8% Pt/TiO_2

Adsorption temperature (K)	Amounts desorbed (µmol/g catalyst)			
	H_2	CO	CO_2	CH_4
300	39	11	9	—
385	220 ± 10	122 ± 6	16.5 ± 1	6.3 ± 0.6
Methanol adsorption at 385	493	300	12.5	23

Methanol Desorption and Reaction

When CH_3OH was adsorbed on the Pt/TiO_2 catalyst at 385 K and a TPD experiment carried out, H_2 and CO desorbed simultaneously in a peak near 500 K, with a H/CO ratio near 3. Methane formed at the same temperature, but with only 6% of the H_2 amplitude. Unreacted CH_3OH desorbed with a peak at 400 K. Thus, as shown in Fig. 8, most of the methanol decomposed to CO and H_2. A small CO_2 signal was seen at high temperature. The total amount of CO and H_2 was larger than that seen for coadsorption of CO and H_2 (see Table 1). For TPR following CH_3OH adsorption at 385 K in H_2, CO and unreacted CH_3OH desorbed and a broad CH_4 peak formed with a maximum at 550 K, as shown in Fig. 9.

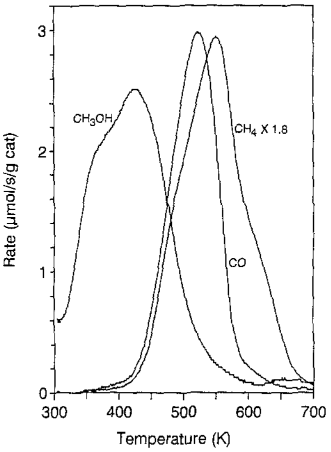

FIG. 9. TPR spectra for CH_3OH adsorbed on 1.8% Pt/TiO_2 at 385 K in H_2 flow.

TITANIA

An attempt was made to adsorb CO and H_2 on TiO_2 alone. The TiO_2 support was pretreated in H_2 with the same procedure as that used for the Pt/TiO_2 catalyst. Carbon monoxide exposure was carried out in H_2 flow at 300 and 385 K. During TPD following CO adsorption at 385 K in H_2 flow, a small amount of CO (0.8 μmol/g TiO_2) and CO_2 (0.4 μmol/g TiO_2) desorbed. Methane (4.7 μmol/g TiO_2) was also seen with a peak temperature of 660 K, but no H_2 desorption was detected.

Methanol readily adsorbed on TiO_2, and heating in H_2 (TPR) following CH_3OH adsorption in H_2 flow at 385 K yielded CO (24 μmol/g TiO_2), CH_4 (120 μmol/g TiO_2), and unreacted CH_3OH (65 μmol/g TiO_2). The CO_2 signal was in the noise level. Most of the CO desorbed in a peak at 680 K, the CH_4 formed in a broad peak at 640 K, while the CH_3OH formed over a wide temperature range. The TPR spectra were quite different from those on Pt/TiO_2. The TPD spectra following CH_3OH adsorption in H_2 flow at 385 K yielded CO, CH_4, and CH_3OH signals that were similar to the TPR results. Hydrogen desorbed in two peaks centered at 490 and 670 K.

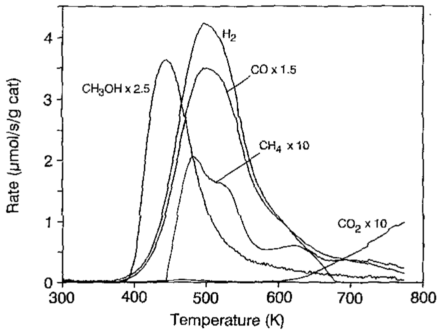

FIG. 8. TPD spectra for CH_3OH adsorbed on 1.8% Pt/TiO_2 at 385 K in H_2 flow. The catalyst was cooled to 300 K in H_2 and then heated in He flow.

DISCUSSION

The TPD and TPR spectra for CO and H_2 coadsorption on Pt/TiO_2 exhibit a number of similarities to those of TPD and TPR experiments on Ni/Al_2O_3 (*11*) and Ni/TiO_2 (*12, 17*). The amount of CO adsorption increases, in the presence of H_2, as the adsorption temperature is raised. Following coadsorption at elevated temperatures, H_2 and CO desorb simultaneously, in an approximate 3 : 1 ratio (H : CO). Thus the processes on Pt/TiO_2 appear to be similar to those reported on supported Ni catalysts: CO adsorbs on Pt and forms a methoxy

(CH_3O) species on the TiO_2 support in an activated spillover process. The CH_3O species is hydrogenated at a different rate from CO adsorbed on the metal. Carbon monoxide on Ni is hydrogenated at a faster rate than CH_3O on Al_2O_3 or TiO_2. However, CO on Pt is hydrogenated at a slower rate than CH_3O on TiO_2 because Pt is a much poorer methanation catalyst than is Ni. The following discussion will justify this explanation and thus show that TiO_2 creates new reaction sites for methanation that are more active than Pt itself. Indeed, the Pt/TiO_2 catalyst is almost as active as a Ni/SiO_2 catalyst during TPR. Dwyer (*8*) proposed that a CH_3O species forms on TiO_2 and is hydrogenated to CH_4 faster than CO is on Pt; our studies confirm this. The creation of new sites on the support may explain the high activity of Pt/TiO_2 catalysts in steady-state kinetic measurements. Vannice and Twu (*6*) concluded that special sites are created on Pt/TiO_2 at the interface. Moreover, IR studies (*18*) showed that H_2 displaced a large fraction of adsorbed CO on Pt/TiO_2, even at 300 K. At steady state, only a small fraction of IR active CO was on the surface of Pt/TiO_2 in the SMSI state, and this may be related to CH_3O being on TiO_2 at steady state.

Adsorbed Methoxy Intermediates

The simultaneous desorption of CO and H_2 during TPD, following coadsorption of CO and H_2 at 385 K on Pt/TiO_2, demonstrates that the CO and H_2 form a complex on the surface. The desorption spectra are quite different from those for CO or H_2 adsorbed alone. The desorption spectra for coadsorption at 385 K are also different from those obtained for coadsorption at 300 K; the process to form CH_3O is activated. Much more CO adsorbs at 385 than at 300 K because of this activated process.

The activated process appears to form a CH_3O species whose decomposition during TPD limits the rate that CO and H_2 appear in the gas phase. The shapes of the CO and H_2 desorption curves are almost identical. Perhaps the clearest evidence that a CH_3O forms on Pt/TiO_2 is that the TPD spectra obtained following CH_3OH adsorption at 385 K (Fig. 8) are similar to those obtained for CO and H_2 coadsorption at 385 K (Fig. 5). The peak temperatures are identical, the shapes are similar, and the H/CO ratio is slightly greater than 3 in each case. The H_2 and CO desorption peaks are somewhat broader for CH_3OH adsorption, but this difference may be due to the higher coverage obtained for CH_3OH adsorption.

Additional results from IR studies (*8, 9*) confirm that CH_3O species form on supported Pt catalysts in the presence of CO and H_2. Dwyer detected a CH_3O species on Pt/TiO_2 with IR (*8*), and Robbins and Marucchi-Soos (*9*) detected CH_3O on a Pt/Al_2O_3 catalyst. Analogy to previous TPD studies on Ni/Al_2O_3 (*13*) and Ni/TiO_2 (*12, 17*) also indicate that a methoxy species forms. For both supported Ni catalysts, H_2 and CO desorbed simultaneously in an approximate 3 : 1 ratio (H : CO). Moreover, CO adsorption in H_2 to form CH_3O was activated on these Ni catalysts and much more CO adsorbed at 385 than at 300 K. Also, the additional CO that adsorbed at 385 K on Ni/Al_2O_3 and Ni/TiO_2 formed CH_4 during TPR in one of the two CH_4 peaks: the one associated with the CH_3O complex.

Location of Methoxy Intermediate

The CH_3O species that forms at 385 K from coadsorbed CO and H_2 is adsorbed on the TiO_2 surface. The amount of CO adsorbed in He at 300 K on Pt/TiO_2 was measured from the amounts of CH_4 and unreacted CO detected during a subsequent TPR. If one CO molecule is assumed to adsorb on each Pt surface atom, then the percentage Pt exposed is 44%. Then, the amount of CO adsorbed in H_2 at 385 K for 60 min exposure corresponds to 2.3 molecules of CO for every Pt atom or 5.3 molecules of CO for every Pt surface atom. Thus, much of the CO must be adsorbed on the TiO_2 support. The difference in the amounts between adsorption at 300 and at

385 K is 165 μmol/g TiO_2, which corresponds to the amount of CH_3O on the TiO_2 support.

Reactivity of Adsorbed Methoxy

On Ni/Al_2O_3 (*11*) and Ni/TiO_2 (*12*), two distinct CH_4 peaks (both narrower than the CH_4 peak from Pt/TiO_2) were observed during TPR in ambient pressure H_2. The low-temperature CH_4 peak was due to hydrogenation of CO adsorbed on Ni and the high-temperature peak was due to hydrogenation of the CH_3O species. At higher H_2 pressures the CH_4 peaks split further apart, and at sufficiently low H_2 partial pressures the two peaks coalesced into one peak (*15*). Hydrogenation of CO on Ni was positive order in H_2 pressure, but hydrogenation of CH_3O was negative order in H_2 pressure for low coverages of CH_3O. At high coverage of CH_3O, the rate of hydrogenation does not exhibit much dependence on H_2 pressure (*19*). A similar dependence on H_2 partial pressure appears to exist on Pt/TiO_2. However, because the CH_3O on TiO_2 is hydrogenated faster than the CO on Pt (the reverse of what was observed on Ni catalysts), the CH_4 peak(s) becomes narrower at 2 atm H_2 pressure and separates into two peaks at low H_2 pressure. That is, as the H_2 pressure was lowered, the CO on Pt was hydrogenated at a much slower rate while the rate of CH_3O hydrogenation did not change much, but much more of the CH_3O decomposed to form CO instead of being hydrogenated to CH_4. Thus, less CH_4 and more CO was observed at low H_2 partial pressure (Fig. 3) than at ambient pressure (Fig. 2). The important point is that two distinct CH_4 peaks are observed.

Other experiments also indicate that the CH_3O on TiO_2 is hydrogenated faster than CO on Pt. When CO was adsorbed on Pt/SiO_2 (*20*), the CH_4 peak during TPR was at a much higher temperature than the CH_4 peak from Pt/TiO_2. On high-purity Pt powder, no CH_4 forms during TPR (*9*). Moreover, Robbins and Marucchi-Soos (*9*) showed directly with IR that CH_3O on Pt/Al_2O_3 was hydrogenated faster than CO on Pt during TPR. Two distinct CH_4 peaks were seen during TPR on Pt/Al_2O_3, and the low-temperature peak was due to CH_3O hydrogenation. As the CO coverage was increased on Pt/Al_2O_3 by adsorption at 380 K, the CH_4 peak temperature for hydrogenation of CH_3O increased. A similar increase was observed for Pt/TiO_2 (Figs. 1 and 2). Dwyer (*8*) observed that the methanation rate on Pt powder increased when TiO_2 was deposited on it, even though the Pt surface area decreased.

Our TPD experiments following adsorption of CH_3OH at 385 K on Pt/TiO_2 indicate that CH_3O forms and decomposes in the same manner as the CH_3O formed by coadsorbed CO and H_2. Similarly, the TPR spectra following CH_3OH adsorbed on Pt/TiO_2 (Fig. 9) are similar to the TPR spectra for CO adsorbed in H_2 at 385 K (Fig. 2). That is, both of these spectra correspond to hydrogenation of CH_3O.

The decomposition of CH_3O, as measured by the appearance of CO and H_2 during TPD following adsorption at 385 K, occurs at the same temperature as the CH_4 peak during TPR for CO adsorption at 300 K. As the CH_3O coverage was increased, by CO adsorption at 385 K, the CH_4 peak temperature measured during TPR increased and appeared at a higher temperature than the CO and H_2 from TPD of CH_3O. The gas phase H_2 apparently inhibited the decomposition of CH_3O; a similar result was seen for Ni/TiO_2 (*17*).

Explanation of TPR Spectra

When CO was adsorbed at 300 K on Pt/TiO_2, the subsequent TPR (Fig. 1) showed a rather broad CH_4 peak. Only a small amount of unreacted CO desorbed. The same CH_4 peak was observed when CO was adsorbed in He flow. Thus, at 300 K, CO adsorbed on the Pt surface and as the temperature was raised in H_2, the CO transferred to TiO_2 to form the CH_3O species. Under these conditions the CH_3O was almost completely hydrogenated to CH_4, starting near 400 K. In contrast, during TPR on Ni/Al_2O_3, only a fraction of the CO adsorbed on Ni transferred to the Al_2O_3 support before the rate of hydrogenation of CO on Ni became significant (*11*). The slower rate of CO hydrogenation on Pt allowed almost all the CO to transfer when CO was originally adsorbed at 300 K.

A higher coverage of CH_3O was obtained by adsorbing CO at 385 K in H_2 flow. For 30 min exposure of CO at 385 K, only some of the CH_3O was hydrogenated to CH_4, however. Higher exposures (60 min) of CO at 385 K did not increase the amount of CH_4 formed during TPR, but the amount of unreacted CO increased significantly and was much larger than the amount of CH_4. Similarly, for CH_3OH adsorption, the amount of unreacted CO was much larger than the amount of CH_4 during TPR; the CO peak temperature was also lower than the CH_4 peak temperature in both cases. The CH_3O that forms (from either CO + H_2 or CH_3OH) thus appears to adsorb at more than one site on the TiO_2 surface. The site where the CH_3O can be readily hydrogenated to CH_4 appears to saturate first. Methanol exposure more readily covered the other site, however, and thus more unreacted CO was observed during TPR for CH_3OH adsorption than that for 60 min of CO adsorption in H_2. Since the amount of CH_4 formed during TPR did not change when the CO adsorption time was increased from 30 to 60 min, but the amount of adsorbed CO was significantly increased, the adsorbed CH_3O does not appear to be blocking sites required for H_2 adsorption. Instead, the additional CO that adsorbs appears to be in a less reactive form on the TiO_2.

The H_2 needed to hydrogenate CH_3O most likely adsorbs and dissociates on Pt, but hydrogenation could be occurring on Pt or on TiO_2. The Pt is needed, however, since the rate of methanation was much slower for CH_3OH adsorbed on TiO_2 without Pt. However, comparison between the TiO_2 of Pt/TiO_2 and TiO_2 alone are difficult because some of the TiO_2 in contact with the Pt is reduced.

The formation of a CD_3O species (by adsorbing CO in D_2 flow) provides some insight into the reaction. Most of the methane products formed during subsequent heating in H_2 were CD_2H_2 and CD_3H. That is, the CD_3O appears to be directly hydrogenated to methane, without first decomposing. It is possible that the methoxy is hydrogenated directly on the TiO_2 surface. However, we cannot rule out the possibility that CD_3O decomposes on Pt, but the exchange between the resulting D atoms and the H atoms that adsorb from the gas phase is slow and thus the CO is hydrogenated by the local concentration of D atoms. The rate of decomposition of CH_3O, as measured by the appearance of CO and H_2 during TPD, appears to be as fast or faster than the rate of hydrogenation. However, adsorbed hydrogen may decrease the decomposition rate.

When CD_3O was formed on Pt/TiO_2, the CH_4 signal (mass 15 in Fig. 4) was quite different from that seen when CH_3O was present; the CH_4 may be due to hydrogenation of CO adsorbed on Pt. This methanation of CO on Pt accounts for the long tail to 650 K in Fig. 2. This is also a further indication that two separate sites for methanation are present on Pt/TiO_2 catalysts.

Transfer from Pt to TiO_2

On Ni/Al_2O_3 (*11*), a clear indication of transfer between Ni and Al_2O_3 was obtained by isotope labeling of the CO. By the use of interrupted reaction or CO exchange on the Ni, one of the sites could be labeled with ^{13}CO and the other with ^{12}CO. Attempts at similar experiments on Pt/TiO_2 were not as successful. The $^{13}CH_4$ and $^{12}CH_4$ signals were identical at ambient pressures, and only slight differences were seen at low pressures. Apparently the transfer from Pt to TiO_2 is rapid, in ambient pressure H_2, at temperatures below where the methanation rate becomes large. Note that on Pt/TiO_2, interrupted TPR removes CO from TiO_2 and adsorption is expected to take place on Pt. Thus, the isotope-labeling experiment is different from that on Ni/Al_2O_3, in which interrupted TPR removed CO from the Ni surface and adsorption took place on Ni.

Though the CH_4 peaks were similar, the ^{12}CO and ^{13}CO signals were significantly different during TPR at low partial pressures of H_2 (Fig. 3), and a small difference was also seen for TPD (Fig. 6). In both cases, the ^{13}CO, which was exposed to the catalyst last, desorbed at lower temperatures. These results may indicate that the ^{12}CO and ^{13}CO are adsorbed on different sites. We mentioned earlier that two types of adsorption sites for CH_3O appear to be present on TiO_2. The rate of transfer between Pt and TiO_2 appears fast, however, in the presence of H_2. On Ni/Al_2O_3 and Ni/TiO_2 the transfer rates were slower. Thus the transfer is a complicated function of the metal, the support, and their interaction.

CONCLUSIONS

Carbon monoxide and hydrogen, when coadsorbed on Pt/TiO_2, form a CH_3O complex on the surface of the TiO_2 support in an activated process. The CH_3O appears to be hydrogenated directly on TiO_2 to form CH_4. The CH_3O species is hydrogenated at a much faster rate than is CO on Pt, and this process may be related to the higher activities exhibited by Pt/TiO_2 catalysts in steady-state methanation. Isotope studies indicate that transfer from Pt to TiO_2 is fast. The TPD and TPR results exhibit similar trends to those reported previously for Ni/Al_2O_3, but because Pt is a much poorer methanation catalyst than Ni, the CO on Pt is hydrogenated at a slower rate than the CH_3O species.

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REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).
2. Demmin, R. A., Ko, C. S., and Gorte, R. J., *J. Phys. Chem.* **89,** 1151 (1985).
3. Dwyer, D. J., Cameron, S. D., and Gland, J., *Surf. Sci.* **159,** 430 (1985).
4. Dwyer, D. J., Robbins, J. L., Cameron, S. D., Dudash, N., and Hardenbergh, J. (Baker, R. T. K., Tauster, S. J., and Dumesic, J. A., Eds.), *ACS Symp. Ser.* **298,** 21 (1986).
5. Resasco, D. E., and Haller, G. L., *J. Catal.* **82,** 279 (1983).
6. Vannice, M. A., and Twu, C. C., *J. Catal.* **82,** 213 (1983).
7. Bracey, J. D., and Burch, R., *J. Catal.* **86,** 384 (1984).
8. Dwyer, D. J., presented at Fall ACS meeting, New York, NY, 1986.
9. Robbins, J. L., and Marucchi-Soos, E., *J. Phys. Chem.* **93,** 2885 (1989).
10. Kester, K. B., Zagli, E., and Falconer, J. L., *Appl. Catal.* **22,** 311 (1986).
11. Glugla, P. G., Bailey, K. M., and Falconer, J. L., *J. Phys. Chem.* **92,** 4474 (1988).
12. Sen, B., and Falconer, J. L., *in* "Proceedings of 2nd International Conference on Spillover" (K. H. Steinberg, Ed.), p. 106. GDR, 1989.
13. Glugla, P. G., Bailey, K. M., and Falconer, J. L., *J. Catal.* **115,** 24 (1989).
14. Sen, B., Mao, T. F., and Falconer, J. L., submitted for publication.
15. Sen, B., and Falconer, J. L., submitted for publication.
16. Falconer, J. L., and Schwarz J. A., *Catal. Rev. Sci. Eng.* **25,** 141 (1983).
17. Sen, B., and Falconer, J. L., *J. Catal.* **122,** 68 (1990).
18. Vannice, M. A., Twu, C. C., and Moon, S. H., *J. Catal.* **79,** 70 (1983).
19. Flesner, R. L., and Falconer, J. L., in preparation.
20. Way, J. D., Masters thesis, University of Colorado, 1980.