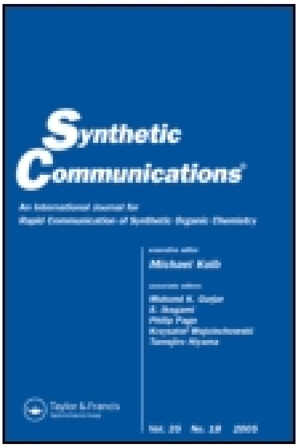


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

HAP-Pd(0): A Highly Efficient Recyclable Heterogeneous Catalyst for the Selective Reduction of Carbon-Carbon Double Bond in α,β-Unsaturated Ketones

Omkar Singh Chambyal [a] , Satya Paul [a] , Tahira Shamim [a] , Monika Gupta [a] , Rajive Gupta [a] & André Loupy [b]
[a] Department of Chemistry, University of Jammu, Jammu, India
[b] Laboratoire des Reactions Sélectives sur Supports, Paris-South University, Orsay, France

Accepted author version posted online: 13 Feb 2012.Version of record first published: 13 Nov 2012.

To cite this article: Omkar Singh Chambyal, Satya Paul, Tahira Shamim, Monika Gupta, Rajive Gupta & André Loupy (2013): HAP-Pd(0): A Highly Efficient Recyclable Heterogeneous Catalyst for the Selective Reduction of Carbon-Carbon Double Bond in α,β-Unsaturated Ketones, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 43:5, 656-667

To link to this article: http://dx.doi.org/10.1080/00397911.2011.605242

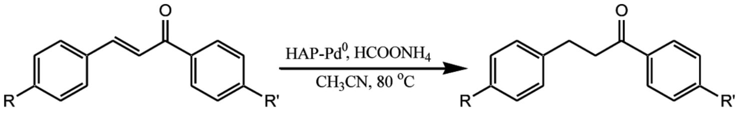
Synthetic Communications®, 43: 656–667, 2013

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2011.605242

HAP-Pd(0): A HIGHLY EFFICIENT RECYCLABLE HETEROGENEOUS CATALYST FOR THE SELECTIVE REDUCTION OF CARBON–CARBON DOUBLE BOND IN α,β-UNSATURATED KETONES

Omkar Singh Chambyal,[1] Satya Paul,[1] Tahira Shamim,[1] Monika Gupta,[1] Rajive Gupta,[1] and André Loupy[2]
[1]*Department of Chemistry, University of Jammu, Jammu, India*
[2]*Laboratoire des Reactions Sélectives sur Supports, Paris-South University, Orsay, France*

GRAPHICAL ABSTRACT



Abstract *A recyclable heterogeneous hydroxyapatite-supported palladium(0) catalyst was prepared by a simple procedure and successfully applied for the selective reduction of carbon–carbon double bond in α,β-unsaturated ketones using $HCOONH_4$ as hydrogen transfer agent. The workup procedure is simple, and the catalyst could be recovered by simple filtration and recycled for five consecutive runs without significant loss of activity.*

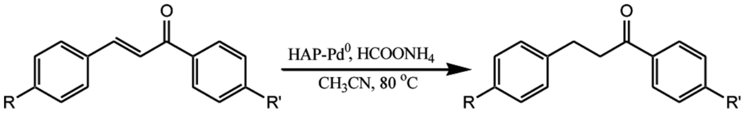
Keywords HAP-Pd(0); heterogeneous catalysis; reductions; selectivity; α,β-unsaturated ketones

INTRODUCTION

Hydrogenation is a most common reaction used in the synthesis of many products across many industrial processes,[1,2] including the petrochemical, pharmaceutical, and food industries. Selective hydrogenation in organic synthesis is a great challenge for chemists. Selective reduction[3–6] of carbon–carbon double bond in α,β-unsaturated carbonyl compounds is a highly desirable organic transformation because it leads to saturated carbonyl compounds, which have a wide range of applications in synthetic and pharmaceutical chemistry. The conventional hydrogenation procedure, although it often offers selective reductions under mild conditions, generally requires a special setup and is always associated with the cautions of using hydrogen gas. Moreover, heterogeneous and homogeneous catalytic transfer hydrogenations have been used extensively in the reduction of a variety of functional

Received May 24, 2011.

Address correspondence to Satya Paul, Department of Chemistry, University of Jammu, Jammu 180 006, India. E-mail: paul7@rediffmail.com



Scheme 1. HAP-Pd^0-catalyzed selective reduction of carbon–carbon double bond in α,β-unsaturated ketones at 80 °C.

groups.[7–9] Transition metals such as Pd, Rh, Pt, Ni, Cu, Ir, and Co and their complexes are commonly used as catalysts for reductions.[10–15] Among these, palladium[16–19] is more advantageous with regard to reaction conditions, activity, selectivity, and yields of final products. Most of the Pd-catalyzed selective reductions have been reported in homogeneous media. For example, $[(t\text{-}Bu_2PH)Pd(P\text{-}t\text{-}Bu_2)]_2$ was reported for the selective reduction of carbon–carbon double bond of α,β-unsaturated ketones, aldehydes, sulfones, and phosphonates in good to excellent yields.[20,21] Palladium-catalyzed selective reduction of α,β-unsaturated carbonyl compounds has also been reported in the presence of triethylsilane in ethanol.[22]

Recently, heterogeneous catalysts[23–28] have emerged as more advantagous over their homogeneous counterparts because of simplified recovery, recyclability, and potential for incorporation in continuous reactors and microreactors. In this context, some heterogeneous palladium catalysts have been developed for the selective reductions, such as the $HCOONH_4$-Pd/C system for the reduction of various functionalities[29] including heterocyclic ring in quinolines,[30] aryl ketones to alcohols,[31] benzyl glycosides,[32] dibenzyl uracils,[33] α,β-unsaturated nitroalkenes,[34] cyclic α,β-unsaturated ketones,[35] aldehydes, sulfones, and phosphonates. Pd-MCM-48, Pd/SiO_2, and Pd/Al_2O_3 have been reported as effective catalysts for the selective hydrogenation of conjugated and isolated C=C of citral in supercritical carbon dioxide[36] using H_2 gas. Recently, polymer-supported palladium nanoparticles[37] have shown excellent activity and selectivity for the hydrogenation of alkynes and alkenes.

Herein, we describe the synthesis of a recyclable heterogeneous hydroxyapatite-supported Pd(0) catalyst and its application for the selective reduction of carbon–carbon double bond in α,β-unsaturated ketones using ammonium formate as hydrogen transfer agent simply by stirring in acetonitrile at 80 °C (Scheme 1).

RESULTS AND DISCUSSION

Hydroxyapatite used for the preparation of hydroxyapatite-supported Pd(0) catalyst (HAP-Pd^0) was prepared according to the literature procedure with slight modification.[38] HAP-Pd^0 was prepared by stirring a mixture of hydroxyapatite and $Pd(OAc)_2$ in ethanol for 3 h, followed by dropwise addition of hydrazine hydrate (80%). To make the reaction medium completely heterogeneous, the catalyst was conditioned by refluxing for 6 h in ethanol, toluene, and acetonitrile (each for 2 h) to remove any physiosorbed palladium acetate. The conditioned catalyst was quite stable and could be used for several days.

The characterization of HAP-Pd^0 was done by X-ray diffraction (XRD), atomic absorption spectrophotometry (AAS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Powder XRD diffraction patterns of HAP-Pd^0 (Fig. 1) exhibited three additional reflections in addition to hydroxyapatite corresponding to $2\theta = 39°$, $46°$, and $65°$, which could be attributed to Pd(0) [Ref. Joint Committee on Powder Diffraction Standards (JCPDS) file: 46–1043]. The amount of the palladium supported on hydroxyapatite was determined by AAS analysis and found to be 1.1 mmol/g.

The surface morphology and distribution of palladium in HAP-Pd^0 were also investigated using TEM and SEM. The TEM micrograph (Fig. 2a) shows the distribution of palladium onto hydroxyapatite, and the average particle diameter was about 20 nm. The SEM image (Fig. 3) indicates that the catalyst consists of hydroxyapatite, possessing an empty space for adsorption of palladium nanoparticles.

To test the activity of HAP-Pd^0 as a completely heterogeneous catalyst for the selective reduction of double bond in α,β-unsaturated ketones, 3-(4-methoxyphenyl) -1-phenylprop-2-en-1-one was selected as the test substrate and the selective reduction was carried out under different set of conditions with respect to different solvents, temperatures, and molar ratios of HAP-Pd^0 and ammonium formate. To select the best solvent as far as selectivity is concerned, the reaction was carried out in toluene, ethanol, water and acetonitrile. The results are summarized in Table 1. It is clear that acetonitrile gave the best results. Further, to select the appropriate reaction temperature, the reaction was carried out at room temperature, 50, and 80 °C. We found that 80 °C was the optimum reaction temperature. After carrying out reactions with different molar ratios of the catalyst, 0.3 g equivalent to 0.33 mol% Pd gave the optimum results under mild conditions. For 1 mmol of α,β-unsaturated ketone, 1.5 g of $HCOONH_4$ was required. Thus, optimum conditions selected are α,β-unsaturated ketone (1 mmol), $HCOONH_4$ (1.5 g), HAP-Pd^0 (0.3 g, 0.33 mol% Pd), acetonitrile (5 mL), and 80 °C as the reaction temperature.

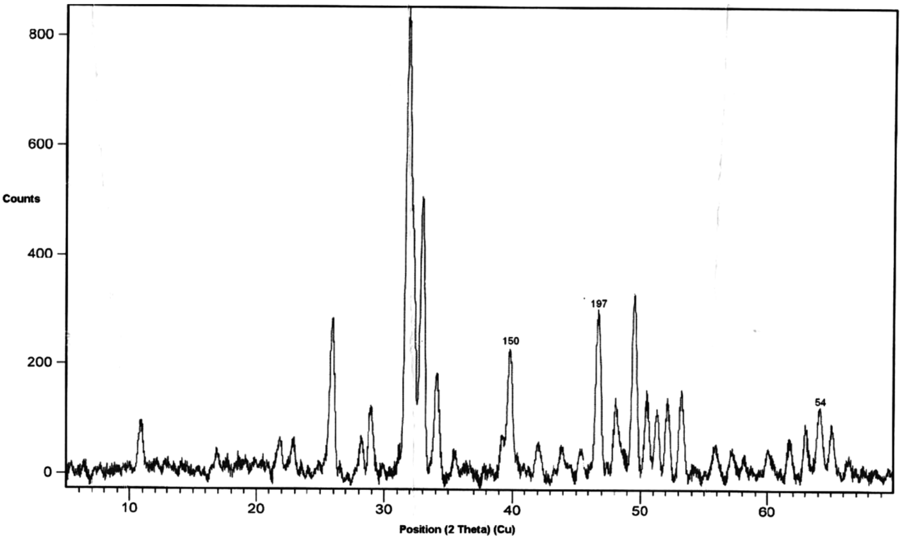
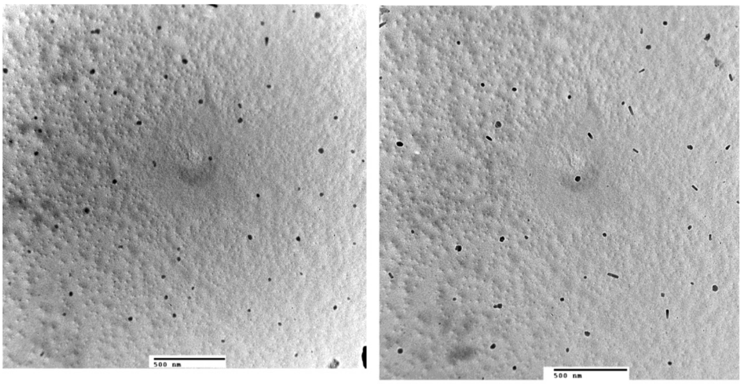


Figure 1. XRD diffraction patterns of HAP-Pd^0.



(a) (b)

Figure 2. (a) TEM micrograph of HAP-Pd^0. (b) TEM micrograph of HAP-Pd^0 after the fifth run.

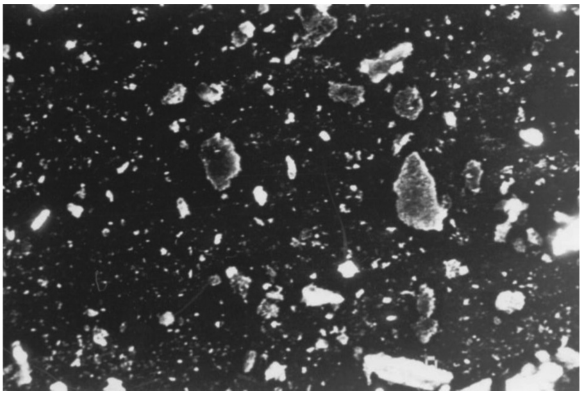


Figure 3. SEM image of HAP-Pd^0.

Table 1. Effect of solvent on the HAP-Pd^0-catalyzed reduction of carbon–carbon double bond in α,β-unsaturated ketones[a]

Entry	Solvent	Time (h)	Yield (%)[b]
1	Toluene	6	40[c]
2	Water	6	35[c]
3	Ethanol	6	50[c]
4	**Acetonitrile**	**6**	**89**

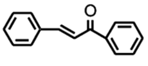
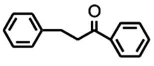
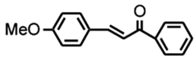
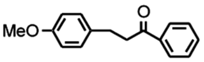
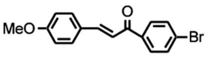
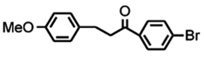
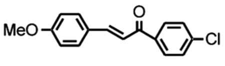
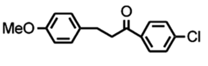
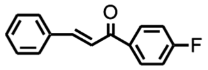
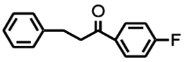
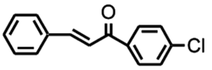
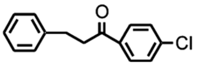
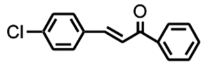
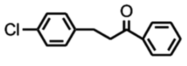
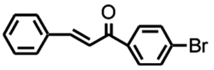
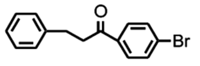
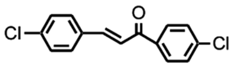
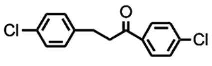
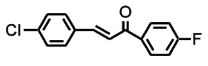
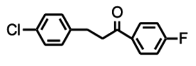
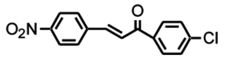
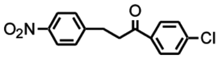
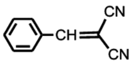
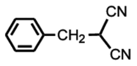
[a] Reaction conditions: 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1 mmol), $HCOONH_4$ (1.5 g), HAP-Pd^0(0.3 g, 0.33 mol% Pd), solvent (5 mL) at 80 °C.

[b] Yield refers to separation based on column chromatography.

[c] The rest being the starting materials.

To demonstrate the versatility of the catalytic process, different enones subsitututed with electron-withdrawing and electron-donating groups were subjected to reduction under the reaction conditions. All the substrate gave good results (Table 2). It is pertinent to mention that no saturated or unsaturated alcohol was detected, which clearly supports the high selectivity of the catalytic process. Further, the developed protocol showed functional group tolerance for easily reducible groups such as NO_2 and CN (entries 11 and 12).

Table 2. HAP-Pd^0-catalyzed selective reduction of carbon–carbon double bond in α,β-unsaturated ketones using $HCOONH_4$ in acetonitrile at 80 °C

Entry	Substrate[a]	Product	Time (h)	Yield (%)[b,c]	Mp/lit. mp (°C)
1			7	87	68–70/68–69[39]
2			6	89	61–62/62–63[39]
3			6.5	87	66–67/67–68[40]
4			6	86	59–60/60–61[41]
5			6.5	90	38–39/37–39[39]
6			7	83	73–74/73–75[39]
7			7.5	86	54–55/53–54[39]
8			8	90	97–98/98–99[42]
9			4.5	85	81–82/82–83[41]
10			6	91	47–49/46–48[39]
11			9	75	65–66
12			9	68	90–91/91–92[43]

[a] The reactions were carried out by stirring a mixture of α,β-unsaturated ketone (1 mmol), $HCOONH_4$ (1.5 g), HAP-Pd^0 (0.3 g, 0.33 mol% Pd), and acetonitrile (5 mL) at 80 °C.

[b] Yield refers to column chromatography yield.

[c] The rest being the unreacted chalcones.

Table 3. Comparison of different supported Pd catalysts for the selective reduction of carbon–carbon double bond in α,β-unsaturated ketones

Entry	Catalyst[b]	Time (h)	Yield (%)[c]
1	Pd/C	6	62
2	Pd/C	15	83[d]
3	Pd/SiO$_2$	6	53
4	Pd/SiO$_2$	15	72[d]
5	Pd/Al$_2$O$_3$	6	58
6	Pd/Al$_2$O$_3$	15	78[d]
7	**HAP-Pd^0**	**6**	**89**

[a] Reaction conditions: 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1 mmol), HCOONH$_4$ (1.5 g), HAP-Pd^0 (0.3 g, 0.33 mol% Pd), acetonitrile (5 mL) at 80 °C.

[b] Pd/C, Pd/SiO$_2$, and Pd/Al$_2$O$_3$ were prepared by a procedure similar to that described for HAP-Pd^0. An amount of the catalyst equivalent to 0.33 mol% Pd was taken for the test reaction.

[c] Yield refers to column chromatography yield, the rest being the starting materials.

[d] Yield refers to maximum yield after 15 h. After this no further conversion was observed.

To compare the activity of HAP-Pd^0 over Pd/SiO$_2$, Pd/Al$_2$O$_3$, and Pd/charcoal, selective reduction of 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one was attempted using HCOONH$_4$ in acetonitrile at 80 °C (Table 3). Pd-HAP^0 was found to be more active, though similar selectivity was observed.

In the case of heterogeneous catalysts, deactivation and recyclability are important issues that need to be addressed. For reductions, this becomes more important.

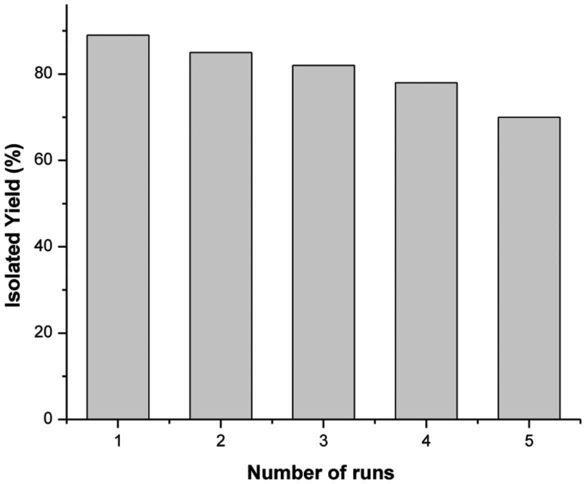


Figure 4. Recyclability of HAP-Pd^0 for the selective reduction of carbon–carbon double bond in 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1 mmol) using HCOONH$_4$ (1.5 g), HAP-Pd^0 (0.3 g, 0.33 mol% Pd), acetonitrile (5 mL) at 80 °C for 6 h.

Thus, a series of five consecutive runs for the reduction of 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one under the reaction conditions for 6 h were carried out with the same catalyst. The results are represented in Fig. 4, which demonstrate that the catalyst is highly stable under the reaction conditions, though catalytic activity drops very little after every use. The drop in activity might not be due to the leaching of palladium because the amount of Pd before and after the fifth use remains almost the same (determined by AAS analysis). The TEM micrographs of the catalyst after the fifth run did not show any loss of uniformity in distribution of Pd over HAP (Fig. 2b). The structural changes on the surface of hydroxyapatite may be responsible for the slight loss of catalytic activity.

CONCLUSION

In conclusion, we have developed a mild and highly efficient method for the selective reduction of carbon–carbon double bond in α,β-unsaturated ketones without affecting the carbonyl group using HAP-Pd^0 and ammonium formate in acetonitrile at 80 °C. Moreover, the catalyst is highly stable and hence recyclable under the reaction conditions.

EXPERIMENTAL

All melting points were determined on a Perfit melting-point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Brucker DPX-200 NMR spectrometer (200 MHz) in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard, and infrared (IR) spectra were recorded on a Perkin-Elmer FTIR spectrophotometer using KBr discs. Mass spectral data was recorded on Bruker Esquire 3000 (ESI), whereas thermal analysis was carried out on a DTG-60 Shimadzu thermal analyzer with heating rate of 10 °C/min. SEM images were recorded using a Jeol T-300 scanning electron microscope, and TEM images were recorded on H7500 Hitachi. Pd content was determined on GBC Avanta-M atomic absorption spectrometer manufactured by GBC Scientific. The catalyst was stirred in diluted. HNO_3 for 10 h, and the resulting filtrate was subjected to AAS analysis.

Preparation of Hydroxyapatite-Supported Palladium(0) [HAP-Pd^0]

Hydroxyapatite was prepared by stirring a solution of diammonium hydrogen phosphate (8 g) in double-distilled water (250 mL) at pH 12 and calcium nitrate [$Ca(NO_3)_2.4H_2O$] (25 g) in double-distilled water (150 mL) for 10 min. The suspension was then further stirred for 4 h at 115 °C, and the solid was filtered off, washed with double-distilled water (500 mL), and then dried in the oven at 95 °C for 5 h. The oven-dried hydroxyapatite was calcined in air at 750 °C for 30 min before use. HAP-Pd^0 was prepared by stirring a mixture of hydroxyapatite (3 g) and $Pd(OAc)_2$ (0.05 g) in ethanol (25 mL) at room temperature for 2 h, followed by addition of hydrazine hydrate (80%, 1.5 mL) dropwise over a period of 20 min. It was further stirred at room temperature for 7 h. The color of the catalyst changed to dark grey, which indicated that Pd(II) was reduced to Pd(0). HAP-Pd(0) was filtered off and washed with ethanol (10 mL) and acetone (3 × 20 mL). To remove any physiosorbed

$Pd(OAc)_2$, the catalyst was conditioned by refluxing for 6 h respectively in ethanol, toluene, and acetonitrile, each for 2 h. Finally, the HAP-Pd(0) was dried in the oven at 95 °C for 5 h and stored in a desiccator.

General Procedure for the Selective Reduction of Carbon–Carbon Bond in α,β-Unsaturated Ketones Using HAP-Pd(0)

Acetonitrile (5 mL) was added to a mixture of α,β-unsaturated ketone (1 mmol), ammonium formate (1.5 g), and HAP-Pd^0 (0.3 g, 0.33 mol% Pd), and the reaction mixture was stirred at 80 °C for an appropriate time (monitored by thin-layer chromatography, TLC). After completion of the reaction, the reaction mixture was cooled to room temperature and filtered. The residue was washed with acetonitrile (2 × 10 mL). The organic solvent was removed under reduced pressure, and product was obtained after passing through column of silica gel and elution with EtOAc–petroleum ether (1:9). The residue was again washed with deionized water (200 mL) followed by acetonitrile (3 × 10 mL) and dried at 100 °C for 2 h. It can be used further for carrying out the reactions.

Spectral Data of Compounds

1,3-Diphenylpropan-1-one (Entry 1). IR (KBr, ν_{max} cm^{-1}): 2933 (aliphatic CH_2 stretch), 1681 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 2.98 (t, 2H, CH_2), 3.33 (t, 2H, CH_2), 7.20–7.55 (m, 10H, Harom); *m*/*z*: 210 (M^+). Anal. calcd. for $C_{15}H_{14}O$: C, 85.71; H, 6.66; O, 7.61. Found: C, 85.70; H, 6.60; O, 7.60.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (Entry 2). IR (KBr, ν_{max} cm^{-1}): 2943 (aliphatic CH_2 stretch), 1687 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 2.94 (t, 2H, CH_2), 3.33 (t, 2H, CH_2), 3.95 (s, 3H, OCH_3), 6.91 (d, 2H, Harom), 7.12–7.85 (m, 7H, Harom); *m*/*z*: 240 (M^+). Anal. calcd. for $C_{16}H_{16}O_2$: C, 79.79; H, 6.71; O, 13.32. Found: C, 79.93; H, 6.72; O, 13.29.

1-(4-Bromophenyl)-3-(4-methoxyphenyl)propan-1-one (Entry 3). IR (KBr, ν_{max} cm^{-1}): 2999 (aliphatic CH_2 stretch), 1682 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.01 (t, 2H, CH_2), 3.34 (t, 2H, CH_2), 3.87 (s, 3H, OCH_3), 6.85 (d, 2H, Harom), 7.20–7.55 (m, 4H, Harom), 7.95 (d, 2H, Harom); *m*/*z*: 318 (M^+), 320 (M + 2). Anal. calcd. for $C_{16}H_{15}BrO_2$: C, 60.21; H, 4.74; O, 10.02. Found: C, 60.20; H, 4.72; O, 10.04.

1-(4-Chlorophenyl)-3-(4-methoxyphenyl)propan-1-one (Entry 4). IR (KBr, ν_{max} cm^{-1}): 2934 (aliphatic CH_2 stretch), 1680 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.04 (t, 2H, CH_2), 3.38 (t, 2H, CH_2), 3.92 (s, 3H, OCH_3), 6.95 (d, 2H, Harom), 7.25–7.68 (m, 4H, Harom), 7.97 (d, 2H, Harom); *m*/*z*: 274 (M^+), 276 (M + 2). Anal. calcd. for $C_{16}H_{15}ClO_2$: C, 69.95; H, 5.50; O, 11.65. Found: C, 69.93; H, 5.49; O, 11.62.

1-(4-Fluorophenyl)-3-phenylpropan-1-one (Entry 5). IR (KBr, ν_{max} cm^{-1}): 2990 (aliphatic CH_2 stretch), 1668 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.08 (t, 2H, CH_2), 3.30 (t, 2H, CH_2), 7.19–7.78 (m, 7H, Harom), 7.99 (d, 2H, Harom);

m/*z*: 228 (M^+). Anal. calcd. for $C_{15}H_{13}FO$: C, 78.93; H, 5.74; O, 7.01. Found: C, 78.90; H, 5.72; O, 7.00.

3-(4-Chlorophenyl)-1-phenylpropan-1-one (Entry 6). IR (KBr, ν_{max} cm^{-1}): 2967 (aliphatic CH_2 stretch), 1683 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.12 (t, 2H, CH_2), 3.37 (t, 2H, CH_2), 7.08–7.78 (m, 7H, Harom), 8.03 (d, 2H,Harom); *m*/*z*: 244 (M^+), 246 ($M + 2$). Anal. calcd. for $C_{15}H_{13}OCl$: C, 73.61; H, 5.31; O, 6.54. Found: C, 73.58; H, 5.28; O, 6.50.

1-(4-Chlorophenyl)-3-phenylpropan-1-one (Entry 7). IR (KBr, ν_{max} cm^{-1}): 2957 (aliphatic CH_2 stretch), 1677 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.12 (t, 2H, CH_2), 3.37 (t, 2H, CH_2), 7.08–7.78 (m, 7H, Harom), 8.03 (d, 2H, Harom); *m*/*z*: 244 (M^+), 246 ($M + 2$). Anal. calcd. for $C_{15}H_{13}OCl$: C, 73.61; H, 5.31; O, 6.54. Found: C, 73.59; H, 5.29; O, 6.56.

1-(4-Bromophenyl)-3-phenylpropan-1-one (Entry 8). IR (KBr, ν_{max} cm^{-1}): 2982 (aliphatic CH_2 stretch), 1668 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.05 (t, 2H, CH_2), 3.29 (t, 2H, CH_2), 7.16–7.73 (m, 7H, Harom), 7.97 (d, 2H, Harom); *m*/*z*: 288 (M^+), 290 ($M + 2$). Anal. calcd. for $C_{15}H_{13}OBr$: C, 62.50; H, 4.51; O, 5.55. Found: C, 62.48; H, 4.48; O, 5.52.

1,3-Bis(4-chlorophenyl)propan-1-one (Entry 9). IR (KBr, ν_{max} cm^{-1}): 2955 (aliphatic CH_2 stretch), 1672 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.00 (t, 2H, CH_2), 3.27 (t, 2H, CH_2), 7.08–7.98 (m, 8H, Harom); *m*/*z*: 278 (M^+), 280 ($M + 2$). Anal. calcd. for $C_{15}H_{12}OCl_2$: C, 75.00; H, 5.00; O, 6.66. Found: C, 74.98; H, 4.97; O, 6.68.

1-(4-Chlorophenyl)-3-(4-fluorophenyl)propan-1-one (Entry 10). IR (KBr, v_{max} cm^{-1}): 2964 (aliphatic CH_2 stretch), 1650 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.02 (t, 2H, CH_2), 3.33 (t, 2H, CH_2), 7.25 (d, 2H, Harom), 7.42–7.85 (m, 4H, Harom), 8.01 (d, 2H, Harom); *m*/*z*: 261 (M^+), 263 ($M + 2$). Anal. calcd. for $C_{15}H_{12}OClF$: C, 68.80; H, 4.58; O, 6.11. Found: C, 68.84; H,4.59; O, 6.10.

1-(4-Chlorophenyl)-3-(4-nitrophenyl)propan-1-one (Entry 11). IR (KBr, v_{max} cm^{-1}): 2974 (aliphatic CH_2 stretch), 1670 (C=O stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.12 (t, 2H, CH_2), 3.39 (t, 2H, CH_2), 7.28–7.37 (d, 2H, Harom), 7.68–7.75 (m, 2H, Harom), 7.99–8.10 (d, 2H, Harom), 8.26–8.34 (d, 2H, Harom); *m*/*z*: 289 (M^+), 291 ($M + 2$). Anal. calcd. for $C_{15}H_{12}O_3ClN$: C, 62.17; H, 4.15; O, 16.58; N, 4.83. Found: C, 62.19; H, 4.16; O, 16.59; N, 4.84.

Benzylmalononitrile (Entry 12). IR (KBr, v_{max} cm^{-1}): 2986 (aliphatic CH_2 stretch), 2255 (CN stretch); ^1H NMR (200 MHz, $CDCl_3$): δ 3.18 (d, 2H, CH_2), 3.76 (t, 1H, CH), 7.12–7.37 (m, 5H, Harom); *m*/*z*: 156 (M^+). Anal. calcd. for $C_{10}H_8N_2$: C, 76.92; H, 5.13; N, 17.95. Found: C, 76.93; H, 5.11; N, 17.92.

ACKNOWLEDGMENTS

We are grateful to Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh, for the SEM, TEM, and XRD and the Head, Institute Instrumentation Centre, Indian Institute of Technology, Roorkee, for AAS analysis.

REFERENCES

1. Blaser, H. U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. Selective hydrogenation for fine chemicals: Recent trends and new developments. *Adv. Synth. Catal.* **2003**, *345*, 103–151.
2. Noyori, R.; Kitamura, M.; Ohkuma, T. Toward efficient asymmetric hydrogenation: Architectural and functional engineering of chiral molecular catalysts. *Proc. Nat. Acad. Sci. U.S.A.* **2004**, *101*, 5356–5362.
3. Neri, G.; Mercadante, L.; Donato, A.; Visco, A.; Galvagno, S. Influence of Ru precursor, support, and solvent in the hydrogenation of citral over ruthenium catalysts. *Catal. Lett.* **1994**, *29*, 379–386.
4. Gallezot, P.; Giroir-Fendler, A.; Richard, D. Chemioselectivity in cinnamaldehyde hydrogenation induced by shape selectivity effects in Pt-Y zeolite catalysts. *Catal. Lett.* **1990**, *5*, 169–174.
5. Englisch, M.; Jentys, A.; Lercher, J. A. Structure sensitivity of the hydrogenation of crotonaldehyde over Pt/SiO_2 and Pt/TiO_2. *J. Catal.* **1997**, *166*, 25–35.
6. Claus, P. Selective hydrogenation of α,β-unsaturated aldehydes and other C=O and C=C bonds containing compounds. *Top. Catal.* **1998**, *5*, 51–62.
7. Brieger, G. B.; Nestrick, T. J. Catalytic transfer hydrogenation. *Chem. Rev.* **1974**, *74*, 567–580.
8. Jonstone, R. A.; Wilby, W. A. H.; Entwistle, I. D. Heterogeneous catalytic transfer hydrogenation and its relation to other methods for reduction of organic compounds. *Chem. Rev.* **1985**, *85*, 129–180.
9. Wang, G. Z.; Backvall, J. E. Ruthenium-catalysed transfer hydrogenation of imines by propan-2-ol. *J. Chem. Soc., Chem. Commun.* **1992**, *14*, 980–981.
10. Lee, H.; An, M. Selective 1,4-reduction of unsaturated carbonyl compounds using $Co_2(CO)_8$–H_2O. *Tetrahedron Lett.* **2003**, *44*, 2775–2778.
11. Sakaguchi, S.; Yamaga, T.; Ishii, T. Y. Iridium-catalyzed transfer hydrogenation of α,β-unsaturated and saturated carbonyl compounds with 2-propanol. *J. Org. Chem.* **2001**, *66*, 4710–4712.
12. Ohta, T.; Kamiya, M.; Kusui, K.; Michibata, T.; Nobutomo, M.; Furukawa, I. Rhodium-catalyzed reduction of esters to alcohols using diphenylsilane. *Tetrahedron Lett.* **1999**, *40*, 6963–6966.
13. Chen, S.; Ferreira, P. J.; Sheng, W.; Yubuuchi, N.; Lawrence, F. A.; Shao-Horn, Y. Enhanced activity for oxygen reduction reaction on “Pt_3Co” nanoparticles: Direct evidence of percolated and sandwich-segregation structures. *J. Am. Chem. Soc.* **2008**, *130*, 13818–13819.
14. Li, T. H.; Wang, C. M.; Yu, S. W.; Liu, X. Y.; Fu, H.; Xie, X. G. Reduction of N_2O by H_2 catalyzed by platinum monocation: A theoretical study. *J. Mol. Str.: Theochem.* **2009**, *902*, 109–113.
15. Khurana, J. M.; Sharma, P. Chemoselective reduction of α,β-unsaturated aldehydes, ketones, carboxylic acids, and esters with nickel boride in methanol–water. *Bull. Chem. Soc. Japan* **2004**, *77*, 549–552.
16. Basu, B.; Bhuiyan, M. M. H.; Das, P.; Hossain, I. Catalytic transfer reduction of conjugated alkenes and an imine using polymer-supported formates. *Tetrahedron Lett.* **2003**, *44*, 8931–8934.
17. Jana, P. P.; Sarma, R.; Baruah, J. B. Reduction of α,β-unsaturated carbonyl compounds by palladium(II) and nickel(II) complexes having nitrogen-containing ligands. *J. Mol. Catal. A: Chem.* **2008**, *289*, 57–60.
18. Keelara, A.; Srinivasa, G. S.; Gowda, D. C. Palladium-catalyzed simple and efficient hydrogenative cleavage of azo compounds using recyclable polymer-supported formate. *Can. J. Chem.* **2005**, *83*, 517–520.

19. Muhammad, O.; Sonavane, S. U.; Sasson, Y.; Chidambaram, M. Palladium/carbon-catalyzed hydrogen transfer reactions using magnesium/water as hydrogen donor. *Catal. Lett.* **2008**, *125*, 46–51.
20. Sommovigo, M.; Alper, H. Mild reduction of α,β-unsaturated ketones and aldehydes with an oxygen-activated palladium catalyst. *Tetrahedron Lett.* **1993**, *34*, 59–62.
21. Cho, I. S.; Yamaga, T.; Ishii, Y. Palladium-catalyzed hydrogenation of α,β-unsaturated sulfones and phosphonates. *J. Org. Chem.* **1994**, *59*, 4027–4028.
22. Mirza-Aghayan, M.; Boukherroub, R.; Bolourtchian, M.; Rahimifard, M. Palladium-catalyzed mild reduction of α,β-unsaturated compounds by triethylsilane. *J. Organometal. Chem.* **2007**, *692*, 5113–5116.
23. Yin, L.; Liebscher, J. Carbon–carbon coupling reactions catalyzed by heterogeneous palladium catalysts. *Chem. Rev.* **2007**, *107*, 133, and references cited therein.
24. Sodhi, R. K.; Paul, S. Nanosized Mn(acac)$_3$ anchored on amino-functionalized silica for the selective oxidative synthesis of 2-arylbenzimidazoles, 2-arylbenzothiazoles, and aerobic oxidation of benzoins in water. *Catal. Lett.* **2011**, *141*, 608–615.
25. Budarin, V.; Clark, J. H.; Hardy, J. J. E.; Luque, R.; Milkowski, K.; Tavener, S. J.; Wilson, A. Starbons: New starch-derived mesoporous carbonaceous materials with tunable properties. *Angew Chem., Int. Ed. Engl.* **2006**, *45*, 3782–3786.
26. Choudhary, D.; Paul, S.; Gupta, R.; Clark, J. H. Catalytic properties of several palladium complexes covalently anchored onto silica for the aerobic oxidation of alcohols. *Green Chem.* **2006**, *8*, 479–482, and references cited therein.
27. Jamwal, N.; Gupta, M.; Paul, S. Hydroxyapatite-supported palladium (0) as a highly efficient catalyst for the Suzuki coupling and aerobic oxidation of benzyl alcohols in water. *Green Chem.* **2008**, *10*, 999–1003.
28. Shamim, T.; Gupta, M.; Paul, S. The oxidative aromatization of Hantzsch 1,4-dihydropyridines by molecular oxygen using surface functionalized silica-supported cobalt catalysts. *J. Mol. Catal. A: Chem.* **2009**, *302*, 15–19.
29. Ram, S.; Ehrenkaufer, R. E. Ammonium formate in organic synthesis: A versatile agent in catalytic hydrogen transfer reductions. *Synthesis* **1988**, 91–94.
30. Balczewski, P.; Joule, J. A. A novel application of ammonium formate/palladium on carbon for selective reduction of the heterocyclic ring in quinolines and isoquinolines. *Synth. Commun.* **1990**, *20*, 2815–2819.
31. Chem, F.-E.; Zhang, H.; Yuan, W.; Zhang, W.-W. A new convenient reduction of aralkyl ketones to alcohols using Raney nickel–ammonium formate. *Synth. Commun.* **1991**, *21*, 107–109.
32. Bieg, T.; Szeja, W. Regioselective hydrogenolysis of benzyl glycosides. *Carbohydr. Res.* **1990**, *205*, c10–c11.
33. Botta, M.; Summa, V.; Saladino, R.; Nicoletti, R. A useful methodology for the regioselective deprotection of 1,3-dibenzyluracils. *Synth. Commun.* **1991**, *21*, 2181–2187.
34. Kabalka, G. W.; Pace, R. D.; Wadgonkar, P. P. Oximes from conjugated nitroalkanes using Pd/C ammonium formate. *Synth. Commun.* **1990**, *20*, 2453–2458.
35. Rao, H. S. P.; Reddy, S. Palladium-assisted transfer hydrogenation of cyclic α,β-unsaturated ketones by ammonium formate. *Tetrahedron Lett.* **1994**, *35*, 171–174.
36. Chatterjee, M.; Chatterjee, A.; Ikushima, Y. Pd-catalyzed completely selective hydrogenation of conjugated and isolated C=C of citral (3,7-dimethyl-2,6-octadienal) in supercritical carbon dioxide. *Green Chem.* **2004**, *6*, 114–118.
37. Park, C. M.; Kwon, M. S.; Park, J. Palladium nanoparticles in polymers: Catalysts for alkene hydrogenation carbon-carbon cross coupling reactions and aerobic alcohol oxidation. *Synthesis* **2006**, 3790–3794.
38. Solhy, A.; Clark, J. H.; Tahir, R.; Sebti, S.; Larzek, M. *Trans*-esterifications catalysed by solid, reusable apatite–zinc chloride catalysts. *Green Chem.* **2006**, *8*, 871–874.

39. Tian, F.; Lu, S. Selective reduction of α,β-unsaturated carbonyl compounds with CO/H_2O catalyzed by selenium under atmospheric pressure. *Synlett* **2004**, 1953–1956.
40. Bhuiyan, M. M. H. Catalytic transfer reduction of electron-deficient alkenes and an imine using potassium formate and catalytic palladium acetate. *Pak. J. Sci. Ind. Res.* **2005**, *48*, 377–380.
41. Zhou, J.-B.; Wang, Y.-L.; Wang, J.-Y. Selective reduction of carbon–carbon double bonds of aryl substituted chalcones with $Zn/CH_3COONH_4/C_2H_5OH/H_2O$. *J. Chem. Res.* **2004**, 118–119.
42. Davey, W.; Hearne, J. A. Chalcones and related compounds, part IX: Preparation and rearrangement of some 1,3-diphenylprop-2-en-1-ols ("chalcols"). *J. Chem. Soc.* **1964**, 4978–4985.
43. Chikashita, H.; Nishida, S.; Miyazaki, M.; Morita, Y.; Itoh, K. In situ generation and synthetic application of 2-phenylbenzimidazoline to the selective reduction of carbon–carbon double bonds of electron-deficient olefins. *Bull. Chem. Soc. Japan* **1987**, *60*, 737–746.