

Methanol Synthesis over Palladium Supported on Silica

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Methanol synthesis activity of palladium supported on four types of silica (Davison 01, 03, 57, and 59) were evaluated at 16 atm and 255°C in a Berty-type reactor. Turnover frequencies (TOF) were determined based on hydrogen chemisorption data. The TOF's for a particular type of silica increased with decreasing metal dispersion, but for equivalent dispersions the silicas had a marked effect, with TOF's following the sequence Pd/SiO₂(59) > Pd/SiO₂(57) > Pd/SiO₂(01,03). Preliminary results on unsupported Pd show that the activity was less than expected on the basis of particle size. Thus, the silica promotes the activity of the Pd, even though the supported metal particles are relatively large and the TOF increases with particle size. Chloride ions enhance activity by stabilizing higher dispersions and by increasing TOF's. Lithium ions effect extensive sintering of the silica support and promote activity by increasing the TOF. The latter increase may, in part, be the result of more efficient use of Pd surface which occurs via the exclusion of small pores. The more active Pd/SiO₂ catalysts were found to be comparable in activity to a commercial methanol synthesis catalyst. © 1986 Academic Press, Inc.

INTRODUCTION

Since the pioneering work of Poutsma *et al.* (1) on the methanol synthesis activity of supported palladium, numerous studies have been carried out to determine the mechanism, the origin of the activity and selectivity, and the promotional effect of Group IA and IIA metal ions. Papers published through 1984 recently have been reviewed (2). The salient features of the supported metal catalysts are the following: (i) very large support effects have been noted which result from variations in the chemical composition and the exact nature of the support (3-6); (ii) provided the support is nonacidic, high selectivities (>90%) for methanol may be achieved; and (iii) the ions Li⁺ and Mg²⁺ are effective in promoting the activity of Pd on certain supports such as silica gel (4, 7, 8).

The large variations in activity which result when different grades of silica gel are employed as the support were of particular interest in this study. For example, Fajula *et al.* (5) observed that Pd supported on

Davison grade 01 silica was almost inactive for methanol formation; whereas, Pd on grade 57, the material used by Poutsma *et al.* (1), was quite active and highly selective. Such factors as metal crystallite size were suggested as being of importance in determining activity (5). Bell and co-workers, however, have concluded that for the Pd/SiO₂ system the crystallite morphology does not depend upon particle size (9). They found no variation of specific activity with dispersion, although they investigated only a range of 10-20% dispersion. By contrast Ichikawa *et al.* (10) observed that only methane was produced over their Pd/SiO₂ catalysts which had dispersions of 79-88%. For a dispersion of 38% methanol was detected, but with a rather poor selectivity.

The promotion of activity by Li⁺ was first observed by Tamaru and co-workers (4), who concluded that the promoter aided in the stabilization of reactive intermediates. Driessen *et al.* (7) likewise noted the promotional effect of Mg²⁺ and La³⁺ on the methanol synthesis activity of Pd/SiO₂ catalysts. Unfortunately, in these two studies

dispersion data was not complete, therefore it is impossible to separate the effect of promoter on dispersion from a more direct influence such as electronic interaction.

Possible promotional effects of chloride ions also have been noted, but the interpretation of results are not straightforward. Catalysts prepared by impregnating SiO₂ with Pd(π -C₃H₅)₂ were much less active than those prepared from PdCl₂, but the types of silica were different in this study (3). Similarly, Driessen *et al.* (7) and Kikuzono *et al.* (4) found that chloride-free catalysts were less active, but again the absence of good dispersion data makes comparisons of specific activity uncertain.

The present work was undertaken in an effort to resolve some of these questions concerning the effects of dispersion and promoter ions on the specific activity. Additional studies were carried out on the nature of the Pd/SiO₂ catalysts to determine the origin of the marked differences in activities which have been observed with the various silicas. As a limiting case of the support effect, the activities of unsupported Pd were briefly investigated. Moreover, for practical reasons the activity of a commercial methanol synthesis catalyst was determined and compared with that of the most active catalyst in this study.

EXPERIMENTAL

Catalyst preparation. Four commercial-grade Davison silicas were used in this study: 01, 03, 57, and 59. According to the manufacturer grades 01 and 03 are identical except for the particle size of the material. Physical properties of the grades 01 and 57 have been previously reported (5), and their surface areas will be discussed more fully in a subsequent section. The Ca, Mg, Na and Fe impurities were present in the SiO₂(01) at levels of 0.006, 0.003, 0.06, and 0.006%, respectively, and in the SiO₂(57) at levels of 0.06, 0.003, 0.07, and 0.007%, respectively.

All catalysts were prepared by an incipient wetness method. Catalysts containing

chloride ions were prepared by dissolving PdCl₂ (Aldrich) in a 1 : 1 mixture of HCl and deionized water. The PdCl₂ solution was then added to the silica (1–1.5 ml/g SiO₂) while stirring in order to wet all the support. The catalysts usually were loaded to a level of 5 wt% Pd; however, several catalysts contained 10 wt% Pd. The impregnated catalyst was allowed to stand overnight in a covered beaker. The material was dried in a rotary evaporator at 55°C for several hours and then in air at 110°C overnight. In a few cases the catalyst was stirred to dryness on a hot plate at 60–70°C.

Chloride-free catalysts were prepared by dissolving a sufficient amount of Pd(OAc)₂ (Aldrich) in acetone and impregnating the support (1.5–2.0 ml/g SiO₂). This material then was treated as described above. For one catalyst an aqueous HNO₃ solution was used instead of acetone. Chloride concentrations were determined by neutron activation analysis.

Lithium was added to the catalysts in one of three ways. Using a method similar to that of Tamaru and co-workers (4), Li and Pd were coimpregnated onto the catalyst. As an alternative, Li₂CO₃ first was added to the SiO₂, followed by evaporation in air and drying in flowing N₂ at 280°C for 12 h. This material then was impregnated with PdCl₂. Thirdly, Pd/SiO₂ catalysts were prepared in the conventional manner, reduced in H₂ (see below), and then impregnated with lithium salts. Other Group IA and IIA metal ions were added using the latter technique.

Prior to reduction the catalysts were heated under vacuum at 150°C for 4 h, and then calcined at 150°C in flowing air for 2 h and at 400°C for 4 h. They subsequently were cooled to 25°C under flowing N₂ and reheated to 300°C under N₂. At 300°C the flow was switched to H₂ for 2 h, and the temperature was increased to 400°C for another 3 h. The catalysts were flushed with N₂ for 15 min, cooled to 25°C under flowing N₂, and stored in air until use.

Catalytic reactor. Kinetic studies were carried out in a 0.5-liter stainless-steel Berty-type reactor (Autoclave Engineers).

A premixed feed gas of $H_2/CO = 2.2$ to 2.4 (Matheson) was passed through beds of activated carbon and chromium on silica prior to entering the reactor. All transfer lines and valves were heated to $>100^\circ C$ to eliminate condensation. Data was taken with 2–10 g of catalyst in the reactor basket.

Prior to measuring conversions, a catalyst was heated under flowing N_2 at 1 atm to $255^\circ C$, which was the standard reaction temperature. The gas hourly space velocity (SV at STP) was approximately $500\ h^{-1}$. Once the temperature had stabilized, the flow was switched to H_2 to condition the catalyst overnight. Subsequently, the reactor was charged with the CO/H_2 mixture to 16 atm. The flow rate during reaction was maintained at a SV of $5000\ h^{-1}$ by means of a backpressure regulator.

Affluent gases were analyzed using a Varian Model 3700 gas chromatograph. Separation was achieved using a Porapak Q column (100–200 mesh, $2\ mm \times 3.6\ m$, $30\ cm^3/min$ He flow) which was connected to the exit of the reactor via a six-way heated sampling valve.

Sorption studies. Hydrogen adsorption measurements were carried out in a conventional volumetric apparatus equipped with a Ruska XR-38 pressure gauge. The samples (0.5 to 1.2 g) were placed in a flow-through cell and outgassed at $25^\circ C$ for 0.5 h and heated to $200^\circ C$. The palladium was reduced in flowing H_2 (1 atm) at $200^\circ C$ for 1 h and at $400^\circ C$ for 2 h. The cell then was evacuated at $400^\circ C$ for 2 h and the sample was cooled to $100^\circ C$ under vacuum. The hydrogen uptake was determined at $100^\circ C$ and at pressures up to 0.26 atm. Under these conditions the β -hydride phase does not exist (11). The isotherms were obtained 30 min after exposure to the gas. The amount of chemisorbed hydrogen was determined by extrapolating the data to zero pressure.

The BET surface areas of the pure silica and the catalysts were determined using nitrogen. Isotherms were determined with the samples at 77 K. Pore diameters were

calculated from the Kelvin equation using gravimetric nitrogen desorption data (12).

RESULTS

As noted previously (5), steady-state activity for methanol synthesis was maintained over long periods. One catalyst was tested for 53 h, and no loss in activity was observed. It was found, however, that a high steady-state activity was attained for the $SiO_2(57)$ catalysts only if the sample size was large ($>5\ g$), which corresponds to a catalyst volume recommended for the Berty reactor. In subsequent sections the reaction rates and turnover frequencies (TOF) will be based on the steady-state activities.

Dispersion effects. Minor, sometimes inadvertent modifications in pretreatment conditions resulted in variations in dispersions which provided an opportunity to study the relationship between particle size and TOF. As indicated in Table 1, the dispersion values, determined from H_2 chemisorption data, significantly decreased as a result of the catalytic reaction. This is believed to be a real decrease in dispersions, rather than an artifact of surface contamination, since dispersions determined from broadening of an X-ray diffraction line of Pd ($2\theta = 40.15^\circ$) generally were in agreement with those determined from H_2 chemisorption data, as shown in Table 1.

As depicted in Fig. 1, for samples prepared from the same precursor ($PdCl_2$) and the same support, the TOF increased with decreasing dispersion (increasing particle size). In going from 32 to 16% dispersion the TOF increased by about a factor of 15 for the $PdCl_2/SiO_2(01,03)$ samples. Although the slope was approximately the same, the increase in TOF was only about 20% in going from 17 to 8% dispersion on the $PdCl_2/SiO_2(57)$ samples. The reaction rates (per kg of catalyst), given in Table 1, decreased with decreasing dispersion for the $PdCl_2/SiO_2(57)$ samples, but increased with decreasing dispersion for the $PdCl_2/SiO_2(01,03)$ samples. That is, in the latter

TABLE I
Dispersion and Activity of Silica-Supported Palladium Catalysts^a

Catalyst	Dispersion %		Activity (moles kg ⁻¹ h ⁻¹)	TOF (N × 10 ³ , sec ⁻¹)
	Fresh	Used		
5% PdCl ₂ /SiO ₂ (59)	20	11	7.9	42
10% PdCl ₂ /SiO ₂ (57) ^b	14(14) ^c	8.3(10)	8.9	31
5% PdCl ₂ /SiO ₂ (57)	34	18	7.6	25
10% PdCl ₂ /SiO ₂ (01)	25(24)	19(22)	4.5	7
5% PdCl ₂ /SiO ₂ (03)	39	16	2.2	8
5% PdCl ₂ /SiO ₂ (01)	31	17	3.4	12
5% PdCl ₂ /SiO ₂ (03)	35	19	1.2	4
5% PdCl ₂ /SiO ₂ (01)	51	22	2.4	6
5% PdCl ₂ /SiO ₂ (01)	48(27)	27(24)	1.4	3
5% PdCl ₂ /SiO ₂ (01)	59	27	0.9	2
5% PdCl ₂ /SiO ₂ (01)	73	32	0.4	0.6
5% Pd(OAc) ₂ /SiO ₂ (57) ^b		10	3.1	18
5% Pd(OAc) ₂ /SiO ₂ (57) + HCl ^b		16	7.0	26
5% Pd(OAc) ₂ /SiO ₂ (01)	5	3	0.3	5
5% Pd(OAc) ₂ /SiO ₂ (01) ^d	17	11	1.0	5

^a Activities and TOF's determined at 255°C, 16 atm, H₂/CO = 2.3, SV = 5,000 h⁻¹; activities based on kg of catalyst; N = molecules CH₃OH produced (metal site)⁻¹ sec⁻¹, except for 10% PdCl₂/SiO₂(57) conversions did not exceed 30% of equilibrium; selectivities for CH₃OH were >90%.

^b Chloride levels for 10% PdCl₂/SiO₂(57), 5% Pd(OAc)₂/SiO₂(57), and 5% Pd(OAc)₂/SiO₂(57) + HCl are 1,000, 130, and 390 μg/g, respectively.

^c Numbers in parentheses indicate dispersions determined from X-ray line broadening.

^d Catalyst prepared in aqueous HNO₃ solution.

case the increase in TOF more than compensated for the decrease in metal surface area.

Support effect. Two types of support effects are evident from the results of Fig. 1.

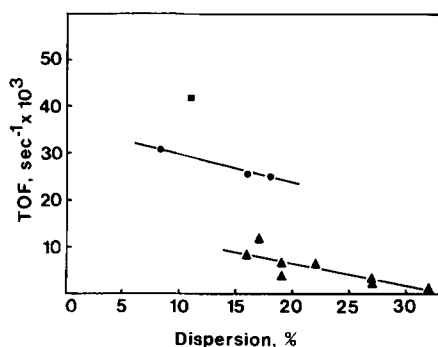


FIG. 1. Variation in TOF for CH₃OH formation with respect to silica support and dispersion: (■) PdCl₂/SiO₂(59), (●) PdCl₂/SiO₂(57), (▲) PdCl₂/SiO₂(01,03). 255°C, 16 atm, H₂/CO = 2.3, SV = 5000 h⁻¹.

The SiO₂(01,03) tends to stabilize the Pd in a higher state of dispersion; however, at similar levels of dispersion the activity of the PdCl₂/SiO₂(57) catalyst was a factor of 2.5 greater than the PdCl₂/SiO₂(01,03) catalyst. The PdCl₂/SiO₂(59) catalyst was even more active than the others.

Effect of chloride ions. Chloride ions likewise have two effects on the catalysts: they enhance the dispersion and the TOF (Table 1). Clearly as a class of materials, the catalysts prepared from Pd(OAc)₂ on SiO₂(01,03) had lower dispersions than those prepared from PdCl₂ on the same silica. Moreover, addition of HCl to the 5% Pd(OAc)₂/SiO₂(57) catalyst increased the dispersion of the used catalyst by 60%. A set of catalysts prepared from Pd(OAc)₂ on SiO₂(01,03) exhibited distinctly lower TOF's than would be expected for their

TABLE 2
Dispersion and Activity of Promoted Palladium Catalysts

Catalyst	Dispersion %		Activity ^a (moles kg ⁻¹ h ⁻¹)	TOF (N × 10 ³ , sec ⁻¹)
	Fresh	Used		
PdCl ₂ /Li ₂ CO ₃ /SiO ₂ (57) ^b	17	13	9.2	42
PdCl ₂ /Li ₂ CO ₃ /SiO ₂ (01) ^b	38	26	6.5	15
Li ₂ CO ₃ /PdCl ₂ /SiO ₂ (03) ^b	34	25	4.9	12
Li ₂ CO ₃ /PdCl ₂ /SiO ₂ (01) ^c	62	41	5.0	7
Li ₂ CO ₃ -PdCl ₂ /SiO ₂ (01) ^b	30	14	2.4	10
PdCl ₂ /Na ₂ CO ₃ /SiO ₂ (01) ^c			1.0	
PdCl ₂ /K ₂ CO ₃ /SiO ₂ (01) ^c			0.8	
PdCl ₂ /MgCl ₂ /SiO ₂ (01) ^c			1.6	
PdCl ₂ /CaCl ₂ /SiO ₂ (01) ^c			1.8	

^a 255°C, 16 atm, H₂/CO = 2.3, SV = 5000 h⁻¹; conversions were less than 30% except for the first two catalysts listed. For these the conversions were 36 and 45%, respectively. All Pd loadings were 5%.

^b Li/Pd = 4; the order of addition is indicated by the sequence; Li₂CO₃-PdCl₂ indicates that the Li and Pd were coimpregnated.

^c Li/Pd = Na/Pd = K/Pd = 2; Mg/Pd = Ca/Pd = 1.

range of dispersions. The Pd(OAc)₂/SiO₂(01) catalyst prepared in an aqueous nitric acid solution also had a lower TOF. More significantly, the Pd(OAc)₂/SiO₂(57) catalyst had a considerably lower TOF than expected from its dispersion, but when a small amount of Cl⁻ was added back, the TOF increased considerably.

Effect of Group IA and Group IIA metal ions. The results of this study (Table 2) show that lithium ions have a positive effect on catalytic activity regardless of the sequence in which they were added. Addition of Li₂CO₃ to a previously reduced PdCl₂/SiO₂(01) catalyst increased the TOF by a factor of 4. Coimpregnation with Li⁺ or addition of Li₂CO₃ before addition of PdCl₂ yielded similar TOF's. The addition of Li⁺ also had a positive effect on the TOF of a PdCl₂/SiO₂(57) catalyst. The anion involved does not appear to be a major factor as catalysts prepared both from Li₂CO₃ and LiCl gave major enhancements in the rates of methanol synthesis. No trends were noted in the ability of Li⁺ to stabilize Pd dispersion. As shown in Fig. 2 the activity

of a PdCl₂/Li₂CO₃/SiO₂(01) series increased as the amount of Li⁺ increased up to a Li/Pd atomic ratio of about unity.

Other Group IA and IIA metal ions likewise yielded rate enhancements as shown in Table 2, but the influence of Li⁺ was significantly greater than the other metal ions. This trend is particularly evident in comparing the promoter effect of Li⁺ with that of Na⁺ and K⁺.

In an effort to understand the role of

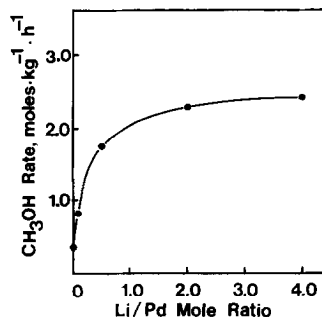


FIG. 2. Variation in reaction rate for CH₃OH formation with respect to Li loading for Li₂CO₃/PdCl₂/SiO₂(01) catalysts.

TABLE 3
Surface Areas of Supports and Catalysts

Catalyst/support	Surface area, ^a m ² /g			
	Unpromoted		Li-Promoted ^b	
	Fresh	Used	Fresh	Used
SiO ₂ (57)	283		173	
SiO ₂ (01)	596			
SiO ₂ (03)	625(27) ^c		82	
5% PdCl ₂ /SiO ₂ (57)	254	226		168 ^d
5% PdCl ₂ /SiO ₂ (03)	368(28)	429(28)	51 ^d	36 ^d
5% PdCl ₂ /SiO ₂ (03)			102 ^e	79 ^e
5% PdCl ₂ /SiO ₂ (57)			174 ^e	176 ^e

^a BET surface area determined from nitrogen adsorption at 77 K; each of the samples had been heated to 400°C for 1–1.5 h.

^b 6.9–7.7 wt% Li₂CO₃.

^c Number in parentheses indicate pore diameters in Å.

^d Li⁺ added to reduced sample.

^e Li⁺ added to SiO₂ first, then Pd²⁺ added.

these promoters the effect of Li on the BET surface area of the catalysts was investigated, and the results are summarized in Table 3. Since Li is known to be a flux for sintering silica, it is not surprising that the surface areas decreased remarkably upon the addition of ca. 7 wt% Li₂CO₃, followed by heating the samples under vacuum from 1 to 1.5 h at 400°C. The surface area of the SiO₂(57) sample decreased by 46%, and the surface area of the SiO₂(03) sample decreased ca. 87%. The BET surface areas of the Pd-loaded catalysts remained essentially unchanged as a result of the methanol synthesis reaction, but further decreases were noted for the Li-promoted SiO₂(03) sample.

Activity of unsupported Pd. Palladium sponge which had a dispersion of 7% for the used catalyst was found to be totally inactive for methanol synthesis. This material, however, was relatively inactive for 1-butene hydrogenation when compared with a supported PdCl₂/SiO₂(03) catalyst. A high-purity palladium powder (Johnson Matthey) having a surface area of 1 m²/g was found to be inactive for methanol synthesis. Both the sponge and the powder were dispersed in quartz wool and sandwiched between layers of SiO₂(57) in the Berty re-

actor. The weight percentage of Pd was 5%. Assuming a TOF of 1 × 10² molec site⁻¹ sec⁻¹, a charge of this material would be expected to catalyze 3 × 10⁻² mol CH₃OH kg⁻¹ h⁻¹, which would have been detected in our system. In one run the Pd powder was mixed with fines of SiO₂(57), ground and then pressed into wafers. This material was placed between layers of silica. The entire mass contained 5% Pd. Methanol was formed over this catalyst (~1 mole CH₃OH kg⁻¹ h⁻¹ where the rate is based on kg of Pd plus silica), along with a small amount of ethanol, but the activity declined over a period of a few hours.

Comparison with a commercial catalyst. For purposes of comparison the methanol synthesis activity of an ICI catalyst was determined in the Berty reactor at 16 atm and 250°C. The feed stream for the commercial catalyst was a mixture of H₂, CO, and CO₂ in the ratio 2.37:1:0.08. The commercial catalyst reached an activity of 10.2 mole kg⁻¹ h⁻¹ after 33 h of operation. On the basis of total catalyst mass this activity is about 1.5 times the activity of the 5% Pd/SiO₂(59) catalyst, corrected to 250°C.

DISCUSSION

The results of this study suggest that a number of factors including particle size, type of silica, presence of chloride ions and the presence of Group IA and Group IIA promoters influence the activity of palladium supported on silica. The positive influence of particle size, which is most evident in the Pd/SiO₂ catalysts, supports the preliminary observations of Ichikawa *et al.* (10) that methanol was found only on catalysts having dispersions <45%. The observation by Hicks and Bell (9) that the TOF for methanol synthesis did not vary for Pd dispersion between 10 and 20% may reflect the use of Cab-O-Sil HS5 silica as a support. Hicks and Bell (13) further noted that the ratio of the more active Pd(100) surfaces to the less active Pd(111) surfaces remained constant on their silica support, although such was not the case for their

Pd/La₂O₃ catalysts. The Pd(100) planes were estimated to be 2.8 times more active than the Pd(111) planes. Although the distribution of Pd planes may indeed vary on our Pd/SiO₂(01,03) catalysts, this could not account for the 20-fold change in activity which was observed for the range of dispersions listed in Table 1.

In comparison with the work of Hicks and Bell (9) it is significant that they observed a TOF of ca. 5×10^{-3} molec site⁻¹ sec⁻¹ under the conditions of our experiment, which agrees well with the TOF's of the Pd/SiO₂(01,03) samples of comparable dispersions. It is also interesting to note that Ryndin *et al.* (3) observed a TOF of 32×10^{-3} molec site⁻¹ sec⁻¹ (extrapolated to our conditions using their rate law (9)) for their Pd/SiO₂(57) catalyst.

By contrast Fajula *et al.* (5) found that their Pd/SiO₂(01) catalyst had a very low dispersion (~4%), and that the catalyst was inactive for methanol synthesis. On the basis of this data and particle size distributions obtained by transmission electron microscopy they concluded that methanol is produced on small size crystallites of Pd. In view of the present study and the results of Ichikawa *et al.* (10) such a conclusion probably is incorrect. In the earlier work (5) the effects of the physical and chemical properties of the support were not adequately considered.

Since Pd particles 70 to 150 Å in diameter have the largest specific activity, one might expect that unsupported forms of Pd having even larger size particles would be more active, but such was not the case. The results reported here for the unsupported catalyst might be suspect because of the problem encountered in working with a small volume of active material in the Bertly reactor; however, Ryndin *et al.* (3) also observed that Pd black had a very small TOF. More recently, under comparable experimental conditions (250°C, 14.6 atm, H₂/CO = 3), except in a plug-flow microreactor, Sudhakar and Vannice (6) have observed a TOF of 2.7×10^{-4} sec⁻¹ for CH₃OH forma-

tion over a high-purity palladium powder, which is two orders of magnitude less than the more active Pd/SiO₂ catalysts of Table 1. The actual methanol synthesis activity of unsupported palladium should be determined on metal films and single crystals, although the experiments to date suggest that the TOF is small unless the Pd is in intimate contact with an oxide.

This observation is supported by the differences in activities which result from variations in the type of silica employed. Clearly, the silica plays a role in determining the activity of the Pd; yet, this effect must be operative on relatively large Pd particles. The low activity of the Pd/SiO₂(01,03) in part may be related to the partial blockage of pores by Pd particles which are located at the pore mouth. The nominal pore diameter of this support is 28 Å, which is considerably smaller than the average Pd particle size (40–70 Å), based on dispersion data. Calculations show that for open pores diffusion would not be rate limiting, but in partially blocked pores diffusion limitations could be a factor. Evidence for pore blocking in the SiO₂(01,03) catalysts is found in the data of Table 3. The decrease in BET surface area from ca. 600 to 400 m²/g for SiO₂(01,03) upon addition and reduction of Pd suggests that metal particles are sealing off pores. Hydrogen is expected to diffuse through the blocking Pd, thus the dispersion data probably reflects the total amount of exposed metal. Pore blocking, however, is not the only factor since differences in methanol synthesis activity were noted previously for Pd/Cab-O-Sil and Pd/SiO₂(57) and in the present study between Pd/SiO₂(57) and Pd/SiO₂(59). Among these catalysts there is no trend between pore diameter and activity.

Both the need for silica and the variation among silicas may be explained if the support is required to stabilize reaction intermediates. Kikuzono *et al.* (4) presented infrared evidence which suggests the role of formate ions as intermediates in methanol synthesis over alkali metal-promoted Pd/

SiO₂ catalysts. One oxygen of the SiO₂ support is believed to be present in the formate ion. They observed the formate ions only on the active Li- and Na-promoted catalysts, but not on the relatively inactive K-promoted or Pd/SiO₂ catalysts. Hicks and Bell (9) likewise failed to observe formate ions on the latter catalyst and argued that these were not intermediates in the reaction. Nevertheless, silica or another support may be required to stabilize intermediates such as formate or methoxide ions. Sudhakar and Vannice (6) reached a similar conclusion based on their comparison of supported and unsupported catalysts; however, their suggestion that the intermediates exist at the Pd-support interface is not consistent with the particle size effect observed here. That is, if the Pd-support interface was important, one would expect to find the highest activity for catalysts having the greatest metal periphery (smallest particles), but such was not the case (Fig. 1). It seems more likely that the entire support surface functions as a reservoir for the intermediates, although the steady state concentration must be small. Experiments are underway in this laboratory in an effort to detect such intermediates on the more active Pd/SiO₂ catalysts.

The positive role of chloride ions, both in stabilizing dispersion and in promoting specific activity has been confirmed. The mode by which Cl⁻ ions promote activity is not so evident, although it is likely that Cl⁻ ions deplete the surface Pd of electrons via an image charge effect. This image charge should strengthen the C—O bond and prevent dissociation of the molecule. Moreover, it would limit the addition of H₂ as a surface hydride which, according to the mechanism of Hicks and Bell (9), would favor the molecular addition of H₂ to CO. One also could argue that Cl⁻ ions result in the stabilization of the Pd^{δ+} species which has been suggested as an active form of palladium in methanol synthesis (see below).

It is surprising that both chloride ions and Group IA ions have the same positive effect

on activity since their electronic effects on Pd are expected to be opposite. The most obvious effect of lithium is to modify the BET surface areas of the catalysts (Table 3). All of the Pd/SiO₂ catalysts were greatly reduced in surface area during reaction, which probably eliminates the smaller pores in the SiO₂(01,03) and the effects associated with pore blocking. Moreover, as suggested by Tamaru and co-workers (4), the stabilization by the promoter of surface intermediates, such as formate ions, may be crucial in the mechanism. Ponec and co-workers favor the formation of active Pd^{δ+} ions which act in concert with Pd⁰ crystallites to form the active surface (7). These Pd^{δ+} species are believed to be stabilized by promoters such as Mg²⁺. Recent XPS studies of Fleisch *et al.* (14) show no evidence for positively charged Pd supported on silica, and Pd supported on La₂O₃, which is a very active catalyst, was more electronegative than bulk Pd. On both unpromoted and Li-promoted Pd/SiO₂(57,59) Deligianni *et al.* (8) were unable to detect any CO infrared bands above 2100 cm⁻¹ which might indicate the presence of Pd^{δ+} sites, although it should be noted that these studies were carried out on fresh catalysts.

In comparing the activity of Pd on different types of silica the influence of impurities should be considered. Earlier results for Pd on SiO₂(57), SiO₂(01), and Cab-O-Sil showed that there was no correlation between metal ion impurities and activity. Pd/Cab-O-Sil fell between Pd/SiO₂(57) and Pd/SiO₂(01) in activity; yet, Cab-O-Sil is substantially purer than the other two silicas. The present work indirectly addresses this question in that the results of Fig. 2 show that a considerable amount of promoter is required to significantly modify activity. Thus, if impurities were to influence the activity their concentrations would have to be larger than the levels found in these silicas.

Finally, Pd/SiO₂ has several characteristics which give it commercial potential. Clearly, Pd/SiO₂ catalysts can be made as

active as a commercial CuO/ZnO/Al₂O₃ catalyst, but only at a considerably greater cost. The Pd/SiO₂ catalysts are more robust with respect to thermal and mechanical shock; thus, they may find application in slurry reactors. In addition the Pd/SiO₂ catalysts may exhibit more sulfur tolerance than the more traditional catalysts, although there is no data in the literature to support this supposition.

CONCLUSIONS

1. The TOF for methanol synthesis increases with increasing particle size of Pd supported on silica. This effect is most evident for the less active Pd/SiO₂ catalysts.

2. Differences in apparent TOF of the catalysts prepared from the three different types of silica may be attributed to (a) stabilization of active intermediates on the support (a positive effect), (b) stabilization of small Pd crystallites (a negative effect), and (c) partial blockage of the Pd surface by Pd particles at the entrance of small pores (a negative effect).

3. Chloride ions promote the activity of Pd/SiO₂ mainly by stabilizing higher dispersion, but the TOF also is increased.

4. Lithium ions promote activity by increasing the TOF. This effect, in part, may be related to sintering of the support which could result in more efficient utilization of the Pd.

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