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Spillover Rate from Pd to Al_2O_3

In previous studies we found that CO and H_2 coadsorbed on Ni/Al_2O_3 can spill over from the Ni to form a CH_3O species on the Al_2O_3 support (*1*). Because the CH_3O was not hydrogenated to CH_4 as fast as CO that was adsorbed on Ni, two distinct CH_4 peaks were observed during temperature-programmed reaction (TPR). Thus, the area of the high-temperature CH_4 peak, which was due to CH_3O hydrogenation, gave a direct measure of how much CH_3O formed during TPR. The amount of spillover was thus readily measured with TPR, and changes in heating rate (*1, 2*) were used to study the rate of spillover.

On Pd/Al_2O_3 (*3*), Pt/Al_2O_3 (*4, 5*), and Pt/TiO_2 (*6*) a similar process occurs, but the rate of CH_3O hydrogenation is faster than the rate of CO hydrogenation on catalysts made from these less-active methanation metals. Thus, during TPR experiments, spillover created CH_3O on the Al_2O_3 or TiO_2 surfaces, and as this CH_3O was hydrogenated to CH_4, sites on the support were made available for more spillover. However, in contrast to the TPR experiments on Ni/Al_2O_3, two distinct CH_4 peaks could *not* be distinguished on Pd/Al_2O_3. This may be because the rate of spillover is fast relative to the rate of CO hydrogenation; Palazov *et al.* (*7*) observed rapid spillover of CH_3O on Pd/Al_2O_3 with infrared spectroscopy.

To measure the rate of spillover on Pd/Al_2O_3, we used interrupted TPR and isotope exchange before a complete TPR experiment. In this approach, ^{12}CO was adsorbed at 300 K and the catalyst temperature was then raised in H_2 flow to facilitate spillover. The heating ramp was interrupted before a significant amount of CH_4 formed, and the sample was quickly cooled to 300 K. Then the catalyst was exposed to ^{13}CO to displace any ^{12}CO that remained on the Pd surface. At room temperature, gas phase CO readily exchanges with adsorbed CO on Pd (*3*). We have also observed previously that gas phase CO does not exchange with CH_3O on Al_2O_3 of Ni/Al_2O_3 (*8*). Thus, any ^{12}CO remaining on the catalyst after exchange was assumed to be present as $^{12}CH_3O$ on the Al_2O_3 surface. The amount of $^{12}CH_4$ that formed during the subsequent TPR was thus a measure of how much ^{12}CO had spilled over to the Al_2O_3 since all the adsorbed $^{12}CH_3O$ was hydrogenated to $^{12}CH_4$. A series of TPR experiments with different interruption temperatures yielded a TPR spectrum for spillover and an estimate of the activation energy for spillover.

The temperature-programmed reaction experiments were carried out at ambient pressure in a flow system. The apparatus and procedures have been described previously (*1, 3, 9*). The following experimental steps were used:

(*1*) *Adsorption.* ^{12}CO was adsorbed on Pd/Al_2O_3 at 300 K for 15 min to obtain saturation coverage in He flow. Under these conditions essentially all the CO is adsorbed on the Pd surface.

(*2*) *Interrupted TPR.* The catalyst temperature was raised at a rate of 1 K/s in H_2 flow at ambient pressure, but heating was stopped at a preselected temperature and the catalyst was rapidly cooled to 300 K before a significant amount of CH_4 formed.

(*3*) *Isotope exchange.* The catalyst was

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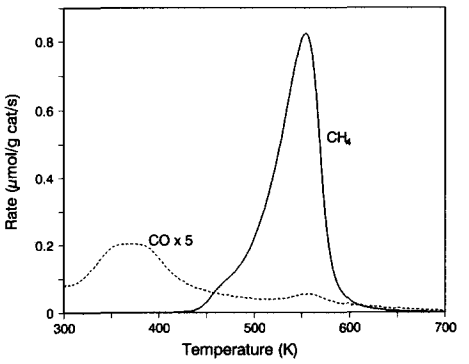

FIG. 1. CO and CH_4 TPR spectra following CO adsorption at 300 K in He for 15 min on 3.7% Pd/Al_2O_3.

then exposed to ^{13}CO at 300 K for 15 min to replace ^{12}CO adsorbed on the Pd by ^{13}CO.

(4) TPR. After exchange, the catalyst temperature was raised from 300 to 773 K in ambient pressure H_2 at a rate of 1 K/s, and the methane ($^{13}CH_4$, $^{12}CH_4$) and carbon monoxide (^{13}CO, ^{12}CO) products were detected with a quadrupole mass spectrometer, which was located immediately downstream from the reactor. A computer allowed multiple mass peaks to be detected simultaneously. Mass 15 was used to detect $^{12}CH_4$ and mass 17 to detect $^{13}CH_4$, and mass 15 was corrected for cracking from $^{13}CH_4$. Small amounts of CO_2 also formed (*3*).

The 3.7% Pd/Al_2O_3 catalyst was prepared by impregnation to incipient wetness of aqueous H_2PdCl_4 onto Kaiser A-201 Al_2O_3. The procedure was described previously (*3*) and is essentially the same as that used by Palazov *et al.* (*7*). The final reduction temperature was 773 K.

At the beginning of the experiments, the reduced catalyst was pretreated for 2 h at 773 K in ambient pressure H_2 flow. To maintain a clean surface, the catalyst was held in H_2 at 773 K for 10 min at the completion of each TPR experiment.

Figure 1 shows TPR spectra for ^{12}CO adsorbed at 300 K for an experiment where no interruption or ^{13}CO exchange was carried out. As reported previously (*3*), almost all the CO adsorbed at 300 K reacted to form CH_4; only a small amount of unreacted CO desorbed at low temperature. Methane started to form at 425 K and the peak temperature was 550 K. The CH_4 spectrum appears to consist of two overlapping peaks, with a small peak centered near 475 K. However, neither variations in heating rate nor H_2 pressure was able to distinguish two CH_4 peaks. The rate of CH_4 formation on Pd/Al_2O_3 is much faster than that reported for Pd/SiO_2 (*10*). When the catalyst was exposed to ^{13}CO at 300 K for 15 min after ^{12}CO adsorption at 300 K, almost no $^{12}CH_4$ was detected. That is, essentially all the ^{12}CO, which was adsorbed on Pd, was displaced by ^{13}CO, and thus 15 min of ^{13}CO exposure was sufficient time for almost complete exchange in our experiments.

A series of $^{12}CH_4$ spectra obtained for TPR experiments, after interrupted TPR to temperatures from 350 to 450 K and subsequent ^{13}CO exchange (as described previously) is shown in Fig. 2. As successively higher interruption temperatures were used before ^{13}CO exposure, increasing amounts of $^{12}CH_4$ were observed during the subsequent TPR because more ^{12}CO spilled over onto Al_2O_3 as interruption temperature increased. The $^{12}CH_3O$ that formed by spill-

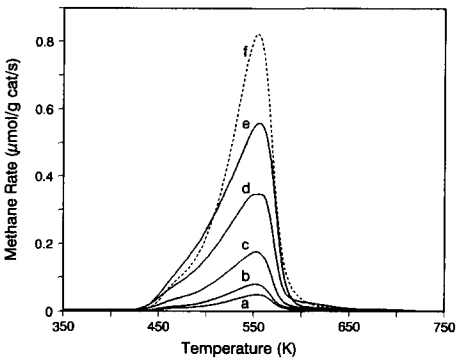

FIG. 2. $^{12}CH_4$ TPR spectra following ^{12}CO adsorption at 300 K in He, interrupted TPR to various temperatures, and ^{13}CO exchange at 300 K in He. The interruption temperatures were: (a) 350 K, (b) 375 K, (c) 400 K, (d) 425 K, and (e) 450 K. Curve (f) is the $^{12}CH_4$ TPR spectrum following ^{12}CO adsorption at 300 K in He without interrupted TPR or isotope exchange.

over did not exchange with gas phase ^{13}CO but it was hydrogenated during the subsequent TPR.

The amount of $^{13}CH_4$ that formed during each of the TPR experiments was approximately the same because the $^{13}CH_4$ amount corresponds to the amount of ^{13}CO that adsorbed on Pd at 300 K. The presence of $^{12}CH_3O$ on Al_2O_3 at these coverages did not significantly affect the hydrogenation rate of ^{13}CO, so the $^{13}CH_4$ spectra were quite similar to the $^{12}CH_4$ spectrum in Fig. 1. The ^{13}CO is also assumed to hydrogenate by first spilling over onto the Al_2O_3; because of the large area available on the Al_2O_3, the rate of ^{13}CO spillover was not significantly inhibited by the presence of $^{12}CH_3O$. Thus the total amount of methane ($^{12}CH_4$ and $^{13}CH_4$) formed during these TPR experiments after interrupted TPR was larger than that seen in Fig. 1. For example, for the TPR experiment shown in Fig. 2e, the total amount of methane was 1.8 times that in Fig. 1.

The amount of $^{12}CH_4$ formed in Fig. 2e shows that 80% of the ^{12}CO spilled over onto Al_2O_3 during the interrupted TPR to 450 K; very little was lost to the gas phase as ^{12}CO or $^{12}CH_4$. The 20% of the originally adsorbed ^{12}CO that remained on the Pd was displaced by ^{13}CO during the exchange step. This means that during a normal TPR following CO adsorption at 300 K (Fig. 1), only 20% of the CO remains on Pd by 450 K. Since spillover continues above 450 K, essentially all the CO is hydrogenated after first spilling over onto the Al_2O_3 to form CH_3O.

The amounts of $^{12}CH_4$ in Fig. 2 are the amounts that spilled over. The concentrations of ^{12}CO remaining on the Pd surface after the interrupted TPR experiments were obtained by the differences between the amounts of $^{12}CH_4$ in Fig. 2 and the amount of $^{12}CH_4$ formed during a normal TPR (Fig. 1). For example, following an interrupted TPR to 400 K and ^{13}CO exchange, 13.9 μmol $^{12}CH_4$/g catalyst formed during the subsequent TPR. Since 49 μmol $^{12}CH_4$/g catalyst formed as shown in Fig. 1, this means that 35.1 μmol ^{12}CO/g catalyst remained *on Pd* after the interrupted TPR to 400 K. These 35.1 μmol ^{12}CO/g catalyst were displaced by ^{13}CO during the exchange step. A plot of the concentration of ^{12}CO remaining on Pd after the interrupted TPR (C_{CO}) versus elapsed time during the interrupted TPR was smooth, and the negative of the slope of that plot ($-dC_{CO}/dt$) was used to estimate the rate of spillover at that ^{12}CO concentration and temperature. Table 1 lists the concentrations and rates. These rates were used to obtain an activation energy by assuming that spillover was first order in C_{CO}. The resulting Arrhenius plot in Fig. 3 gave an activation energy of 43 ± 5.5 kJ/mol (99% confidence limits) and a preexponential factor of 5.2×10^3 s^{-1}. For comparison, the leading edge analysis (*11, 12*) was used to estimate an activation energy of 125 kJ/mol for $^{12}CH_3O$ hydrogenation on Al_2O_3.

The activation energy and preexponential factor for spillover were used to generate a continuous plot of spillover rate versus temperature by numerical intergration. This plot (dashed line in Fig. 4) shows that CO is essentially completely removed from Pd by 500 K during a standard TPR. The spillover curve shows good agreement with the rates measured from the concentration versus time plot (points in Fig. 4). The area under the dashed curve, up to a given temperature, corresponds to the amount of spillover for a given interruption temperature (last column

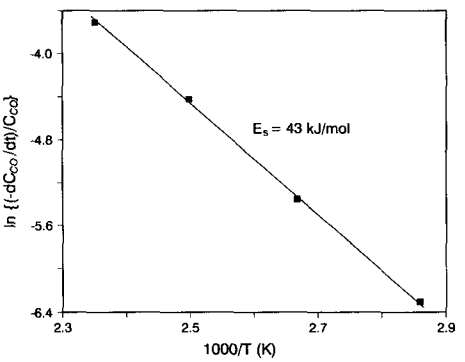

FIG. 3. Arrhenius plot of ln $\{(-dC_{CO}/dt)/C_{CO}\}$ versus inverse interruption temperature.

TABLE 1

CO Surface Coverage on Pd and Spillover Rate

Interruption temperature (K)	$^{12}CH_4$ amount from Fig. 2 (μmol/g catalyst)	C_{CO} (μmol/g catalyst)	$-\frac{dC_{CO}}{dt}$ (μmol/g catalyst/s)	$^{12}CH_4$ amount from Fig. 4 (μmol/g catalyst)
300	0	49.0	—	0
350	3.6	45.5	0.09	1.9
375	6.0	43.0	0.23	5.9
400	13.9	35.1	0.43	14.3
425	27.4	21.6	0.54	27.7
450	40.8	8.2	—	41.1

in Table 1) and this shows good agreement with the measured amounts. The amount of spillover during the cool-down period, although small compared to that during the temperature rise, may introduce some error into the measurements. Figure 4 shows that the spillover rate is faster than the hydrogenation rate until 475 K, at which point not much CO is left to spillover. Thus, only one CH_4 peak was seen during TPR because almost all the CO on Pd had spilled over onto Al_2O_3. These TPR results indicate that CH_3O hydrogenation might play an important role during steady-state methanation on Pd/Al_2O_3. However, the difference in the H_2/CO ratio between TPR and steady-state experiments could significantly affect the surface processes.

These experiments do not provide any information on how the CH_3O is hydrogenated. Hydrogen to hydrogenate the CH_3O could spill over onto the Pd or the hydrogenation could occur at the Pd–Al_2O_3 interface.

Spillover to form CH_3O on Al_2O_3 from CO and H_2 on Pd is fast relative to CH_3O or CO hydrogenation below 475 K. An activation energy for spillover of 43 kJ/mol was estimated. Because the activation energy for methanation is higher, at higher temperatures, CH_3O hydrogenation is expected to be faster than spillover. Interrupted TPR combined with isotope exchange is an effective technique for studying the spillover process.

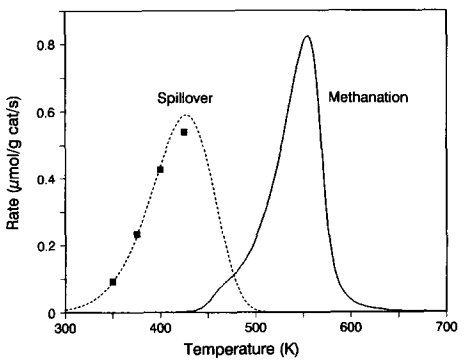

FIG. 4. The spillover rate during TPR (dashed line) is compared to the methanation rate during TPR (solid line). The solid points correspond to the rates measured from the concentration versus time curves.

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