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Partial hydrogenation of 1,3-cyclooctadiene catalyzed by palladium-complex catalysts immobilized on silica

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Abstract

Silica-immobilized Pd-complex catalyst was prepared and applied to the hydrogenation of 1,3-cyclooctadiene (1,3-COD). The characterization of catalyst was conducted by EA, ICP-AES, TG, differential TG and XPS analyses. The result revealed that Pd-complexes were successfully immobilized on the silica support. The resulting catalyst was found to be more active and selective than the commercial Pd/C catalyst and the unsupported Pd-complex catalysts for the partial hydrogenation of 1,3-COD to cyclootene (COE). The introduction of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) ligand to Pd-complex gave rise to a considerable increase of 1,3-COD conversion with the COE selectivity of higher than 99 mol%. Such an excellent catalytic performance can be attributed to electronic and geometric effects caused by the interaction between tmeda ligand and Pd atoms in the silica-immobilized Pd-complex catalyst.

Keywords: Immobilization; Pd-complex catalysts; Partial hydrogenation; 1,3-Cyclooctadiene; *N*,*N*,*N*′,*N*′-tetramethylethylenediamine

1. Introduction

Transition metal complexes have been widely used as catalysts for homogeneous and heterogeneous hydrogenation reactions. It was reported that higher activity and selectivity could be attained with these catalysts than with the conventional ones. In addition, metal complex-based catalysts were shown to be active under mild reaction conditions [1].

Among various hydrogenation reactions, much attention has been directed to the selective hydrogenation of olefins [2–4], especially to the partial hydrogenation of cyclodienes that leads to the formation of natural products such as biologically active compounds [5]. Hence, a large number of heterogeneous catalysts have been applied to this reaction, such as Pd/C [6], Pd/C_{60} [7] and bimetals (Pd–Pb and Pd–Cu) supported on different solids [8,9]. On the other hand, several authors have reported alternative catalysts operated under homogeneous conditions, mainly complexes of transition metals such as Pd [10], Rh [11] and Ru [12]. These homogeneous noble metal complex catalysts generally showed higher selectivity compared to the supported ones. However, the former have significant shortcomings because of their inherent homogeneous nature; e.g. expensive transition metals and ligands should be recovered by careful and costly purification of the solutions obtained after reaction [13].

In order to overcome such limitations, much effort has been devoted to the design of effective catalysts or to bridging the gap between homogeneous and heterogeneous catalyses by the variation of application phase, i.e. “heterogenized”, “immobilized”, or “anchored” catalysis [14]. In recent years, Richmond et al. [15] reported that mononuclear methylpalladium complexes immobilized on silica were found to be more active for the cyclization of aminoalkynes than their mononuclear analogues. Furthermore, Pd-aminosilane complexes grafted on MCM-41 showed a high reaction rate and a high regioselectivity for the hydrogenation of dienes with hydroxyl groups [16]. On the other hand, the palladium tetra-coordinated complex supported on alumina proved to be more active and selective than unsupported complex and Lindlar catalyst (Pd/$CaCO_3$ modified with $Pb(OAc)_2$). This feature could be attributed to electronic and geometric effects involved with a possible interaction between coordinated species and support [1,17–19].

In the present work we have prepared Pd-complexes immobilized on silica and applied the resulting catalysts to the partial hydrogenation of 1,3-cyclooctadiene (1,3-COD). The resulting catalysts have been characterized by EA,

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ICP-AES, TGA and XPS analyses. In addition, the effect of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) ligand, which was added to Pd-complexes immobilized on silica, has been investigated on the basis of XPS analysis and catalytic activities for the partial hydrogenation of 1,3-COD.

2. Experimental

2.1. Catalyst preparation

Commercial catalyst Pd/C (1 wt.% Pd) was supplied by Aldrich. Unsupported Pd-complex catalysts were synthesized by the methods described in the literature. These are (tmeda)$PdCl_2$ [20], $(tmeda)_2Pd$ [21] and (tmeda)Pd$[APSi(OEt)_3]_2$ [22], where AP represents “aminopropyl”.

Silica-supported Pd-complex catalysts were prepared according to the following steps: (1) grafting of aminopropyl linker on silica support; (2) anchoring of Pd precursor to the aminopropyl silica; (3) introduction of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) ligand to the Pd-complex immobilized on silica. The overall synthesis procedure is depicted in Fig. 1.

In a typical procedure, 3-aminopropyltriethoxysilane ($APSi(OEt)_3$; 1.5 ml) was grafted on 500 mg of silica under reflux of xylene (30 ml) in the Schlenk apparatus. The mixture was refluxed for 12 h, filtered and washed with xylene several times to ensure that no unreacted species remain. The white solid product ($APSi/SiO_2$) was dried in vacuo at 353 K for 24 h. Then, Pd precursor (K_2PdCl_4; 0.23 mmol of Pd) was complexed with $APSi/SiO_2$ (500 mg; 0.45 mmol NH_2), followed by stirring the mixture with distilled water (30 ml) under nitrogen for 24 h. The obtained yellow solid ($Pd(APSi)_2/SiO_2$) was filtered, washed with distilled water three times and dried in vacuo. Finally, the coordination of tmeda ligand to this solid was carried out in a manner similar to the preparation of $Pd(APSi)_2/SiO_2$. The resulting product was designated as (tmeda)$Pd(APSi)_2/SiO_2$.

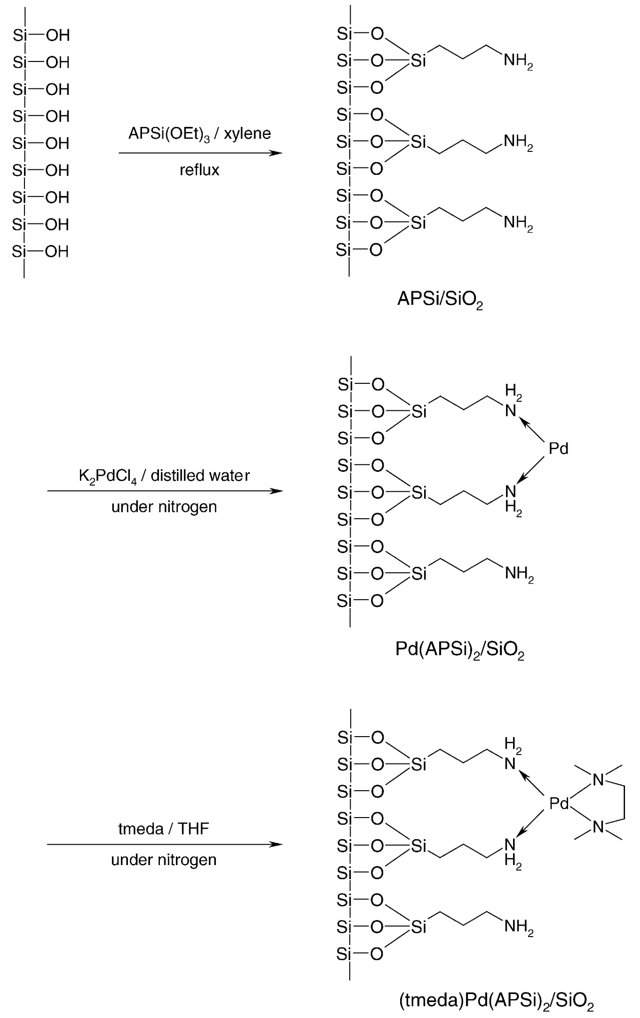

Fig. 1. Schematic diagram for the synthesis procedure of silica-immobilized Pd-complex catalysts.

2.2. Catalyst characterization

The amounts of amine and Pd in the prepared samples were measured with elemental analysis (EA; EA-1110) and ICP-AES (Shimadzu ICPS-1000IV), respectively, as presented in Table 1. Thermogravimetric (TG) measurement was performed on a TGA-2050 in 4% O_2/N_2 flow (40 ml/min) with a heating rate of 10 K/min. Differential TG results were calculated by differentiating the resulting TG curves with respect to temperature.

X-ray photoelectron spectra (XPS) were measured on an ARIESARSC 10MCD 150 by using an Mg Kα anode (1253.6 eV). The samples were mounted on a double-sided adhesive tape and evacuated to ca. 1.33×10^{-3} Pa (1×10^{-5} Torr) at a room temperature in the pretreatment chamber and then transferred to the analyzer chamber maintained at 1.33×10^{-7} Pa (1×10^{-9} Torr). Binding energies were referenced to the C 1s peak at 284.5 eV as an internal standard.

Table 1
Amounts of nitrogen atom and palladium atom characterized by elemental analysis and ICP-AES, respectively

	N atom		Pd atom	
	$Pd(APSi)_2/SiO_2$	(tmeda)$Pd(APSi)_2/SiO_2$	$Pd(APSi)_2/SiO_2$	(tmeda)$Pd(APSi)_2/SiO_2$
Theoretical (mmol/g)	0.94	1.88	0.47	0.47
Experimental (mmol/g)	0.91	1.76	0.37	0.36
Experimental (wt.%)	1.48	2.88	0.5	0.5

2.3. Catalytic hydrogenation

The reactor with 10 mg of the catalyst in ethanol (7 ml) was purged with hydrogen (5 ml/min, 1 atm) for 30 min and then 1 ml of 1,3-COD (1 mmol) in ethanol was added with a micro-syringe. The partial hydrogenation of 1,3-COD was started with magnetic stirring ($t = 0$). Liquid samples of this suspension were taken periodically with a filtering syringe and analyzed by a Varian CP-3380 gas chromatography (GC) equipped with an FID and a Carbowax 20M capillary column. Identification of reaction products was performed by using a mass spectrometer. The direct hydrogenation of cyclooctene (COE) was carried out in a similar manner.

The recovery of catalysts was carried out according to a procedure similar to that reported elsewhere [23]. The catalyst recovered by filtration was washed successively with ethanol and filtered off. After being dried in vacuo, the catalyst was reused three times.

3. Results and discussion

3.1. TGA and differential TGA (DTGA)

Fig. 2(a) shows TG curves of the three samples, APSi/SiO_2, Pd$(APSi)_2/SiO_2$ and (tmeda)Pd$(APSi)_2/SiO_2$, in the temperature range from 30 to 750 °C. There is little difference in the three TG curves observed at temperatures below 150 °C, where the weight loss originates from the removal of volatile hydrocarbons and water [24]. This indicates that Pd-complex catalysts immobilized on SiO_2 may be stable below 100 °C. However, the total weight losses of the three samples are very much different because the aminopropyl linker introduced to catalysts, the tmeda ligand and residues (e.g. aminopropyl and amine), which are not bound to Pd atom, are oxidized in the range of 200–700 °C.

To investigate the oxidation processes of such organics, the TG curves were differentiated with respect to the

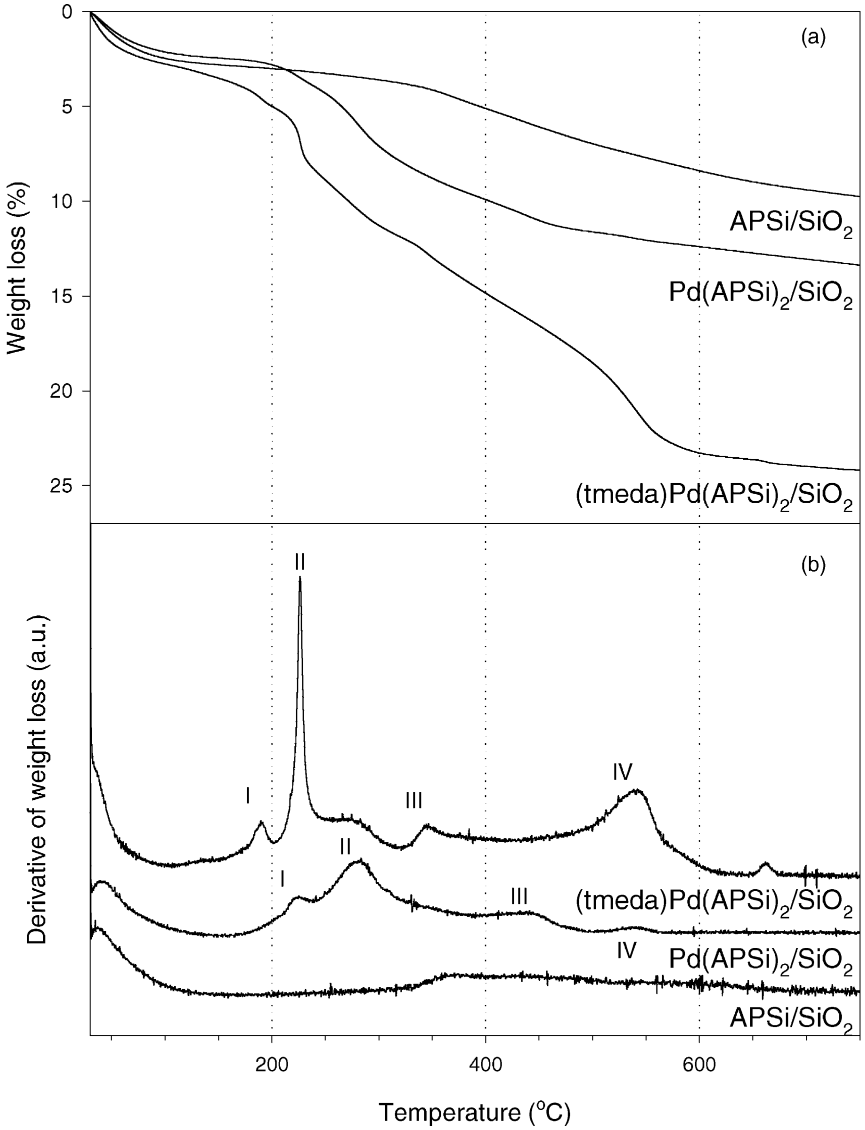

Fig. 2. TG curves (a) and their corresponding differential TG curves (b) of the three samples; APSi/SiO_2, Pd$(APSi)_2/SiO_2$ and (tmeda)Pd$(APSi)_2/SiO_2$.

temperature as shown in Fig. 2(b). From the differential TG curve of (tmeda)Pd$(APSi)_2/SiO_2$ sample, four major peaks are observed in different temperature regions: below 200 °C (I); 200–250 °C (II); 300–400 °C (III); above 500 °C (IV). The peaks I and II indicate the losses of AP groups affected by the anchored Pd. On the basis of the peak positions, the peak I may be considered to represent the loss of AP groups electronically influenced by neighboring palladium metals while the peak II represents the loss of AP groups directly bound to Pd. On the other hand, these peaks are observed at lower temperatures than those for $Pd(APSi)_2/SiO_2$ sample, and this suggests that electron-donating tmeda ligand makes the bond between AP groups and Pd weak [24–26]. In comparison to the differential TG curve of $APSi/SiO_2$, the peak III of (tmeda)Pd$(APSi)_2/SiO_2$ sample may be attributed to the loss of aminopropyl groups and amine of tmeda that are not bound to Pd. The difference in the peak temperatures between the two samples may be caused by the coordination of tmeda on $APSi/SiO_2$. The peak IV observed above 500 °C for (tmeda)Pd$(APSi)_2/SiO_2$ sample may be attributed to the tmeda ligand and residues that are bound to Pd.

3.2. Partial hydrogenation of 1,3-cyclooctadiene

The silica-supported Pd-complex catalyst ($Pd(APSi)_2/SiO_2$)) was applied to the partial hydrogenation of 1,3-COD at 20 °C and the result is shown in Fig. 3. The conversion of 1,3-COD reaches almost 100 mol% with the COE selectivity of about 92 mol% at the reaction time of 40 min. Such a high selectivity would be hardly achievable with the commercial Pd/C catalyst, which produces COE with the selectivity of about 70 mol%. Hence, it is evident that the catalyst prepared with 0.5 wt.% loading of Pd is more active for the partial hydrogenation of 1,3-COD compared to the commercial Pd/C catalyst. The improved catalytic performance can be attributed to the relatively easy accessibility of substrate to Pd metal atoms that are located in the remote position from the silica support (cf. Fig. 1). Similar results were reported for the Pd nanoparticle [27] or for Pt/Pd bimetallic nanoparticle catalysts [28], which can be explained by the efficient chemisorption of electron-rich substrate to the electron-deficient metal clusters.

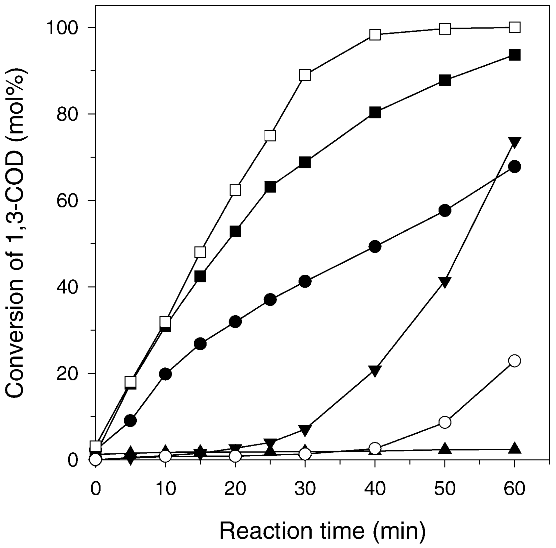

Fig. 3. Catalytic activities obtained for the partial hydrogenation of 1,3-COD over various catalysts; $Pd(APSi)_2/SiO_2$ (□), Pd/C (○), (tmeda)$PdCl_2$ (■), $(tmeda)_2Pd$ (●), (tmeda)Pd$[APSi(OEt)_3]_2$ (π), $Pd(OAc)_2$ (θ).

Fig. 3 shows the catalytic activities obtained from various Pd-complex catalysts. Concerning the conversion of 1,3-COD, all the unsupported catalysts are less active than the $Pd(APSi)_2/SiO_2$ catalyst, except for the (tmeda)$PdCl_2$ catalyst. This indicates that $Pd(APSi)_2/SiO_2$ is more stable and active than its homogeneous analogues.

3.3. Effect of tmeda ligand on the silica-supported Pd-complex catalysts

It was reported that the catalytic activity could be improved by the introduction of another ligand to Pd-complex catalysts [29]. The tmeda ligand was known to be a very particular ligand chelating to Pd, which is ascribed to its steric characteristics, flexibility and electronic properties [30].

As shown in Fig. 4, the addition of tmeda ligand leads to a considerable increase of reaction rate for the partial hydrogenation of 1,3-COD. It was observed that the COE selectivity at the complete conversion of 1,3-COD was higher than 99%. These results may be explained in terms of the optimal balance between adsorption and desorption affinities and/or the ligand effect on the silica-supported Pd-complex catalysts [29,30].

To confirm the high selectivity of immobilized Pd-complex, the desired product COE was directly hydrogenized to cyclooctane (COA) over the three catalysts, Pd/C,

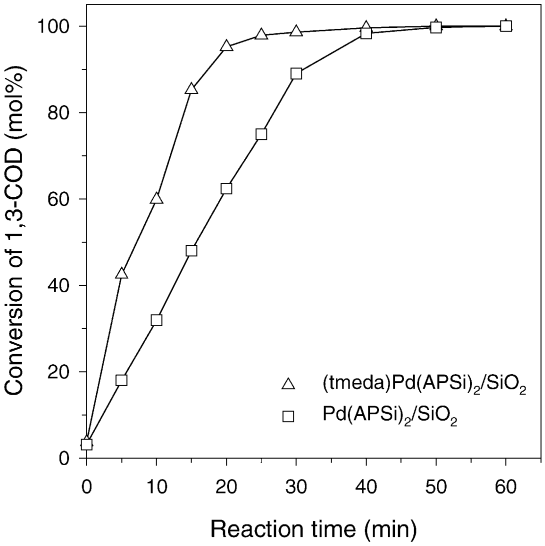

Fig. 4. Effect of the tmeda ligand on the catalytic activity for the partial hydrogenation of 1,3-COD.

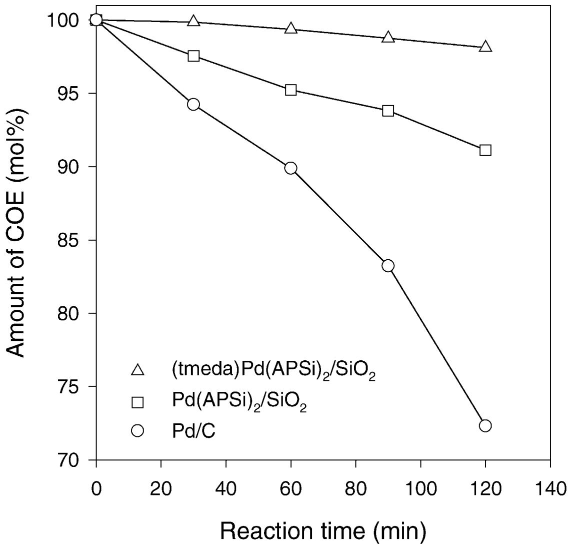

Fig. 5. Reaction results obtained for the hydrogenation of COE on the three catalysts.

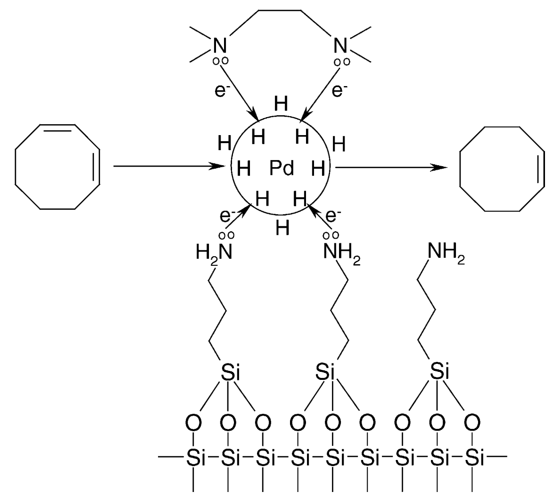

Fig. 6. Reaction mechanism for the partial hydrogenation of 1,3-COD on the catalyst (tmeda)Pd(APSi)$_2$/SiO$_2$.

Pd(APSi)$_2$/SiO$_2$ and (tmeda)Pd(APSi)$_2$/SiO$_2$. As shown in Fig. 5, the hydrogenation rate of COE to COA is very low over (tmeda)Pd(APSi)$_2$/SiO$_2$ and such a low hydrogenation rate may have contributed to the high COE selectivity [$S\,(\%) \cong 100$ up to complete conversion of 1,3-COD]. The hydrogenation rate was also reported to be low in the direct hydrogenation of COE over the pumice-supported palladium catalysts [31]. Accordingly, these results suggest that the tmeda ligand not only suppresses the adsorption of 1,3-COD, which is π-donor substrate, on Pd atom but also facilitates the desorption of COE produced by the hydrogenation of 1,3-COD. It is speculated that the high activity and selectivity of (tmeda)Pd(APSi)$_2$/SiO$_2$ catalyst is brought about by the increased electron density of Pd atom (electronic effect) as well as the increased effect of steric hindrance (geometric effect) by the coordination of tmeda ligand as depicted in Fig. 6.

XPS analysis was carried out to investigate the electronic effect for the hydrogenation of 1,3-COD. Fig. 7 shows the corresponding Pd 3d spectra of the prepared catalysts before and after the partial hydrogenation of 1,3-COD. The Pd 3d$_{5/2}$ BE of Pd(APSi)$_2$/SiO$_2$ and (tmeda)Pd(APSi)$_2$/SiO$_2$ before the partial hydrogenation are 334.8 and 334.2 eV, respectively. The Pd 3d$_{5/2}$ BE of (tmeda)Pd(APSi)$_2$/SiO$_2$ is 0.6 eV lower than that of Pd(APSi)$_2$/SiO$_2$ and this difference was maintained after the reaction. Such a difference in BE was brought about by the coordination of tmeda ligand on Pd [32,33] and made the electron density of the Pd atom increase. This effect should then decrease the adsorption affinity on the electron-rich dienes on the Pd atom and thus makes the desorption of product easier. Consequently, the overall reaction would be controlled by the surface reaction to yield a high catalytic activity. Indeed, a similar electronic effect has been reported by XPS analysis for Pd/SiO$_2$ doped with alkali metal ions, Pd/SiO$_2$ modified with TiO$_2$, and Pd/SiO$_2$ promoted with Nb and Ce oxides [17,34,35].

3.4. Recycling tests

The activity of the immobilized metal complex catalyst may be decreased due to the loss of active metal complexes during the reaction [23,35,36]. In order to see if it can be recycled, the catalyst was recovered by evaporating the reaction mixture in a Schlenk apparatus with a vacuum pump. The recovered catalyst was washed thoroughly with the reaction solvent, ethanol, and dried in vacuo.

As one can observe in Table 2, the conversion of 1,3-COD tended to decrease slightly over the recovered catalyst as the catalyst recycle was repeated. However, the catalytic activity

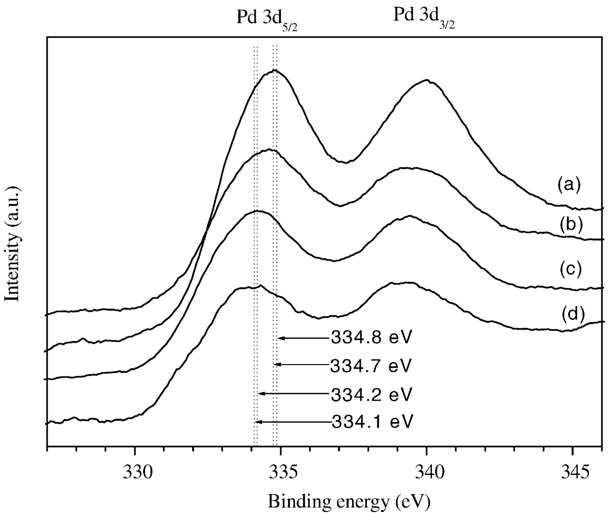

Fig. 7. XPS spectra of Pd 3d in Pd(APSi)$_2$/SiO$_2$ and (tmeda)Pd(APSi)$_2$/SiO$_2$ catalysts before and after the partial hydrogenation of 1,3-COD: (a) Pd(APSi)$_2$/SiO$_2$ (before); (b) Pd(APSi)$_2$/SiO$_2$ (after); (c) (tmeda)Pd(APSi)$_2$/SiO$_2$ (before); (d) (tmeda) Pd(APSi)$_2$/SiO$_2$ (after).

Table 2
Catalytic activities of recycled catalyst for the partial hydrogenation of 1,3-COD

Recycle	Conversion at 30 min (%)
Fresh, (tmeda)Pd$(APSi)_2/SiO_2$	98.5
1	96.8
2	95.9
3	87.9

was easily recovered when additional fresh catalyst was supplemented for the loss during recycling. This indicates that silica-supported Pd-complex catalysts can be reused without apparent loss of catalytic activity. Also, these catalysts were found to be stable under the present reaction conditions because no metal leaching was observed in the course of reaction.

4. Conclusions

Silica-immobilized Pd-complex catalyst was prepared and applied to the partial hydrogenation of 1,3-cyclooctadiene (1,3-COD). The preparation of catalyst was carried out by a simple scheme, i.e. (1) introduction of aminopropylsilane on silica, (2) complexation of Pd with the aminopropylsilane, and (3) coordination of tmeda. The results of characterization of the prepared catalysts supported the stable immobilization of Pd-complex on silica.

The resulting heterogenized Pd-complex catalysts showed higher activity and selectivity than their homogeneous analogues or commercial Pd/C in the partial hydrogenation of 1,3-COD. In particular, the coordination of tmeda on Pd complex results in a remarkable improvement of the catalytic performance. Presumably, the tmeda not only suppresses the adsorption of 1,3-COD on Pd atom but also facilitates desorption of the COE produced by the hydrogenation of 1,3-COD. The electronic influence between the Pd atom and amine ligands is responsible for the promotional effect of the catalytic behavior as confirmed by XPS analysis. The silica-immobilized Pd-complex catalyst can be reused without apparent loss of catalytic activity.

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References

[1] P.C. L'Argentiere, E.A. Cagnola, M.E. Quitoga, D.A. Liprandi, Appl. Catal. A 226 (2002) 253.
[2] P.C. L'Argentiere, E.A. Cagnola, D.A. Liprandi, M.C. Martinez, C.S. Lecea, Appl. Catal. A 172 (1998) 41.
[3] L.F. Liotta, A.M. Venezia, A. Martorana, G. Deganello, J. Catal. 171 (1997) 177.
[4] G. Deganello, D. Duca, L.F. Liotta, A. Martorana, A.M. Venezia, A. Benedetti, G. Fagherazzi, J. Catal. 151 (1995) 125.
[5] J.G. Ulan, W.F. Maier, J. Org. Chem. 52 (1987) 3132.
[6] D. Lennon, R. Marshall, G. Webb, S.D. Jackson, Stud. Surf. Sci. Catal. 130 (2000) 245.
[7] R. Yu, Q. Liu, K.L. Tan, G.Q. Xu, S.C. Ng, T.S. Andy, J. Chem. Soc., Faraday Trans. 93 (1997) 2207.
[8] M.A. Volpe, P. Rodriguez, C.E. Gigola, Catal. Lett. 61 (1999) 27.
[9] L. Guczi, Z. Schay, G. Stefler, L.F. Liotta, G. Deganello, A.M. Venezia, J. Catal. 182 (1999) 456.
[10] J.M. Kerr, C.J. Suckling, Tetrahedron Lett. 29 (1988) 5545.
[11] R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 98 (1976) 2143.
[12] Y. Shvo, I. Goldberg, D. Czerkie, D. Reshef, Z. Stein, Organometallics 16 (1997) 133.
[13] R.A. Sheldon, R.S. Downing, Appl. Catal. A 189 (1999) 163.
[14] C. Coperet, M. Chabanas, R.P. Arroman, J.M. Basset, Angew. Chem. Int. Ed. 42 (2003) 157.
[15] M.K. Richmond, S.L. Scott, H. Alper, J. Am. Chem. Soc. 123 (2001) 10521.
[16] S. Shimazu, N. Baba, N. Ichikuni, T. Uematsu, J. Mol. Catal. A 182/183 (2002) 343.
[17] J.H. Kang, E.W. Shin, W.J. Kim, J.D. Park, S.H. Moon, Catal. Today 63 (2000) 183.
[18] E.W. Shin, C.H. Choi, K.S. Chang, Y.H. Na, S.H. Moon, Catal. Today 44 (1998) 137.
[19] P.C. L'Argentiere, E.A. Cagnola, D.A. Liprandi, M.C. Román-Martinez, C. Salinas-Martinez de Lecea, Appl. Catal. A 172 (1998) 41.
[20] Y.-J. Kim, J.-C. Choi, K. Osakada, J. Organomet. Chem. 491 (1995) 97.
[21] Y.-J. Kim, D.-H. Kim, J.-Y. Lee, S.-W. Lee, J. Organomet. Chem. 538 (1997) 189.
[22] Y.-J. Kim, Y.-S. Kwak, S.-W. Lee, J. Organomet. Chem. 603 (2000) 152.
[23] Y.-M. Chung, H.-K. Rhee, Catal. Lett. 82 (2002) 249.
[24] V.B. Valodkar, G.L. Tembe, M. Ravindranathan, R.N. Ram, H.S. Rama, J. Mol. Catal. A 202 (2003) 47.
[25] P. Sivasamy, M. Meenakshisundaram, C.T. Vijayakumar, J. Anal. Appl. Pyrol. 6869 (2003) 51.
[26] W.J. Kim, E.W. Shin, J.H. Kang, S.H. Moon, Appl. Catal. A 251 (2003) 305.
[27] O.D. Quintero, S. Martinez, Y. Henriquez, L. D'Ornelas, H. Krentzien, J. Osuna, J. Mol. Catal. A 197 (2003) 185.
[28] Y.-M. Chung, H.-K. Rhee, Catal. Lett. 85 (2003) 159.
[29] Y.M. Chung, W.S. Ahn, P.K. Lim, J. Catal. 173 (1998) 210.
[30] G. Sanchez, J.L. Serrano, J. Garcia, G. Lopez, J. Perez, E. Molins, Inorg. Chim. Acta 287 (1999) 37.
[31] G. Deganello, D. Duca, A. Martorana, G. Fagherazzi, J. Catal. 150 (1994) 127.
[32] L.M. Gomez-Sainero, X.L. Seoane, J.L.G. Fierro, A. Arcoya, J. Catal. 209 (2002) 279.
[33] P.C. L'Argentiere, M.G. Canon, N.S. Figoli, Appl. Surf. Sci. 89 (1995) 63.
[34] D.C. Lee, J.H. Kim, W.J. Kim, J.H. Kang, S.H. Moon, Appl. Catal. A 244 (2003) 83.
[35] J. John, M.K. Dalal, R.N. Ram, J. Mol. Catal. A 137 (1999) 183.
[36] F. Benvenuti, C. Carlini, M. Marchionna, A.M.R. Galletti, G. Sbrana, J. Mol. Catal. A 145 (1999) 221.