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Sol-Gel Synthesis, Characterization and Catalytic Activity of Pd Supported on Silica and Siloxane-Modified Silica

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Palladium supported on silica, Pd-SiO_2, and on siloxane-modified silica, Pd-$(CH_3)_2SiO{\cdot}SiO_2$, were synthesized by sol-gel method. They were characterized by infrared spectroscopy X-ray diffraction spectrometry, magnetic susceptibility and BET surface area measurements. XRD confirmed that metallic Pd on the siloxane-modified silica and on silica supports adopted face centered cubic structure. IR data of the modified system indicated that the intensity of hydroxyl stretching band due to silanol moiety and water was dramatically decreased, and the methyl group is structurally intact. The BET surface area measurements showed that the surface area of the modified silica system is smaller than that of the silica system. In the liquid-phase hydrogenation of phenylacetylene over Pd/SiO_2 and $Pd/(CH_3)_2SiO_2{\cdot}SiO_2$ systems, Pd/SiO_2 catalysts exhibited higher catalytic actiivity than the modified silica catalysts.

INTRODUCTION

Inorganic supports such as silica, alumina and aluminosilicates have been reported in a large number of catalytic reactions[1–5]. Such supports are characterized by the presence of hydroxyl (—OH), hydroxylate (—O^-) and bridging oxygen (—O—) groups in their bulk and surface structures. The hydroxyl functionality has been exploited to anchor organometallic and inorganic catalysts on the support surface[6–12]. Its concentration on the catalyst surface has been shown to play a significant role in various catalytic processes such as hydroformylation, water-gas shift, polymerization and hydrogenation reactions[5,6]. Low concentration of the hydroxyl functionality results in the formation of isolated active sites needed for substrate binding. The number of hydroxyl functionality in the support can be altered by either introducing various alkali metal ions into the catalyst matrix or by methylating the hydroxyl groups[6–10]. Such modifications are reported to alter the number of surface active sites, surface area, porosity and stability of the catalyst.

Polysiloxane {(—SiR_x—O_y—)$_m$, where x = 1 or 2; y = 4 – x; R = methyl or pheny} is an important class of inorganic polymers[13,14]. They are chemically inert,

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thermally stable, exhibit good surface properties and are known to incorporate metal ions[13–15]. In this study, the hydroxyl functionality concentration is controlled by incorporating siloxane [—O—$Si(CH_3)_2$—O—] moiety into the silica support structure. Sol-gel method was adopted to achieve this goal[7–10, 16–18]. Palladium supported on siloxane-modified silica, Pd—$Si(CH_3)_2O{\cdot}SiO_2$, catalysts were prepared by simultaneous hydrolysis and polycondensation of tetraethoxysilane [$Si(OEt)_4$] and diethoxydimethylsilane [$SiMe_2(OEt)_2$] in the presence of varying amounts of $PdCl_2$ salt. Subsequent calcination and reduction allows Pd(0) to be evenly entrapped into the polymeric network.

Liquid-phase hydrogenation of phenylacetylene was taken as a model catalytic reaction to evaluate the catalytic properties of the siloxane-modified versus the silica catalysts. The influence of metal loading, temperature, concentration of the substrate and hydrogen pressure on catalytic activity and selectivity is reported.

EXPERIMENTAL

All chemicals used are of reagent grade and were used without further purification. Tetraethoxysilane, $PdCl_2$, and dichlorodimethylsilane were obtained from Fluka, Ferak Laboral, and Janssen Chemica, respectively.

Infrared (FT-IR) spectra were recorded on a Perkin-Elmer (Spectrum 2000) spectrometer. The unloaded and Pd-loaded catalysts were dried at 70°C before they were compressed into KBr pellets. The magnetic susceptibility measurements were done using a magnetic susceptibility balance (Sherwood Scientific). X-ray diffraction measurements were performed on a Philips (PW, 1729) generator connected to P.M. 8203 recorder in the range of $2\theta = 3°–65°$ using Cu ($K_{\alpha,\lambda} = 1.5418$ Å) source. BET surface area measurements were performed on 0.2000 g samples for all of the unloaded (SiO_2 and $Me_2SiO{\cdot}SiO_2$) and loaded (Pd/SiO_2 and $Pd/Me_2SiO{\cdot}SiO_2$) supports using a single point N_2-adsorption BET apparatus.

Analysis of the reaction mixtures was performed on a Pye-Unicam gas chromatograph with an FID detector, using stainless steel column (1.5 m, 6 mm) packed with 10% PEGA (polyethylene glycol adipate) supported on acid- washed diatomite "C" (mesh, 100–120). Zero grade nitrogen at a flow rate of 30 mL/min was used as a carrier gas. The injector, oven and detector temperatures were maintained at 250, 120 and 300°C, respectively. Data were collected on an electronic integrator (Spectra Physics Data Jet).

Preparation of Unloaded Silica Support: 18.5 mL (82.4 mmol) of tetraethoxysilane was added to a magnetically stirred mixture containing 20 mL distilled water and 10 mL absolute ethanol. The pH of the solution was adjusted with HCl to less than 1 and then refluxed for 4–5 h during which tetraethoxysilane hydrolyzed and polycondensed. The solvent was evaporated on a water bath maintained at 80–85°C. The obtained gel was allowed to stand in air overnight, then dried at 100°C in an oven for a few hours. The solid was powdered using a hand mortar and then calcined.

Preparation of Pd supported on Silica: A stock solution of $PdCl_2$ was

prepared by dissolving 1.5110 g (8.52 mmol) of the palladium salt in 500 mL HCl/distilled water. For the preparation of 5 g of the 1% Pd/SiO_2 catalyst, 27.60 mL (0.470 mmol $PdCl_2$) of the above solution was mixed with an equal volume of absolute ethanol. The pH of this solution was then adjusted to less than 1 with HCl. Then, 18.5 mL (82.4 mmol) of tetraethoxysilane was added dropwise. The magnetically stirred solution was heated to reflux for 4–5 h. The solvent was evaporated on a water bath until a gel was formed. It was allowed to stand overnight in air and then oven-dried at 100°C for several hours. The obtained solid ($PdCl_2$ supported on silica) was powdered using a hand mortar and then subjected to calcination and reduction. Similarly, 0.05%, 0.1%, 0.5% and 5% samples were prepared by taking appropriate amounts of $PdCl_2$(aq.) solution.

Preparation of Unloaded Siloxane-Modified Silica: 8.1 mL (66.8 mmol) of dichlorodimethylsilane was added to a magnetically stirred solution of 18.5 mL (82.4 mmol) tetraethoxysilane in 25 mL absolute ethanol. Immediately the dichloro-derivative reacts with ethanol forming diethoxydimethylsilane. The reaction mixture was warmed on a water bath maintaned at 70°C for 2–3 h during which simultaneous hydrolysis and polycondensation of diethoxydimethylsilane and tetraethoxysilane derivatives took place by absorbing moisture from air. Ethanol was evaporated and the formed gel was left to stand overnight in air. 25 mL of 95% ethanol was added and warmed for 2 h after which the solvent was evaporated to dryness. The siloxane-silica network was dried at 80–85°C for few hours. The unloaded support was powdered and then calcined.

Preparation of Pd-Supported Siloxane-Modified Silica: To prepare 10 g of the 1% Pd/modified-SiO_2 catalyst, 0.17 g (0.958 mmol) of $PdCl_2$ was suspended in 25 mL absolute ethanol. The magnetically stirred suspension was warmed for 30 min. 18.5 mL (82.4 mmol) of tetraethoxysilane followed by 8.1 mL (66.8 mmol) of dichlorodimethylsilane was added dropwise and the reaction was warmed at 70°C for 2–3 h. As hydrolysis and polycondensation proceeds, the solution becomes colloidal in which $PdCl_2$ salt is unformly dispersed. Ethanol was then evaporated and the formed gel was left to stand overnight in air. 25 mL of 95% ethanol was added to the gel and warmed for 2–3 h during which hydrolysis and polycondensation processes were completed. The solvent was removed and the gel was dried at 80–85°C for a few hours. The solid was powdered and then subjected to calcination and reduction. Analogous procedures were used to prepare 0.1%, 0.5% and 5% Pd catalysts.

Calcination and Reduction: Calcination was carried out in a glass fixed-bed flow reactor. The catalyst was placed in the reactor over which oxygen gas was passed at flow rate of 100 mL/min. The temperature was maintained at 450°C for 1 h. Then, helium gas was introduced for 5 min followed by hydrogen gas at a flow rate of 30 mL/min for 4 h at 450°C. At this stage the palladium salt was reduced to the metallic state. The reactor was cooled to room temperature under helium atmosphere. Catalysts were activated before use by heating at 450°C, under hydrogen atmosphere, for 1 h, and then cooled to room temperature.

Liquid-Phase Hydrogenation of Phenylacetylene: 100 mL samples of

phenylacetylene in cyclohexane of different concentrations (0.092, 0.276, 0.552, 0.828 or 1.656 M) were hydrogenated over 0.5 g catalyst samples of different metal loadings. These reactions were performed under various conditions of temperature (30, 40, 50 and 60°C) and hydrogen pressure (20, 30, 40 and 60 psi) in a stainless steel Parr hydrogenator (Parr-4842) with a Watlow-945 controllor. The reaction progress was monitored by taking *ca.* 0.5 mL samples at 10 min. intervals for G.C. analysis.

RESULTS AND DISCUSSION

Synthesis of Pd-SiO_2 and Pd-$Me_2SiO{\cdot}SiO_2$ Catalysts: All catalysts and supports were prepared by sol gel method. This method was adopted for the preparation of several Ru, Pt and Pd catalysts[7-10]. To ensure high dispersion of Pd into the support, $PdCl_2$ was added to the reaction mixture before or during the hydrolysis step, This produces strong interaction between the $PdCl_2$ precursor and the hydroxyl groups of the silanols[7]. Extensive Pd-silanol interaction occurs in the silica system, whereas in the siloxane-silica system it occurs to a much lower extent. Moreover, the dispersion of metallic Pd occurs to a larger extent into the silica support compared to the siloxane-modified silica. Lopez and coworkers[7] studied such interaction by UV-visible and IR spectroscopy and concluded that the interaction between silica gel and palladium precursor has an important effect on the specific area of the catalyst.

Infrared Spectroscopy: FT-IR spectral data of the unloaded sol-gel SiO_2 and $Me_2SiO{\cdot}SiO_2$ supports, and all Pd-containing catalysts are recorded in the 4000–400 cm^{-1} range (Table-1). Characteristic strong and broad bands centered at 3500 cm^{-1} were observed. They are attributed to the stretching frequency of bonded and free hydroxyl groups (ν(O—H)) of silanol and water. Bands in the 1650 cm^{-1} region attributed to occluded water of the gel were also observed. The peaks at 1080, 960 and 800 cm^{-1} regions are assigned to antisymmetric stretching of Si—O—Si ($\nu(Si—O—Si)_{asym}$), silanol stretching (ν(Si—OH)) and symmetric stretching frequencies of Si—O—Si ($\nu(Si—O—Si)_{sym}$), respectively. Similar IR bands were also observed for siloxane-silica system. The silanol stretching bands shift to higher frequencies in the modified system. Additional bands due to stretching frequencies of C—H and Si—C appeared for the modified system at 2900 cm^{-1} and 850 cm^{-1} regions, respectively. The presence of C—H and Si—C stretching frequencies in siloxane-modified support and catalysts clearly suggests that calcination and reduction processes did not eliminate the methyl group of the siloxane moiety. Thus Si—CH_3 moiety is a predominant structural feature of the loaded and unloaded siloxane-silica support. Consequently, the number of hydroxyl groups available on the support surface decrease. The low polar character of the methyl group reduces the water content in the system. This is also evident from the low intensity broad features in the 3500 cm^{-1} region due to the stretching frequency of O—H group.

TABLE-1
FT-INFRARED SPECTRAL DATA (cm^{-1}) FOR Pd/SiO_2 AND $Pd/Me_2SiO{\cdot}SiO_2$ CATALYSTS

Catalyst	ν(OH)	ν(Si—O—Si) (asym)	ν(Si—OH)	ν(Si—O—Si) (sym)	ν(Si—C)	δ(Si—OH)
(A)						
SiO_2	3476 s, br	1086 vs	962 m	800 m	a	462 s
0.1% Pd/SiO_2	3515 s, br	1083 vs	965 m	796 m	a	457 s
0.5% Pd/SiO_2	3592 s, br	1081 vs	960 m	800 m	a	452 s
1% Pd/SiO_2	3563 s, br	1080 vs	944 m	805 m	a	447 s
5% Pd/SiO_2	3475 s, br	1086 vs	962 m	800 m	a	457 s
(B)						
$Me_2SiO{\cdot}SiO_2$ [b]	3459 w, br	1096 vs	1042 s	811 s	852 s	441 s
0.5% $Pd/Me_2SiO{\cdot}SiO_2$	3459 w, br	1102 vs	1048 s	805 s	850 s	432 s
1% $Pd/Me_2SiO{\cdot}SiO_2$	3459 w, br	1095 vs	1052 s	805 s	849 s	437 s
5% $Pd/Me_2SiO{\cdot}SiO_2$	3459 w, br	1081 vs br	–	805 s	860 s	447 s

[a]Absent

[b]C—H stretching frequencies in 2900 cm^{-1} region are observed.

Infrared spectroscopy provides a direct evidence for the support hydroxyl groups-metal interaction (Si—OH····Pd) on the support surface[7]. The position of the band at 460 cm^{-1} region due to silanol moiety shifts to lower frequency upon Pd/—OH interaction. This shift increases as metal loading increases. However, the Pd-hydroxyl group interaction has decreased for the 5% metal loading due to increased metal clustering.

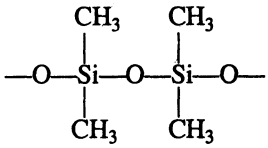
BET Surface Area Measurements: BET surface area data obtained for both catalytic systems are shown in Table-2. In general, the BET surface area of the siloxane-silica system is less than that obtained for the silica system. This is evident for the unloaded support where the surface area of the former system was 165 m^2/g whereas that of the latter was 270 m^2/g. A similar trend was also observed for the Pd-loaded systems where the surface area ranged from 290–500 m^2/g for the siloxane-silica system and 680–900 m^2/g for the silica system. The presence of two methyl groups in the modified system limits the crosslinking to two sites, which in turn decreases the porosity. However, the tetraethoxysilane has four sites available for hydrolysis and polycondensation (crosslinking) which has led to an increase in porosity.

In both systems Pd loading caused an increase in the porosity of the support and hence in the BET surface area. This observation suggests that the metal is incorporated into the framework structure of the support. Moreover, the total surface area decreases as metal loading increases due to metal clustering. It is important to note that the effect of Pd-loading on the surface area of the modified system was irregular and hence the presence of methyl group caused irregular metal clustering.

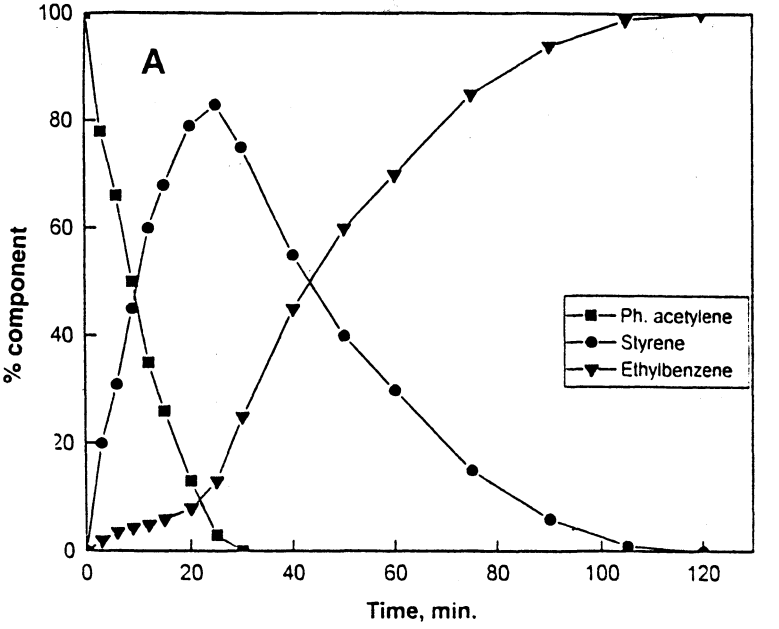
X-ray Diffraction Analysis: X-ray diffraction analysis was carried on 5% Pd supported on silica, 5% Pd supported on siloxane-modified silica and the corresponding unloaded supports. The broad peaks for the support materials indicate that both supports are amorphous. Palladium on both supports exhibits two sharp diffraction peaks located at $2\theta = 21.4°$ and 27.8°. These two peaks are characteristic of face-centered cubic (FCC) Pd(0) assigned to (111) and (210) planes[7]. Comparison between the peak position and width in both systems shows that Pd(0) particle size is practically the same.

Magnetic Susceptibility Measurements: Magnetic susceptibility measurements performed on all samples showed that all catalysts and unloaded supports are diamagnetic, and thus Pd is present in the metallic state[19].

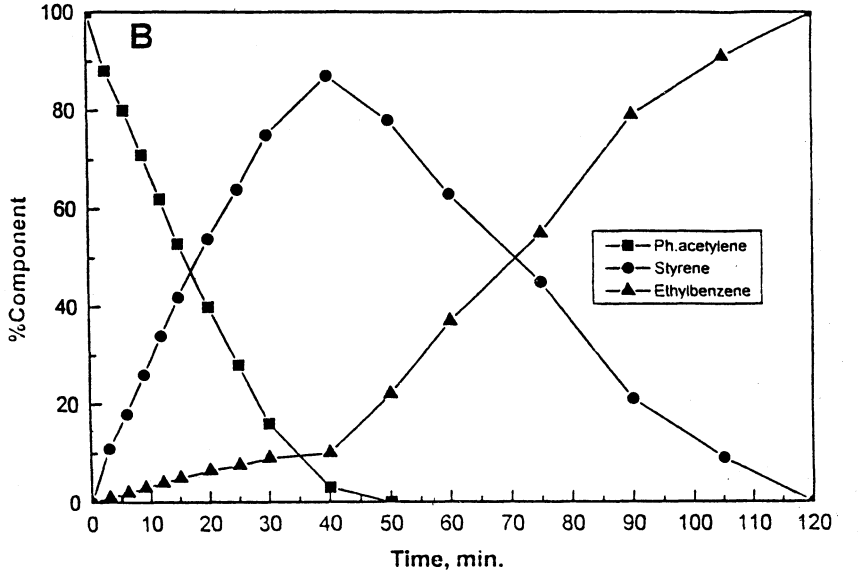
Structure: The detailed structure of the Pd-siloxane silica catalysts is not known. However, information gathered from BET surface area measurements, infrared, XRD and magnetic measurements shows that it is undoubtedly porous metalllic Pd(0) with a FCC structure, and that the methyl groups are structurally intact. The major structural features of the modified support are the decrease in the hydroxyl groups concentration. This decreases the possibility of having *vicinal* hydroxyl groups and consequently the active sites (binding and catalytic) are isolated. The low concentration of hydroxyl groups on the support surface results in low dispersion of Pd(0) and therefore more metal clustering. Moreover, the presence of hydrophobic methyl groups on the surface of the catalyst support weakens its interaction with water and consequently its sorption ability towards water diminishes.



Catalytic Activity and Selectivity: The catalytic data obtained for the liquid-phase hydrogenation of phenylacetylene over Pd-supported on silica and siloxane-silica are reported in Tables-2 and 3. The hydrogenation reaction was found to be zero and first order with respect to phenylacetylene and hydrogen, respectively. All catalysts have shown two-step hydrogenation behaviour when phenylacetylene is first converted to styrene and consequently to ethylbenzene (Fig. 1). Such observation is consistent with the reported catalytic behaviour of metallic Pd[19]. The dependence of catalytic activity and selectivity, and the activation energy, E_a, on the nature of the support and on the metal loading are obvious (Table-2 and Fig. 2). Pd-siloxane-silica catalysts show lower activity than Pd-silica catalysts. The higher E_a and lower catalytic activity for the Pd-siloxane-silica catalysts clearly indicate that hydroxyl groups on the support surface play a considerable role in the catalytic process. These results are in agreement with the observation of Collin *et al.*[20] for the olefin polymerization catalyzed by metallocene on hydroxylated, partially and completely dehydroxylated alumina and silica. However, the selectivity is slightly affected by the nature of the support.



A. The hydrogenation profile of phenylaceteylene over 0.5% Pd/SiO_2



B. The hydrogenation profile of phenylaceteylene over 0.5% Pd/modified SiO_2

Fig. 1 Typical profile of liquid-phase hydrogenation reaction of phenylacetylene (0.276 M, 30°C, 50 psi hydrogen pressure) over 0.5% Pd/SiO_2 (A) and 0.5% $Pd/Me_2SiO{\cdot}SiO_2$ (B).

TABLE-2
RATE OF LIQUID-PHASE HYDROGENATION REACTION OF 0.276 M PHENYLACETYLENE AT 30°C AND 50 psi HYDROGEN PRESSURE OVER Pd/SiO_2 (A) AND $Pd/Me_2SiO{\cdot}SiO_2$ (B) CATALYSTS[a]

Catalyst	BET (m^2/g)[b]	Activity[b]	Selectivity[c]	E_a[d]
(A) SiO_2	270	–	–	–
0.1% Pd/SiO_2	900	1.16×10^{-2}	85	18.22
0.5% Pd/SiO_2	836	3.42×10^{-2}	82	12.17
1.0% Pd/SiO_2	778	1.02×10^{-1}	80	11.22
5.0% Pd/SiO_2	680	2.07×10^{-1}	79	11.00
(B) $Me_2SiO{\cdot}SiO_2$	165	–	–	–
0.1% $Pd/Me_2SiO{\cdot}SiO_2$	470	e	e	e
0.5% $Pd/Me_2SiO{\cdot}SiO_2$	500	1.64×10^{-2}	88	27.36
1.0% $Pd/Me_2SiO{\cdot}SiO_2$	290	2.01×10^{-2}	80	29.90
5.0% $Pd/Me_2SiO{\cdot}SiO_2$	455	1.05×10^{-1}	63	11.70

[a]Reaction rates in M/min were obtained from [phenylacetylene] *vs.* time plots.
[b]The catalyst activity was calculated as rate per gram catalyst (mol L^{-1} min^{-1} g^{-1})
[c]The catalyst selectivity is calculated as (% styrene/% conversion) × 100% at the time where [phenylacetylene] first becomes zero, % conversion is the sum of % styrene and % ethylbenzene.
[d]Energy of activation of kJ/mole as obtained from ln k *vs.* 1/T Arrhenius plots.
[e]Relatively inactive.

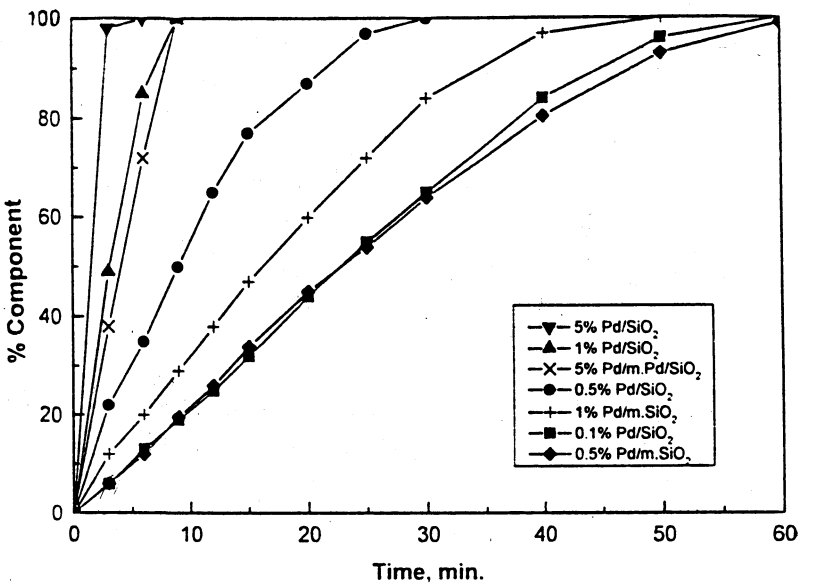


Fig. 2 % Conversion for the liquid-phase hydrogenation reaction of 0.267 M phenylacetylene in cyclohexane over 0.1%, 0.5%, 1% and 5% Pd/SiO_2 and 0.5%, 1% and 5% $Pd/Me_2SiO{\cdot}SiO_2$ at 30°C and 50 psi hydrogen pressure.

The catalytic activity of both systems increases with increasing hydrogen pressure (Table-3). However, the half-hydrogenation selectivity slightly declines with increasing hydrogen pressure. This increase in activity and decline in selectivity is due to the fact that hydrogen becomes more available and complete hydrogenation becomes more feasible[21]. It is noteworthy that the Pd-siloxane-silica system is generally much less selective than the silica system (Table-2 and 3). The effect of temperature on the catalytic properties was also examined. It is evident from the catalytic data that activity increases and selectivity decreases as a function of temperature for both catalytic systems (Table-3).

Conclusions

Simultaneous hydrolysis and polycondensation of a mixture of $Si(OEt)_4$ and $Me_2Si(OEt)_2$ in the presence of Pd salt provide a controlled route to structurally isolated hydroxyl groups and ultimately to isolated Pd(0) catalytic sites. The porosity, structure and concentration of the hydroxyl groups on the catalyst surface can be controlled by appropriate selection of $Si(OEt)_4/Me_2Si(OEt)_2$ ratio. This type of modification can also be tuned to involve the surface only or both the surface and bulk of the catalyst support. The surface can be modified by reaction of $Me_2Si(OEt)_2$ with preformed Pd-SiO_2 catalyst whereas the latter can be done using varying amounts of $Me_2Si(OEt)_2$ and $Si(OEt)_4$.

TABLE-3
LIQUID-PHASE HYDROGENATION REACTION OF PHENYLACETYLENE OVER 5% Pd/SiO_2 (A) AND 5% $Pd/Me_2SiO{\cdot}SiO_2$ (B) AT DIFFERENT TEMPERATURES AND HYDROGEN PRESSURES[a]

H_2	Pressure (psi)[b]	Activity[c]	Selectivity[d] (%)		Temperature (°C)[e]	Activity[c]	Selectivity[d] (%)
(A)	20	4.46×10^{-2}	95	(A)	30	0.117	92
	30	6.74×10^{-2}	94		40	0.144	89
	40	9.72×10^{-2}	93		50	0.173	87
	50	1.17×10^{-1}	92		60	0.190	85
	60	1.24×10^{-1}	91				
(B)	20	3.7×10^{-2}	79	(B)	30	0.096	75
	30	6.4×10^{-2}	77		40	0.106	72
	40	8.4×10^{-2}	77		50	0.124	70
	50	9.6×10^{-2}	75		60	0.147	68
	60	1.08×10^{-1}	72				

[a][phenylacetylene] = 1.656 M.
[b]Reaction temperature = 30°C.
[c]The catalyst activity is expressed as rate of conversion of phenylacetylene per minute per gram catalyst (mol L^{-1} min^{-1} g^{-1}).
[d]The catalyst selectivity is calculated as (% sytrene/% conversion) × 100% at the time where [phenylacetylene] first becomes zero, % conversion is the sum of % styrene and % ethylbenzene.
[e]Hydrogen pressure = 50 psi.

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REFERENCES

1. G.C. Bond, Heterogeneous Catalysis and Appications, Oxford University Press, New York (1987).
2. Y.I. Yermakov and V. Likholobov, Homogeneous and Heterogeneous Catalysis, VNU Science Press, Utrecht, The Netherlands (1987).
3. Y. Iwazawa and B.C. Gates, *Chemtech.*, **19,** 173 (1989).
4. K. Soga and M. Kaminaka, *Makromol. Chem.*, **194,** 1745 (1993).
5. R.K. Grasselli and J.F. Brazdil (Eds.), Solid State Chemistry in Catalysis, ACS Symposium Series, 279, American Chemical Society (1985).
6. T. Marks, *Acc. Chem. Res.*, **25,** 57 (1992).
7. T. Lopez, M. Asomoza, P. Bosch, E. Garcia-Figueroa and R. Gomez, *J. Catal.*, **138,** 463 (1992).
8. T. Lopez, A. Lopez Gaona and R. Gomez, *J. Non-Cryst. Solids*, **110,** 170 (1989).
9. T. Lopez, A. Romero and R. Gomez, *J. Non-Cryst. Solids*, **127,** 105 (1991).
10. T. Lopez, L. Herrera, R. Gomez, W. Zou, K. Robinson and R.D. Gonzalez, *J. Catal.*, **136,** 621 (1992).
11. P.G. Harrison, *J. Organomet. Chem.*, **542,** 141 (1997).
12. Yu.T. Struchkov and S.V. Lindeman, *J. Organomet. Chem.*, **448,** 9 (1995).
13. R. Murugavel, A. Voigt, U. Walawalker and H. Roesky, *Chem. Rev.*, **96,** 2205 (1996).
14. R. Murugavel, V. Chandrasekhar and H. Roesky, *Acc. Chem. Res.*, **29,** 183 (1996).
15. I.E. Sheat, C.E. Garraher (Jr.), C.U. Pittman, M. Zelddin and B. Currel, Inorganic and Metal Containing Polymeric Materials, Plenum Press, New York (1990).
16. D. Avnir, *Acc. Chem. Rev.*, **28,** 328 (1995).
17. C.J. Brinker, D.E. Clark and D.R. Ulrich (Eds.), Better Ceramics Through Chemistry, III, *Material Research Society Symposium Proceedings*, **121** (1988).
18. L.H. Larry and K.W. Jon, *Chem. Rev.*, **90,** 33 (1990).
19. S.D. Jackson and L.A. Shaow, *Appl. Catal. Letters*, **134,** 91 (1996).
20. S. Collins, W.M. Kelly and D.A. Holden, *Macromolecules*, **25,** 1780 (1992).
21. W. Zou and R.D. Gonzalaez, *J. Catal.*, **133,** 202 (1992).

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