JOURNAL OF CATALYSIS 91, 104–115 (1985)

Kinetics of Methanol and Methane Synthesis over Pd/SiO_2 and Pd/La_2O_3

ROBERT F. HICKS[1] AND ALEXIS T. BELL

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemical Engineering, University of California, Berkeley, California 94720

Received April 2, 1984; revised September 18, 1984

A study of the kinetics of methanol and methane synthesis over Pd/SiO_2 and Pd/La_2O_3 has been carried out. The activation energy and the orders with respect to H_2 and CO partial pressures are found to be essentially the same for methanol synthesis over both catalysts. This suggests that the methanol reaction mechanism is unaffected by support composition. The higher specific activity of Pd/La_2O_3 relative to Pd/SiO_2 for methanol synthesis is believed to be due to small differences in the relative strengths of H_2 and CO adsorption. The rate expressions for methane synthesis over Pd/La_2O_3 and Pd/SiO_2 differ significantly. This strongly suggests that the methanol reaction mechanism for the two catalysts is different, or alternatively that the mechanism is the same but the rate-limiting step is different.

INTRODUCTION

The performance of supported Pd catalysts for the synthesis of CH_3OH has been discussed recently by a number of authors (*1–9*). Of particular interest has been the observation that support composition has a strong influence on both the activity and selectivity of Pd. It has been reported that the specific activity and selectivity is particularly high when Pd is supported on La_2O_3 (*2, 3*). Hicks and Bell (*10–12*) have recently undertaken a series of investigations of La_2O_3- and SiO_2-supported Pd, aimed at understanding how support composition influences the catalytic properties of Pd. For Pd/SiO_2, X-ray photoelectron spectra (*10*), infrared spectra of adsorbed CO (*11*), and measurements of the adsorption stoichiometries of H_2 and CO (*11*) indicated the complete absence of any metal–support interaction. By contrast, similar techniques applied to Pd/La_2O_3 clearly revealed the presence of metal–support interactions. The influence of the support was expressed through an increase in the electronic charge density at the metal surface and a reduction in both the capacity and strength of CO chemisorption. These effects were ascribed to a partial coverage of the Pd crystallites by small patches of partially reduced support material.

The effects of Pd dispersion and crystallite morphology on the catalytic properties of a series of Pd/La_2O_3 and Pd/SiO_2 catalysts have also been investigated by Hicks and Bell (*12*). Metal dispersion was measured by H_2–O_2 titration. Crystallite morphology was characterized by the distribution of Pd(100) and Pd(111) surfaces, as identified from *in situ* infrared spectra of bridge-bonded CO. For a fixed crystallite morphology, the turnover frequency for CH_3OH formation was found to be independent of Pd dispersion for both SiO_2- and La_2O_3-supported Pd. With La_2O_3-supported Pd, the crystallite morphology changed in a systematic manner as the Pd weight loading increased. Examination of these catalysts revealed that the CH_3OH turnover frequency was a factor of 2.5 higher for a low-weight loading catalyst exhibiting primarily

---

[1] Present address: Research Division, W. R. Grace & Company, 7379 Route 32, Columbia, Maryland 21044.

0021-9517/85 $3.00

TABLE 1

Activation Energies and Preexponential Factors for Pd/SiO_2 and Pd/La_2O_3 Catalysts

Catalyst	D_{Pd}[a] (%)	A_{CH_3OH}[b] (s^{-1})	E_{CH_3OH} (kcal/mol)	A_{CH_4}[b] (s^{-1})	E_{CH_4} (kcal/mol)
0.75% Pd/SiO_2	17	5.6×10^5	20.3	7.3×10^9	33.9
2.00% Pd/SiO_2	21	5.9×10^4	17.8	3.5×10^6	24.4
5.10% Pd/SiO_2	16	8.5×10^4	18.2	3.8×10^7	26.8
0.20% Pd/La_2O_3[c]	5	5.5×10^6	19.7	7.8×10^{12}	37.6
0.70% Pd/La_2O_3	18	4.9×10^6	20.3	3.1×10^{11}	35.5
1.90% Pd/La_2O_3	16	6.7×10^6	20.8	1.2×10^{12}	36.7
5.00% Pd/La_2O_3	9	5.4×10^6	20.7	1.1×10^{12}	35.6

[a] Dispersion of used catalysts.
[b] Calculated for $P_{H_2} = 7.0$ atm and $P_{CO} = 3.0$ atm.
[c] Prepared from $Pd(\pi\text{-}C_3H_5)_2$ as reported in (*3*).

Pd(100) surfaces than for a high-weight loading catalyst exhibiting primarily Pd(111) surfaces. It was also noted that the CH_3OH turnover frequency increased linearly with the proportion of Pd(100) surfaces. From a comparison of a Pd/SiO_2 and a Pd/La_2O_3 catalyst with nearly equivalent morphologies, it was established that the CH_3OH turnover frequency for Pd/La_2O_3 is 7.5 times greater than that for Pd/SiO_2. The effects of Pd dispersion and morphology on the turnover frequency for CH_4 formation were also examined. It was found that dispersion had no effect for Pd/SiO_2 catalysts. For the Pd/La_2O_3 catalysts, the CH_4 turnover frequency decreased with increasing Pd dispersion.

The aim of the present investigation is to identify the effects of Pd dispersion, Pd morphology, and support composition on the kinetics of methanol and methane synthesis. These studies were carried out with the same Pd/SiO_2 and Pd/La_2O_3 catalysts used previously (*10–12*). The results reported here are discussed in the light of previous studies of CO hydrogenation over Pd, and a possible mechanism for the synthesis of methanol is proposed.

EXPERIMENTAL

The preparation procedures for the catalysts used in this study are given in Refs. (*10, 11*). The Pd/SiO_2 samples were prepared by incipient wetness impregnation of Cab-O-Sil HS5 silica (BET surface area = 300 m^2/g) with H_2PdCl_4. The Pd/La_2O_3 samples were prepared by ion exchange of fully hydrated La_2O_3 (BET surface area = 11 m^2/g) with H_2PdCl_4. All samples were dried in a vacuum oven at 338 K, calcined in a 21% O_2/He mixture for 2 hr at 623 K, and reduced in H_2 for 3 hr at 523 K. After reduction, the samples were stored in a desiccator.

The concentration of exposed Pd atoms was determined by H_2–O_2 titration, using the pulsed-flow technique (*11*). The Pd weight loading was determined by X-ray fluorescence and quantitative analysis. In Table 1 are listed the Pd weight loading and Pd dispersion, D_{Pd} for each of the samples used in this study. The Pd dispersions were measured after the catalysts had been exposed to methanol synthesis conditions.

Rate data were taken with 0.1 g of catalyst contained in a tubular microreactor which was made of copper. The reactor was heated in a fluidized sand bath. Reaction products were analyzed by gas chromatography using a Varian 3700 gas chromatograph equipped with a 3-m stainless-steel column packed with Chromosorb 107. Fresh catalyst samples were reduced in H_2 at 573 K for 3 hr and then conditioned in a mixture of 70% H_2 and 30% CO at 523 K and 10 atm for 10 hr. During the first few hours of the conditioning period, the activity of both Pd/SiO_2 and Pd/La_2O_3 decreased rapidly. At the end of 10 hr, the activity of the Pd/La_2O_3 catalyst reached a stable level, whereas the activity of Pd/SiO_2 continued to decrease slowly. To compensate for the further loss of activity of Pd/SiO_2, the rates of reaction were measured periodically for a standard set of reaction conditions. Throughout the range of conditions for which rate data were taken, the synthesis gas flow rate to the reactor was adjusted to maintain differential conversion. It should be noted that the methanol concentration in the effluent stream rarely exceeded 1% of the equilibrium value.

Methanol and methane were the only products observed using the Pd/La_2O_3 catalysts. With the Pd/SiO_2 catalysts, small amounts of dimethyl ether were observed in addition to methanol and methane. The rate of dimethyl ether formation varied inversely with the synthesis gas flow rate indicating that this product is formed via the dehydration of methanol (*5*). The intrinsic rate of methanol synthesis was determined by summing the observed rate of methanol formation and twice the rate of dimethyl ether formation. This sum was found to be independent of synthesis gas flow rate.

Infrared spectra of species adsorbed on the catalyst surface under reaction conditions were obtained using a specially designed cell. Details concerning the cell construction and the procedures used to acquire spectra may be found in references (*12, 13*).

RESULTS

Listed in Table 1 are the preexponential factors and the apparent activation energies for methanol and methane synthesis determined for Pd/SiO_2 and Pd/La_2O_3 catalysts of different Pd loadings. All of the rate measurements on which these activation energies are based were made at temperatures between 498 and 548 K. It is evident that the support composition has a small effect on the apparent activation energy for methanol synthesis. Moreover, for a given support composition, the values obtained for the different Pd weight loadings are in good agreement with one another. The average activation energy for CH_3OH formation is 18.8 ± 1.3 kcal/mol for Pd/SiO_2 and 20.4 ± 0.5 kcal/mol for Pd/La_2O_3. The results in Table 1 indicate, however, that support composition does affect the apparent activation energy for CH_4 synthesis. The Pd/La_2O_3 samples show little variation with metal loading, and can be characterized by an average value of 36.4 ± 1.0 kcal/mol. By contrast, the Pd/SiO_2 samples exhibit two values of the activation energy for CH_4 formation: 25.6 ± 1.7 kcal/mol for the 2.0 and 5.1% Pd/SiO_2 samples; and 33.9 kcal/mol for the 0.75% Pd/SiO_2 sample.

The dependence of the turnover frequencies for CH_3OH and CH_4 synthesis, N_{CH_3OH} and N_{CH_4}, on the partial pressures of H_2 and CO are shown in Figs. 1 and 2 for 2.0% Pd/SiO_2, and in Figs. 3 and 4 for 1.9% Pd/La_2O_3. The data in these figures were used to determine power-law rate expressions for N_{CH_3OH} and N_{CH_4}. For 2.0% Pd/SiO_2, the rates are given by

$$N_{CH_3OH} = k_1 P_{H_2}^{0.75} P_{CO}^{0.15} \tag{1}$$

$$N_{CH_4} = k_2 P_{H_2}^{0.70} P_{CO}^{-0.40} \tag{2}$$

and for 1.9% Pd/La_2O_3, the rates are given by

$$N_{CH_3OH} = k_{1'} P_{H_2}^{0.75} P_{CO}^{0.10} \tag{1'}$$

$$N_{CH_4} = k_{2'} P_{H_2}^{0.15} P_{CO}^{-0.05} \tag{2'}$$

Comparison of Eqs. (1) and (1′) indicates that the H_2 and CO pressure dependencies of the rate of methanol synthesis are virtually the same for 2.0% Pd/SiO_2 and 1.9% Pd/La_2O_3. This fact combined with the close agreement of the activation energies for CH_3OH formation over Pd/SiO_2 and Pd/La_2O_3, suggests that the mechanism of

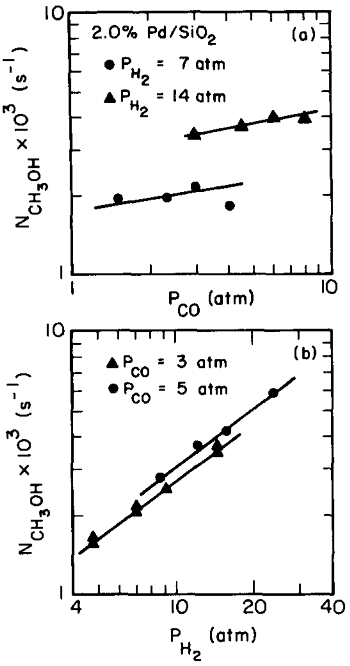

FIG. 1. The dependence of the methanol turnover frequency for 2.0% Pd/SiO_2 on (a) the CO pressure and (b) the H_2 pressure. T = 523 K.

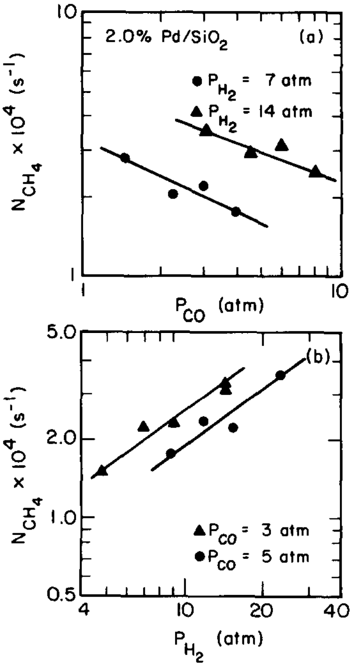

FIG. 2. The dependence of the methane turnover frequency for 2.0% Pd/SiO_2 on (a) the CO pressure and (b) the H_2 pressure. T = 523 K.

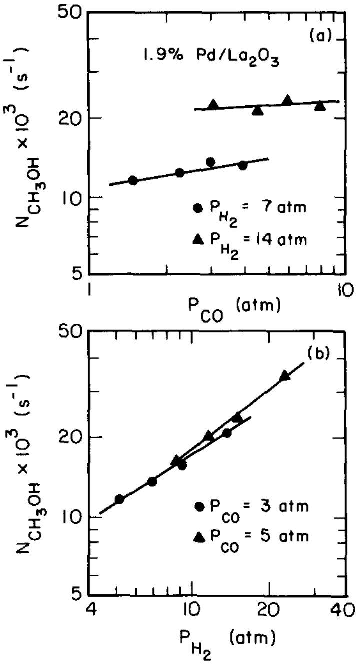

FIG. 3. The dependence of the methanol turnover frequency for 1.9% Pd/La_2O_3 on (a) the CO pressure and (b) the H_2 pressure. T = 523 K.

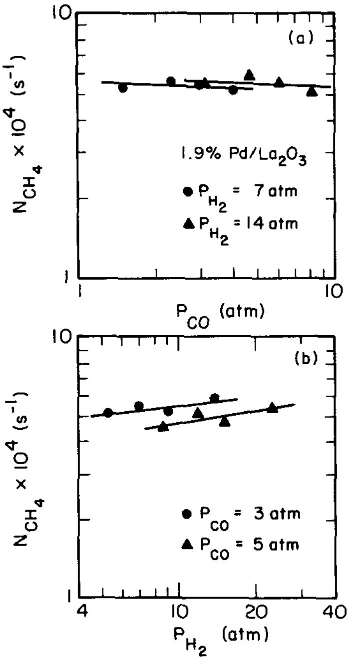

FIG. 4. The dependence of the methane turnover frequency for 1.9% Pd/La_2O_3 on (a) the CO pressure and (b) the H_2 pressure. T = 523 K.

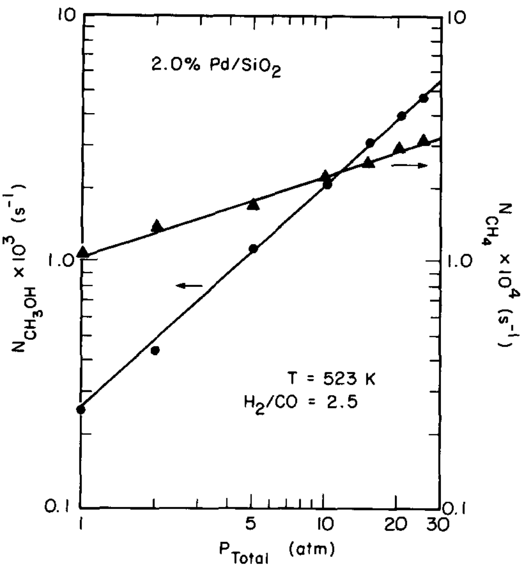

FIG. 5. The dependence of the methanol and methane turnover frequencies on total pressure, for 2.0% Pd/SiO_2.

methanol formation is the same for both catalysts. Conversely, comparison of Eqs. (2) and (2′) shows that the composition of the support has a strong influence on the H_2 and CO pressure dependence of the rate of methane formation and, as was noted earlier, the activation energies for methane formation are quite different on the two supports. These results suggest that the mechanism of methane formation on Pd/SiO_2 and Pd/La_2O_3 may not be the same.

The dependence of N_{CH_3OH} and N_{CH_4} on the total pressure was determined and is shown in Figs. 5 and 6 for 2.0% Pd/SiO_2 and 1.9% Pd/La_2O_3, respectively. These data were obtained at total pressures of 1 to 25 atm, for a fixed H_2/CO ratio of 2.5. Power-law rate expressions determined from these data are given by

$$N_{CH_3OH} = k_3 P^{0.95} \tag{3}$$

$$N_{CH_4} = k_4 P^{0.30} \tag{4}$$

for 2% Pd/SiO_2 and by

$$N_{CH_3OH} = k_{3'} P^{0.85} \tag{3'}$$

$$N_{CH_4} = k_{4'} P^{-0.05} \tag{4'}$$

for 1.9% Pd/La_2O_3. Comparison of Eqs. (3) and (4) with Eqs. (1) and (2), and comparison of Eqs. (3′) and (4′) with Eqs. (1′) and (2′), shows that the dependence of N_{CH_3OH} and N_{CH_4} on total pressure is virtually the same, regardless of whether it is determined from experiments in which the total pressure is varied or from experiments in which the partial pressures of H_2 and CO are varied separately.

Infrared spectra of adsorbed species were recorded over the same range of reaction conditions used to establish the kinetics of methanol and methane synthesis. The features observed were identical to those reported previously (*12*). For both SiO_2- and La_2O_3-supported Pd, the only bands attributable to species adsorbed on Pd were those associated with CO. The positions of the bands for CO adsorbed on Pd/SiO_2 were 2075 and 1965 cm^{-1}, and for Pd/La_2O_3, 2060, 1955, and 1900 cm^{-1}. Neither the positions nor intensities of these bands changed with reaction temperature or reactant partial pressures. From these observations it was concluded that the catalyst surface is saturated by adsorbed CO for all of the reaction conditions used in the experiments reported here.

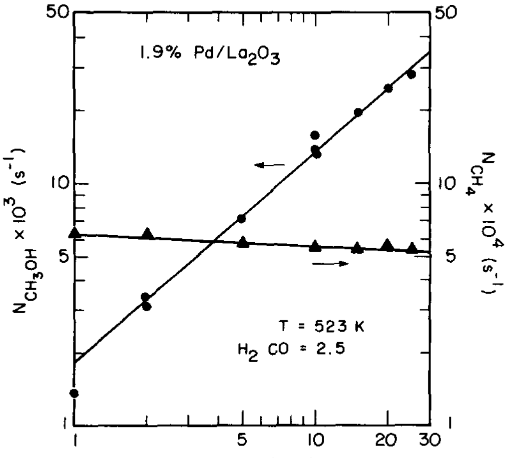

FIG. 6. The dependence of the methanol and methane turnover frequencies on total pressure, for 1.9% Pd/La_2O_3.

TABLE 2

Comparison of the Rate Laws Reported in the Literature for CO Hydrogenation over Supported Pd

Reference	Catalyst	E_i (kcal/mol)		Order w.r.t. H_2		Order w.r.t. CO	
		CH_3OH	CH_4	CH_3OH	CH_4	CH_3OH	CH_4
Ryndin *et al.* (*3*)	1.5% Pd/SiO_2	17.2	24.1	—	—	—	—
Wang *et al.* (*14*)	4.8% Pd/SiO_2	—	27.0	—	0.7	—	0.15
Fajula *et al.* (*5*)	4.6% Pd/SiO_2	—	—	2.2	—	−0.4 −1.1	—
This work	2.0% Pd/SiO_2	17.8	26.8	0.75	0.7	0.15	−0.4
Ichikawa (*2*)	2.9% Pd/La_2O_3	13.0	29.0	1.0	1.0	0.4	−0.4
Ryndin *et al.* (*3*)	0.2% Pd/La_2O_3	14.0	24.9	—	—	—	—
This work	1.9% Pd/La_2O_3	20.8	36.7	0.75	0.15	0.1	−0.005

DISCUSSION

A comparison of the rate parameters determined in this work with those reported in the literature is given in Table 2. For Pd/SiO_2, there is a fair degree of agreement between different authors concerning the activation energies for CH_3OH and CH_4 synthesis. However, the agreement with regard to the orders in H_2 and CO partial pressures is not good. Fajula *et al.* (*5*) have reported that the rate of CH_3OH synthesis is 2.2 order in H_2 and either −0.4 or −1.1 order in CO, depending on whether the total pressure was above or below 15 atm. In the present studies, no change in the CO order was observed for total pressures ranging from 1 to 25 atm (see Figs. 5 and 6). Comparison of the rate law for methane synthesis over Pd/SiO_2 reported here with that given by Wang *et al.* (*14*) shows close agreement in the order with respect to H_2, but a large difference in the order with respect to CO.

The spread in reported activation energies for methanol and methane synthesis over Pd/La_2O_3 is greater than that for Pd/SiO_2. On the other hand, the dependence of the rate of methanol synthesis on H_2 and CO partial pressures determined by Ichikawa (*2*) and those presented here are reasonably close. The level of agreement is, in fact, surprising when one recalls that all of Ichikawa's measurements were performed with reactant partial pressures below 1 atm. The dependencies of the rate of methane synthesis on H_2 and CO partial pressures reported by Ichikawa (*2*) show little agreement with those determined in the present study.

Many factors may contribute to the differences in rate laws shown in Table 2. These include the technique for catalyst preparation, the nature of the Pd precursor, the Pd loading and/or dispersion, the source of the support, and the manner of catalyst pretreatment. In this regard, it should be noted that two grades of silica were used to prepare the Pd/SiO_2 catalysts listed in Table 2. In the work of Ryndin *et al.* (*3*) and in the present work, Cab-O-Sil HS5 silica was used, whereas Davison grade 57 silica was used in the studies reported by Fajula *et al.* (*5*) and Wang *et al.* (*14*). It has been reported by Fajula *et al.* (*5*) that large differences in the activity and selectivity of Pd for methanol synthesis occur depending on the grade of silica used. In the present work, catalysts of varying Pd loadings and dispersion were prepared from a single source of silica, employing a common preparation technique. Thus, the effects of support composition, metal loading, and dispersion could be studied in a systematic fashion.

Hicks and Bell (*12*) have recently reported that the turnover frequency for methanol synthesis over SiO_2- and La_2O_3-supported Pd is independent of Pd dispersion, for dispersions between 10 and 20%. However, the turnover frequency does depend on the Pd morphology. At 523 K, 10 atm pressure, and H_2/CO ratio of 2.5, the methanol turnover frequency of Pd/La_2O_3 increases from 7.5×10^{-3} to $16.0 \times 10^{-3}\ s^{-1}$ as the proportion of Pd(100) surfaces increases from 10 to 85%. It is to be noted that the shift in Pd morphology is affected by increasing the Pd weight loading. Thus, 0.7% Pd/La_2O_3 contains 85% Pd(100) and 15% Pd(111) surfaces, while 8.8% Pd/La_2O_3 contains 10% Pd(100) and 90% Pd(111) surfaces. Inspection of Table 1 indicates that as the metal loading is changed, and hence, the Pd morphology is changed, the apparent activation energy for methanol synthesis remains constant. These data suggest, therefore, that the mechanism of methanol synthesis does not depend on the structure of the crystallite planes exposed.

Hicks and Bell (*12*) also noted that for a fixed Pd morphology, the rate of methanol synthesis over Pd/La_2O_3 is 7.5 times higher than over Pd/SiO_2. This difference is attributable totally to the influence of metal–support interactions (*12*) on the properties of Pd/La_2O_3. The results presented here show that the higher activity of Pd/La_2O_3 cannot be ascribed to differences in either the activation energy or the orders in H_2 and CO partial pressures. This observation, combined with the similar behaviors of the two catalysts with regard to variations in Pd dispersion, strongly suggests that the mechanism of methanol synthesis is the same for Pd supported on SiO_2 and La_2O_3. Assuming that this is so, the observed differences in methanol synthesis activity are quite possibly due to factors such as the proportion of total Pd surface sites active for methanol synthesis, or to the magnitude of the rate and equilibrium parameters associated with the elementary steps in the reaction mechanism.

The idea that only a fraction of all surface Pd sites are active for methanol synthesis has been proposed by Ponec and co-workers (*4, 7–9*). In studies with MgO-promoted Pd/SiO_2, it was observed that the increase in methanol activity with increasing MgO promotion was paralleled very closely by an increase in the amount of Pd^{n+} ions extractable by acetylacetonate. Based on this evidence, Ponec proposed that Pd^{n+} centers are essential for the synthesis of methanol and play a role similar to that of Cu^+ ions in Cu/ZnO catalysts (*15, 16*).

While the results reported by Ponec and co-workers (*4, 7–9*) are significant and highly suggestive, we do not believe that they provide a satisfactory basis for explaining the differences in methanol synthesis activity with Pd crystallite morphology and support composition, reported by us. Several reasons can be given for this opinion. First, if it is assumed that ionic centers are required for methanol synthesis, and that such centers occur on the surface of Pd crystallites, then it would be necessary for the proportion of ionic sites to be independent of changes in Pd dispersion. Otherwise the methanol turnover frequency would not be independent of the Pd dispersion over both Pd/SiO_2 and Pd/La_2O_3. The requisite constraint is quite demanding, and it seems unlikely that the proportion of ionic sites would remain fixed as the weight loading of Pd on both supports is varied from 0.25 to 9.0%, and the dispersion is varied from 10 to 20% (*12*). The dependence of methanol turnover frequency on Pd morphology is also difficult to reconcile with the idea that synthesis occurs at ionic sites, since this would necessitate that the proportion of such sites be higher on Pd(100) than on Pd(111) surfaces. Finally, XPS spectra of the reduced Pd/SiO_2 and Pd/La_2O_3 catalysts used in the present studies showed no evidence for positively charged Pd (*10*). Quite to the contrary, Pd supported on SiO_2 exhibited bulk-like electronic properties, while Pd supported on La_2O_3 was more electronegative than bulk Pd. The latter characteristic is ascribed to charge transfer from patches of partially reduced support residing on the surface of the Pd crystallites.

Our investigations of Pd/SiO_2 and Pd/La_2O_3 suggest that other factors may be responsible for the changes in methanol turnover frequency with Pd morphology and support composition. The Pd morphology might affect the rate by changing the geometry of the active site, or by changing the strengths of H_2 and CO adsorption. Regarding this latter effect, infrared studies clearly show the CO adsorption strength is sensitive to the type of crystallite plane exposed. At high coverages of CO, the frequency of the infrared band for CO adsorbed on Pd(100) is about 50 cm^{-1} higher than that for CO adsorbed on Pd(111) (*11, 12*). This indicates that the Pd–CO π-bond is stronger for CO adsorbed on (111) surfaces. Desorption experiments further reveal that at high CO coverages, CO desorbs more rapidly from Pd(100) than from Pd(111) (*11, 17*).

The support composition might also be expected to alter the strengths of H_2 and CO adsorption. Investigations of Pd/La_2O_3 have provided convincing evidence that patches of partially reduced support reside on the Pd crystallites of this catalyst (*10–12*). Infrared observations of CO desorption have found that these patches weaken the Pd–CO bond, most likely by delocalized charge transfer to the Pd surface (*11*). Moreover, this effect on the Pd surface appears to be retained during methanol synthesis. Carbon monoxide desorption experiments conducted after the cessation of methanol synthesis show that CO desorbs much faster from Pd/La_2O_3 than from Pd/SiO_2 (*17*). Preliminary results of H_2 thermal desorption experiments indicate that H_2 is more strongly bound on Pd/La_2O_3 than Pd/SiO_2 (*18*). Finally, it has recently been observed that CO will not displace H_2 preadsorbed on Pd/La_2O_3 but will completely displace H_2 preadsorbed on Pd/SiO_2. As will be shown below, in the context of a discussion of the mechanism of methanol synthesis, small changes in the strengths of H_2 and CO adsorption as a consequence of changes in crystallite morphology or support composition could very easily account for differences in the methanol turnover frequency.

Identification of the factors that influence methane synthesis is even more difficult than identification of the factors influencing methanol synthesis. The data presented here clearly show that the kinetics of methane synthesis are quite different for Pd/SiO_2 and Pd/La_2O_3. Of particular note is that the activation energy is about 10 kcal/mol greater on the latter catalyst. It was also shown in an earlier study (*12*) that while the turnover frequency for methane synthesis is independent of Pd dispersion for Pd/SiO_2, the turnover frequency decreases significantly with increasing dispersion for Pd/La_2O_3. All of these observations suggest that either the mechanism of methane formation, or the rate-controlling step in the mechanism is different. Further work is required to establish which of these two interpretations is more nearly correct.

Mechanism

The mechanism by which methanol is formed over Pd has been discussed by several authors. Rabo and co-workers (*1, 19*) have proposed that molecularly adsorbed CO reacts with H atoms directly to produce CH_xO species which then undergo additional hydrogenation to produce methanol. The suggestion that CO reacts without rupture of the C–O bond is supported by the observation that CO does not readily dissociate on Pd (*19*). Fajula *et al.* (*5*) have also described a mechanism in which CO reacts associatively and have proposed that the rate-limiting step is the simultaneous addition of four H atoms. This step was chosen to explain the observation of a second-order dependence of the CH_3OH synthesis rate on H_2 partial pressure. A somewhat different mechanism has been proposed by Kikuzono *et al.* (*6*), to rationalize the synthesis of methanol over alkali metal-promoted Pd/SiO_2. It was suggested that CO first reacts with an OH group to form a formate ion which is stabilized by the basic metal oxide promoter. Methanol is then assumed to be formed by the reduction of the formate ion. A mechanism involving formate was postulated based on infrared observation of formate ions and other adsorbed species during methanol synthesis.

The assumption that CH_3OH synthesis proceeds via associatively adsorbed CO is supported by the isotopic tracer studies of Takeuchi and Katzer (*20*). It was observed that when a 50–50 mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ is passed over a Rh/TiO_2 catalyst, the principal products formed are $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$. While similar experiments have not been reported for Pd, it seems reasonable to expect that the results would be identical.

It appears unlikely that formate ions are primary intermediates in the synthesis of methanol over Pd/SiO_2 and Pd/La_2O_3. As noted earlier, the close similarity in the kinetics of methanol synthesis over Pd/SiO_2 and Pd/La_2O_3 suggests that the synthesis mechanisms on both catalysts are identical. While *in situ* infrared studies (*17*) have revealed the presence of formate species on Pd/La_2O_3, none were observed on Pd/SiO_2. These studies also showed that formate ions could be formed by passing CO and H_2 over La_2O_3 in the absence of Pd. However, in this case, no CH_3OH is formed.

The synthesis of methanol over Pd most likely proceeds via stepwise hydrogenation of adsorbed CO. A mechanism which gives rise to kinetics consistent with those observed for Pd/SiO_2 and Pd/La_2O_3 is shown in Fig. 7. Carbon monoxide is assumed to adsorb in a bridging fashion between adjacent Pd atoms. Hydrogen adsorbs on sites different from those that adsorb CO (designated M_h in the figure). Initially H_2 adsorbs in the molecular state, but then rapidly dissociates to form adsorbed H atoms. It is proposed that the rate-determining step is the reaction of adsorbed CO with molecularly adsorbed H_2 to form a hydroxymethylene intermediate. This intermediate is then rapidly hydrogenated to a CH_3O intermediate and finally methanol. Atomically adsorbed hydrogen is assumed to participate in these last two steps.

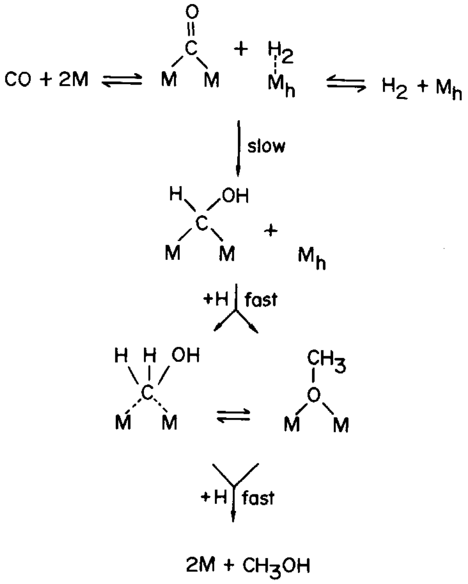

FIG. 7. Proposed scheme for the conversion of CO and H_2 to methanol.

In writing the scheme shown in Fig. 7, it is assumed that bridge-bonded CO is the reactive form of adsorbed CO. Studies by Bradshaw and Hoffmann (*21–23*) of CO adsorption on Pd single crystals have shown that CO adsorbs in the bridge-bonded form on Pd(100) and Pd(111) surfaces at high coverages. Comparison of the infrared spectra of CO adsorbed on Pd(100) and Pd(111) surfaces with those of CO adsorbed on supported Pd reveals that the same sites exist on the surface of the supported Pd crystallites (*24*). Since the specific activity for methanol synthesis is found to correlate with the distribution of bridge-bonded CO adsorbed on Pd(100) and Pd(111) surfaces (*12*), it is concluded that the reactive species is bridge-bonded CO.

Infrared studies of CO adsorption on Pd/SiO_2 and Pd/La_2O_3 have revealed that at saturation coverage the stoichiometry for bridge-bonded CO is one CO molecule per

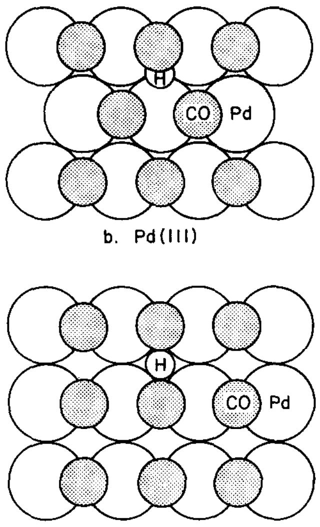

FIG. 8. A schematic representation of H_2 and CO adsorption on Pd(100) and Pd(111).

surface Pd atom (*11*). Illustrations of CO adsorption at this level on both Pd(100) and Pd(111) surfaces are shown in Fig. 8. Examination of this figure suggests that while the spacing between the nearest neighbor CO molecules is small, there is sufficient room to accommodate adsorbed hydrogen. The most likely positions for H_2 adsorption are the surface hollows. These sites possess fourfold symmetry on the (100) surface and threefold symmetry on the (111) surface. The selection of such sites is consistent with the results of Ertl and co-workers (*25, 26*) for H_2 adsorption on Pd(100) and Pd(111) surfaces. The conclusion that CO and H_2 adsorption occur on distinctly different types of sites is further indicated by recent isotopic displacement studies (*27*) which show that in the presence of gas-phase CO and H_2, the surface of Pd black is covered by a monolayer of CO and nearly a monolayer of H atoms.

There is only indirect evidence for the existence of molecularly adsorbed H_2 on the surface of Pd. Behm *et al.* (*26*) have found that the kinetics of H_2 adsorption and desorption from a Pd(100) surface is best interpreted by a precursor-state model. In such a model, it is assumed that H_2 adsorbs initially as a molecule and then translates over the surface until it dissociates. The coverage by molecularly adsorbed H_2 would be expected to be small if there are many pairs of vacant sites at which dissociation could take place. Saturation of the Pd surface with adsorbed CO might be expected to increase the coverage by adsorbed H_2 by inhibiting the translation of the H_2 molecules to sites required for dissociation.

The scheme proposed in Fig. 7 is also consistent with what is known about the adsorption and decomposition of CH_3OH on Pd single-crystal surfaces (*28, 29*). The adsorption of CH_3OH on Pd(100) and Pd(111) at 300 K leads to the formation of CO and H_2. When the adsorption temperature is reduced to 77 K, Christmann and Demuth (*28*) report that part of the adsorbed CH_3OH is converted to a methoxide group. As the temperature is raised, most of the methoxide desorbs as CH_3OH. However, a small amount remains on the surface and at higher temperatures is converted via a sequence of reactions to CO and H_2. It is therefore apparent that the formation of methanol from a methoxide group is a rapid reaction, as is indicated in Fig. 7.

An expression for the kinetics of CH_3OH synthesis can readily be developed on the basis of the mechanism shown in Fig. 7. The turnover frequency for methanol synthesis is given by

$$N_{CH_3OH} = k\theta_{CO}\theta_{H_2}, \qquad (5)$$

where k is the rate coefficient for the rate-limiting step, and θ_{CO} and θ_{H_2} are the surface coverages of CO and H_2. Based on the infrared spectra discussed earlier, θ_{CO} is taken to be unity. Since H_2 molecules and H atoms adsorb on the same sites, while CO molecules adsorb on different sites, the coverage of molecularly adsorbed H_2 is given by

$$\theta_{H_2} = \frac{K_{H_2}P_{H_2}}{1 + K_{H_2}P_{H_2} + (K_H P_{H_2})^{1/2}}, \quad (6)$$

where K_{H_2} and K_H are the equilibrium constants for the molecular and dissociative adsorption of hydrogen. Since the dissociation of H_2 is strongly favored on Pd (*25, 26*), it is assumed that $K_{H_2}P_{H_2} \ll (K_H P_{H_2})^{1/2}$. Substitution of Eq. (6) into Eq. (5), and introduction of the assumption concerning the relative significance of molecularly and atomically adsorbed hydrogen gives

$$N_{CH_3OH} = \frac{kK_{H_2}P_{H_2}}{1 + (K_H P_{H_2})^{1/2}}. \quad (7)$$

Equation (7) predicts that the rate of CH_3OH synthesis is zero order in CO and between one and one-half order in H_2. This agrees reasonably well with the kinetics for both Pd/SiO_2 and Pd/La_2O_3 reported here.

An alternative mechanism to that shown in Fig. 7 can be proposed in which H atoms add sequentially to CO. In this case, the concerted addition of the first two H atoms to CO could be viewed as a rate-limiting step. Such a mechanism yields a kinetic expression for methanol synthesis which varies from zero to first order with respect to H_2, depending on whether the coverage of atomic hydrogen is high or low. Although this mechanism cannot be ruled out, there is some evidence to suggest that it may not be operative on Pd. As discussed above, isotopic tracer studies have found that the Pd surface is covered by nearly a monolayer of hydrogen in the presence of gas-phase H_2 and CO (*27*). A high coverage of H atoms implies that the order with respect to H_2 should be near zero, instead of 0.75 as is observed.

The form of Eq. (7) suggests that differences in N_{CH_3OH}, occurring with changes in crystallite morphology and support composition, could be attributed to changes in the magnitude of k, K_{H_2}, and/or K_H. The changes in these parameters would not need to be particularly large. Thus, for example, if the energetics of the system were altered such that the apparent activation energy changed by 2 kcal/mol, the methanol turnover frequency would change by a factor of 7.5 at 523 K. This is exactly the ratio of the methanol turnover frequencies for Pd/La_2O_3 relative to Pd/SiO_2 when both catalysts have the same average crystallite morphology. To establish the validity of this interpretation would require measurements of the activation energies for methanol synthesis with much more accuracy than those made in the present study.

CONCLUSIONS

The activation energy and the orders with respect to H_2 and CO partial pressures are essentially the same for methanol synthesis over Pd/SiO_2 and Pd/La_2O_3, suggesting that the reaction mechanism is not affected by support composition. The observed higher specific activity of Pd/La_2O_3 relative to Pd/SiO_2 is ascribed to small differences in the relative strengths of H_2 and CO adsorption. The rate expressions for methane synthesis over Pd/SiO_2 and Pd/La_2O_3 differ significantly. This difference is taken as an indication that the reaction mechanisms for the two catalysts are different or that the mechanism is the same but the rate-limiting step is different.

A mechanism for methanol synthesis over Pd has been proposed which suggests that the rate-limiting step is the reaction of adsorbed H_2 with adsorbed CO to form a hydroxymethylene intermediate. Rate expressions for methanol synthesis derived on the basis of this mechanism are consistent with those observed experimentally for both Pd/SiO_2 and Pd/La_2O_3.

ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of the Basic Energy Sciences, U.S. Department of Energy under Contract De-AC03-76SF00098.

REFERENCES

1. Poutsma, M. L., Elek, L. F., Ibarbia, P. A., Risch, A. P., and Rabo, J. A., *J. Catal.* **52,** 157 (1978).

2. Ichikawa, M., *Shokubai* **21,** 253 (1979).

3. Ryndin, Yu. A., Hicks, R. F., Bell, A. T., and Yermakov, Yu. I., *J. Catal.* **70,** 287 (1981).
4. Poels, E. K., van Broekhoven, E. H., van Barneveld, W. A. A., and Ponec, V., *React. Kinet. Catal. Lett.* **18,** 223 (1981).
5. Fajula, F., Anthony, R. G., and Lunsford, J. H., *J. Catal.* **73,** 237 (1982).
6. Kikuzono, Y., Kagami, S., Naito, S., Onishi, T., and Tamaru, K., *Faraday Discuss. Chem. Soc.* **72,** 135 (1982).
7. Ponec, V., *Stud. Surf. Sci. Catal.* **11,** 63 (1982).
8. Poels, E. K., Koolstra, R., Geus, J. W., and Ponec, V., *Stud. Surf. Sci. Catal.* **11,** 233 (1982).
9. Driessen, J. M., Poels, E. K., Hindermann, J. P., and Ponec, V., *J. Catal.* **82,** 26 (1983).
10. Fleisch, T. H., Hicks, R. F., and Bell, A. T., *J. Catal.* **87,** 398 (1984).
11. Hicks, R. F., Yen, Q.-J., and Bell, A. T., *J. Catal.* **89,** 498 (1984).
12. Hicks, R. F., and Bell, A. T., *J. Catal.*, in press.
13. Hicks, R. F., Kellner, C. S., Savatsky, B. J., Hecker, W. C., and Bell, A. T., *J. Catal.* **71,** 216 (1981).
14. Wang, S.-Y., Moon, S. H., and Vannice, M. A., *J. Catal.* **71,** 167 (1981).
15. Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., Bulko, J. B., and Kobylinski, T. P., *J. Catal.* **56,** 407 (1979).
16. Mehta, S., Simmons, G. W., Klier, K., and Herman, R. G., *J. Catal.* **57,** 339 (1979).
17. Hicks, R. F., and Bell, A. T., unpublished results.
18. Rieck, J. S., and Bell, A. T., unpublished results.
19. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53,** 295 (1978).
20. Takeuchi, A., and Katzer, J. R., *J. Phys. Chem.* **85,** 937 (1981).
21. Bradshaw, A. M., and Hoffmann, F. M., *Surf. Sci.* **72,** 513 (1978).
22. Ortega, A., Hoffmann, F. M., and Bradshaw, A. M., *Surf. Sci.* **119,** 79 (1982).
23. Hoffmann, F. M., *Surf. Sci. Rep.* **3,** 107 (1983).
24. Sheppard, N., and Nguyen, T. T., "Advances in Infrared and Raman Spectroscopy" (R. J. H. Clark and R. E. Hester, Eds.), Vol. 5. Heyden & Sons, London, 1978.
25. Conrad, H., Ertl, G., and Latta, E. E., *Surf. Sci.* **41,** 435 (1974).
26. Behm, R. J., Christmann, K., and Ertl, G., *Surf. Sci.* **99,** 320 (1980).
27. Winslow, P., and Bell, A. T., unpublished results.
28. Christmann, K., and Demuth, J. E., *J. Chem. Phys.* **76,** 6308, 6318 (1982).
29. Gates, J. A., and Kesmodel, L. L., *J. Catal.* **83,** 437 (1983).