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The Activity of Pd(110) for Methanol Synthesis[1]

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The synthesis of methanol from CO and H_2 has been studied over unsupported, single-crystal Pd(110) at pressures of 72.3–244 KPa, temperatures of 493–553 K, and a H_2/CO ratio of 3.9, in a combined high-pressure reactor/UHV surface analysis chamber. At 244 KPa the reaction exhibited linear Arrhenius behavior with an activation energy of 18.4 ± 1.9 kcal/mol, and a pre-exponential factor of 8×10^4 s^{-1}. These values are in good agreement with values reported for supported Pd/SiO_2. At 553 K the reaction was roughly first order in total pressure (1.2 ± 0.2) over the pressure range studied. Specific rates (turnover frequencies) observed in this study, extrapolated to pressures typical of most methanol synthesis work (1–1.5 MPa), are in good agreement with rates observed for Pd dispersed on "noninteracting" supports such as SiO_2, and some basic supports such as ZnO and MgO. These rates are higher than those observed over Pd supported on zeolite and acidic supports (e.g., PdNaY and Al_2O_3), but much lower than those observed on highly active La_2O_3-supported Pd. In addition, no dimethyl ether product was detected on Pd(110), though it is a significant product on many acidic supports. Thus, Pd metal is an active methanol synthesis catalyst, and no specific support interaction is required. Highly interacting supports exhibit rates and/or selectivities substantially different from those of Pd(110).

The selective synthesis of methanol from CO and H_2 is a process of major industrial importance because of the use of methanol as a chemical intermediate, its potential use as a starting material for fuel production, and many other applications (*1, 2*). The most commonly employed industrial catalysts are based on Cu supported on ZnO, or a mixture of ZnO and other oxides such as Cr_2O_3. Accordingly, most studies into the mechanism of methanol synthesis have focused on Cu/ZnO catalysts. The thermodynamics of the reaction require high pressures over a narrow temperature range for both high selectivity and activity. The addition of small amounts of CO_2 and H_2O in the product streams (with the added complication of the water–gas shift reaction) and the complexity of the catalyst itself have made elucidation of the reaction mechanism difficult.

It has been demonstrated that under certain conditions Pd is also an active methanol synthesis catalyst, and that the nature of the support has great influence on both the rate and selectivity (*3*). Early work by Poutsma *et al.* (*4*), using silica-supported Pd, showed that under typical methanol synthesis conditions (1–100 MPa, 523–598 K) Pd exhibits high selectivity and activity toward the production of methanol. However, Vannice and Garten (*5*) showed that at atmospheric pressure and similar temperatures, Pd is an active and selective catalyst for methanation when supported on alumina. The work of Ichikawa and co-workers (*6*) has shown strong support effects for group VIII metals in methanol synthesis. In addition to the effects of typical oxide supports, Tamaru and co-workers (*7*) have reported large promotion effects due to the addition of alkali metals to Pd catalysts. In this study methanol was produced at less than atmospheric pressures while previous studies done in this pressure regime did not detect any methanol (*5, 8, 9*).

Typical of the strong effects observed on

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different supports are the studies by Bell and co-workers (*10, 11*) which reported that Pd supported on La_2O_3 is one to two orders of magnitude more active than Pd on supports such as SiO_2, TiO_2, ZnO, MgO, Al_2O_3, and ZrO_2. The selectivity of these catalysts varied from 44 to almost 100%. Similarly, studies by Lunsford and co-workers (*12*) found total CO conversions to vary by a factor of 40, while selectivities varied from 100% methane to 97% methanol, depending on the support. Thus, within similar temperature and pressure regimes, results from different laboratories have often found Pd to be a good methanation catalyst or good methanol synthesis catalyst (for example (*5*) and (*4, 7*), respectively). In a recent review by Lunsford (*3*) the effects of support, preparation technique, and alkali metal addition have been summarized.

In order to interpret the effect of reaction conditions properly, it is necessary to establish the activity of unsupported Pd. It has recently been demonstrated (*13*) that the activity of Cu-based methanol synthesis catalysts can be directly related to the total copper surface area, the support having been shown to have little effect on the activity of the metal catalyst. Furthermore, under synthesis conditions, the Cu metal was shown to be partially oxidized (*13*), implying that the Cu metal, and not the support, is primarily responsible for the catalytic activity. In this study we present results which show the methanol synthesis activity of unsupported Pd metal using a well-characterized Pd(110) single-crystal catalyst.

The experiments were performed in a combined UHV surface analysis/high-pressure reactor described previously (*14*). The system consists of a UHV surface analysis chamber equipped with Auger electron spectroscopy (AES), an ion sputter gun, and a quadrupole mass spectrometer, connected to a high-pressure (<300 KPa) batch microreactor.

The Pd(110) sample was supplied by Metal Crystals & Oxides Ltd., and was oriented to within ±0.5° of the (110) plane. The Pd(110) sample was mounted on the arm of a retractable bellows which allowed the sample to be transferred *in vacuo* between the two chambers of the apparatus. The sample measured 1 cm in diameter by 0.1 cm thick and was heated resistively by two 0.051-cm tungsten wires spot-welded to the back of the crystal. The temperature was measured by a 0.08-mm chromel–alumel thermocouple spot-welded to the bottom edge. The sample was cleaned by being transferred into the high-pressure reactor, into which 2.14 KPa of CO and 1.07 KPa of O_2 were introduced, and heating the crystal to 600 K for 2 min to remove C and S impurities. This procedure was repeated one to three times. After transfer to the UHV analysis chamber, AES was used to verify that the surface was free of all detectable impurities.

Gas chromatography with flame ionization detection (FID) was used for product analysis. The reactants used were Matheson research-grade carbon monoxide (99.99%) and hydrogen (99.999%). The hydrogen was used without further purification. The CO was purified by being passed slowly through a glass wool-filled trap submerged in a 2-methylbutane slush (108 K) to remove metal carbonyls. H_2 and CO were charged into a steel pressure vessel in a 3.9 : 1 H_2/CO ratio and allowed to mix for at least 24 h before an experiment.

After the surface cleanliness was verified by surface analysis, the sample was translated into the reaction chamber. Next, the reactor was charged to the desired pressure with the H_2/CO mixture (244 KPa for the temperature dependence experiments). The sample was then heated to the reaction temperature within 30 s and held at the desired temperature to ±0.5 K by an RHK TM-310 temperature programmer for 4 to 24 h depending on the temperature. After completion of a run the reactor gas was evacuated through a 77 K trap and the condensed products were analyzed by the

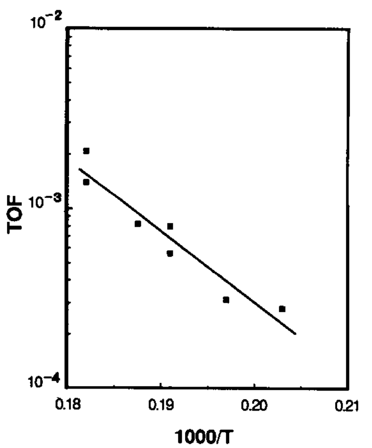

FIG. 1. Turnover frequency (CH_3OH molecules produced/Pd surface atoms-s) versus inverse temperature at a total pressure of 244 kPa and 3.9:1 H_2/CO mixture. A least squares fit yields an activation energy of 18.4 ± 1.9 kcal/mol, and a pre-exponential factor of 8×10^4.

GC. Concentration of the products in this manner allowed for detection of fewer than 10^{13} methanol molecules. Methane was not quantitatively collected because of its appreciable vapor pressure at 77 K. The background activity of the heating leads and thermocouple was determined to be negligible by using a stainless steel slug of approximately the same size as the Pd(110) crystal.

Figure 1 shows an Arrhenius plot of the reaction rate, expressed as the turnover frequency (TOF), molecules of CH_3OH produced per Pd surface atom per second (i.e., not the total CO conversion). The total Pd surface atoms were determined using a Pd(110) surface density of 9.3×10^{14} atoms/cm^2. The rate shows approximately linear Arrhenius behavior with an activation energy of 18.4 ± 1.9 kcal/mol, with a pre-exponential factor of 8×10^4 s^{-1} over the temperature range of 493 to 553 K, and at a pressure of 244 KPa. Dimethyl ether, which would have been completely trapped with the methanol product, was not detected in any experiment. Accounting for instrument sensitivity, conversion to dimethyl ether was less than 5%.

After reaction, submonolayer quantities of carbonaceous residue, generally 0.05 to 0.25 monolayers, were detected by AES. Significant absorbtion of hydrogen into the bulk, determined by postreaction temperature-programmed desorption, was not observed. Small amounts (0 to 2% of a monolayer) of nickel carbonyls were detected by AES after 12 to 24 h of reaction despite careful trapping of the CO reactant. As a result, methanation activity and selectivity to methane could not be accurately determined in these experiments, since the small amounts of Ni could contribute significantly to the methane production.

For reaction times of 6 to 24 h, the methanol production rate exhibited steady-state behavior. Synthesis rates were reproducible to ±25%; however, methane production rates for similar conditions varied by up to a factor of four. This is a further indication that much of the methane produced was due to minute amounts of nickel carbonyls.

Figure 2 shows the variation of rate with pressure at 553 K. Methanol production

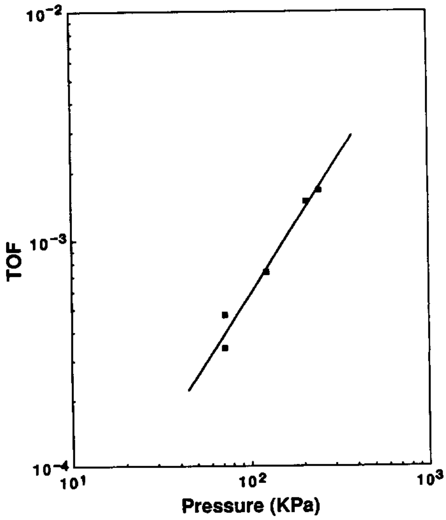

FIG. 2. Turnover frequency plotted as a function of total pressure at 553 K, for a 3.9:1 H_2/CO mixture. The order of reaction in total pressure determined by a least squares fit of the data is 1.2 ± 0.2.

TABLE 1

Comparison of Selected Supported Pd Catalysts with Pd(110)

Catalyst	TOF × 1000 (s^{-1})[a]	E_a (kcal/mol)	Selectivity (%)	Reference
1.7%Pd/SiO_2	1.7	—	100	[12][b]
4.0%Pd/SiO_2	18.1	—	96.5	[12][b]
1.5%Pd/SiO_2	2.3	17.2	91.6	[10][c]
7.9%Pd/SiO_2	18.5	14.1	98.3	[10][c]
5.1%Pd/SiO_2	5.4	18.2	89.8	[11][d]
Pd(110)	4.2	18.4 ± 1.9	—	This work[e]
Pd(110)	13.3	18.4 ± 1.9	—	This work[f]
0.2%Pd/La_2O_3	99.1	19.7	99	[10][c]
0.2%Pd/ZnO	8.4	17.6	99.8	[10][c]
0.5%Pd/TiO_2	4.2	16.0	44.1	[10][c]
1.5%Pd/Al_2O_3	2.6	14.2	33.2	[10][c]
5.4%PdHY	<1	—	2.0	[12][b]
2.4%PdNaY	0	—	0	[12][b]

[a] TOF's are for methanol production only and not for total CO conversion.

[b] Conditions: 553 K, 1.52 MPa, $H_2/CO = 2.8–2.4$.

[c] Conditions: 523 K, 1.01 MPa, $H_2/CO = 2.3$.

[d] Conditions: 553 K, 1.01 MPa, $H_2/CO = 2.3$.

[e] Conditions: 523 K, $H_2/CO = 3.9$, pressure extrapolated (based on experimentally determined dependence in Fig. 2) to 1.01 MPa. Compare with Refs. (*10, 11*).

[f] Conditions: 553 K, $H_2/CO = 3.9$, pressure extrapolated to 1.52 MPa. Compare with Ref. (*12*).

was approximately first order (1.2 ± 0.2) in pressure from 72.3 to 244 KPa and a $H_2:CO$ ratio of 3.9:1. This dependence agrees well with the total pressure dependence found by Hicks and Bells (*10, 11*) on Pd/SiO_2, but is significantly lower than the approximately second-order dependence observed over Pd/SiO_2 for pressures of 0.5 to 1.5 MPa observed by Lunsford and co-workers (*12*).

It is instructive to compare results obtained on Pd(110) with those obtained on various supported catalysts. Table 1 shows values for the specific activities, activation energies, and selectivities for supported Pd, and values obtained in this work. For comparison of specific activities, the data in this study have been scaled to pressures commonly used in studies on supported Pd, using the experimentally determined pressure dependence. At 523 K and 1.01 MPa we estimate a TOF of 4.2×10^{-3} s^{-1} and, at 553 K and 1.52 MPa, a TOF of 13×10^{-3} s^{-1}. The activation energy determined in this study, 18.4 kcal/mol, is in good agreement with values of 17.2 to 19.7 for Pd on "noninteracting" supports such as SiO_2 and basic supports such as ZnO and La_2O_3 (excepting the one value for 7.9% Pd/SiO_2 (*10*)). In addition the pre-exponential factor determined for Pd(110) agrees well with reported values for Pd/SiO_2 of 6×10^4 to 6×10^5 (*11*). The activation energy for Pd(110) is, however, significantly different from values obtained on acidic Al_2O_3 and TiO_2 supports. The absence of any dimethyl ether product in our study agrees well with selectivity data on basic supports, which mostly show >90% selectivity to methanol and <5% selectivity to dimethyl ether. This implies that production of large quantities of dimethyl ether can be directly related to support-induced effects and not to the Pd metal.

Thus, our extrapolated rates and kinetic parameters are in good agreement with those of "noninteracting" supports, such as SiO_2, considering the large variations observed in the supported catalyst data. The rates on Pd(110) are significantly lower than the TOF's reported for 0.2% Pd/La_2O_3 (99×10^{-3}) and for a series of Pd/La_2O_3 catalysts with 0.2 to 5% loading ($30–80 \times 10^{-3}$ s^{-1}) (*11*). The activation energy for Pd(110), however, is similar to that of Pd supported on La_2O_3. In contrast, the rates on Pd(110) are much higher than the rates reported on acidic zeolites by Lunsford and co-workers (*12*). In addition, acidic and zeolite supports exhibit low selectivities to methanol (*12*), and/or high selectivities to dimethyl ether (*10*). These results support the proposal by Hicks and Bell (*11*) that the methanol reaction mechanism is unaffected by the support composition on basic supports; the variation in specific activities of each catalyst possibly being attributed to small variations in the H_2 and CO binding energies. However, in some cases, large support effects, due to different preparations which add ions, e.g., Cl^-, to the catalyst, have been shown for typically noninteracting supports such as silica (*3*).

In view of the complexity of separating support effects from the activity of Pd metal, our results show that there is no requirement for a specific support interaction, e.g., support-induced creation of Pd^{+1} sites, for methanol production, as has been proposed for Cu/ZnO synthesis catalysts (*15*). While many supports exhibit specific rates and activation energies similar to those on Pd(110), large deviations such as those observed for La_2O_3 (*11*), PdNaY (*12*), or Pd/Al_2O_3 (*4*) indicate that large metal support interaction effects can be important. It is not well understood if these enhancements are due strictly to electronic modification of Pd by the support or if the presence of specific sites on the support has a significant effect on the activity. Experiments which introduce controlled modifications to well-characterized Pd surfaces may afford insight into these effects.

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