

Effects of Metal-Support Interactions on the Synthesis of Methanol over Palladium

YU. A. RYNDIN,¹ R. F. HICKS, AND A. T. BELL

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

AND

YU. I. YERMAKOV

Institute of Catalysis, Novosibirsk 630090, USSR

Received October 16, 1980; revised March 20, 1981

The synthesis of methanol and other products from CO and H₂ was studied over Pd catalysts prepared by adsorption of Pd(π -C₃H₅)₂ on MgO, ZnO, La₂O₃, γ -Al₂O₃, SiO₂, TiO₂, and ZrO₂ as well as over a SiO₂-supported Pd catalyst prepared from PdCl₂ and Pd black. Both the activity and selectivity of Pd were affected strongly by the nature of the support and the composition of the Pd precursor. The specific activity for methanol synthesis decreased in the order Pd/La₂O₃ \gg Pd/SiO₂ [derived from PdCl₂] > Pd/ZrO₂ > Pd/ZnO \approx Pd/MgO > Pd/TiO₂ > Pd/Al₂O₃ \approx Pd/SiO₂ [derived from Pd(π -C₃H₅)₂] \gg Pd black, while the specific activity for hydrocarbon synthesis decreased in the order Pd/TiO₂ \approx Pd/ZrO₂ > Pd/La₂O₃ > Pd/Al₂O₃ \approx Pd/SiO₂ [derived from PdCl₂] \approx Pd/SiO₂ [derived from Pd(π -C₃H₅)₂] \approx Pd black \gg Pd/MgO \approx Pd/ZnO. Dimethyl ether production was observed over four of the catalysts and the activity for formation of this product decreased in the order Pd/Al₂O₃ \gg Pd/TiO₂ \gg Pd/MgO \approx Pd/ZrO₂. The effects of support composition on the catalytic properties of Pd are discussed in the light of current ideas concerning metal-support interactions and the acid-base properties of the support.

INTRODUCTION

The selective synthesis of methanol from CO and H₂ over Group VIII metals has been reported in several recent studies (1-5). Poutsma *et al.* (1) have demonstrated that both silica- and alumina-supported Pd catalyzed the hydrogenation of CO to methanol with high selectivity. Methane formation was found to be significant only outside the temperature-pressure regime for which methanol formation is thermodynamically favorable. The behaviors of Pt and Ir were similar but these metals were less active than Pd. The authors suggested that the attainment of high methanol selectivities might be attributed to the inability of all

three metals to chemisorb CO dissociatively at reaction temperatures, compared to other Group VIII metals. The synthesis of methanol over Rh, Pd, Ir, and Pt has also been investigated by Ichikawa (2-5) in a series of studies carried out at atmospheric pressure. This work has shown that catalyst activity and selectivity depend not only on the choice of metal, but also on the composition of the metal precursor and acid/base properties of the metal oxide support. On a given support much higher methanol activities and selectivities were obtained by pyrolysis of transition metal complexes (e.g., Rh₄(CO)₁₂, Ir₄(CO)₁₂, [Pt₁₅(CO)₃₀] · [NET₄]₂, etc.) than by reduction of halogen-containing compounds (e.g., RhCl₃ or H₂PtCl₆). High methanol activity and selectivity was fur-

¹ Permanent address: Institute of Catalysis, Novosibirsk 630090, USSR.

ther favored by the use of moderately basic supports such as MgO, La₂O₃, Y₂O₃, and Nd₂O₃. Utilization of strongly basic or acidic supports such as Li₂O, SiO₂, TiO₂, and WO₃ greatly suppressed the synthesis of methanol and elevated somewhat the synthesis of methane.

The objectives of the present research were to explore further the effects of support composition on the specific activity of Pd for the synthesis of methanol and other products. These studies were carried out at 10 atm over the temperature range of 323 to 573 K. Supported Pd catalysts were prepared on SiO₂, Al₂O₃, TiO₂, ZrO₂, ZnO, MgO, and La₂O₃ by reacting bis- π -allylpalladium, Pd(π -C₃H₅)₂, with the hydroxyl groups present on the support surface. The selection of this preparative procedure was motivated by the desire to achieve intimate contact between the precursor and the support and was suggested by previous studies (6, 7) showing that high precursor dispersion could be realized on SiO₂ and Al₂O₃. In addition, it was anticipated that by avoiding the presence of halogen in the precursor, more active catalysts might be prepared than those derived from PdCl₂ (1, 4).

EXPERIMENTAL

Supports

A summary of the supports used in this work, the conditions of their pretreatment, and their source are listed in Table 1. Enhancement of the surface area of La₂O₃ was carried out by hydrolysis of nonporous La₂O₃ (Ventron Corporation, 99.9% purity) at 353 K with subsequent filtering and drying in air at 373 K, following the method outlined in Ref. (8). The powdered La(OH)₃ was then pressed into a tablet and dehydrated under vacuum at 573 K. The porous La₂O₃ thus obtained was rehydrated at 298 K with water vapor and then again dehydrated at 493 K under vacuum before impregnation.

Porous ZrO₂ was prepared by coagulation of a colloidal suspension of ZrO₂

(Nyacol Inc.) and scrupulous washing of the precipitate with large quantities of distilled water. After drying in air at 373 K, the ZrO₂ powder was pressed into a tablet and dehydrated under vacuum at 773 K. The average size of the zirconia particles in the original suspension was about 500 Å, which corresponds to a final surface area of not more than 20 m²/g for the dried material.

Prior to impregnation by the palladium complex all of the supports were dehydrated under vacuum at 10⁻³ Torr for 15 hr at the temperatures indicated in Table 1. The dehydration temperature was selected based on infrared studies of the surfaces of the oxides used (8-11) and was chosen to maximize the concentration of isolated surface hydroxyl groups, capable of reacting with Pd(π -C₃H₅)₂.

Synthesis of bis- π -Allylpalladium

bis- π -Allylpalladium was obtained by reacting (C₃H₅PdCl)₂ (Strem Chemicals, Inc.) with a solution of C₃H₅MgCl in diethyl ether at 298 K in an inert atmosphere (6). After distillation of the ether the product compound was extracted with pentane and filtered. Further purification of the Pd(π -C₃H₅)₂ was achieved by vacuum sublimation. The yield of the final complex was ~85%, based upon the initial quantity of (C₃H₅PdCl)₂ used.

Catalyst Preparation

The vacuum-dehydrated supports were impregnated with a pentane solution of Pd(π -C₃H₅)₂. A rapid irreversible adsorption of the complex was observed during impregnation, which was accompanied by a fading of the initially yellow-green solution of the complex and a coloration of the support. Following impregnation, the remaining pentane solution was decanted, and the catalyst was washed free of unreacted complex using fresh portions of pentane. The catalyst was then dried under vacuum at 298 K for 3 hr. Finally, the catalyst was reduced in hydrogen at 573 K for 15 hr.

TABLE 1
 Support and Catalyst Characteristics

Catalyst	Source of support	Support surface area (m ² /g) ^a	Dehydration temp. (K)	Pd loading (wt%)	D_{Pd}	Catalyst charge (g)
Pd/MgO	Mallinckrodt	100	873	0.3	0.20	0.57
Pd/ZnO	Kadox 25	10	723	0.3	0.50	1.10
Pd/ γ -Al ₂ O ₃	Kaiser S-201	250	873	2.1	0.40	0.55
Pd/La ₂ O ₃	Ventron	14 ^b	493	0.2	0.23	1.04
Pd/SiO ₂ (I)	Davison 70	250	873	1.5	0.36	0.28
Pd/SiO ₂ (II) ^c	Davison 57	—	—	7.9 (4.6) ^c	0.17 (0.26) ^d	0.05
Pd/TiO ₂	Degussa P-25	50	673	0.5	0.35	0.56
Pd/ZrO ₂	Nyacol	20	773	0.3	0.48	1.88
Pd black	—	—	—	—	0.003	0.10

^a Reported by support manufacturer.

^b Reported by Rosynek and Magmeson (8).

^c Obtained from Union Carbide (1)—Pd loading reported as 4.6%.

^d D_{Pd} based on a Pd loading of 4.6%.

The catalysts derived from Pd(π -C₃H₅)₂ were compared with two other catalysts. The first was a Pd/SiO₂ catalyst prepared by incipient wetness impregnation of Davison 57 silica gel with an aqueous solution of PdCl₂. This catalyst was obtained from the Union Carbide Corporation and is identical to that described by Poutsma *et al.* (1). The second catalyst was a palladium black (Strem Chemicals, Inc.).

Catalyst Characterization

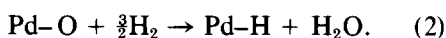
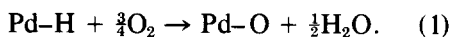
The palladium content of each catalyst was determined by X-ray fluorescence and was found to be in good agreement with the metal loadings determined from the amount of palladium complex adsorbed by the supports. The palladium content of silica-supported catalyst obtained from Union Carbide was found to be 7.9% rather than 4.6%, as had been reported by Poutsma *et al.* (1).

Palladium dispersions for most of the catalysts were measured by H₂-O₂ titration, using the pulsed flow technique (12-14) to avoid problems associated with H₂ adsorption (15). Evacuated catalyst samples were placed in the adsorption appa-

ratus without prior exposure to air. In the presence of flowing H₂, each catalyst sample was heated to 573 K over a 1-hr period and then maintained at 573 K for 12 hr. At the end of this period the hydrogen flow was stopped, and the catalyst was exposed to a flow of argon for 1 hr at 573 K. The catalyst was then cooled to room temperature over a 30-min period.

A different procedure was used to pre-treat the palladium black sample. This catalyst was first heated in flowing argon at 373 K for 1 hr to drive off adsorbed water and then reduced in flowing H₂ at 573 K for 30 min. At the end of this period the sample was again purged in flowing argon for 1 hr.

The reduced catalyst samples were titrated first with oxygen, then with hydrogen, and finally with oxygen a second time, each titration being carried out at room temperature. For Pd supported on SiO₂, Al₂O₃, ZrO₂, and MgO, the O₂ uptakes during the first and second oxygen titrations were nearly identical and equal to one-half the H₂ uptake during the hydrogen titration. This ratio of the O₂ and H₂ titers is in agreement with that expected from the stoichiometries of reactions 1 and 2 (12, 13).



The consistency of the two oxygen titers indicates that very little adsorbed H_2 is lost during the argon purge following reduction. For Pd supported on TiO_2 , ZnO , and La_2O_3 , the uptake of O_2 during the first oxygen titration was greater than the uptake during the second titration by 40, 65, and 70%, respectively, suggesting that a part of the O_2 taken up during the first titration is used to replace oxygen lost from the support during reduction. It was observed, though, that the H_2 uptake during the hydrogen titration was twice the O_2 uptake during the second oxygen titration in agreement with the stoichiometries of reactions 1 and 2. In view of this, the Pd dispersions for all of the catalysts were determined by averaging the results of the hydrogen titration and the second oxygen titration.

Hydrogen-oxygen titration could not be used on the Pd black or Pd/ SiO_2 catalyst obtained from Union Carbide because these materials exhibited a large weak adsorption of hydrogen well above the stoichiometric amount, possibly due to β -hydride formation (14, 16). For these catalysts dispersion was determined solely by oxygen titration.

The dispersions of all of the catalysts used in this study are listed in Table 1. For the sake of subsequent discussion, the two SiO_2 -supported catalysts have been designated as Pd/ SiO_2 (I) and Pd/ SiO_2 (II), to differentiate between the use of Pd(π - C_3H_5)₂ and PdCl₂, respectively, as the metal precursor. It is significant to note that the dispersions for those catalysts prepared by adsorption of Pd(π - C_3H_5)₂ lie between 0.2 and 0.6. These results indicate that the atomic dispersion of Pd which can be achieved when the complex is reduced at room temperature cannot be retained when reduction is carried out at elevated temperatures. This conclusion is in agreement with that reported earlier for SiO_2 - and

Al_2O_3 -supported Pd (6) and indicates that the other supports used in this work are no more effective than SiO_2 and Al_2O_3 for stabilizing the dispersion of Pd.

Catalyst Evaluation

Catalyst testing was carried out in a tubular microreactor made of stainless steel. Between 0.05 and 1.88 g (see Table 1) of reduced catalyst, in the form of a powder with particles of about 0.50 to 0.25 mm in diameter, was loaded into the reactor. The reactor was then flushed with helium, and the catalyst was reduced in hydrogen at 573 K. The hydrogenation of CO was conducted at a total pressure of 10 atm using a 3:1 mixture of H_2 to CO, over the temperature range of 423 to 573 K. The gas flow rate was typically 200 STP cm^3/min . Products were analyzed with a Varian 3700 gas chromatograph fitted with a 1-m \times 2-mm column packed with Chromosorb-106 and a flame ionization detector. The column temperature was raised from 318 to 513 K at a rate of 10 K/min.

An analysis of the reaction products was conducted 10 min following the onset of reaction, after which the catalyst was reduced for 30 min in hydrogen before reintroducing the reaction mixture. If the analyses of consecutive runs at a given temperature were not reproduced, runs were continued until a stationary state of the catalyst was attained, at which point the dependence of catalyst activity on temperature was explored. Following this, the catalyst temperature was returned to that used initially and the catalyst activity was compared with the initially measured values.

RESULTS

Methanol and C_1 through C_6 hydrocarbons were observed as the primary products for all the catalysts tested and only occasionally were traces of ethanol detected. For Pd supported on Al_2O_3 , TiO_2 , ZrO_2 , and MgO, dimethyl ether was also observed. Carbon monoxide conversions and product distributions determined at 523

K are given in Table 2. It is significant to note that the conversions are small in all cases and lie well below the equilibrium conversion of 10% for the conditions indicated.

During the evaluation of the catalysts, it was observed that activity of some of the catalysts either increased or decreased with repeated use, the nature and extent of these changes depending on the composition of the support. Figure 1 illustrates the manner in which the activities for methanol and total hydrocarbon synthesis change as a function of the number of runs conducted using SiO₂- and ZnO-supported catalysts. It is observed that while the methanol activity of the Pd/SiO₂ catalyst is constant the hydrocarbon activity declines to an asymptotic level after ten runs. The Pd/ZnO catalyst exhibits the reverse behavior and in this case it is the methanol activity which increases to an asymptotic level. The stability behavior of the remaining catalysts is summarized in Table 3. With the exception of Pd/SiO₂ (I), all of the catalysts exhibit a stable activity for hydrocarbon synthesis. A somewhat different pattern is observed for the synthesis of methanol. In most cases a stable activity is achieved after three or

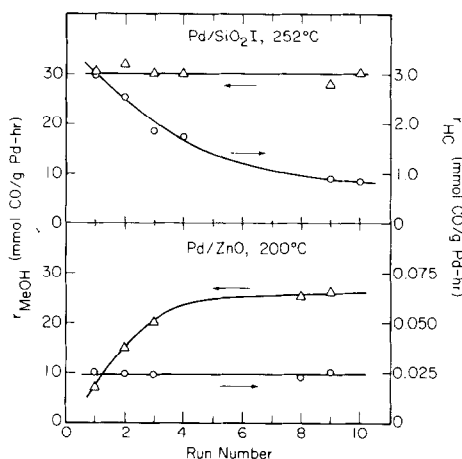


FIG. 1. Dependences of the methanol and hydrocarbon formation rates over Pd/SiO₂ (I) and Pd/ZnO as functions of the number of consecutive runs performed.

TABLE 2
Catalytic Properties of Supported and Unsupported Pd

Catalyst	CO conv. (%)	E_a (kcal/mole)		Turnover freq. ($\times 10^3$ s ⁻¹)				S (%)				
		CH ₃ OH	CH ₃ OCH ₃	CH ₄ + C ₂₊	CH ₃ OH	CH ₃ OCH ₃	CH ₄	C ₂₊	CH ₃ OH	CH ₃ OCH ₃	CH ₄	C ₂₊
Pd black	0.01	10.2	—	23.3	0.60	0	0.07	0.13	75.0	0	8.8	16.2
0.3% Pd/MgO	0.1	16.6	23.4	26.9	7.70	0	0.02	0.01	98.4	1.2	0.3	0.2
0.2% Pd/ZnO	0.4	17.6	—	24.5	8.40	0	0.01	0.01	99.8	0	0.1	0.1
1.5% Pd/Al ₂ O ₃	0.1	14.2	24.6	25.9	2.61	4.920	0.26	0.07	33.2	62.7	3.3	0.8
0.2% Pd/La ₂ O ₃	0.5	14.0	—	24.9	99.10	0	0.50	0.53	99.0	0	0.5	0.5
1.5% Pd/SiO ₂ (I)	0.1	17.2	—	24.1	2.33	0	0.08	0.13	91.6	0	3.4	5.0
7.9% Pd/SiO ₂ (II)	1.5	14.1	—	25.7	18.51	0	0.28	0.03	98.3	0	1.5	0.2
0.5% Pd/TiO ₂	0.3	16.0	23.5	23.2	4.20	0.819	4.00	0.50	44.1	8.6	42.1	5.2
0.3% Pd/ZrO ₂	0.7	15.2	22.9	24.0	11.40	0.070	3.40	0.37	74.7	0.5	22.3	2.5

Note. Reaction conditions: $T = 250^\circ\text{C}$; $P = 10$ atm; $\text{H}_2/\text{CO} = 3$; $Q = 200$ cm³(STP)/min.

TABLE 3

Stability of Supported and Unsupported Pd

Catalyst	Cat. stability		
	CH ₃ OH	CH ₃ OCH ₃	CH ₄ + C ₂ +
Pd black	Stable	—	Stable
0.3% Pd/MgO	Inc.	Stable	Stable
0.3% Pd/ZnO	Inc.	—	Stable
1.5% Pd/Al ₂ O ₃	Inc.	Stable	Stable
0.2% Pd/La ₂ O ₃	Stable	—	Stable
1.5% Pd/SiO ₂ (I)	Stable	—	Dec.
7.9% Pd/SiO ₂ (II)	Stable	—	Stable
0.5% Pd/TiO ₂	Inc.	Stable	Stable
0.3% Pd/ZrO ₂	Inc.	Stable	Stable

Note. Reaction conditions: $T = 250^\circ\text{C}$; $P = 10$ atm; $\text{H}_2/\text{CO} = 3$; 200 cm³(STP)/min.

four runs, during which the activity increases severalfold. However, for Pd/SiO₂ (I), Pd/SiO₂ (II), and Pd/La₂O₃, stable activity is reached within the first 10-min reaction period. For those catalysts which produce dimethyl ether, the activity of ether formation remains constant as the number of runs increases.

Arrhenius plots for the synthesis of methanol, dimethyl ether, and total hydrocarbons are shown in Figs. 2 through 4, and apparent activation energies determined from these plots are given in Table 2. It is evident that the support composition has a strong influence on the catalyst activity.

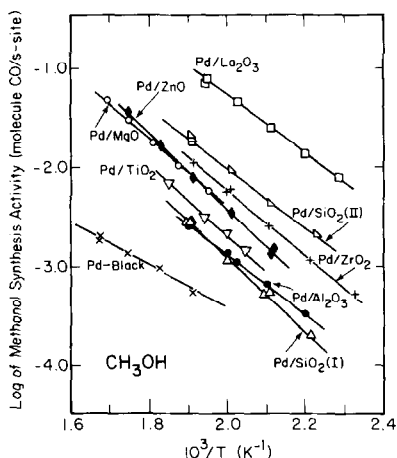


FIG. 2. Arrhenius plots for the formation of methanol: $P = 10$ atm; $\text{H}_2/\text{CO} = 3$.

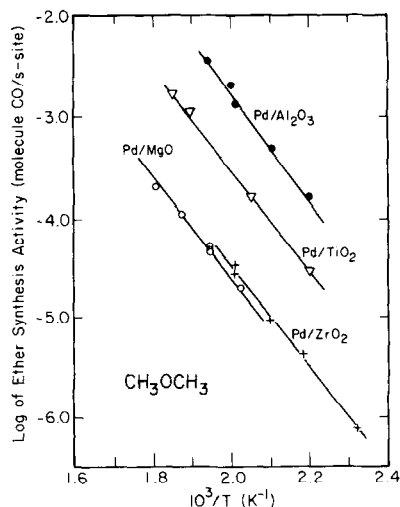


FIG. 3. Arrhenius plots for the formation of dimethyl ether: $P = 10$ atm; $\text{H}_2/\text{CO} = 3$.

The specific activity for methanol synthesis decreases in the order Pd/La₂O₃ \gg Pd/SiO₂ (II) $>$ Pd/ZrO₂ $>$ Pd/ZnO \approx Pd/MgO $>$ Pd/TiO₂ $>$ Pd/Al₂O₃ \approx Pd/SiO₂ (I) \gg Pd black. The apparent activation energy for this process is 15.8 ± 1.8 kcal/mole for the supported catalysts, but is 10.2 kcal/mole for Pd black. However, there is no clear-cut correlation between specific activity and

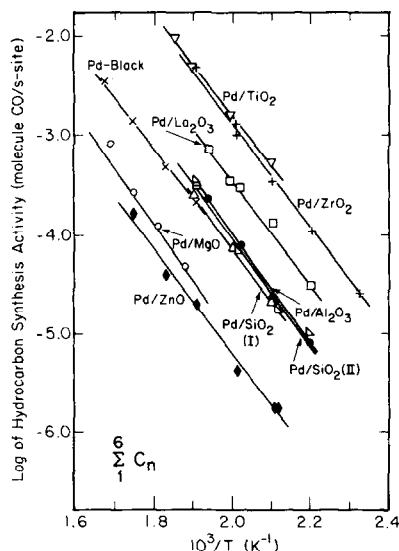


FIG. 4. Arrhenius plots for the formation of hydrocarbons: $P = 10$ atm; $\text{H}_2/\text{CO} = 3$.

activation energy. Dimethyl ether formation is observed over only four of the catalysts examined, and the specific activity for the formation of this product is observed to decrease in the order $\text{Pd}/\text{Al}_2\text{O}_3 \gg \text{Pd}/\text{TiO}_2 \gg \text{Pd}/\text{MgO} \approx \text{Pd}/\text{ZrO}_2$. The apparent activation energy for dimethyl ether formation is 24.0 ± 0.5 kcal/mole and does not appear to depend very strongly on the nature of the support. The support composition is also seen to affect the specific activity of Pd for the formation of hydrocarbons but in a manner different from that in which it affects the methanol synthesis activity. As seen in Fig. 4, the specific activity for total hydrocarbon formation decreases in the order $\text{Pd}/\text{TiO}_2 \approx \text{Pd}/\text{ZrO}_2 > \text{Pd}/\text{La}_2\text{O}_3 > \text{Pd}/\text{Al}_2\text{O}_3 \approx \text{Pd}/\text{SiO}_2$ (II) $\approx \text{Pd}/\text{SiO}_2$ (I) $\approx \text{Pd}$ black $\gg \text{Pd}/\text{MgO} \approx \text{Pd}/\text{ZnO}$. The apparent activation for hydrocarbon formation is 24.0 ± 1.5 kcal/mole and is approximately the same for supported and unsupported Pd.

The composition of the support also affects the product distribution. As may be seen in Table 2, methanol selectivities of 92 to 100% are obtained when Pd is supported on SiO_2 , MgO , La_2O_3 , and ZnO . Very little, if any, dimethyl ether is formed over these catalysts. A high selectivity to oxygenated products, 95.9%, is also observed for the Al_2O_3 -supported catalyst, but in this in-

stance the methanol selectivity is only 32.5%, the balance of oxygenated products being dimethyl ether. The TiO_2 - and ZrO_2 -supported catalysts stand out from all the others because of their low selectivities for the formation of oxygenated products and their correspondingly high selectivities for hydrocarbon formation. Palladium black exhibits a similar behavior to these latter two catalysts.

Figure 5 and Table 2 show that the support composition has a strong influence on the distribution of hydrocarbons formed. As may be seen in Fig. 5 in most instances the percentage of CO converted to a hydrocarbon containing n carbon atoms decreases monotonically as n increases. Exceptions to this pattern are found for the MgO -, Al_2O_3 -, and La_2O_3 -supported catalysts, which produce higher yields of C_6 hydrocarbons than anticipated. Attention is also drawn to the TiO_2 - and ZrO_2 -supported catalysts since the methane selectivity is particularly high for these catalysts. Table 2 shows that the specific activity for methane synthesis over these catalysts is much greater than that observed for any of the remaining catalysts.

DISCUSSION

The observed increase in the activity of Pd when it is supported on metal oxides parallels in some respects the observations reported by Vannice (17). In studies conducted at atmospheric pressure he noted that the methanation activity of Pd supported on SiO_2 and $\eta\text{-Al}_2\text{O}_3$ was higher than that of Pd black and that the activity increased in the order $\text{Pd}/\eta\text{-Al}_2\text{O}_3 \gg \text{Pd}/\text{SiO}_2 > \text{Pd}$ black. The results presented in Table 2 show that the hydrocarbon synthesis activity does increase somewhat when Pd is supported on SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ but that a much more dramatic increase is observed in activity for the synthesis of oxygenated products. The failure of Vannice (17) to observe methanol formation is not surprising since his studies were conducted at temperatures of 548 K

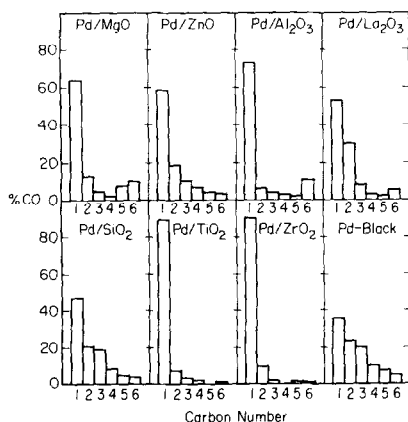


FIG. 5. Percentage of the CO converted to hydrocarbons containing one to six carbon atoms: $T = 250^\circ\text{C}$; $P = 10$ atm; $\text{H}_2/\text{CO} = 3$.

and above. Equilibrium calculations show that at 1 atm and such high temperatures the formation of methane will be favored strongly over the formation of methanol (1).

The exceptionally high methanol synthesis activity of Pd/La₂O₃ relative to the other catalysts tested confirms the results obtained by Ichikawa (4) in studies conducted at atmospheric pressure. The activation energies for methanol formation are also in good agreement—a value of 13.0 kcal/mole being reported by Ichikawa and a value of 14.0 kcal/mole being found in the present work. However, it is significant to note that the activity of the Pd/La₂O₃ catalyst used in the present studies appears to be considerably higher than that of the catalyst prepared by Ichikawa starting from PdCl₂. Examination of Table 4 shows that if Ichikawa's results are extrapolated to the conditions of the present studies, it is concluded that the catalyst used in the present work is 20-fold more active for methanol synthesis and about 2-fold more active for methane synthesis. A part of this difference may be ascribed to the differences in Pd loading. Ichikawa observed that with increasing Pd content the methanol activity reached a maximum value at about 0.5% and then decreased to an asymptotic level for loadings between 1 and 5%, the ratio of the maximum activity to that observed at

loadings of a few percent being about 3. The remaining portion of the difference between Ichikawa's catalyst and that described here is very likely associated with differences in the nature of the palladium precursor and the origin and pretreatment of the support. Thus, Ichikawa observed (4) that the methanol synthesis activity of supported Pt catalysts was five to ten times lower when H₂PtCl₆ was used as the source of Pt than when [Pt₃(CO)₆]₃₋₅ · [NEt₄]₂ was used as the precursor.

The differences between the two Pd/SiO₂ catalysts examined in this work might also be ascribed to the effects of metal dispersion and the origin of the materials used to prepare the catalyst. The extent to which each of these factors plays a role is unknown and must await further investigation. It is significant to note, though, that Maxted and Ali (18) have observed that the activity of Pd for the hydrogenation of cyclohexene depends on the composition of the support, the origin of the support, and the loading of Pd.

The present knowledge of the interactions between Pd and metal oxide supports is inadequate to permit the development of a satisfactory interpretation for the effects of support composition on the activity of Pd for the synthesis of methanol and hydrocarbons. However, since there has been some discussion in the recent literature concern-

TABLE 4
Comparison of Pd/La₂O₃ Catalysts

Ref.	Catalyst	E _a (kcal/mole)		Reaction rate (mmole/hr · g Pd)	
		CH ₃ OH	CH ₄	CH ₃ OH	CH ₄
Ichikawa (4)	2.9% Pd/La ₂ O ₃	13.0	29.0	40.3 ^a	1.96 ^b
This work	0.2% Pd/La ₂ O ₃	14.0	24.9	871.0	4.70

Note. Reaction conditions: $T = 250^{\circ}\text{C}$; $P = 10$ atm; $\text{H}_2/\text{CO} = 3$.

^a Extrapolated from measurements made at $T = 200^{\circ}\text{C}$; $P = 1$ atm; $\text{H}_2/\text{CO} = 2$ using the relationship $r_{\text{CH}_3\text{OH}} = k_1 P_{\text{H}_2} P_{\text{CO}}^0 \exp(-13000/RT)$, given in Ref. (4).

^b Extrapolated from measurements made at $T = 200^{\circ}\text{C}$; $P = 1$ atm; $\text{H}_2/\text{CO} = 2$ using the relationship $r_{\text{CH}_4} = k_2 P_{\text{H}_2} P_{\text{CO}}^{-0.4} \exp(-29000/RT)$ given in Ref. (4).

ing the influence of metal-support interactions on the chemisorptive and catalytic properties of transition metals, it is instructive to review these efforts in order to determine whether the conclusions drawn might help to explain at least a part of the present results.

Strong evidence for the influence of metal-support interactions on the chemisorption of H_2 and CO has been presented recently by Tauster *et al.* (19, 20). Their results have shown that the H_2 and CO chemisorption capacities of Ru, Rh, Pd, Os, Ir, and Pt supported on TiO_2 (19) and the H_2 chemisorption capacity of Ir supported on TiO_2 , V_2O_3 , Nb_2O_5 , and Ta_2O_5 decrease with an increase in the temperature at which the supported metal is reduced in hydrogen. Electron microscopy and X-ray diffraction showed that these losses in chemisorption capacity were not due to metal agglomeration. It was suggested, therefore, that reduction at high temperatures gives rise to a strong metal-support interaction (SMSI) and that the occurrence of SMSI properties depends on the ease with which the metal oxide can be reduced.

Tauster *et al.* (19) proposed that the SMSI properties of TiO_2 might be explained in terms of metal-metal bonding between the noble metal and titanium cations or, alternatively, the formation of intermetallic compounds. Support for the first of these possibilities has been presented by Horsley (21), based on SCF- $X\alpha$ molecular orbital calculations for molecular cluster models of Pt/ TiO_2 . These calculations favor a structure in which Pt atoms are inserted into surface oxygen vacancies in the support, with bonding between the titanium cations and the Pt atoms. Horsley suggested that if the Pt-Ti bonds were stronger than the Pt-Pt bonds, then Pt atoms would be preferentially attracted to surface anion vacancies formed by reduction of TiO_2 rather than to other Pt atoms. Such an occurrence would explain the epitaxial growth of thin rafts of Pt atoms on TiO_2 (22). It was speculated

that the absence of corner atoms of steps in the rafts of Pt atoms might explain the suppression of H_2 chemisorption, since such sites have been claimed to be necessary for the dissociative chemisorption of H_2 (23).

The relevance of SMSI effects to the present work is unclear. Of the supports used here, only TiO_2 has been demonstrated to exhibit SMSI activity, and, based on the work of Tauster and Fung (20) with Ir/ TiO_2 , one could anticipate that Pd/ TiO_2 reduced at 573 K should exhibit such activity. However, since the H_2 chemisorption capacity of this catalyst was not unusually low, SMSI effects cannot be invoked automatically. This does not rule out the possibility, though, that Pd on TiO_2 and on other supports experiences weaker metal-support interactions which, while not markedly affecting the chemisorption characteristics of the metal, may still influence its catalytic properties.

On the basis of results obtained by Figueras *et al.* (24) and Van Hardeveld and Hartog (25), Vannice (17) has suggested that the higher methanation activities of Al_2O_3 - and SiO_2 -supported Pd, compared to Pd black, might be ascribed to an enhanced formation of weakly bound, linearly adsorbed CO species. It was reasoned that such an enhancement could be due to a decrease in metal crystallite size or to a metal-support electron transfer which might result in the stabilization of surface structures not normally present on large metal crystallites. While such an explanation might also be invoked to explain the higher hydrocarbon synthesis activities observed using the La_2O_3 -, ZrO_2 -, and TiO_2 -supported palladium catalysts described here, the experimental evidence needed to support such an interpretation is not available.

In the studies reported by Ichikawa (2-5) it was suggested that the acidity or basicity of the support has a significant influence on the selectivity of the products formed from CO and H_2 . Basic supports were observed

to promote the formation of oxygenated products while acidic supports favored the formation of hydrocarbons. Examination of the present results in terms of the acidity or basicity of the support confirms that the highest methanol selectivities are observed on the most basic oxide supports (e.g., La_2O_3 , MgO , ZnO). The case of $\gamma\text{-Al}_2\text{O}_3$ is anomalous however, since a high selectivity for oxygenated products is observed over a support which is strongly acidic. Thus, it is not clear to what extent acidity or basicity of the support plays a dominant role in defining the selectivity of supported Pd.

A clearer relationship can be established between support acidity and the formation of dimethyl ether. The results presented in Table 2 and Fig. 3 show that the highest activities for dimethyl ether formation are exhibited by Pd supported on $\gamma\text{-Al}_2\text{O}_3$ and TiO_2 . Both supports are acidic (26) and are known to catalyze the formation of dimethyl ether during the decomposition of methanol (27, 28). The lower rate of dimethyl ether formation over TiO_2 compared to Al_2O_3 is most likely attributable to the lower strength and concentration of acid sites on TiO_2 (26). Consistent with this trend, it is observed that very little dimethyl ether is formed for Pd supported on MgO or ZrO_2 , materials which exhibit very small concentrations of acid sites, and that the formation of dimethyl ether is totally suppressed when Pd is supported on basic oxides such as ZnO and La_2O_3 or on a neutral oxide such as SiO_2 . It is noted further that studies of methanol decomposition over MgO (29), ZnO (30), and rare earth oxides (31) also show dimethyl ether formation to be insignificant. On the basis of these observations, it is concluded that the dimethyl ether observed in these studies results from the decomposition of methanol, subsequent to its formation.

The exceptionally high activities of Pd/ TiO_2 and Pd/ ZrO_2 for the synthesis of methane, noted in Table 2 and Figs. 5, agree with Ichikawa's (4) observations at 1

atm, but the origin of this specificity cannot readily be explained. One possibility is that a substantial portion of the methane formed over these catalysts arises from a decomposition of methanol. Carrizosa *et al.* (28) have reported that methanol will decompose over rutile at 523 K, to produce coke and methane but that coke decomposition on anatase occurs only at temperatures in excess of 673 K. Since the TiO_2 used in the present studies consists of 87% anatase and 13% rutile (32), it is possible that methanol decomposition on the rutile phase might form methane and carbon. Since hydrogen is always present in the gas phase, the carbon might be expected to undergo rapid hydrogenation instead of producing coke. The extent to which such processes might occur on ZrO_2 is uncertain; however, it seems reasonable to expect TiO_2 and ZrO_2 to exhibit similar characteristics, since both Ti and Zr are part of Group IVB.

CONCLUSIONS

The results presented in this study indicate that the activity and selectivity of supported Pd catalysts for CO hydrogenation are strongly influenced by the composition of the support and differ significantly from those of Pd black. Utilization of basic metal oxide supports such as MgO , ZnO , and La_2O_3 favors the formation of methanol, the selectivity to this product exceeding 98%. High methanol selectivity (98%) is also observed for Pd supported on SiO_2 , a neutral oxide. When an acidic metal oxide such as Al_2O_3 , TiO_2 , or ZrO_2 is used as the support, the methanol selectivity is suppressed at the expense of forming hydrocarbons. Acidic sites on the support also appear to be responsible for converting a part of the methanol formed to dimethyl ether. The manner in which the acid/base properties of the support express their influence on the catalytic properties of Pd is not understood at present. An electronic interaction between the metal and the support is suggested but it appears that this

interaction is not of the SMSI-type discussed in the literature (19, 20).

Other factors besides the support composition may also influence the activity and selectivity of Pd, among these being the nature of the Pd precursor, the loading and/or dispersion of Pd, the source of the support, and the manner of catalyst pretreatment. Thus, for example, the exceptionally high activity and selectivity of the Pd/La₂O₃ catalyst described in these studies may be due to its preparation by reaction of Pd(π -C₃H₅)₂ with hydroxyl groups present on the support. The extent to which each of the factors noted exerts an effect on catalyst performance is not yet established and must await further investigation.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Jule A. Rabo of the Union Carbide Corporation for donation of the catalyst sample designated as Pd/SiO₂ (II). This work was supported by the National Science Foundation under Grant 78-18989-BELL-ZF 04/80 and by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-ENG-48.

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., *J. Chem. Soc. Chem. Commun.*, 566 (1978).
3. Ichikawa, M., *Bull. Chem. Soc. Japan* **51**, 2268, 2273 (1978).
4. Ichikawa, M., *Shokubai* **21**, 253 (1979).
5. Ichikawa, M., and Shikakura, K., Preprints, The Seventh International Congress on Catalysis, Tokyo, July 1-2, 1980.
6. Yermakov, Yu. I., *Catal. Rev. Sci. Eng.* **13**, 77 (1976).
7. Ryndin, Yu. A., Ph.D. thesis, Institute of Catalysis, Novosibirsk, USSR, 1977.
8. Rosynek, M. P., and Magmeson, D. T., *J. Catal.* **46**, 402 (1977).
9. Anderson, P. J., *Trans. Faraday Soc.* **61**, 2754 (1965).
10. Lewis, K. E., *Trans. Faraday Soc.* **62**, 204 (1966).
11. Tretyakov, N. E., and Pozdnyakov, D. V., *Russ. J. Phys. Chem.* **44**, 107 (1970).
12. Benson, J. E., Hwang, H. S., and Boudart, M., *J. Catal.* **30**, 146 (1973).
13. Freel, J., *J. Catal.* **25**, 139 (1962).
14. Gruber, H. L., *Anal. Chem.* **34**, 1828 (1962).
15. Farrauto, R. J., *AIChE Symp. Ser. No. 143* **70**, 9 (1974).
16. Aben, P. C., *J. Catal.* **10**, 224 (1968).
17. Vannice, M. A., *J. Catal.* **40**, 129 (1975).
18. Maxted, E. B., and Ali, S. I., *J. Chem. Soc.*, 4137 (1961).
19. Tauster, S. I., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100**, 170 (1978).
20. Tauster, S. J., and Fung, S. C., *J. Catal.* **55**, 29 (1978).
21. Horsley, J. A., *J. Amer. Chem. Soc.* **101**, 2870 (1979).
22. Baker, R. T. K., Prestridge, E. B., and Garten, R. L., *J. Catal.* **56**, 390 (1979).
23. Christmann, K., and Ertl, G., *Surface Sci.* **60**, 365 (1976).
24. Figueras, F., Gomez, R., and Primet, M., *Advan. Chem. Ser.* **121**, 480 (1973).
25. Van Hardeveld, R., and Hartog, F., in "Advances in Catalysis," Vol. 23, p. 75. Academic Press, New York/London, 1972.
26. Tanabe, K., "Solid Acids and Bases." Academic Press, New York, 1970.
27. Matsushima, T., and White, J. M., *J. Catal.* **44**, 183 (1976).
28. Carrizosa, I., Munvera, G., and Castañar, S., *J. Catal.* **49**, 265 (1977).
29. Foyt, D. C., and White, J. M., *J. Catal.* **47**, 260 (1977).
30. Ueno, A., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **67**, 2585 (1971).
31. Rosynek, M. P., *Catal. Rev. Sci. Eng.* **16**, 111 (1977).
32. Gravelle, P. C., Juillet, F., Meriaudeau, P., and Teichner, S. J., *Discuss. Faraday Soc.* **52**, 140 (1971).