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Layered double hydroxides supported nano palladium: An efficient catalyst for the chemoselective hydrogenation of olefinic bonds

Lakshmi Kantam M*, Parsharamulu T, Manorama S.V.

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India

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ABSTRACT

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1. Introduction

Chemoselective hydrogenation of olefinic double bonds is an indispensable tool for the synthesis of natural products, pharmaceuticals, and functional materials [1-3]. The most promising method for performing these transformations are by employing transition metals particularly palladium under catalytic conditions using molecular hydrogen. Many of these processes were realized using Pd/C in combination with various additives like pyridines. amines, ammonium acetate, ammonia, and diphenylsulfide that results in the selective reduction of olefinic bond in presence of aromatic halogens [4,5], aromatic carbonyls [4,5], epoxides [6], benzyl [7-10], benzyl esters [11], and N-Cbz protective groups [11]. Selective hydrogenations of substituted γ -amino α , β -unsaturated esters were accomplished without affecting the benzyl ester or benzyl ether functionality using Pd/C in EtOAc in absence of additives [12]. Notably, Felpin and Fouquet has reported the selective hydrogenation of olefins by in situ generated Pd⁰/C catalyst from Pd(OAc)₂ and charcoal in methanol [13].

A chemoselective hydrogenation method was demonstrated by Hirota et al. using finely dispersed palladium catalyst in silk-fibroin [14]. In addition, hydrogenation of olefins was accomplished using Pd nanoparticles in water-in-CO₂ and water-in-oil microemulsion as catalysts [15,16]. Ihm et al. showed the potential application of Pd(II) complexes supported on a modified macroporous polymer bead for the hydrogenation of olefins [17]. Similarly, Zecca et al. used the ion-exchange resins-supported palladium catalyst for the same reaction [18]. Manorama et al. disclosed a promising catalytic protocol for hydrogenation of nitro arenes, azides and olefins employing Pd immobilized on the surface of amine-terminated Fe₃O₄ and NiFe₂O₄ nanoparticles [19]. Dendrimer-encapsulated palladium nanoparticles were also explored for the chemoselective hydrogenation of olefins with modest success [20]. All these reports reveal the important requirement for an improved catalytic system for the chemoselective hydrogenation of olefin in presence of various sensitive functional groups.

Chemoselective hydrogenation of olefinic double bonds in the presence of various functional groups

using layered double hydroxides supported nanopalladium (LDH-Pd⁰) catalyst is described. LDH-Pd⁰

was recovered quantitatively by simple filtration and reused several times with consistent activity and

Recently, we have reported the chemoselective hydrogenation of olefinic bond using a Pd/Mg-La mixed oxide catalyst [21]. In continuation to these studies, herein we report the chemoselective hydrogenation of olefinic double bonds at room temperature with good to excellent yields using heterogeneous LDH-Pd⁰ catalyst (Scheme 1). This protocol tolerates a wide variety of functional group with excellent selectivity. Earlier, our group has reported the synthesis and characterization of layered double hydroxides supported nanopalladium catalyst (LDH-Pd⁰) and its activity in Suzuki, Heck, Sonogashira, and Stille type coupling reactions of chloroarenes [22]. LDHs have received much attention in view of their potential usefulness as materials [23-26], anion exchangers and more importantly as catalysts [27-34]. The LDH consists of alternating cationic $M(II)_{1-x}M(III)_x$ (OH)₂^{x+} and anionic $A^{n-x}H_2O$ layers [35]. The positively charged layers contain edge-shared metal M(II) and M(III) hydroxide octahedra, with charges neutralized by A^{n-} anions located in the interlayer spacing or at the edges of the lamellae. Small hexagonal LDH crystals with

^{*} Corresponding author. Tel.: +91 40 2719 3510; fax: +91 40 2716 0921. *E-mail address:* mlakshmi@iict.res.in (L.K. M).

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 $R = H, Cl, CH_3, OCH_3, NO_2, NH_2$

 R^{1} = H, Ph, COPh, COOH, COH, COOCH₃, CH₂OH, CN

Scheme 1. Chemoselective hydrogenation of olefinic bonds over LDH-Pd⁰ catalyst.

 $Mg_{1-x}Al_x(OH)_2(Cl)_x \cdot zH_2O$ composition were synthesized following the existing procedures (here x = 0.25) [22].

2. Experimental

2.1. General

All the chemicals were purchased from Sigma Aldrich or Alfa Aesar Company and used without further purification. Thin-layer chromatography was performed on Merck-precoated silica gel 60-F254 plates. All the other solvents were obtained from commercial sources and purified using standard methods. The particle size and external morphology of the samples were observed on a Philips TECNAI F12 FEI transmission electron microscope (TEM). NMR spectra were recorded on a Bruker Avance (300 MHz), Varian (500 MHz) spectrometer using TMS as an internal standard in CDCl₃. XPS spectra were recorded on a KRATOS AXIS 165 equipped with Mg K_{α} radiation (1253.6 eV) at 75 W apparatus using Mg K_{α} anode and a hemi spherical analyser. The C 1s line at 284.6 eV was used as an internal standard for the correction of binding energies. The X-ray diffraction (XRD) patterns of the fresh and used samples were obtained on a Rigaku Miniflex X-ray diffractometer using Ni filtered Cu K_{α} radiation (λ = 0.15406 nm), at a scan rate of 2° min⁻¹, with the beam voltage and beam current of 30 kV and 15 mA, respectively.

2.2. Preparation of Mg-Al-Cl (LDH) support

The preparation of LDH (Mg–Al–Cl) was carried out following the reported procedure [34]. A mixture of MgCl₂·6H₂O (30.49 g, 0.15 mmol) and AlCl₃· Θ H₂O (12.07 g, 0.05 mmol) was dissolved in 200 mL of deionized water. To this aqueous solution, 100 mL of NaOH (2 M) solution was slowly added at 25 °C and further 2 M NaOH solution was added to maintain a pH of 10 under nitrogen flow. The resulting suspension was stirred overnight at 70 °C. The solid product was isolated by filtration, washed thoroughly with deionized water and dried overnight at 80 °C.

2.3. Preparation of LDH-PdCl₄

The preparation of LDH-PdCl₄ was based on the literature procedure [22]. LDH-Cl (Mg:Al=3:1, 1.5 g) was suspended in 150 mL of aqueous Na₂PdCl₄ (0.441 g, 1.5 mmol) solution and stirred at 25 °C for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 500 mL of water and vacuum dried to obtain 1.70 g of LDH-PdCl₄.

2.4. Preparation of LDH-Pd⁰

The preparation of LDH-Pd⁰ was based on the literature procedure [36]. LDH-PdCl₄ (1 g) was reduced with hydrazine hydrate (1 g, 20 mmol) in ethanol (10 mL) for 3 h at room temperature, filtered and washed with ethanol to give LDH-Pd⁰ as an air stable black powder (0.89 mmol of Pd/g).

2.5. Characterization of LDH-Pd⁰

The catalyst was well characterized by XRD, TEM and XPS analysis (see supporting information (SI)). The XRD patterns of the fresh and used LDH-Pd⁰ catalysts (Fig. 1(a) and (b), see SI) revealed the presence of both LDH (Mg–Al–Cl) and metallic Pd phases. The diffraction peaks at 2θ = 40.21, 46.62 [ICSD # 87-0639] are corresponding to the metallic Pd species and those at 2θ = 11.20, 22.41, 34.51, 38.30, 60.20, 61.60 are due to the LDH support. Studies of XRD pattern indicate that the catalyst and support maintain the crystal structure after the reaction. Similarly the XPS data of catalyst shows the characteristic peaks at 335.60 eV and 340.76 eV corresponding to Pd 3d5/2 and Pd 3d3/2. Moreover, the position of the Pd phases of the catalyst after the reaction is unchanged at 335.65 eV and 341.02 eV.



Fig. 1. TEM images of the LDH-Pd⁰: (a) fresh catalyst, Inset shows the corresponding SAED pattern of Pd nanoparticle and (b) used catalyst.



Scheme 2. Chemoselective hydrogenation of (E)-chalcone over LDH-Pd⁰ catalyst.

Screening of reaction parameters for the hydrogenation of chalcone.^a

Entry	Catalyst	Solvent	Time (h)	Yield (%) ^b	
1	LDH-Pd ⁰	Ethanol	2.5	96	
2	LDH-Pd ⁰	Ethanol	10	96	
3	LDH-Pd ⁰	Toluene	4	96	
4	LDH-Pd ⁰	Methanol	4	96	
5	LDH-Pd ⁰	Ethyl acetate	4	96	
6	LDH-Pd ⁰	Water	10	82	
7	LDH-Pd ⁿ	Ethanol	5	94	
8	Pd/C	Ethanol	2.5	60 ^c	

^a *Reaction conditions*: (E)-chalcone (2 mmol), 15 mg of LDH-Pd⁰ catalyst (0.67 mol% of palladium), solvent (10 mL), stirring under one atmosphere of hydrogen pressure at room temperature.

^b Isolated yields.

Table 1

^c Commercial 5% Pd/C catalyst was used.

2.6. General procedure for the hydrogenation of different unsaturated compounds

In a typical reaction, 0.015 g of catalyst and 2 mmol of the reactant were taken in 10 mL of ethanol under hydrogen atmosphere. The reaction was monitored by thin-layer chromatography (TLC). After complete disappearance of the starting material, the catalyst was separated by simple filtration and the solvent was removed under reduced pressure to obtain the pure product.

3. Results and discussion

3.1. Screening of catalysts and solvents

To know the catalytic activity of LDH-Pd⁰ catalyst for the hydrogenation reaction, we performed a reaction with (E)-chalcone using ethanol as a solvent at room temperature under one atmosphere hydrogen pressure (Scheme 2). Interestingly, the reaction proceeded with complete chemoselectivity and only the olefinic bond was reduced. Further we studied various reaction parameters for hydrogenation of (E)-chalcone using LDH-Pd⁰ as a catalyst and molecular hydrogen as the reducing agent at room temperature to develop a better catalytic system and the results are summarized in Table 1.

Next, we screened different solvents for the hydrogenation of (E)-chalcone (Table 1, entries 2–6). However, all the reactions proceeded smoothly and gave good yields at longer reaction times. Notably, similar result was obtained when LDH-Pd^{II} catalyst was used for the reaction (Table 1, entry 7). On the other hand only moderate yields of the desired product was observed along with the concomitant undesired side product (1,3-diphenylpropan-1-ol) when commercially available 5% Pd/C was used as catalyst (Table 1, entry 8).

3.2. Scope of the reaction

With the optimized reaction conditions in hand, the scope of the reaction was extended to different unsaturated compounds as summarized in Table 2. As shown, various unsaturated compounds were reduced selectively with yields ranging from 85% to 98% (Table 2, entries 1-21). The catalyst exhibited high activity in the case of non-functionalized aromatic olefins (Table 2, entries 2-4, and 17). Thus styrene, 4-methyl styrene, transstilbene and 2-vinylnaphthalene were successfully converted to ethyl benzene, 1-ethyl-4-methylbenzene, 1,2-diphenylethane, and 2-ethylnaphthalene, respectively, with 92-95% yield. In case of 4chlorostyrene, only the olefinic double bond was reduced and the formation of dehalogenated product was not observed (Table 2. entry 5). Importantly, carbonyl moiety was not affected and only olefinic double bond was reduced selectively in the hydrogenation of cyclic α , β -unsaturated ketones (Table 2, entries 7). Moreover, sterically hindered tri substituted olefinic ketones such as ionone (Table 2, entry 6), pulegone (Table 2, entry 8), and isophorone (Table 2, entry 9) reduced selectively at the olefinic bond to give corresponding alkanes with high yields. Hydrogenation of α,β -unsaturated aldehydes such as cinnamaldehyde and α -methyl-cinnamaldehyde proceeded chemoselectively to furnish the desired products (Table 2, entries 10 and 11). In a similar way, α , β -unsaturated carboxylic acids and esters underwent chemoselective hydrogenation of olefinic bond to afford the corresponding acids and esters in good yields (Table 2, entries 13, 14 and 16). Interestingly, 1-ethyl-4-methoxybenzene also hydrogenated selectively without affecting the methoxy group (Table 2, entry 18). Hydrogenation of diphenylacetylene gave dibenzyl product with 96% yield (Table 2, entry 19). For terminal and disubstituted alkenes this catalytic system afforded good yields and selectivity. Finally, we observed hydrogenation of olefinic double bond substrates with nitro and nitrile functionalities. Mixture of products was obtained in the case of 3-nitro styrene (Table 2, entry 21). Nitro group was reduced to give 3-ethylamine with 75% vield. Under Pd/C-catalyzed hydrogenation condition nitrile functionality is known as reducible functionality. In this case only olefinic bond was reduced selectively using LDH-Pd⁰ catalyst with E-cinnamonitrile as a substrate (Table 2, entry 15). Thus, this protocol tolerates a wide variety of functional groups like keto, aldehyde, acids, esters, alcohol, halogen, ether and cyano in the substrates.

3.3. Recycling of the catalyst

The reusability of LDH-Pd⁰ catalyst was examined for the chemoselective hydrogenation of methyl cinnamate. It is noteworthy to mention that the LDH-Pd⁰ catalyst showed consistent activity and selectivity up to 5 cycles. After each cycle, LDH-Pd⁰ was recovered by simple filtration, washed, air-dried and used directly for the next cycle without further purification. All the cycles showed consistent yield and selectivity for the hydrogenation reaction. The Pd metal content of the fresh and used catalyst was found to be 9.48% and 9.32%, respectively, as measured by ICP AES, which suggested that leaching was minimal.

The TEM images of the catalyst before and after the catalytic reaction is shown in Fig. 1(a) and (b). The Pd nanoparticles seen as dark particles are dispersed on the LDH support. Pd is confirmed by the SAED (selected area electron diffraction) pattern as shown in the inset of Fig. 1(a) and its corresponding d values agree with the JCPDS data. Further as seen from the micrographs there is no significant difference observed in the morphologies of fresh and used catalysts.

Table 2
Selective hydrogenation of different unsaturated compounds. ^a

Entry	Substrate	Product	Time (h)	Yield (%)	Entry	Substrate	Product	Time (h)	Yield (%)
1			2.5	96	12	ОН	ОН	2.5	96
2			1.5	95	13	Contraction of the second seco		2	96, 92 ^b
3	\bigcirc	\bigcirc	1	92	14	ОН	ОН	4	92
4			1	92	15	CN	CN	2	96
5	ci Ci	CI	2	96	16	он он он	OH TOH O	2	98
6			2.5	94	17			2.5	92
7	\bigcirc	\bigcirc°	1.5	92	18		· C	2.5	94
8		×∽° ^ℓ	2	95	19			2	94
9			2	96	20	H ₂ N	H ₂ N	2.5	90
10	С Н	O H	2	94,	21	K NO2	$ \begin{array}{c} + \\ NH_2 \\ NO_2 \\ A \\ B \end{array} $	3	A=75
11	О Н	С Н	2	94					<i>B</i> = 25

^a *Reaction conditions*: substrate (2 mmol), 15 mg of LDH-Pd⁰ catalyst, ethanol (10 mL), stirring under one atmosphere hydrogen pressure at room temperature. ^b Yield at 5th cvcle.

4. Conclusion

In conclusion, a heterogeneous LDH-Pd⁰ catalyzed chemoselective hydrogenation of olefinic double bonds in the presence of other functional groups at room temperature has been successfully developed. The solid catalyst easy to handle can be readily recovered and reused, thus making this procedure more environmentally acceptable. We believe that this methodology may find widespread use in organic synthesis for the chemoselective hydrogenation of double bonds.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata. 2012.08.017.

References

- S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley-Interscience, New York, 2001.
- [2] M. Hudlickey, Reductions in Organic Chemistry, 2nd ed., American Chemical Society, Washington, DC, 1996.
- [3] P.N. Rylander, Hydrogenation Methods, Academic, New York, 1985.
- [4] A. Mori, Y. Miyakawa, E. Ohashi, T. Haga, T. Maegawa, H. Sajiki, Org. Lett. 8 (2006) 3279–3281.
- [5] A. Mori, T. Mizusaki, Y. Miyakawa, E. Ohashi, T. Haga, T. Maegawa, Y. Monguchi, H. Sajiki, Tetrahedron 62 (2006) 11925–11932.
- [6] H. Sajiki, K. Hattori, K. Hirota, Chem. Eur. J. 6 (2000) 2200-2204.
- [7] B.P. Czech, R.A. Bartsch, J. Org. Chem. 49 (1984) 4076–4078.
- [8] H. Sajiki, Tetrahedron Lett. 36 (1995) 3465-3468.
- [9] H. Sajiki, H. Kuno, K. Hirota, Tetrahedron Lett. 38 (1997) 399-402.
- [10] H. Sajiki, K. Hattori, K. Hirota, J. Org. Chem. 63 (1998) 7990-7992.
- [11] A. Mori, Y. Miyakawa, E. Ohashi, T. Haga, T. Maegawa, H. Sajiki, Org. lett. 8 (2006) 3279-3281.
- [12] D. Misiti, G.D. Monache, Synthesis (1999) 873–877.
- [13] F.X. Felpin, E. Fouquet, Chem. Eur. J. 16 (2010) 12440-12445.
- [14] T. Ikawa, H. Sajiki, K. Hirota, Tetrahedron 61 (2005) 2217-2231.
- [15] H. Ohde, C.M. Wai, H. Kim, J. Kim, M. Ohde, J. Am. Chem. Soc. 124 (2002) 4540–4541.
- [16] B. Yoon, H. Kim, C.M. Wai, Chem. Commun. (2003) 1040-1041.
- [17] Y.-D. Jo, J.-H. Ahn, S.-K. Ihm, Polym. Int. 44 (1997) 49–54.
- [18] M. Zecca, R. Fisera, G. Palma, S. Lora, M. Hronec, M. Kralik, Chem. Eur. J. 6 (2000) 1980–1986.
- [19] D. Guin, B. Baruwati, S.V. Manorama, Org. Lett. 9 (2007) 1419–1421.
- [20] Y. Niu, L.K. Yeung, R.M. Crooks, J. Am. Chem. Soc. 123 (2001) 6840-6846.
- [21] M.L. Kantam, R. Kishore, J. Yadav, M. Sudhakar, A. Venugopal, Adv. Synth. Catal. 354 (2012) 663–669.

- [22] B.M. Choudary, S. Madhi, N.S. Chowdari, M.L. Kantam, B. Sreedhar, J. Am. Chem. Soc. 124 (2002) 14127.
- [23] S. Miyata, Clays Clay Miner. 31 (1983) 305.
- [24] P.K. Dutta, M. Puri, J. Phys. Chem. 93 (1989) 367.
 [25] L.M. Parker, N.B. Milestone, R.H. Newman, Ind. Eng. Chem. Res. 34 (1995) 1196. [26] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11 (1991) 173.
- [27] B.M. Choudary, M.L. Kantam, A. Rahman, ChV. Reddy, K.K. Rao, Angew. Chem.
- Int. Ed. 40 (2001) 763. [28] M.L. Kantam, B.M. Choudary, ChV. Reddy, K.K. Rao, F. Figueras, Chem. Commun.
- (1998) 1033. [29] B.M. Choudary, N.S. Chowdari, S. Madhi, M.L. Kantam, Angew. Chem. Int. Ed. 40 (2001) 4620.
- [30] B.M. Choudary, N.S. Chowdari, K. Jyothi, M.L. Kantam, J. Am. Chem. Soc. 124 (2002) 5341.
- [31] B.M. Choudary, N.S. Chowdari, M.L. Kantam, K.V. Raghavan, J. Am. Chem. Soc. 123 (2001) 9220.
- [32] B.F. Sels, D.De Vos, M. Buntinx, F. Pierard, A. Kirsch-De Mesmaeker, P.A. Jacobs, Nature 400 (1999) 855.
- [33] B.F. Sels, D.De Vos, P.A. Jacobs, J. Am. Chem. Soc. 123 (2001) 8350.
- [34] S. Miyata, Clays clay Miner. 23 (1975) 369.
- [35] F. Trifiro, A. Vaccari, in: G. Alberti, T. Bein (Eds.), Comprehensive Supramolecular Chemistry, vol. 7, Pergamon, New York, 1996, p. 251.
- [36] M.L. Kantam, P. Srinivas, K.B. Shiva Kumar, R. Trivedi, Catal. Commun. 8 (2007) 991-996.