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Li^+ Promotion of Pd/SiO_2: The Effect on Hydrogenation, Hydrogenolysis, and Methanol Synthesis

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A novel but fairly simple approach has been used to elucidate the effect of Li^+ promotion of 5 wt% Pd/SiO_2 [$(Li/Pd)_{atomic}$ = 0, 1, 2, 4] by using a set of three distinct reactions (CO hydrogenation, isobutylene hydrogenation, and ethane hydrogenolysis) in addition to H_2 TPD, CO chemisorption, XRD, and TEM. The results were used to indicate the degree of metal surface blockage by the promoter and to better understand how Li^+ goes about affecting Pd catalysis, especially CO hydrogenation which is known to be greatly modified.

Li^+ promotion decreased the strength of H_2 adsorption and enhanced CO adsorption on Pd/SiO_2. Additionally, it significantly decreased the hydrogenation (in the presence of CO) and ethane hydrogenolysis activities of Pd/SiO_2 relative to those of the unpromoted catalyst, with the activities decreasing monotonically with increasing Li^+ loading. Isobutylene hydrogenation results suggest Li^+ blockage of some of the active Pd sites. Steady-state isotopic transient kinetic analysis (SSITKA) of isobutylene hydrogenation in the presence of CO indicates that surface coverage by CO was significantly enhanced by Li^+ promotion. The simultaneous enhancement and suppression of CO and H_2 adsorption, respectively, coupled with active site blockage by Li^+ resulted in olefin hydrogenation appearing to behave like a structure sensitive reaction. Ethane hydrogenolysis results indicate a nonuniform distribution of the promoter on Pd as well as its probable dispersion on the surface of the support as well. Despite the fact that site blockage resulted in a decrease in the hydrogenation and ethane hydrogenolysis activities of $Li-Pd/SiO_2$ ($Li/Pd = 1$), an increase in the rate of methanol formation was observed. This increase in the methanol formation rate with low levels of Li^+ promotion can be attributed to an increase in the number of active sites or in the coverage of the active sites by the surface intermediates since TEM indicated no change in Pd particle size distribution. Higher loadings of Li^+ ($Li/Pd \geq 2$) resulted in a decrease in methanol formation. © 1995 Academic Press, Inc.

INTRODUCTION

The catalytic properties of supported Pd can be greatly modified by using a variety of promoters. For example, various reports in the literature have shown that group IA and IIA oxide promotion can significantly alter the activity and selectivity of Pd/SiO_2 catalysts for CO hydrogenation (1–6). Some of these promoters (Li^+, Na^+, Mg^{++}) enhance the activity for methanol synthesis during CO hydrogenation, whereas others (K^+, Rb^+ Cs^+) suppress it. However, it is difficult to understand the effect of promotion based on various reports in literature for the Pd/SiO_2 catalysts prepared using different SiO_2 supports since the presence of even small quantities of impurities has been found to significantly affect the methanol synthesis activity of a catalyst (7, 8). Additionally, there is still a controversy about whether or not the active site for methanol synthesis is Pd^0, Pd^+, or the silica support itself (1, 6, 7, 9).

Kikuzono *et al.* (1) and Kelly *et al.* (5) have reported that, of IA and IIA promoters, Li^+ has the highest enhancement effect on Pd/SiO_2 for the synthesis of methanol. Alkali promotion has been shown to modify hydrogenation, CO dissociation, and chain growth probabilities on group VIII metals (10–13). However, Li^+ promotion of Pd/SiO_2 only selectively increases the activity for methanol synthesis (1, 5). This suggests that Li^+ promotion does not influence the CO dissociation and chain growth abilities of Pd/SiO_2. The effect of Li^+ promotion on the hydrogenation ability of Pd/SiO_2 and the promoter distribution on the catalyst are still not well understood.

Ethane hydrogenolysis is a structure sensitive reaction which has been extensively used to study supported metal and bimetallic catalysts. Structure-sensitive reactions can be useful for characterizing decoration of metal surface structures by catalyst promoters or poisons (14, 15). Structure sensitivity for a reaction depends on the size of the ensemble required for the reaction and/or on the orienta-

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tion of the metal surface atoms. In particular, structure sensitivity increases with an increase in the ensemble size required for reaction. Ethane hydrogenolysis has been reported to require a large reaction site ensemble on the order of 12 metal surface atoms (16, 17) and has been used successfully with hydrogen chemisorption to investigate potassium dispersion on a series of K^+-promoted Ru/SiO_2 catalysts (15).

Olefin hydrogenation can be used to probe the hydrogenation activity of catalysts. Usually, hydrogenation rates on metal catalysts are significant at even low temperatures. The presence of even small amounts of CO, however, tends to reduce the hydrogenation activity due to the fact that CO competes for adsorption sites. Hydrogenation activity in the presence of CO is especially important in determining selectivity for catalysts used in CO hydrogenation.

This paper reports the results of a study of Li^+ promotion of Pd/SiO_2 using three reactions to explore the modification of the Pd: CO hydrogenation, isobutylene hydrogenation, and ethane hydrogenolysis. CO hydrogenation was used to delineate the effect of Li^+ on methanol synthesis activity; isobutylene hydrogenation in the presence of a small amount of CO was used to analyze the effect of promotion on hydrogenation activity as well as to estimate the surface blockage; and ethane hydrogenolysis was used to determine the degree of the dispersion of Li^+ on the catalysts. H_2 TPD was performed to understand the effect of promotion on hydrogen adsorption. Steady-state isotopic transient kinetic analysis (SSITKA) was used to estimate the surface coverage of CO for the promoted and the unpromoted catalysts under the reaction conditions used for isobutylene hydrogenation. Coupled with TEM characterization, these results permit us to better understand how Li^+ promotion affects Pd catalysis.

EXPERIMENTAL

A series of SiO_2 (Davison grade 59) supported, Li^+-promoted Pd catalysts was prepared with Li/Pd atomic ratios of 0, 1, 2, and 4. In order to minimize any effect due to metal particle size distribution variation for different levels of promotion, a single batch of reduced 5 wt% Pd/SiO_2 was prepared and aliquots of this material were subsequently promoted with Li^+. The base catalyst was prepared by incipient wetness impregnation using an aqueous solution of $PdCl_2$ (Aldrich). The impregnated catalyst was dried in an oven for 5 h at 90°C and then calcined at 400°C for 4 h using a ramp rate of 2°C/min in an air (hydrocarbon-free) flow of 60 cc/min. The calcined catalyst was subsequently reduced in a H_2 (UHP grade) flow of 80 cc/min at 400°C for 5 h followed by passivation by air at room temperature. A ramp rate of 2°C/min to 400°C was used. This treated base catalyst was then promoted with aqueous solutions of $LiNO_3$ (Aldrich) to produce catalysts with the desired Li/Pd ratios. The unpromoted catalyst, with Li/Pd = 0 and referred to by Pd/S2, was impregnated with only distilled water. The promoted catalysts, referred to by the designation Li*X*/Pd/S2 where *X* indicates the nominal Li/Pd atomic ratio, were dried for 5 h and rereduced following the reduction procedure described above. The promoter will be referred to as Li^+ since it was in its cationic form. The exact Li species varies depending on the presence of H_2O and CO during reaction.

CO chemisorption was carried out at 25°C for all the catalysts. However due to uncertainty about possible CO chemisorption suppression and/or CO interaction with Li^+ in the promoted systems, this result was only used to determine the amount of exposed Pd (using $CO_{irrev}/Pd_s = 1$) and to calculate the average metal particle size for the unpromoted catalyst (18). X-ray diffraction line broadening using Cu K_α radiation was also used for all the catalysts to determine the average Pd particle size via the Scherrer equation with correction for instrumental line broadening (19).

Samples of three catalysts (Pd/S2, Li1/Pd/S2, and Li4/Pd/S2) were examined using a JEOL 2000EXII transmission electron microscope. The estimated point-to-point resolution of this instrument is 0.14 nm. Suitable transmission specimens were prepared by dispersing the catalyst powders in iso-butanol and placing a drop of the suspension onto a holey carbon film. Using this approach, it was possible to locate sections of the catalyst which protruded over the edge of the carbon, thereby permitting an examination of the catalyst without interference from the substrate. Electron micrographs were taken of several regions of a given specimen and the size distribution plots constructed from the measurements of over 500 particles in each system.

For H_2 TPD, 20 mg of prereduced catalyst was rereduced at 400°C following the procedure described before for catalyst reduction. The catalyst was then cooled down to room temperature under H_2 flow. To flush the gas phase and any weakly sorbed H_2, He was allowed to flow through the catalyst at 25°C for 10 min. TPD was performed by heating the sample from room temperature to 600°C using a ramp rate of 15°C/min under a 20 cc/min flow of a 5% Ar in He gas mixture. Ar was used as an internal standard. A mass spectrometer was used for TPD effluent gas analysis.

CO hydrogenation reaction studies were carried out in a 0.305 in. (1 in. = 2.54 cm) i.d., stainless-steel U-tube, fixed-bed, microreactor capable of working up to 10 atm pressure. Details of the reaction system and the experimental procedure are given elsewhere (28) and are summarized briefly here. Prior to reaction, 1 g of reduced catalyst was treated *in situ* in a H_2 flow of 50 cc/min at 400°C for 5 h using a ramp rate of 2°C/min. Reaction was carried out under differential conditions; i.e., conversions were kept below 2%. The reactor was operated at 200°C and 7 atm pressure. A total flow rate of the H_2/CO mixture ($H_2/CO = 1$) of 30 cc/min was used. All of the lines in the reaction system were kept at 175°C to avoid any product condensation. Mass and heat transfer did not appear to have an effect on the reaction rate determined.

A similar experimental setup was used for isobutylene (IB) hydrogenation and ethane hydrogenolysis except that a 1/4 in. i.d., Pyrex U-tube, fixed-bed, micro-reactor was used. The prereduced catalyst was treated *in situ* in flowing H_2 (40 cc/min) by heating it at 2°C/min to 400°C and holding for 5 h. For isobutylene hydrogenation, the reactor was filled with 30 mg of catalyst and operated at 1.7 atm pressure and 120–150°C. A flow of $H_2:IB:He:CO$ maintained at 28 : 7 : 63 : 1 cc/min was used. Isobutylene hydrogenation was carried out in the presence of a small fraction of CO since it was of interest to characterize the hydrogenation activities of the catalysts under CO hydrogenation conditions.

For ethane hydrogenolysis, 50 mg of catalyst was used, and the flow of $H_2:C_2H_6:He$ was kept at 20 : 0.2 : 89.8 cc/min. Reaction was carried out at 1.7 atm and 360–400°C. Conversion was kept below 10%. Reaction periods of 5 min were used to avoid complications due to deposited carbon, and the catalyst was bracketed at reaction temperature with H_2 for 15 min between every reaction period.

All of the products were analyzed on-line using a Varian 3700 gas chromatograph equipped with a flame ionization detector. For CO hydrogenation a Porapak-Q column was used, whereas for the other two reaction studies a Megabore GS alumina PLOT (porous layer open tubular) column was used.

The isotopic transients were measured using the system described elsewhere (21) and briefly described here. It consisted of a Pyrex, fixed-bed micro-reactor and an on-line Leybold–Inficon Auditor-2 mass spectrometer (MS) equipped with a high speed data acquisition system interfaced to a 386-PC. During steady-state isobutylene hydrogenation in the presence of CO, two gas streams, having the same gas composition and flow rates except one having ^{12}CO and other ^{13}CO, were switched from one to another without disturbing the steady-state operation of the reaction. A trace of Ar was present in the ^{12}CO stream in order to permit the determination of gas phase hold-up.

RESULTS

CO chemisorption uptakes and the average Pd particle sizes determined by CO chemisorption, XRD, and TEM are summarized in Table 1. The addition of Li^+ resulted in an increase in the CO uptake of the catalysts. CO uptake was used to determine the amount of exposed Pd and the average particle size of Pd for the unpromoted catalyst. Since all the catalysts were prepared from a single prereduced Pd/SiO_2 base catalyst, it might be hypothesized that the average Pd particle sizes for all of the catalysts would be similar. The TEM results provide a definitive conclusion about the variation in Pd particle size with promotion (Table 1, Figs. 1–6). From inspection of the particle size distribution plots (Figs. 4–6), it is apparent that the addition of small concentrations of lithium ($Li/Pd \leq 1$) to the Pd/SiO_2 had very little effect on the metal particle size distribution. Thus, the average Pd metal particle size was essentially identical for Pd/S2 and Li1/Pd/S2 (47 and 48 Å). However, as evident in Fig. 3 and the average Pd particle size for Li4/Pd/S2 (77 Å), higher Li^+ concentrations seemed to favor a significant increase in particle size. Examination of the Pd particles at high magnifications revealed that the electron density across a given particle was uniform, indicating that flat structures rather than the energetically preferred hemispherical form were extant. The Pd particles seemed to acquire a faceted outline with the hexagonal shape being predominant. Furthermore, it was frequently possible to discern the textural features of the underlying silica support through the particles, confirming that they were relatively thin. These characteristics point to the existence of a significant interaction with the support that may be created during the final hydrogen reduction step in the catalyst preparation procedure. As expected, the average particle sizes based on XRD were higher than those obtained from CO chemisorption or TEM due to fact that XRD, using a Cu K_α source, is not able to detect crystallites less than 40–50 Å. However, these XRD-based numbers did not vary significantly with the level of promotion.

H_2 TPD profiles for the unpromoted base and Li1/Pd/S2 catalysts are shown in Fig. 7. The major peak of H_2 desorption from the Pd/S2 base catalyst was located at about 235°C, whereas for Li1/Pd/S2 it was at 160°C.

The CO hydrogenation activity of all the catalysts changed considerably with time-on-stream and reached steady-state after 10–20 h of reaction. Time-on-stream behaviors of these catalysts are shown in Fig. 8, and the steady-state results are summarized in Table 2. Such a variation in activity with time-on-stream has been reported also by other researchers (6, 22, 23). In all cases, the main product observed was methanol with selectivities greater than 90% for all the catalysts studied, and this did not vary significantly with time-on-stream. Methane and trace amounts of other hydrocarbons were also observed. A comparison of the rates of CO conversion shows that the lowest level of Li^+ promotion ($Li/Pd = 1$) enhanced the activity of Pd for CO hydrogenation by a factor of ca. 2. However, higher levels of Li^+ promotion ($Li/Pd \geq 2$) gave reduced activities.

Table 3 gives the steady-state rates of isobutylene hydrogenation at 120°C in the presence of a small amount of CO (0.017 atm) as well as the apparent activation energies for reaction. It can be readily seen that olefin hydrogena-

TABLE 1

Properties of Li^+-Promoted Pd/SiO_2 Catalysts

Catalyst	Pd[a] (wt%)	Li[a] (wt%)	Li/Pd[a] atomic ratio	CO_{irrev}[b] chemisorption (μmol/g)	Pd average particle size (Å)		
					CO Chem.[c]	XRD[d]	TEM[e]
Pd/S2	5.01	0	0	105	42	147	47
Li1/Pd/S2	5.01	0.26	0.8	139	—	135	48
Li2/Pd/S2	5.01	0.62	1.9	122	—	139	—
Li4/Pd/S2	5.01	1.14	3.6	125	—	131	77

[a] Based on ICP analysis, Pittsburgh Applied Research Center.

[b] Maximum error ±7%.

[c] Based on CO_{irrev} chemisorption on the base, unpromoted catalyst.

[d] Maximum error ±6%.

[e] Determined based on the size distribution of over 500 particles.

tion activity decreased monotonically with increased Li^+ loading. The activation energies were somewhat higher for the promoted catalysts than for the unpromoted base catalyst, possibly due to the fact that the conversions were lower and more differential, but did not vary significantly with promotion level. In the absence of CO, isobutylene was completely hydrogenated to isobutane at 120°C on all of the catalysts studied.

Normalized steady-state isotopic transients for Ar and CO on the Li1/Pd/S2 catalyst under isobutylene hydrogenation reaction conditions are shown in Fig. 9. Average surface residence time (τ) for CO is given by the area between the ^{13}CO and Ar (marking gas phase holdup in the system) transients (21). The concentration of surface CO is determined by

$$N_{CO} = \tau_{CO} \cdot F_{CO},$$

where F_{CO} is the flow rate of CO. The CO surface coverage for the Pd/S2 base and the Li1/Pd/S2 catalysts are given in Table 4. It should be noted that the determination of surface concentrations of species by SSITKA does not require any assumptions since the calculation is based on a simple mass balance.

Table 5 gives the rates of ethane hydrogenolysis for the different catalysts at 370°C as well as the apparent activation energies. As in the case for isobutylene hydrogenation, activity decreased with increased Li^+ loading. The activation energies were somewhat higher for the two highest levels of promotion.

DISCUSSION

Since all of the Li^+-promoted catalysts were prepared from a single prereduced Pd/SiO_2 base catalyst, it was expected that the Pd average particle size would not change significantly for the promoted catalysts. This supposition was verified by the TEM results for Li/Pd ≤ 1. However, high loadings of Li^+ (Li/Pd = 4) resulted in an increase in the average Pd particle size. This decrease in Pd dispersion may have resulted due to the large amounts of HNO_3 formed during reduction of $LiNO_3/Pd/SiO_2$. CO chemisorption showed an increase in the CO uptake upon promotion which often indicates an increase in metal dispersion. However, the TEM results clearly show that this was not the case. The higher CO uptake upon promotion was most probably due to the generation of new CO adsorption sites at the promoter–metal interface, to the direct interaction of CO with the promoter, or to a redistribution of the CO adsorption adstate. The last possibility has been proposed by Rieck and Bell (24) who attributed changes in the CO TPD behavior of alkali-promoted Pd/SiO_2 catalysts to an increase in the proportion of linearly-adsorbed CO relative to bridge-adsorbed CO. The similarity in the average Pd particle size of the unpromoted Pd/SiO_2 calculated from CO chemisorption to that from TEM results, however, suggests that this may only account for part of the difference.

The shift in the H_2 desorption peak towards lower temperature during TPD upon Li^+ promotion suggests that Li^+ promotion reduced the strength of H_2 adsorption on the Pd/SiO_2 catalyst.

The observed increase in the rate of methanol formation during CO hydrogenation as a result of a low level of Li^+ promotion is in good agreement with what has been reported earlier (1, 5, 25). However, the observed decrease in the activity of the catalyst with the higher loadings of Li^+ (Li/Pd ≥ 2) is not in agreement with the results of Kelly *et al.* (5). They found that the activity of a Li–Pd/SiO_2 series increased as the Li/Pd ratio was increased to

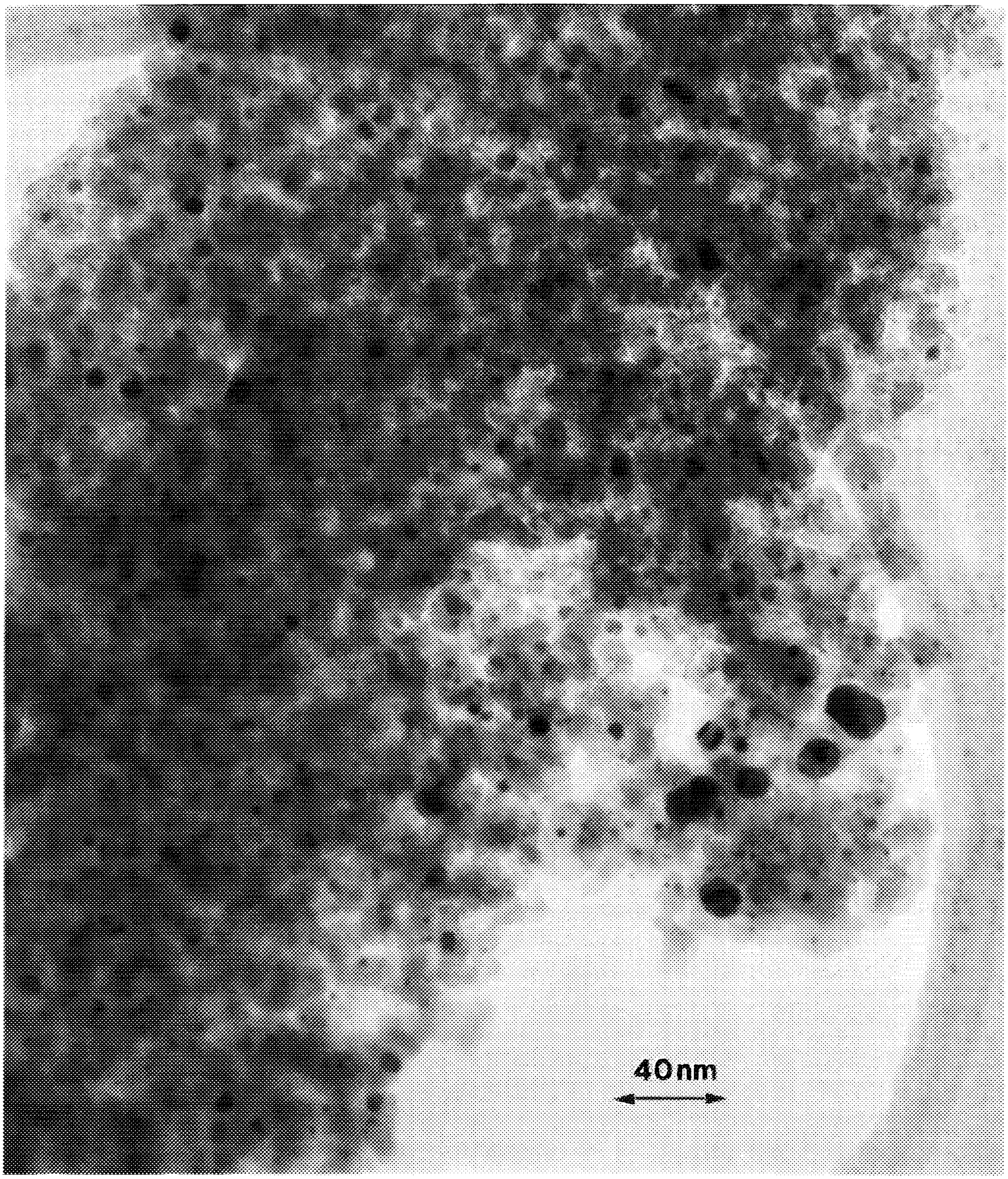

FIG. 1. TEM micrograph of the unpromoted Pd/S2 catalyst.

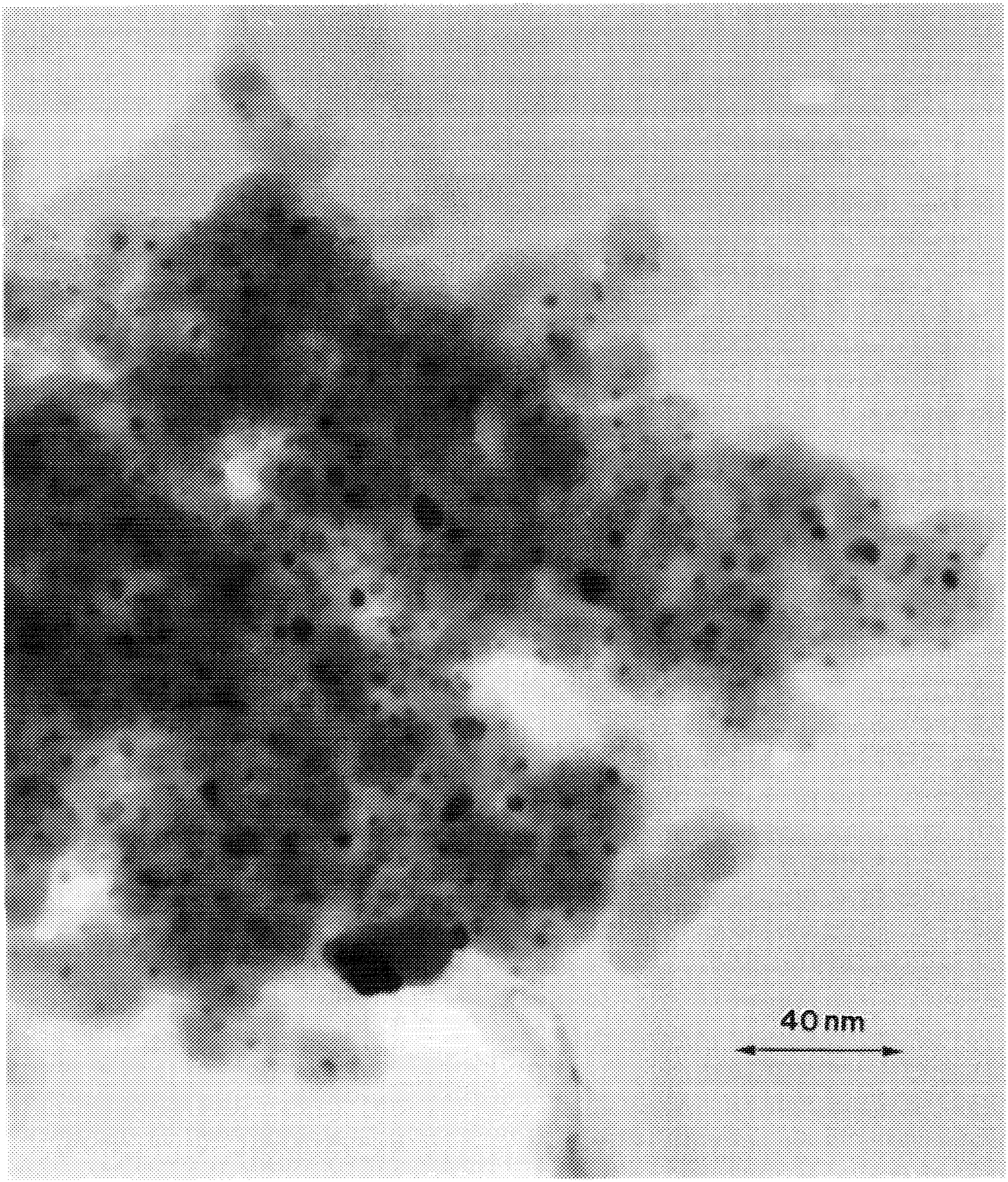

FIG. 2. TEM micrograph of the promoted Li1/Pd/S2 catalyst.

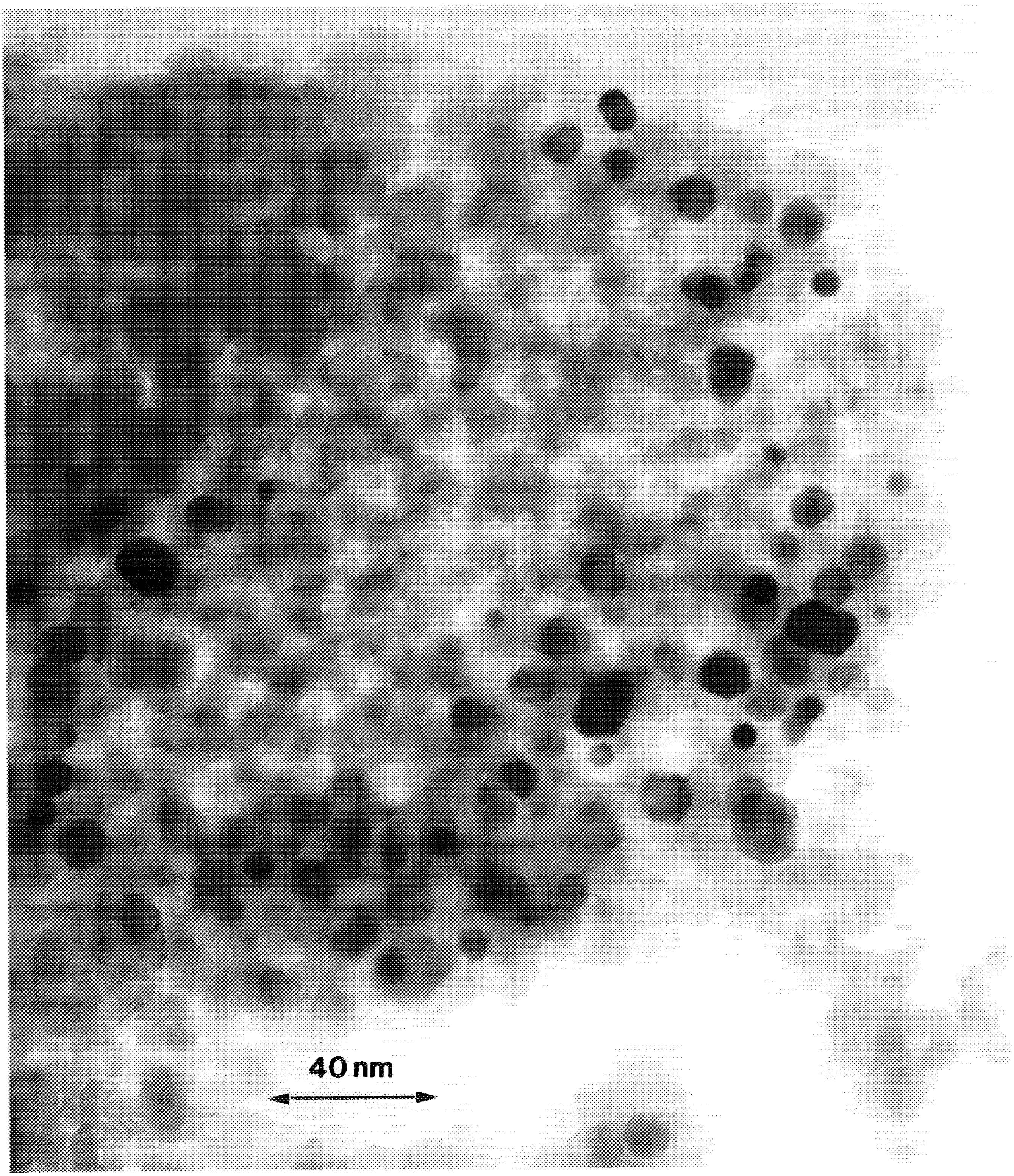

FIG. 3. TEM micrograph of the promoted Li4/Pd/S2 catalyst.

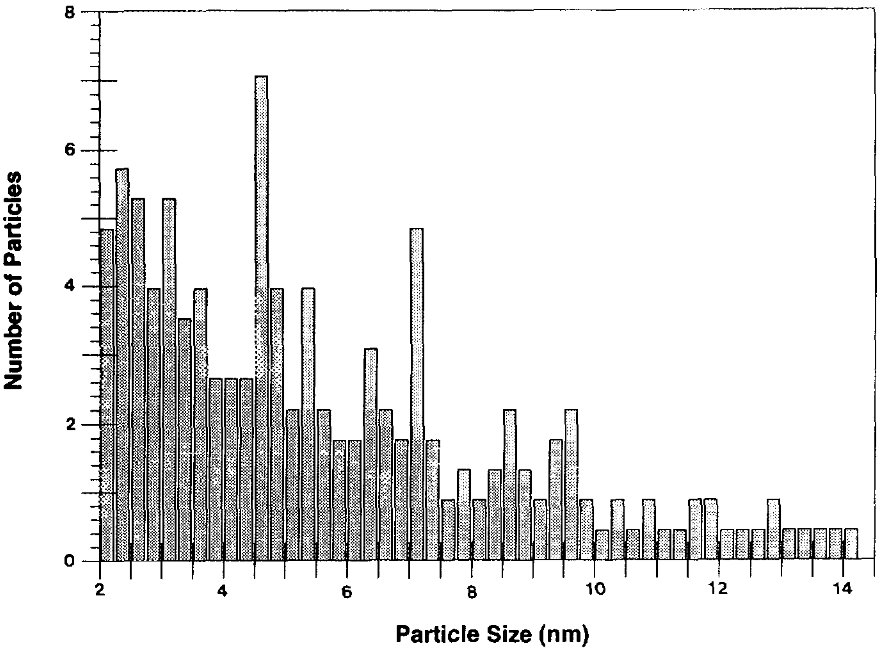

FIG. 4. Pd particle size distribution of Pd/S2 determined by TEM.

about unity and that further increases in Li^+ loading did not have any additional significant effect on the activity of the catalyst. This discrepancy in behavior may be attributed to differences in the catalysts due to preparation procedure, to different kinds of SiO_2 used as support, to Pd dispersion, to pretreatment, and/or to the nature of the Li^+ precursor used for promotion. Catalysts prepared by Kelly *et al.* (5) for studying the effect of Li^+ loading were prepared by sequential impregnation in which Li_2CO_3 was first added to the support before addition of the metal precursor. Such a presence of alkali species prior to metal particle formation is well known to result in higher metal dispersions. Kelly *et al.* also found a 10-fold decrease in activity of unpromoted Pd/SiO_2 when the metal dispersion

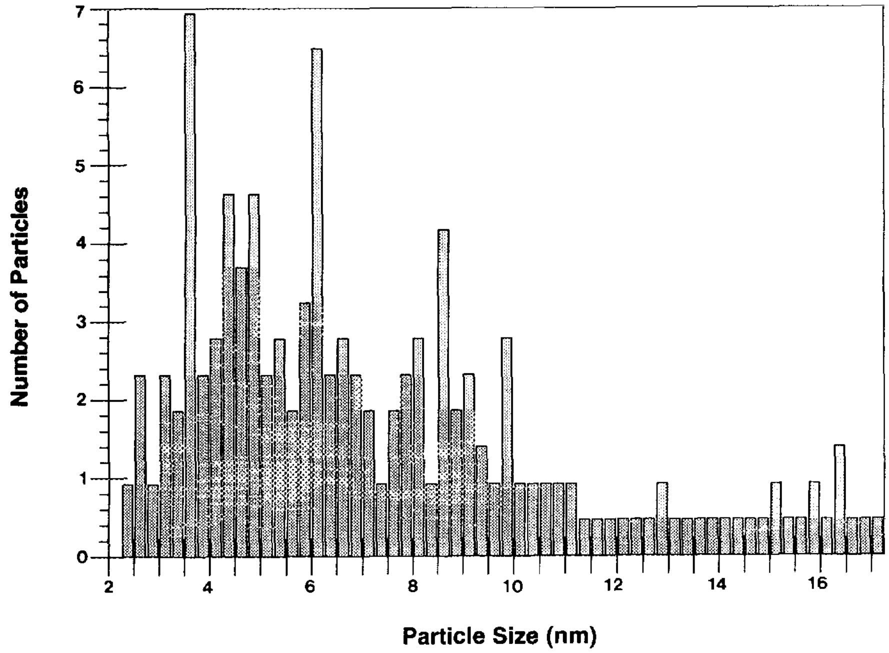

FIG. 5. Pd particle size distribution of Li1/Pd/S2 determined by TEM.

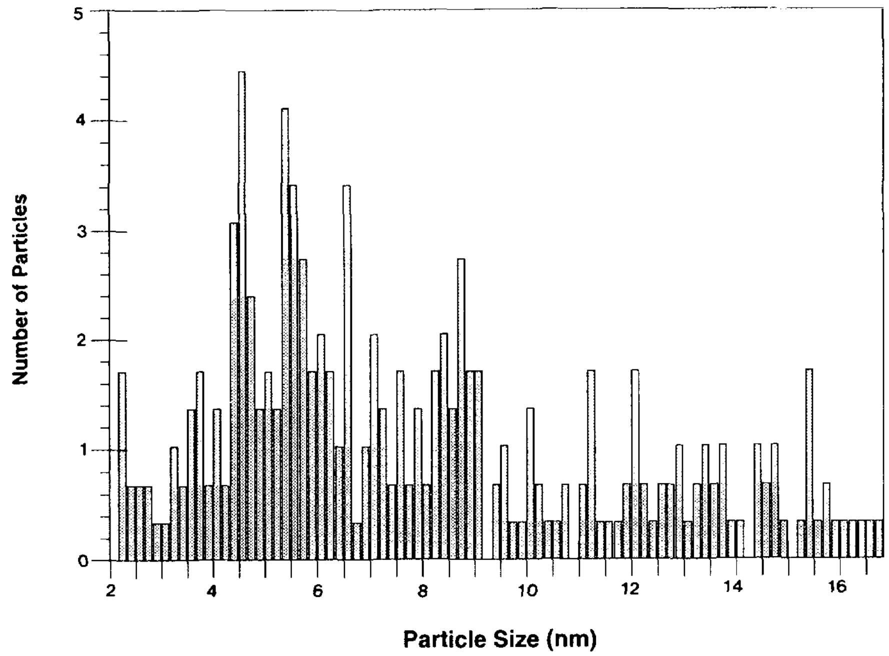

FIG. 6. Pd particle size distribution of Li4/Pd/S2 determined by TEM.

was increased from 25 to 73%. However, the variation in metal dispersion for the series of Li^+-promoted catalysts was not reported. Activity and selectivity of Pd/SiO_2 is also known to be very sensitive to the kind of SiO_2 used as the support (5, 22, 25). The SiO_2 used as the support for Pd by Kelly *et al.* was different from the one used in this study.

Figure 10 summarizes the effect of Li^+ promotion on the rates of the various reactions studied relative to that for the unpromoted base Pd/SiO_2 catalyst. Although a low level of Li^+ promotion (Li/Pd = 1) enhanced the activity for methanol formation, the rates for the other two reactions, ethane hydrogenolysis and isobutylene hydrogenation, decreased significantly. However, higher levels of Li^+ promotion also decreased the activity of the catalyst for methanol synthesis. A decrease in isobutylene hydro-

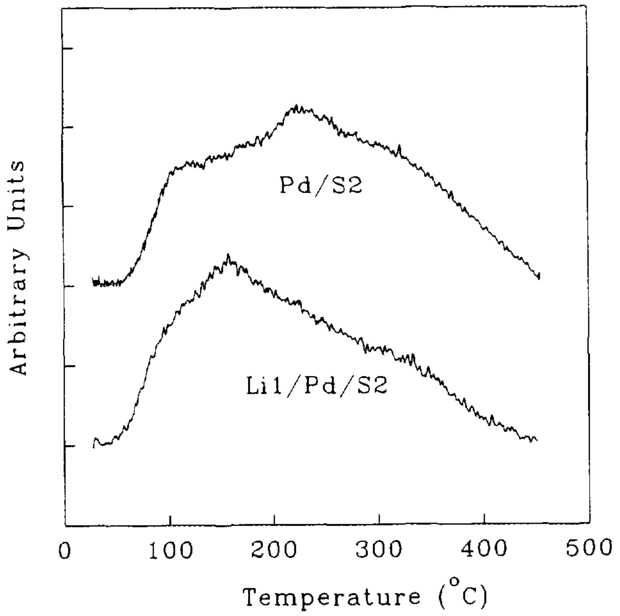

FIG. 7. H_2 TPD profiles for the Pd/S2 and Li1/Pd/S2 catalysts.

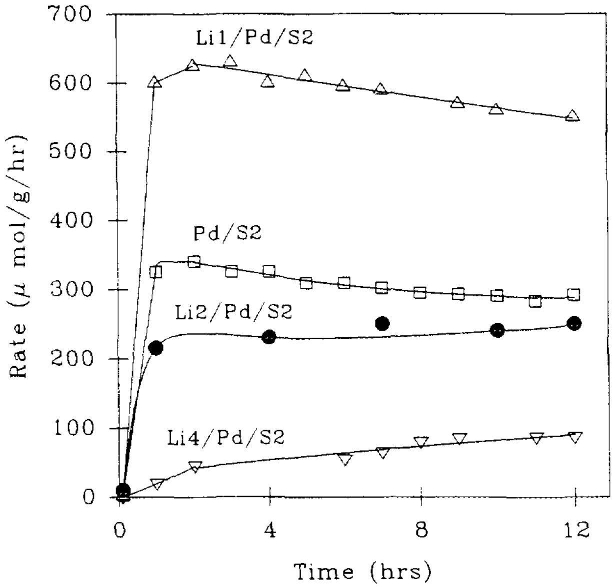

FIG. 8. Rate of methanol formation at 200°C over Li^+-promoted Pd/SiO_2 catalysts.

TABLE 2

CO Hydrogenation Reaction Characteristics on Li^+-Promoted Pd/SiO_2 Catalysts[a,b]

		Selectivities (mol%)						
			Hydrocarbons					
Li/Pd	Rate[c] (μmol/g/h)	MeOH	C_1	C_2	C_3	C_4	C_5	C_6
0	290	96.3	2.8	0.6	0.3	—	—	—
1	573	96.8	1.2	1.0	0.6	0.4	—	—
2	265	91.9	5.1	1.2	0.8	0.5	0.3	0.2
4	93	94.2	4.4	1.2	0.2	—	—	—

[a] $P = 7$ atm, $H_2/CO = 1$, $T = 200°C$.
[b] After 12 h of reaction.
[c] Maximum error ±9%.

genation during its addition to methanol synthesis on Pd/SiO_2 has also been found for high loadings of Li^+ (Li/Pd $\geq$ 4) (20).

A promoter can act on a supported metal catalyst, assuming no change in metal particle size distribution, either by: (a) modification of the surface sites due to the chemical nature of the additive, or (b) blockage of the surface sites by the physical presence of the additive. Physical blockage of the surface active sites by a promoter would have the greatest effect on those reactions requiring large ensembles of surface atoms and should have a lesser effect on those reactions which do not require large ensembles. Examination of Fig. 10 shows that, although some sites were blocked at even the lowest Li^+ loading, as evidenced by the decrease in the rate of ethane hydrogenolysis, the enhancement effect on methanol synthesis due to Li^+ promotion was more significant resulting in an overall increase in its rate of formation. This enhancement could be due to an increase in reaction rate per site due to stabilization of intermediates for the synthesis of methanol as reported earlier in literature (1). However, a recent study in our laboratory of Li^+ promotion of methanol synthesis on Pd using isotopic transient kinetics has indicated that the concentration of the active intermediates leading to methanol increases for this low level of Li^+ promotion (26). Even though the average rate of reaction of these intermediates was found to decrease upon promotion, the overall rate increased because of the significant increase in concentration of intermediates. The decrease in the rate of methanol formation

TABLE 3

Effect of Li^+ Promotion on the Isobutylene Hydrogenation Activity of Pd/SiO_2 in the Presence of CO

Li/Pd	IB conversion[a] (%)	Rate[b,c] (mmol/g/h)	E_{app}[c] (kcal/g mol)
0	17.5	55.5	13
1	11.9	24.8	17
2	5.4	17.2	18
4	1.1	3.3	16

[a] % Conversion of isobutylene.
[b] Steady-state rates: Catalyst wt. = 50 mg, $T = 120°C$, $P = 1.7$ atm, H_2:IB:He:CO = 28:7:63:1 cc/min.
[c] Maximum error ±5%.

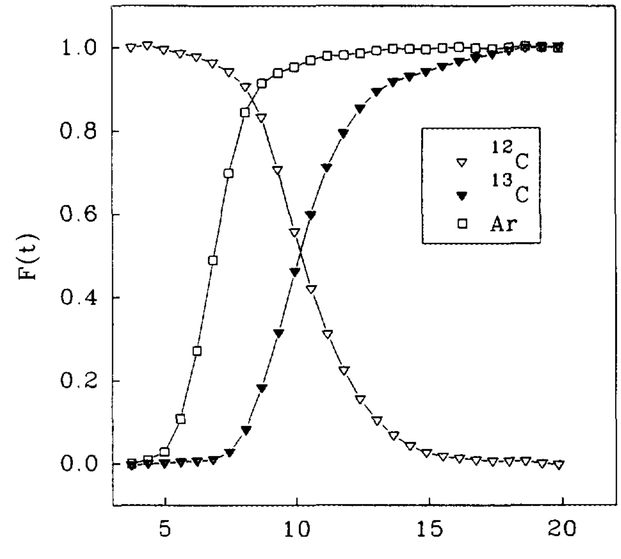

FIG. 9. CO isotopic transients during steady-state isobutylene hydrogenation over Li1/Pd/S2 under standard reaction conditions at 120°C.

TABLE 4

Effect of Li$^+$ Promotion on CO Adsorption on Pd/SiO$_2$

Li/Pd[a] (atomic)	CO$_{irrev}$ chem.[b] (μmol/g)	CO surface coverage[c] (μmol/g)	θ_{CO}[d]
0	105	16	0.15
1	139	80	0.76

[a] Nominal loading.

[b] Static CO chemisorption at 25°C.

[c] Measured by SSITKA during isobutylene hydrogenation in the presence of CO at 120°C.

[d] Based on static CO chemisorption at 25°C on the unpromoted base catalyst.

for higher levels of Li$^+$ promotion (Li/Pd $\geq$ 2) suggests that, at these Li/Pd ratios, blockage of the surface sites due to the physical presence of the promoter dominates any chemical effect, at least for the catalysts prepared by this sequential technique.

For both ethane hydrogenolysis and isobutylene hydrogenation (with CO addition) there was a monotonic decrease in catalytic activity with increasing Li$^+$ loading. This decrease can be attributed in large part to metal site blockage by the promoter. However, the similarity in behavior for the two distinctly different kinds of reactions, one of which is very structure sensitive (ethane hydrogenolysis) and the other relatively structure insensitive (isobutylene hydrogenation), indicates that site blockage may not be necessarily the only reason for the suppression in the hydrogenation activity. While the curves in Fig. 10 for ethane hydrogenolysis and olefin hydrogenation in the presence of CO appear to overlap, no significant conclusions can be drawn about their exact positions. Rather, it is important to note the similar rapid declines in the relative activities with Li$^+$ loading for both structure sensitive and, normally, insensitive reactions.

TABLE 5

Effect of Li$^+$ Promotion on the Ethane Hydrogenolysis Activity of Pd/SiO$_2$

Li/Pd	Conversion (%)	Rate[a,b] (mmol/g/h)	E_{app}[b] (kcal/g mol)
0	9.9	125	67
1	3.8	48.1	66
2	2.0	25.6	75
4	0.3	3.3	74

[a] Total reaction time = 5 min, Catalyst wt. = 50 mg, T = 370°C, P = 1.7 atm, H_2:C_2H_6:He = 20:0.2:89.8 cc/min.

[b] Maximum error ±5%.

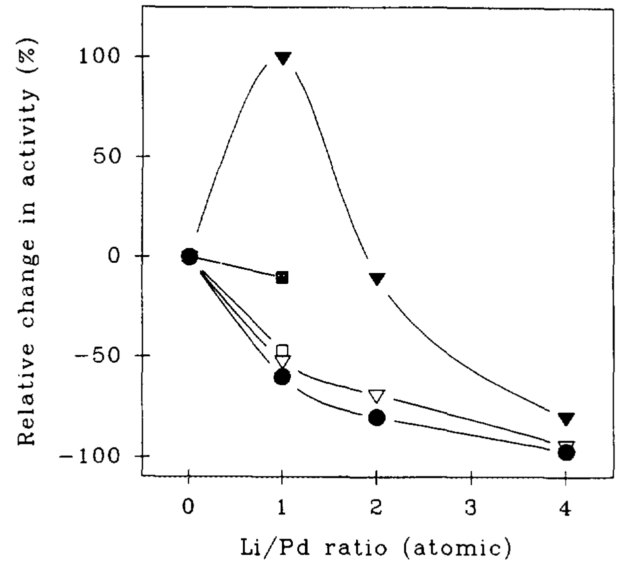

FIG. 10. Effect of Li$^+$ promotion on the rate of various reactions over Pd/SiO$_2$ relative to the unpromoted base catalyst [Li/Pd ratio is the overall nominal value]. ▼, CO hydrogenation (200°C); ●, ethane hydrogenolysis (370°C); ▽, isobutylene hydrogenation (w. CO, 120°C); ■, 1-butene hydrogenation (w/o CO, 20°C) (Ref. 28); □, 1-butene hydrogenation (w. CO, 120°C) (Ref. 28).

In the absence of CO, isobutylene was completely hydrogenated at 120°C. The significant reduction in the hydrogenation activity when CO was present, even at low partial pressures, is known to be due to the competitive adsorption of CO (27). Alkali promoters are known to increase the metal–carbon bond strength of CO adsorbed on group VIII metals (27). An increase in the metal–carbon bond strength means that CO is even more competitive with hydrogen for chemisorption sites, thus decreasing the overall hydrogenation activity of the catalyst by CO site blockage. This site blockage by CO would be higher for the Li$^+$-promoted catalysts relative to the unpromoted catalyst. This is further verified by the CO surface coverages obtained under the isobutylene hydrogenation reaction conditions using steady-state isotopic transient kinetic analysis. These results indicate a significantly enhanced CO coverage (16 vs 80 μmol/g) for the Li1/Pd/S2 catalyst. In a similar study of the effect of alkali promotion of Pd/SiO$_2$ on 1-butene hydrogenation, it was demonstrated that the effect of alkali promotion in suppressing hydrogenation activity was much more profound in the presence of CO than in its absence (28). Results from the same study for the effect of Li$^+$ promotion (Li/Pd = 1) on 1-butene hydrogenation, supporting the argument of enhanced suppression of hydrogenation activity in the presence of CO, are displayed in Fig. 10. Thus, the decrease in hydrogenation activity comparable to that for ethane hydrogenolysis was not only due to Li^+ site blockage but also to enhanced CO adsorption and a decrease in the strength of H_2 adsorption as indicated by H_2 TPD.

Stair (29) has shown that basic promoters also decrease the adsorption strength of unsaturated hydrocarbons on transition metal surfaces. Hence, it is also possible that, as a result of Li^+ promotion, not only hydrogen but also olefin adsorption may have been affected. We have no direct results to permit such a conclusion; however, in the study on the effect of group IA and IIA species promotion on 1-butene hydrogenation on Pd/SiO_2 (28), it was found that a substantial fraction of the 1-butene was isomerized to *cis*- and *trans*-2-butene. Although, as result of promotion, hydrogenation activity of Pd/SiO_2 decreased considerably, the *cis*/*trans* ratio remained essentially unchanged (and not thermodynamically equilibrated), suggesting a possible lack of any significant effect on 1-butene adsorption on Pd/SiO_2.

It is well known that CO and olefins adsorb competitively with H_2 on group VIII metal surfaces. However, the relative ease of adsorption of CO and olefins in the presence of H_2 is not known. During the isotopic switch experiments, the partial pressure of isobutylene was reduced to half of the value used in the hydrogenation experiments ($P_{IB}:P_{CO} = 3.5:1$). For both catalysts (Li/Pd = 0 and 1), the CO surface coverages were found to be very similar, corresponding to saturation surface coverage ($\approx$120–130 μmol/g). On the other hand, for higher partial pressures of isobutylene ($P_{IB}:P_{CO} = 7:1$), some of the surface CO was apparently displaced by isobutylene resulting in surface coverages of CO much lower than saturation coverages. The high CO coverage for $P_{IB}:P_{CO} = 3.5:1$ suggests that CO adsorbs preferentially over isobutylene on the Pd surface. This information also provides indirect evidence that, in an isobutylene, CO, and H_2 mixture, the ease of adsorption of each gas on a Pd surface in decreasing order is CO > isobutylene > H_2.

The activation energies for ethane hydrogenolysis on the unpromoted and Li1/Pd/S2 catalysts were similar to the value reported by Sinfelt (30). They were somewhat higher for the catalysts with Li^+ promotion. By comparing the ethane hydrogenolysis activities of the unpromoted and the promoted catalysts (see Table 5), it is evident that there was a monotonic decrease in activity with increasing Li^+ loading. For the highest level of promotion (Li/Pd = 4), the Pd catalyst had lost almost all of its activity. However, considering the fact that, even for a high loading such as Li/Pd = 2, Li^+ did not completely block the Pd surface for this structure sensitive reaction, it can be assumed that the Li^+ was not uniformly dispersed on the Pd surface. If the promoter had been uniformly distributed on the metal surface, then a complete loss of activity would have been expected for a catalyst with Li/Pd equal to ca. 0.1. It is possible that the Li^+ species preferentially covered some of the metal planes and/or formed islands on the metal surface leading to nonuniform distribution. However, it is obvious that much of the Li^+ was sitting on the surface of the support since the rate was only 80% reduced for Li/Pd = 2. This is in agreement with the conclusions of Rieck and Bell (24) that, for a series of alkali-promoted Pd/SiO_2, only a fraction of the promoter was covering the surface of Pd.

The proposed mechanisms for methanol formation on Pd reported in the literature involve the addition of H atoms to adsorbed CO and subsequent hydrogenation of the CH_xO surface intermediates (31–34). The simultaneous increase in the rate of methanol formation (for Li/Pd = 1) and the decrease in the rate of hydrogenation seen here agrees with those proposed mechanisms where the rate-determining step(s) do not involve the hydrogenation of surface CH_xO species (31–33). These results may also imply that the sites involved in hydrogen adsorption and responsible for hydrogenation are different from the ones involved in CO adsorption and methanol formation. The same has been suggested by Hicks and Bell (32). As mentioned earlier, a recent study from our lab based on steady-state isotopic transient kinetic analysis (26) has found that the increase in the rate of methanol formation upon Li^+ promotion for Li/Pd = 1 is because of an increase in the concentration of surface intermediates leading to methanol, rather than an increase in the intrinsic rate constant for methanol formation. In fact, a measure of the intrinsic reaction rate of the surface intermediates actually decreases, although this may be due to the fact that, as calculated, it includes a possible dependence on hydrogen surface coverage. The decrease in the rate of isobutylene hydrogenation for Li/Pd = 1 agrees well with these findings. This increase in the concentration of surface intermediates as a result of Li^+ promotion is probably only valid for methanol formation and not for other reactions like olefin hydrogenation.

CONCLUSIONS

In order to better understand how Li^+ promotion affects Pd catalysts, three distinct types of reactions were studied over a series of Li^+-promoted Pd/SiO_2 catalysts; CO hydrogenation, isobutylene hydrogenation (a structure insensitive reaction), and ethane hydrogenolysis (a structure sensitive reaction). While one must be cautious in interpretation of the results since catalyst surfaces can be changed to some degree under different reaction conditions, utilization of these three reactions has provided a greater insight into the breath of Li^+ modification of supported Pd surfaces. Based on the experimental results and the preceding discussion, the following conclusions can be drawn:

(i) Li$^+$ promotion significantly enhances the adsorption of CO and decreases the strength of H_2 adsorption on Pd/SiO$_2$.

(ii) Li$^+$ promotion dramatically decreases the olefin hydrogenation (in the presence of CO) and ethane hydrogenolysis activities of Pd/SiO$_2$ relative to the unpromoted catalyst, and the activities decrease monotonically with increasing Li$^+$ loading. The decrease in isobutylene hydrogenation activity results indicate blockage of some of the active Pd sites. However, the similarity in behavior for the two distinctly different kinds of reactions, one of which is very structure sensitive (ethane hydrogenolysis) and the other relatively structure insensitive (olefin hydrogenation), indicates that site blockage may not be necessarily the only reason for the suppression in the hydrogenation activity. As a result of enhanced CO adsorption and weakened H_2 adsorption combined with some active site blockage by the promoter, the results for isobutylene hydrogenation in the presence of CO imitate those of a structure-sensitive reaction.

(iii) Ethane hydrogenolysis results indicate a possible distribution of the promoter between the Pd surface and the surface of the support. It is also highly likely, as shown before for K$^+$ on Ru (15), that Li$^+$ is nonuniformly dispersed on the Pd surface.

(iv) Despite the decrease in the olefin hydrogenation activity of Li$^+$-promoted Pd/SiO$_2$ (Li/Pd = 1) as a result of blockage of some of the active Pd sites by the promoter and perhaps, more especially, by the stronger CO adsorption, low levels of Li$^+$ promotion increase the rate of methanol formation. This increase in the rate of methanol formation can be attributed to an increase in the number of active sites or in the coverage of the active sites by the intermediates (26). For Li$^+$ addition to prereduced Pd/SiO$_2$, higher levels of Li$^+$ promotion (Li/Pd $\geq$ 2) cause a decrease in methanol synthesis activity.

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