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Short communication

Aerobic dehydrogenation of cyclic ketones into corresponding phenols catalyzed by heterogeneous Pd nanocatalysts

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ABSTRACT

The Pd, Ni, Ni-Sn, Cu and Ag@Pd nanocatalyst having different shape and size were used for direct dehydrogenation of cyclic ketones to the corresponding phenols in the presence of O_2 as the oxidant. Among all catalyst tested, metallic Pd-1 nanoparticles exhibited excellent catalytic performance both in presence and absence of p-toluenesulfonic acid. The dehydrogenation of cyclohexanone catalyzed by Pd-1 nanocatalyst led to a 93% yield of the desired cyclohexenone and phenol. X-ray diffraction (XRD) and transmission electron microscopy (TEM) confirmed that there was no change in morphology, crystal phases and particles size of Pd-1 nanocatalyst after the reaction.

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1. Introduction

The transformation of cyclohexanones into corresponding phenols is a fundamental reaction in organic chemistry. Phenols and its derivatives are commonly used in pharmaceuticals, bulk chemicals and polymers [1]. The preparation of phenols from ketones has been investigated previously [2–10]. Condensation of acyclic ketones with β-ketoaldehydes or β-diketones enable direct access to phenols but low product yields, limited access to starting materials, and formation of isomeric products have restricted the utility of these procedures [2]. The dehydrogenation of cyclic ketones affords cyclic enones or aromatic alcohol via removal of 1 or 2 equivalent of H_2, respectively. Methods for formation of phenols via dehydrogenation of cyclohexenones typically use undesirable stoichiometric reagents, such as DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone); use stepwise procedures, such as bromination/dehydrobromination; or require harsh reaction conditions (≥200 °C) that limit functional group compatibility [2–8,11]. Recently, the group of Stahl presented a Pd-based homogeneous system using O_2 as the terminal oxidant for the aromatization of substituted cyclohexanones. Later a thorough investigation of the Pd $(TFA)_2$/2-Me_2Npy-catalyzed dehydrogenation of cyclohexanones and cyclohexenones, showing that an initial, highly active molecular Pd (II) species generate soluble Pd nanoparticles that serve as the active catalyst during steady-state dehydrogenation of the substrate [12–14]. In contrast, no effective heterogeneous catalytic method for dehydrogenation of substituted and unsubstituted cyclohexanones exist. Its great opportunity to create nanoparticle-based heterogeneous catalytic system for this important transformation. The heterogeneous catalyst can be easily separated from the reaction mixture by simple filtration and recycled several times. Here, we report a different Pd, Ni, Ni-Sn, Cu and Ag-Pd heterogeneous nano-catalyst systems, for direct dehydrogenation of cyclohexanones (1a) and 3-methyl-cyclohexanone (2a) to the corresponding phenols, in the presence of O_2 as the oxidant.

2. Experimental

2.1. Materials

Sodium borohydride ($NaBH_4$), ethylene glycol ($HOCH_2CH_2OH$), polyvinylpyrrolidone with an average molecular weight of 10,000 (PVP), acetone (CH_3COCH_3), ethanol (C_2H_5OH), L-ascorbic acid ($C_6H_8O_6$), palladium acetate (Pd $(CH_3COO)_2$), potassium bromide (KBr), p-toluenesulfonic acid ($CH_3C_6H_4SO_3H$), cyclohexanone ($C_6H_{10}O$), cyclohexenone (C_6H_8O), toluene ($C_6H_5CH_3$), mesitylene ($C_6H_3(CH_3)_3$), ethyl acetate ($CH_3COOC_2H_5$), acetic acid (CH_3COOH), dimethylformamide ($(CH_3)_2NC(O)H$), dimethylacetamide ($CH_3C(O)N(CH_3)_2$), 1-methyl-2-pyrrolidinone (C_5H_9NO), phenol (C_6H_6O), 3-methyl phenol (C_7H_8O) were purchased from Sinopherm Chemical Reagent Co. Ltd., palladium nitrate hydrate ($Pd(NO_3)_2 \cdot 2H_2O$) from Aladdin, sodium tetrachloropalladate ($Na_2PdCl_4 \cdot nH_2O$) from

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Shanxi Kaida Chemical Engineering Co. Ltd., copper acetate monohydrate (Cu $(CH_3COO)_2 \cdot H_2O$) from Shanghai Chemical Reagent Company, sodium sulfate (Na_2SO_4) from Shanghai Rich Joint Chemical Reagent Co. Ltd., 3-methyl cyclohexanone ($CH_3C_6H_9O$) from Tokyo Chemical Industry Co. Ltd., 3-methyl cyclohexenone ($CH_3C_6H_7O$) from Energy Chemical, p-anisaldehyde from Aladdin Chemistry Co. Ltd., and nickel (II) formate dihydrate (Ni $(HCOO)_2 \cdot 2H_2O$) and silver nitrate ($AgNO_3$) from Alfa Aesar.

2.2. Methods

2.2.1. Preparation and catalytic application of nanoparticles

All commercially available compounds and solvents were purchased and used as received. Pd-3 [19–20], Cu, Ni and Ni-Sn [21], Pd-1 and Ag@Pd [22], and Pd-2 [23] nanocatalysts were prepared according to condition suggested in literature.

In a typical dehydrogenation reaction, catalyst (2.8 to 5.1 mol%), p-toluenesulfonic acid (15 mol%), the cyclic ketone (0.5 mmol) and DMSO (0.5 ml) were added to a 10 ml Schlenk tube loaded with stir bar. The tube was sealed with a rubber septum and O_2 was bubbled through the solution for 10 min at room temperature. The reaction was heated in an oil bath to 80 °C with vigorous stirring under a balloon of O_2 for given time. After the completion of the reaction, the reaction mixture was filtered. Then, the residue was extracted with ethyl acetate. The organic layer was washed with water while using p-toluenesulfonic acid, dried over Na_2SO_4 and the solvent was removed under vacuum. The products were identified with GC–MS analysis.

In case of using high pressure reactor, catalyst (2.8 to 5.1 mol%), p-toluenesulfonic acid (15 mol%), the cyclic ketone (0.5 mmol) and DMSO (1 ml) were placed in a reactor. After purging the pressure reactor with O_2, the reactor was loaded with given O_2 pressure (25 °C). The reaction was heated to 80 °C with vigorous stirring for given time. After the completion of the reaction, the reaction mixture was filtered. Then, the residue was extracted with ethyl acetate.

3. Results and discussion

The metallic Pd-PVP (Pd-1), Pd-oleylamine (Pd-2), Pd cube (Pd-3), Cu-PVP and Ni-PVP nanoparticles having different particle sizes, and bimetallic Ag@Pd coreshell, and Ni-Sn nanoparticle were successfully synthesized by various methods using different reaction conditions such as stabilizing agent, reducing agents, solvents, reaction temperature etc. The synthesis conditions used for the production of nanoparticles are summarized in Table 1. Nanoparticles ware characterized by powder X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM) and energy dispersive X-ray analysis (EDX). The average particle sizes of the Pd-1, Pd-2, Pd-3, Ni, Ni-Sn, and Cu were obtained around 3.1 nm, 4.2 nm, 7 nm, 13 nm, 8 nm and 98 nm respectively. XRD patterns of Pd-1 and Pd-2 nanoparticles are shown in Fig. 1. Four main characteristic diffraction peaks at $2\theta = 39.21$, 45.87, 68.11 and 82.07° correspond to the (111), (200), (220) and (311) crystal planes of metallic Pd, confirming the formation of Pd nanoparticles

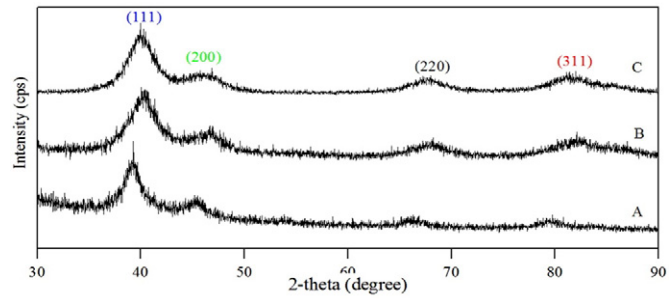


Fig. 1. Powder XRD patterns of A = Pd-2, B = Pd-1 and C = Pd-1 after reaction.

with no visible impurity phases such as PdO. The broadening of peaks in the XRD diffractogram is inversely correlated with short crystallite size of the nanoparticles [15–17]. The detailed experimental procedures and experiment data for nanoparticles preparation are included in supplementary information.

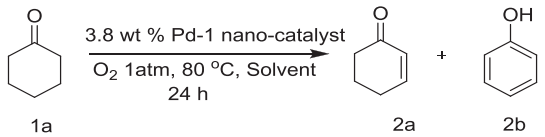
The dehydrogenation of cyclohexanone to the corresponding phenols catalyzed by different nanocatalysts in the presence of O_2 as the oxidant was investigated. Our initial studies targeted the identification of non-acidic reaction conditions for aerobic dehydrogenation of cyclohexenone. Aiming to ultimately assess the solvent effects on the aerobic dehydrogenation of cyclohexanone, we first explored the influence of several solvents in the reaction with cyclohexanone. Table 2 summarizes the results from the aerobic dehydrogenation of cyclohexanone with Pd-1 nanoparticles conducted in several solvents under 1 atm O_2 (RT) at 80 °C for 24 h. The results reveal that the reaction depends heavily upon the solvent. Among different solvents, Pd-1 showed the best conversion in DMSO (Table 1, entry 6). Then, various catalysts were tested for the dehydrogenation of cyclohexanone to the corresponding phenols in dimethylsulfoxide (DMSO) as the solvent under 1 atm of O_2 at 80 °C (Table 3). The tested catalysts include Pd-1, Pd-2, Pd-3, Ni, Ni-Sn, Cu, and Ag@Pd nanoparticles. The metallic Pd-1 nanoparticles exhibited excellent catalytic performance as compared with Ni, Ni-Sn, Cu and Ag@Pd nanoparticles. We found that 3.1 nm Pd-1 nanoparticles were a highly active heterogeneous catalyst for the dehydrogenation of cyclohexanone. In case of Ni, Ni-Sn and Ag@Pd nano-catalysts, addition of organic acid such as *p*-toluenesulfonic acid and increase of O_2 pressure also failed to increase the yield of the phenol product significantly (Table 3, entries 7 to 12). The dehydrogenation of cyclohexanone in the absence of catalyst was quite slow resulted in no conversions after 24 h (Table 3, entry 1).

In case of Pd-1, addition of organic acid such as *p*-toluenesulfonic acid and increase of O_2 pressure also increase the yield of the phenol product. When O_2 pressure increased from 1 to 5 atm the phenol yield from 15 to 49% was increased and further increase in the O_2 pressure up to 10 atm also increased product yield and phenol yield (Table 3, entries 3 to 5). The Pd-1 catalyst at low O_2 pressure favors formation of cyclohexenone, whereas at high O_2 pressure promotes highly selective formation of phenol (Table 3, entries 3 to 5).

Table 1
Reaction conditions for the preparation of Pd, Ag@Pd, Ni, Ni-Sn and Cu nanoparticles.

Nanoparticles	Precursors (mol l^{-1})	Protecting agent	Reducing agent	Reaction solvent	T (°C)	Reaction Time (min)
Pd	Palladium (II) nitrate hydrate (0.0016)	PVP	–	Ethylene glycol	120	120
Ag@Pd	Palladium (II) nitrate hydrate (0.0016) Silver (II) nitrate (0.023)	PVP	–	Ethylene glycol	90	120
Pd	Palladium (II) acetate (0.0005)	Oleylamine	–	Ethylene glycol	200	120
Pd	Sodium tetrachloropalladate	PVP	L-Ascorbic acid	Water	80	180
Ni	Nickel (II) formate dehydrate (0.03)	PVP	$NaBH_4$	Ethylene glycol	195	150
Ni-Sn	Nickel (II) formate dehydrate (0.03) Tin (II) chloride dehydrate (0.01)	PVP	$NaBH_4$	Ethylene glycol	198	150
Cu	Copper (II) acetate monohydrate (0.037)	PVP	$NaBH_4$	Ethylene glycol	190	150

Table 2
Solvents screening for the aerobic dehydrogenation of cyclohexanone catalyzed by Pd-1 nano-catalyst.



Entry	Solvent	Yield (%) 2a	2b	Product yield %
1	Toluene	1	<1	<2
2	Mesitylene	–	–	–
3	DMF	1.3	<1	<3
4	DMA	11	2.3	13
5	Acetic acid	40.5	12.6	53
6	DMSO	39	15	54
7	1-Methyl-2-pyrolidone	3	<1	<4
8	Water	1.6	<0.4	<2

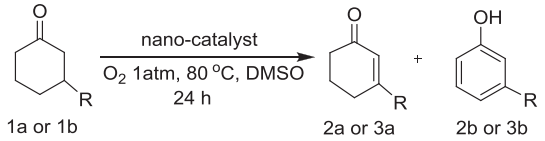
Reaction conditions; substrate 0.5 mmol, 3.8 wt% Pd-1 nanocatalyst, 1 atm O_2 pressure, 80 °C, 24 h.

With the increase in the concentration of Pd-1 nanocatalyst up to 5.1 mol% the catalytic activity towards the dehydrogenation of cyclohexanone was increased (Table 3, entries 2 to 3). The use of *p*-toluenesulfonic acid led to a substantial increase in the yield of phenol as compared to that where no additive was used (Table 3, entries 3 and 13). The best results were obtained by using 15 mol% *p*-toluenesulfonic acid with Pd-1 nanocatalyst in dimethylsulfoxide (DMSO) under 1 atm of O_2 at 80 °C (Table 3, entry 14). This catalyst system led to a 93% yield of the desired enone 2 and phenol 3. After optimization of the reaction conditions for Pd-1 nanocatalyst, we prepared Pd-2 and Pd-3 nanocatalyst. These catalysts have different method of preparation, stabilizing agents, particle size and shapes. Pd-1 nanocatalysts reported here exhibited higher catalytic activity for the dehydrogenation of cyclohexanone to the corresponding phenols in dimethylsulfoxide as compare to Pd-2 and Pd-3 nano-catalysts. The order of activity at 80 °C was Pd-1 > Pd-2 > Pd-3 nano-catalyst in DMSO (Table 3, entries 14, 17 and 19). In the view of industrial purposes, reusability of the catalyst was tested by carrying out repeated runs of the reaction on the same batch of the catalyst. In order to regenerate the catalyst, after each run, it was separated by a filtration, washed several times with deionized water, acetone and ethyl acetate. Then, it was dried under vacuum at 30 °C and reused in the subsequent run. The catalyst can be reused without any significant loss of activity. XRD and TEM results confirmed that there is no change in morphology, particle size and XRD pattern of the Pd-1 nanoparticle after reaction (Figs. 1 and 2). According to other researchers, polyvinylpyrrolidone capped noble metal, when heated, may lead to deactivation [18]. However, we tested the PVP-stabilized Pd-nanocatalysts at 80 °C, and found no evidence for its decomposition.

4. Conclusions

In summary, we have identified a Pd nanocatalyst heterogeneous system that enables direct dehydrogenation of cyclic ketones to the corresponding phenols in the presence of O_2 as the oxidant. The tested catalysts include Pd-1, Pd-2, Pd-3, Ni, Ni-Sn, Cu, and Ag@Pd. The metallic

Table 3
Catalyst optimization for aerobic dehydrogenation of cyclic ketones.



Entry[1a]	Nano-catalyst (wt.%)	Additives/TSOH	T (°C)	P (atm)	Time h	Yield (%) 2a or 3a	2b or 3b	Product Yield %
1	No catalyst	–	80	1	24	–	–	0
2	Pd-1 (2.5)	–	80	1	24	25.2	14.2	39.4
3	Pd-1 (3.8)	–	80	1	24	39	15	54
4	Pd-1 (3.8)	–	80	5	24	25	49	74
5	Pd-1 (3.8)	–	80	10	24	20	55	75
6	Cu (3.8)	–	80	1	24	<2	<1	<3
7	Ni (3.8)	–	80	10	24	0	23	23
8	Ni (3.8)	15%	80	1	24	<1	<0.5	<1
9	Ni-Sn (3.8)	–	80	10	24	0.5	13.3	13.8
10	Ni-Sn (3.8)	15%	80	1	24	9.6	0.8	10.4
11	Ag-$Pd_{core\ shell}$ (3.8)	–	80	1	24	15.4	2.3	17.7
12	Ag-$Pd_{core\ shell}$ (3.8)	15%	80	5	24	0.6	18	18.6
13	Pd-1 (3.8)	15%	80	1	24	29	39	68
14	Pd-1 (5.1)	15%	80	1	48	15	78	93
15[1b]	Pd-1(5.1)	15%	80	1	24	0	61	61
16[1b]	Pd-1(5.1)	15%	80	1	48	0	39	39
17	Pd-2 (5.1)	15%	80	1	48	10	53	63
18[1b]	Pd-2 (5.1)	15%	80	1	48	0	39	39
19	Pd-3 (5.1)	15%	80	1	48	31	<1	32

Reaction conditions; substrate 0.5 mmol [where cyclohexanone (1a), 3 methyl cyclohexanone (1b), cyclohexenone (2a), phenol (2b), 3-methyl cyclohexenone (3a), 3-methyl phenol (3b)], 3.8 wt% nanocatalyst, 1 atm O_2 pressure, 80 °C, 24 h. Yield were determined by using p-anisoldehyde as internal standard.

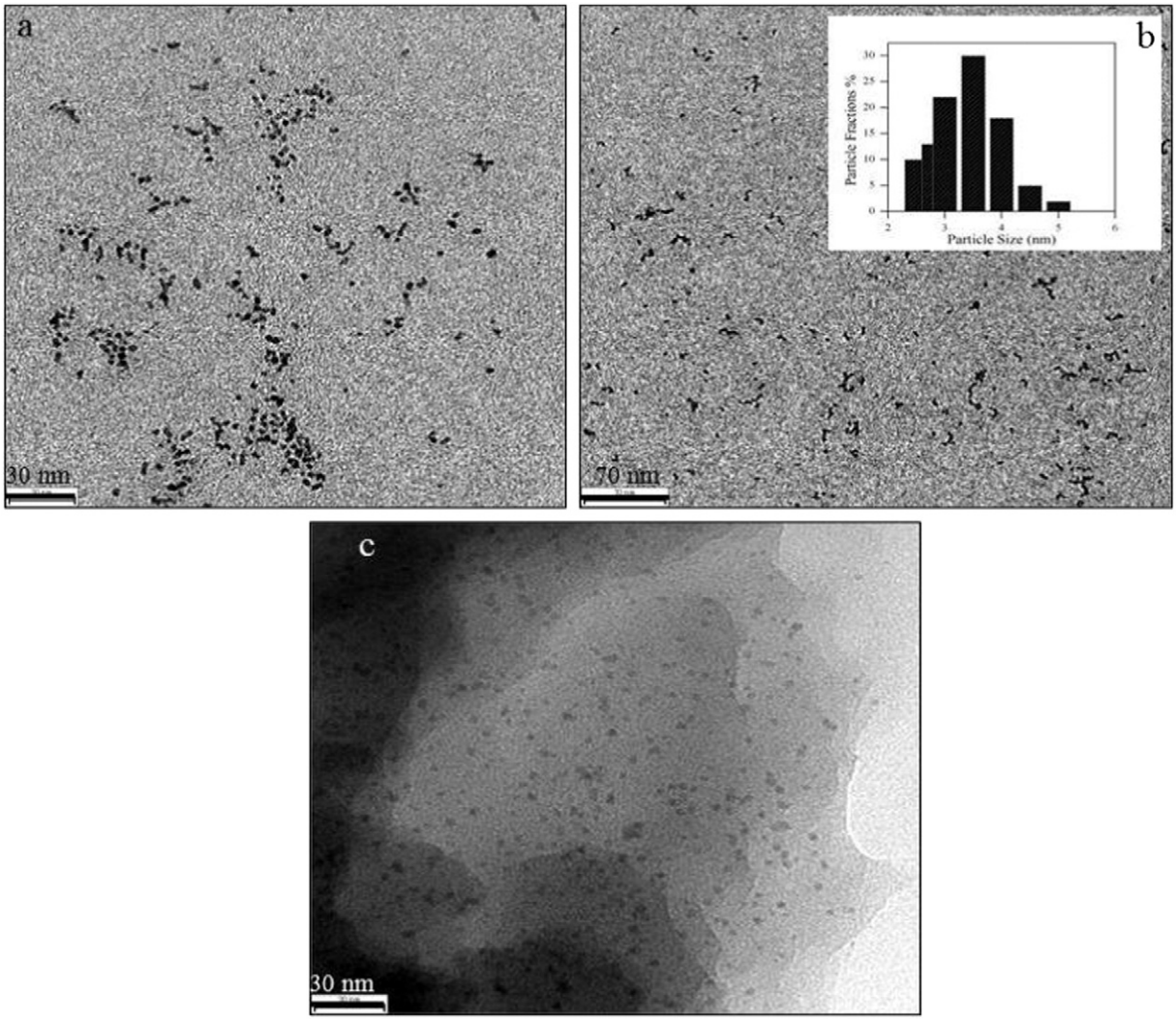


Fig. 2. (a TEM image of Pd-1, (b) their size distribution (3.1 nm) and (c) TEM image of Pd-1 after catalysis reaction.

Pd-1 nanoparticles exhibited excellent catalytic performance as compared with Pd-2, Pd-3, Ni, Ni-Sn, Cu and Ag@Pd nanoparticles. When O_2 pressure increased from 1 to 5 atm the phenol yield from 15 to 49% was increased and further increase in the O_2 pressure up to 10 atm also enhanced product yield and phenol yield. The best results were obtained by using (15 mol%) *p*-toluenesulfonic acid with Pd-1 nanocatalyst in dimethylsulfoxide (DMSO), under 1 atm of O_2 at 80 °C. The ability to replace stoichiometric reagents with O_2 as an oxidant has important implications for large scale applications of these methods in pharmaceutical and fine chemical synthesis.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2016.10.019.

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