JOURNAL OF CATALYSIS **103**, 46–54 (1987)

# The Influence of Dispersion on the Interactions of $H_2$ and CO with Pd/$SiO_2$

JEFFERY S. RIECK AND ALEXIS T. BELL

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

Received September 10, 1985; revised July 6, 1986

The influence of dispersion on the interactions of $H_2$ and CO with Pd/$SiO_2$ has been investigated. The distribution of $H_2$ adstates changes with dispersion, due possibly to a change in the morphology of the Pd crystallites or in the coordination of adsorbed H atoms with the Pd atoms. The ratio of linearly held CO to bridge-bonded CO decreases with the dispersion, as does the ratio of Pd(100) to Pd(111) planes on the surfaces of the Pd crystallites. CO dissociation occurs preferentially from bridge sites and proceeds more readily with decreasing dispersion. Consistent with this, the turnover frequency for methanation increases with decreasing dispersion.

## INTRODUCTION

The influence of dispersion on the activity and selectivity of supported Pd catalysts has been the subject of several recent investigations. Hicks and Bell (*1*) have reported that the turnover frequency for methane formation over Pd/$SiO_2$ and Pd/$La_2O_3$ increased with decreasing dispersion. This trend is qualitatively consistent with that reported by other authors for Ni, Fe, Ru, and Rh (*2–11*). Hicks and Bell (*1*) noted that the turnover frequency for methanol synthesis is independent of metal dispersion but is sensitive to the structure of the planes exposed at the surface of the Pd particles. Pd(100) planes were found to be 2.8 time more active for methanol synthesis than Pd(111) planes. In contrast to the results of Hicks and Bell (*1*), Ichikawa *et al.* (*12*) have reported that the turnover frequency for methane formation over Pd/$SiO_2$ increases with increasing metal dispersion, and Kelly *et al.* (*13*) have observed that the turnover frequency for methanol synthesis increases with decreasing dispersion.

The present investigation was undertaken in an effort to clarify the influence of Pd dispersion on the hydrogenation of CO to methane. Studies were carried out with a single sample of Pd/$SiO_2$ which was sintered to achieve different dispersions. The strengths of $H_2$ and CO chemisorption were characterized by temperature-programmed desorption (TPD). Catalyst activity as a function of dispersion was determined from differential conversion data taken as a function of temperature.

## EXPERIMENTAL

*Apparatus.* The apparatus used for the present study has been described previously (*14–16*). The catalysts were placed in a quartz microreactor which could be heated at up to 1 K/s. The desorbing gas was swept from the microreactor by a continuous flow of carrier gas. Analysis of the effluent flow was performed with a quadrupole mass spectrometer. The transfer time from the microreactor to the mass spectrometer was less than 1.5 s. A microprocessor-based data acquisition system was used to direct the mass spectrometer to a series of preselected masses and to record the signal intensity at each mass setting. The catalyst temperature was also recorded by the data acquisition system.

*Materials.* The Pd/$SiO_2$ catalyst was prepared by ion exchange as described in Refs. (*17, 18*). A solution of $Pd(NH_3)_4Cl_2$ in de-

0021-9517/87 $3.00

ionized water was added dropwise to a slurry of Cab-O-Sil HS-5 silica in deionized water at 298 K. The pH of the slurry was adjusted to 12 by the addition of $NH_4OH$. The slurry was filtered, and the filter cake was washed with deionized water and dried at room temperature under vacuum. The Pd-containing precursor was decomposed by heating to 623 K at 0.1 K/s in a flow of 300 $cm^3$/min of 21% $O_2$ in He. The temperature was maintained at 623 K for 2 h, and the catalyst was evacuated and cooled to room temperature under vacuum. The weight loading of Pd was 0.66% as determined by X-ray fluorescence.

The dispersion of Pd in the catalyst was determined by the temperature used for reduction of the calcined material. Each sample of $Pd/SiO_2$ was heated in a flow of 250 $cm^3$/min of $H_2$ at a rate of 0.1 K/s up to the desired reduction temperature and then maintained at that temperature for 2 h. By increasing the reduction temperature from 473 to 1073 K, dispersions between 85 and 20% could be achieved. The dispersion of each catalyst was measured by $H_2$–$O_2$ titration and equivalent dispersions were obtained from either the $H_2$ and $O_2$ titers. The dispersion of the least dispersed catalyst ($D_{Pd}$ = 20%) was confirmed by XRD line-broadening. Further confirmation of the dispersion measurements were obtained by measuring the amounts of irreversibly adsorbed $H_2$ and CO on each sample. Consistent with previous measurements in this laboratory (*1*), the $H/Pd_s$ ratio was 1.07 ± 0.13 and the $CO/Pd_s$ ratio was 0.99 ± 0.04. No systematic variation in these stoichiometric ratios was observed with changes in Pd dispersion.

Helium and $H_2$ were purified to remove $O_2$ and water; and CO was purified to remove metal carbonyls, water and $CO_2$. Details of the purification procedures are given in Ref. (*19*). The absence of impurities in these gases was established by mass spectrometry.

*Experimental procedure.* The procedures followed are similar to those used in Ref. (*19*). A sample of catalyst which had been presintered to obtain the desired dispersion was placed in the microreactor. The amount of surface Pd present was kept constant between experiments at $2.0 \times 10^{-6}$ mol based on $H_2$–$O_2$ titration. The mass and particle size were selected to avoid transport effects (*20*). The catalysts were then reduced in $H_2$ for 2 h at 573 K. For temperature-programmed desorption (TPD) experiments, adsorption was performed by pulsing $H_2$ or CO through the catalyst bed. A carrier flow rate of 50 $cm^3$/min of He was used, and the heating rate was 1 K/s for these experiments. The relative activities of the catalysts for CO hydrogenation were determined by ramping the catalyst temperature at 1 K/s in a flow of 75 $cm^3$/min of $H_2$ and 25 $cm^3$/min of CO. Following each experiment, the mass spectrometer was calibrated against He mixtures containing specified concentrations of $H_2$ and CO.

The absolute rates of desorption are based on the number of surface Pd atoms present calculated from $H_2$–$O_2$ titration. The moles of gas desorbing during an experiment were calculated by first integrating the spectra to find the peak areas, and then multiplying by the proper calibration factor. The initial coverages were found by dividing the number of moles desorbed by the moles of surface Pd present based on $H_2$–$O_2$ titration.

## RESULTS

### $H_2$ and CO TPD

The TPD spectra for $H_2$ desorption from 0.66% $Pd/SiO_2$ are given in Fig. 1 for samples with dispersions of 76, 51, and 28%. The initial coverage by adsorbed H atoms, $\theta_H^0$, is based on the amount of $H_2$ desorbed up to 873 K. The saturation coverages are close to 1.3, independent of the dispersion. For a dispersion of 76%, there is a prominent peak at 398 K. This is accompanied by shoulders at 463 and 573 K. Decreasing the dispersion to 51% by sintering the catalyst results in a change in the distribution of ad-

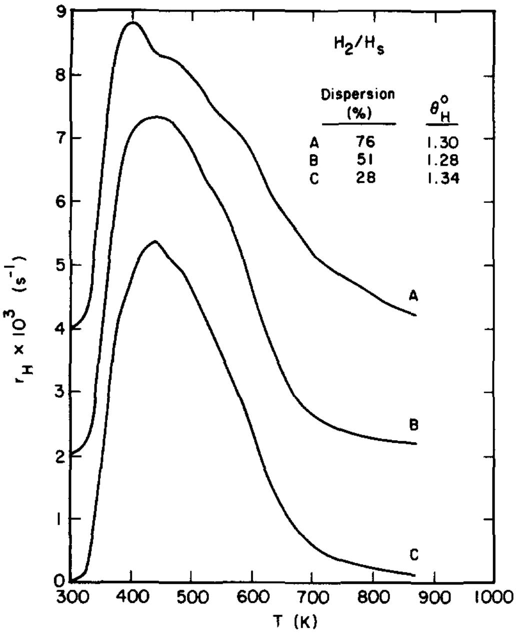

FIG. 1. Effects of dispersion on the TPD of $H_2$ from 0.66% Pd/$SiO_2$.

states for $H_2$ adsorption. The peak at 398 K decreases in intensity, and the most prominent feature is now centered at 448 K. In addition, the high temperature peak at 573 K is less clearly resolved. A further decrease in the dispersion to 28% does not significantly change the $H_2$ TPD spectrum. Both the shape and position of the spectrum for desorption from the 28% dispersion sample agree with those given in Ref. (*19*) for $H_2$ desorption from Pd/$SiO_2$ with dispersions of 35 and 18%.

The CO desorption spectra for 0.66% Pd/$SiO_2$ samples with dispersions of 77, 63, and 28% are given in Fig. 2. Also included in Fig. 2 are the spectra for the $CO_2$ evolved during CO desorption. Since no $H_2$ desorption was observed during these experiments, the appearance of $CO_2$ cannot be attributed to the water–gas shift reaction, and is, therefore, attributed to the disproportionation of CO on the catalyst surface with the stoichiometry: $2\ CO_{ads} \rightarrow C_{ads} + CO_2$. The initial coverage of CO, $\theta^0_{CO}$, given in Fig. 2 is taken to be the amount of CO desorbed, $\theta_{CO}$, plus twice the amount of $CO_2$ produced. The equivalent coverage of CO converted to $CO_2$ is given by $\theta_{CO_2}$.

The spectrum for CO desorption from Pd/$SiO_2$ with 77% dispersion shown in Fig. 2 consists of four peaks located at 380, 463, 668, and 778 K. These peak locations are in good agreement with those reported previously for Pd/$SiO_2$ (*19*). The saturation coverage is 0.99 of a monolayer of CO. Decreasing the dispersion results in a shift in the distribution of CO binding states, although the saturation coverage by CO stays constant. When the dispersion is decreased to 63%, the two low temperature peaks decrease greatly in magnitude. This coincides with a large increase in the magnitude of the two high temperature peaks. However, the positions of the four peaks do not change. Decreasing the dispersion to 28% results in a further decrease in the low temperature peaks, and the coalescence of the two high temperature peaks into a single broad peak centered at 728 K.

Figure 2 shows that all three catalysts produced significant amounts of $CO_2$ during CO TPD. The catalyst with 77% dispersion converts 0.22 of a monolayer equivalent of CO into $CO_2$, while the samples with 63 and 28% dispersion convert 0.14 and 0.13 of a

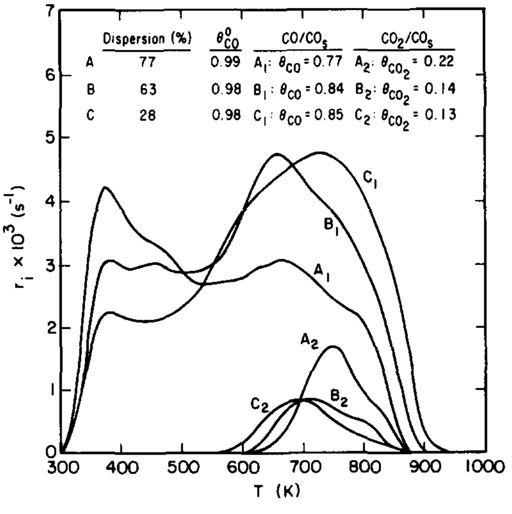

FIG. 2. Effects of dispersion on the desorption products observed during CO TPD from 0.66% Pd/$SiO_2$: (a) CO, (b) $CO_2$.

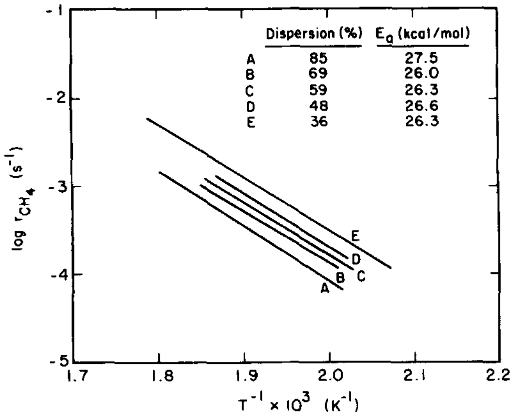

FIG. 3. Arrhenius plots showing the effects of dispersion on the turnover frequency for methanation over 0.66% $Pd/SiO_2$: $P = 1$ atm, $H_2/CO = 3/1$.

monolayer, respectively. Thus, the amount of CO which dissociates during the temperature ramp decreases with decreasing dispersion. It is significant to note, though, that CO dissociation occurs at progressively lower temperatures as the dispersion is decreased. The onset of $CO_2$ production occurs at 578 K for the 28% dispersion sample, while $CO_2$ desorption begins at 618 and 638 K over the samples with 63 and 77% dispersion, respectively. The temperature for which $CO_2$ production reaches a maximum increases in the same order: 28% (698 K) < 63% (713 K) < 77% (753 K).

### *Comparison of Activities for CO Methanation*

The dependence of the methanation activity of each catalyst on temperature was determined by ramping the catalyst temperature at 1 K/s in a flowing mixture of synthesis gas. During the temperature ramp, no products other than methane and $H_2O$ were detected. An Arrhenius plot of the turnover frequency for methanation is given in Fig. 3. The active area for each sample is based on the dispersion of the fresh sample determined by $H_2$–$O_2$ titration. Since the high dispersion catalysts are very sensitive to sintering in the presence of $H_2O$, experiments were conducted to ascertain over what temperature range the dispersion remains stable. The catalyst temperature was ramped in the synthesis gas mixture up to a given temperature, and the temperature ramp was halted. The catalyst was then rereduced at 573 K, and the dispersion redetermined using $H_2$–$O_2$ titration. These experiments showed that the catalyst dispersions were stable at temperatures below 523 K. Therefore, the effects of dispersion on the activities of the catalysts should be considered only for temperatures below 523 K.

Figure 3 reveals that the turnover frequency for methanation increases monotonically with decreasing Pd dispersion. This trend is shown very clearly in Fig. 4, which illustrates further the appearance of a plateau in the turnover frequency for dispersions below about 36%. The activation energies for methanation are listed in Fig. 3. For dispersions between 85 and 36%, $E_a$ lies between 26.0 and 27.5 kcal/mol, and there appears to be no systematic variation in $E_a$ with dispersion.

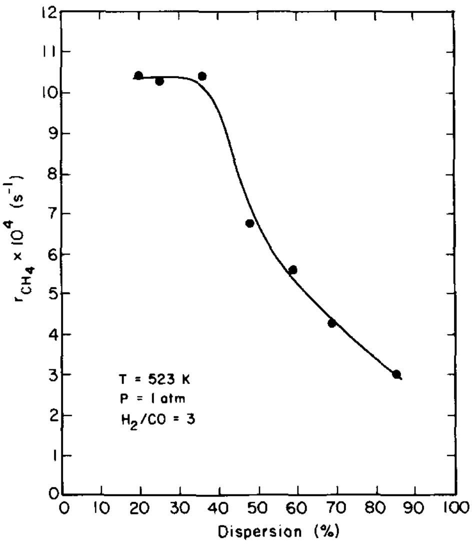

FIG. 4. Effects of dispersion on the turnover frequency for methanation over 0.66% $Pd/SiO_2$: $T = 523$ K, $P = 1$ atm, $H_2/CO = 3$.

## DISCUSSION

### *$H_2$ TPD*

The spectra for $H_2$ desorption in Fig. 1 show that the saturation coverage of $H_2$ does not change with dispersion. For the range of dispersions from 28 to 76%, the saturation coverage is about 1.3. This is somewhat higher than that measured by static chemisorption ($H/Pd_s = 1.07$) and that observed by Hicks *et al.* (*21*) and Rieck and Bell (*19*) for $Pd/SiO_2$ prepared by impregnation ($H/Pd_s = 0.93$ to 1.1). The most likely cause for the 17% higher value of $H/Pd_s$ obtained from $H_2$ TPD spectra is the incomplete removal of adsorbed $H_2$ during the evacuation of the catalyst, prior to initiation of the temperature ramp (*19*). It is of some interest to note, though, that hydrogen coverages in excess of unity have been noted in studies conducted with single crystals. Behm *et al.* (*23*) have reported that the saturation coverage of Pd(100) by H atoms corresponds to 1.35 of a monolayer, while Cattania *et al.* (*24*) have shown that the Pd(110) surface can adsorb 1.5 of a monolayer of H atoms.

The changes in the $H_2$ desorption features with decreasing dispersion indicate that changes in the distribution of H adstates occur as the catalyst is sintered. The peak locations of 398, 463, and 573 K are in good agreement with those previously reported for $Pd/SiO_2$ (*19*). The peak at 398 K is very well resolved for high dispersions, but becomes an unresolved shoulder as the dispersion is decreased. In addition, the peak at 573 K become less well resolved as the catalyst is sintered. The changes in the distribution of H adstates may be explained in two ways. First, a change in the surface morphology of the Pd crystallites may occur as the catalyst is sintered. The CO infrared studies of Hicks *et al.* (*21*) showed that on $Pd/SiO_2$ the surfaces of the Pd crystallites are composed of Pd(111) and Pd(100) planes. The activation energies for desorption of $H_2$ from these surfaces are 20.8 kcal/mol (*25*) and 24.5 kcal/mol (*23*), respectively. Rieck and Bell (*19*) showed that a Pd surface consisting of these two planes should exhibit multiple desorption peaks for $H_2$ TPD. Thus, a change in the surface morphology occurring with the change in dispersion would change the $H_2$ desorption spectrum. A second explanation involves the coordination of H adatoms with the surface Pd atoms. For the Pd(100) surface, adsorption of H atoms into fourfold coordinated sites is favored (*23*), whereas threefold coordination is favored for the Pd(111) surface (*25*). On both of these surfaces, bridge-bonding and adsorption on top of Pd atoms can also occur (*23*, *25*). Since the proportions of four and threefold adsorption sites decrease with increasing dispersion, adsorption into on-top sites and bridge-bonded sites should be more prevalent on the smaller particles. The lower strength of adsorption for these states would explain the decrease in the peak at 398 K as the dispersion decreases.

### *CO TPD*

The locations of the four peaks for CO desorption observed in Fig. 2 are in good agreement with those previously reported by Rieck and Bell (*19*) for $Pd/SiO_2$. By comparing their CO TPD spectra with the infrared observations of Hicks *et al.* (*21*), Rieck and Bell (*19*) were able to assign individual peaks in the TPD spectra to specific modes of CO adsorption. Using these peak assignments, we attribute the two peaks at 380 and 463 K to linearly adsorbed CO, and the peaks at 668 and 778 K to bridge-bonded CO on Pd(100) and Pd(111) planes, respectively. Figure 2 shows, therefore, that as the dispersion decreases, the amount of linearly bonded CO decreases the amount of bridged bonded CO increases. This trend is in good agreement with the infrared observations of Ichikawa *et al.* (*12*). The spectra in Fig. 2 also show that the peak at 778 K increases relative to that at 668 K as the dispersion decreases, indicating that the proportion of Pd(111) sites relative to Pd(100) sites increases with decreasing dispersion. Such a trend is consistent with what one expects, if the Pd crystallites are treated as perfect cuboctahedrons. Calculations by van Hardeveld and Hartog (*26*) show that as the dispersion decreases, the fraction of $C_9$ sites, which are characteristic of Pd(111) planes, increases faster than the fraction of $C_8$ sites, which are characteristic of Pd(100) planes.

The saturation coverage of $Pd/SiO_2$ by CO was observed to be a monolayer, independent of dispersion and in good agreement with our static chemisorption measurements. Thus, although the TPD spectra reveal large changes in the amount of bridge-bonded relative to linearly held CO, the overall adsorption stoichiometry remains constant at one CO molecule per surface Pd atom. This agrees with the infrared studies of $Pd/SiO_2$ by Hicks *et al.* (*21*) which showed that the ratio of CO to Pd is close to one, although the surfaces consisted of 90% bridge-bonded CO.

Figure 2 shows that the temperature for the onset of $CO_2$ formation decreases systematically with decreasing dispersion. If it is assumed that $CO_2$ is formed via the dissociation of a molecule of adsorbed CO followed by the rapid reaction of the nascent 0 atom with a second molecule of CO, then the rate of $CO_2$ formation is controlled by the rate of CO dissociation. The results in Fig. 2 then suggest that CO dissociation occurs more rapidly on large, rather than small, particles. Furthermore, since at the temperatures where $CO_2$ formation is observed, CO desorption is exclusively from bridge sites, we are led to conclude that CO dissociation occurs preferentially from bridge sites. This interpretation is consistent with recent theoretical calculations of the activation energy for CO dissociation carried out by Baetzold (*27*). His results show that there is considerable anisotropy in the activation energy for dissociative chemisorption of CO on fcc(111) surfaces. The activation energy is smallest for dissociation from bridge sites and greatest for dissociation from hollow sites. Dissociation from on-top sites shows a significantly greater barrier than that for dissociation from bridge sites. Since the proportion of CO desorbing from bridge sites increases with decreasing dispersion (see Fig. 2), the downscale shift in the temperature for the onset of CO dissociation (and hence the appearance of $CO_2$) with decreasing dispersion can be attributed to an increase in the fraction of bridge sites and the coincident decrease in the activation energy for dissociation from such sites.

### *Activity for CO Hydrogenation*

The formation of $CH_4$ from CO over Pd is believed to proceed via the dissociation of CO to form adsorbed carbon and the subsequent hydrogenation of this species. Previous studies by Rieck and Bell (*19, 28, 29*) of $Pd/SiO_2$, $Pd/TiO_2$, and rare earth oxide-promoted $Pd/SiO_2$ have shown that the carbon formed by the dissociation of CO is much more easily hydrogenated than molecular CO. This supports the premise that CO dissociation is the rate-limiting step for methanation.

Rieck and Bell (*19, 28, 29*) have also shown that there is a correlation between the turnover frequency for methanation and the temperature for the onset of CO disproportionation during CO TPD—the lower the temperature for the onset of CO disproportionation, the higher the turnover frequency for methanation. A similar trend is observed in the present work if one compares the results presented in Fig. 2 with those in Figs. 3 and 4. Since, as discussed above, the decrease in the temperature for the onset of CO disproportionation with decreasing Pd dispersion can be attributed to an increase in the proportion of bridge sites, it is reasonable to propose that the increase in methanation turnover frequency with decreasing Pd dispersion is due to the same cause. Thus, we propose that as the size of the Pd particles increases the fraction of exposed sites capable of dissociating CO increases and, for this reason, the methanation turnover frequency increases with decreasing Pd dispersion. It should be noted that such an interpretation is consistent with the absence of a significant change in the activation energy for methanation with changes in Pd dispersion. The proposed interpretation is also consistent with the calculations of van Hardeveld and Hartog (*26*) for the distribution of adsorption sites as a function of metal particle size. Assuming that the Pd crystallites have the shape of cubooctahedrons, the fraction of $C_9$ and $C_8$ sites (characteristic of Pd(111) and Pd(100) planes, respectively) decreases from 0.72 to 0.25 as the dispersion increases from 37 to 84%. The extent of the decrease in the fraction of $C_9$ plus $C_8$ sites with increasing Pd dispersion is in reasonably good agreement with the decrease in the methanation turnover frequency seen in Fig. 4.

As was discussed previously, with decreasing Pd dispersion not only does the proportion of $C_9$ plus $C_8$ sites increase but in addition the proportion of $C_9$ sites increases relative to the proportion of $C_8$ sites. What this means is that with increasing particle size the fraction of Pd(111) planes increases more rapidly relative to the fraction of Pd(100) planes. The absence of any significant change in the activation energy with dispersion suggests then that the activation energies for methanation on Pd(111) and Pd(100) planes are comparable. This conclusion agrees with that of Kelley and Goodman (*30*) who observed identical turnover frequencies and activation energies for CO methanation over Ni(111) and Ni(100) single crystal surfaces.

The results presented here are consistent with those of Hicks and Bell (*1*) but contradict those presented recently by Ichikawa *et al.* (*12*). For Pd supported on Davison 62 silica gel, their data showed equivalent turnover frequencies for catalysts with dispersions of 100 and 75%, and a threefold lower turnover frequency for a catalyst with a dispersion of 45%. Ichikawa *et al.* (*12*) also compared their results with those of two separate studies of Pd/$SiO_2$ catalysts reported by Vannice (*31, 32*). In the first of these (*31*), Cab-O-Sil was used as the support and the Pd dispersion was 46%, whereas in the second study (*32*), Davison 57 silica gel was used as the support and the dispersion was 20%. The activity data reported by Vannice (*31, 32*) indicated a nearly threefold lower turnover frequency for the 20% dispersion catalyst relative to the 46% dispersion catalyst. Based on these results, Ichikawa *et al.* (*12*) concluded that the turnover frequency for CO methanation over Pd decreases with decreasing Pd dispersion. Since they also observed that a larger proportion of CO undergoes dissociation on small Pd particles than on large Pd particles, they proposed that the trend in methanation turnover frequency with Pd dispersion could be associated with the ease with which CO dissociates.

The reason for the diametrically opposite conclusions regarding the effects of Pd dispersion on methanation turnover frequency reported here and by Ichikawa *et al.* (*12*) are difficult to explain. It is the opinion of the present authors that the data on which Ichikawa *et al.* (*12*) have based their conclusion may be affected by the fact that different silica supports and methods of catalyst preparation were used for three of the four catalyst samples. Fajula *et al.* (*33*), Deligianni *et al.* (*34*), and Kelly *et al.* (*13*) have shown that the activity of silica-supported Pd is strongly influenced by the source and grade of the silica, and it is not unreasonable to expect that even different batches of the same silica may not yield equivalent results. A further point to note is that in comparing results from different studies it is important to establish the length of time the catalyst was on stream before its activity was measured. In this connection, Ichikawa *et al.* (*12*) make no mention of whether their rate data and those of Vannice (*31, 32*) were determined after an equivalent length of time under reaction conditions.

Finally, we wish to note that both in the study reported by Ichikawa *et al.* (*12*) and that presented here, the amount of $CO_2$ produced during CO TPD increased with increasing dispersion. This trend cannot be rationalized at present and will require further investigation. It should be noted, though, that the amount of $CO_2$ formed, while related to the number of sites available for CO dissociation, is also influenced by other factors such as the CO coverage and the vacancy fraction at the temperature of CO dissociation. Thus, one cannot use the amount of $CO_2$ formed during CO TPD as a direct measure of CO dissociation sites and hence as an indicator of catalyst activity for methanation. The results of this study and those reported previously (*19*, *28*, *29*) suggest that a better indicator of methanation activity is the temperature for the onset of CO disproportionation.

## CONCLUSIONS

The present studies indicate that the adsorptive and catalytic properties of $Pd/SiO_2$ are influenced by the Pd dispersion. The distribution of $H_2$ adstates changes with dispersion, due possibly to a change in the morphology of the Pd crystallites or in the coordination of adsorbed H atoms with the Pd atoms. The ratio of linearly held CO to bridge-bonded CO decreases as the dispersion decreases, as does the ratio of Pd(100) to Pd(111) planes on the surfaces of the Pd crystallites. CO dissociation occurs preferentially from bridge sites and proceeds more readily with decreasing dispersion, due to an increase in the proportion of bridge sites on the Pd crystallites. The turnover frequency for CO methanation parallels the rate of CO dissociation, so that higher methanation rates are observed with decreasing Pd dispersion.

## ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract DE-AC03-76SF0098.

## REFERENCES

*1*. Hicks, R. F., and Bell, A. T., *J. Catal.* **90,** 205 (1984).

*2*. Bartholomew, C. H., Pannell, R. B., and Butler, J. L., *J. Catal.* **65,** 335 (1980).

*3*. Bhatia, S., Bakhshi, N. N., and Mathews, J. F., *Canad. J. Chem. Eng.* **56,** 575 (1978).

*4*. Coenen, J. W. E., Schats, W. M. T. M., and van Meerten, R. Z. C., *Bull. Soc. Chim. Belg.* **88,** 435 (1979).

*5*. Boudart, M., and McDonald, M. A., *J. Phys. Chem.* **88,** 2185 (1984).

*6*. Jung, H.-J., Walker, P. L., Jr., and Vannice, M. A., *J. Catal.* **75,** 416 (1982).

*7*. Jung, H.-J., Vannice, M. A., Mulay, L. N., Stanfield, R. M., and Delgass, W. N., *J. Catal.* **76,** 208 (1982).

*8*. Kellner, C. S., and Bell, A. T., *J. Catal.* **75,** 251 (1982).

*9*. King, D. L., *J. Catal.* **51,** 386 (1978).

*10*. Dalla Betta, R. A., Piken, A. G., and Shelef, M., *J. Catal.* **40,** 173 (1975).

*11*. Underwood, R. P., and Bell, A. T., unpublished results.

*12*. Ichikawa, S., Poppa, H., and Boudart, M., *J. Catal.* **91,** 1 (1985).

*13*. Kelly, K. P., Tatsumi, T., Uematsu, T., Driscoll, D. J., and Lunsford, J. H., *J. Catal.*, in press.

*14*. Low, G., and Bell, A. T., *J. Catal.* **57,** 397 (1979).

*15*. Uchida, M., and Bell, A. T., *J. Catal.* **60,** 204 (1979).

*16*. Chin, A. A., and Bell, A. T., *J. Phys. Chem.* **87,** 3700 (1983).

*17*. Benesi, H. A., Curtis, R. M., and Studer, H. P., *J. Catal.* **10,** 328 (1968).

*18*. Boronin, V. S., Nikulina, V. S., and Poltorak, O. M., *Russ. J. Phys. Chem.* **37,** 626 (1963).

*19*. Rieck, J. S., and Bell, A. T., *J. Catal.* **96,** 88 (1985).

*20*. Rieck, J. S., and Bell, A. T., *J. Catal.* **85,** 143 (1984).

*21*. Hicks, R. F., Yen, Q.-J., and Bell, A. T., *J. Catal.* **89,** 498 (1984).

*22*. Benson, J. E., Hwang, H. S., and Boudart, M., *J. Catal.* **30,** 146 (1973).

*23*. Behm, R. J., Christmann, K., and Ertl, G., *Surf. Sci.* **99,** 320 (1980).

*24*. Cattania, M. G., Penka, V., Behm, R. J., Christmann, K., and Ertl, G., *Surf. Sci.* **126,** 382 (1983).

*25*. Conrad, H., Ertl, G., and Latta, E. E., *Surf. Sci.* **41,** 435 (1974).

*26*. van Hardeveld, R., and Hartog, F., *Surf. Sci.* **15,** 189 (1969).

*27*. Baetzold, R. C., *J. Chem. Phys.* **82,** 5724 (1985).

*28.* Rieck, J. S., and Bell, A. T., *J. Catal.* **99,** 262 (1986).

*29.* Rieck, J. S., and Bell, A. T., *J. Catal.* **99,** 278 (1986).

*30.* Kelley, R. D., and Goodman, D. W., *Prep., Div. Fuel Chem., Amer. Chem. Soc.* **25,** 43 (1980).

*31.* Vannice, M. A., *J. Catal.* **40,** 129 (1975).

*32.* Vannice, M. A., Wang, S.-Y., and Moon, S. H., *J. Catal.* **71,** 152 (1981).

*33.* Fajula, F., Anthony, R. G., and Lunsford, J. H., *J. Catal.* **73,** 237 (1982).

*34.* Deligianni, H., Mieville, R. L., and Peri, J. B., *in* "Proceedings, 8th International Congress on Catalysis," Vol. V, p. 243. Berlin, 1984.