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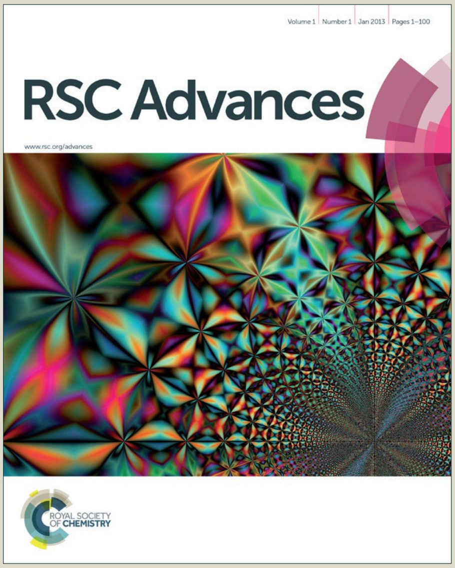

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COMMUNICATION

Fe_3O_4 nanoparticles as a new efficient co-catalyst for Pd(II) in Wacker oxidation of styrene using H_2O_2 as an oxidant

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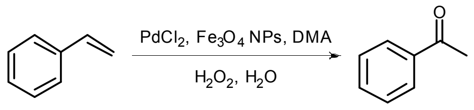
A new highly selective and environment-friendly Wacker oxidation process employing $PdCl_2/Fe_3O_4$ nanoparticles in H_2O at 100 °C using H_2O_2 as an oxidant has been developed. This approach has some advantages such as copper free reaction conditions, green solvent, high yield, excellent selectivity and green oxidant.

Acetophenone as a simplest aromatic ketone is released from a number of both human-made as well as natural sources. Recently, the applications of this compound have been extended into various research fields, such as: 1) in perfumery to impart an orange-blossom-like odor; 2) catalyst for the polymerization of olefins; 3) in organic syntheses especially as a photosensitizer; 4) specialty solvent for plastics and resins; 5) chemical intermediate for the odorant, ethyl methyl phenylglycidate, the riot control agent, 2-chloroacetophenone, 2-bromoacetophenone for dyes, 3-nitroacetophenone, synthesis of pharmaceuticals; 6) flavoring agent in non-alcoholic beverages, ice cream, candy, baked goods, gelatins and puddings, chewing gum, in tobacco; 7) fragrance ingredient in soaps, detergents, creams, lotions, perfumes; 8) solvent for synthesis of pharmaceuticals, rubber, chemicals, dyestuffs and corrosion inhibitors.[1] Currently acetophenone mainly comes as a by-product of cumene oxidation to cumene hydroperoxide for the synthesis of phenol-acetone. The other methods of acetophenone manufacturing are: oxidation of ethylbenzene, acetylation of benzene with acetylchloride in presence of aluminum chloride, catalytically from acetic and benzoic acids, from benzene and acetic anhydride, by-product in the Hock phenol synthesis and Wacker oxidation of styrene.[2]

Wacker oxidation is an efficient strategy for the industrial production of ketones and aldehydes from ethylenic compounds which was originally focused on the conversion of ethylene to acetaldehyde in the presence of a catalytic amount of $PdCl_2$ and $CuCl_2$ in a mixture of water and an organic solvent.[3] Wacker oxidation generally proceed using a Pd(II) catalyst, Cu species and excess O_2 or hydrogen peroxide as an oxidant. Recently the conversion of olefins to corresponding carbonyl products through the Wacker oxidation has been frequently used in many synthetic plans.[4] The reaction has been investigated for the efficient oxidation of a variety of substrates in various reaction conditions. The original conditions required the reaction to be carried out in water containing HCl, and showed some limitations such as a low reaction rate and poor selectivity due to formation of unwanted side product(s). Formation of chlorinated compounds[5] due to rearrangement followed by nucleophilic addition of the chloride anion and corrosion of the reactor are other drawbacks.[4] To overcome these limitations, many efforts have been focused on Wacker oxidation to discovery of better catalysts, ligands, co-catalyst conditions,[6] new solvents including ionic liquids,[7] new oxidant systems using molecular oxygen,[8] and copper free reaction conditions.[9-11]

Since Pd(II) was reduced to Pd(0) during the Wacker reaction, species such as Cu(II) and Fe(III) assisted to the reoxidation of Pd(0) to Pd(II) to prevent the quenching of the oxidation process. It is believed that in chloride-free aqueous media, neither Cu(II) nor Fe(III) salts are effective in reoxidizing of Pd(0).[12]

In continuation of our efforts to development of new catalytic system,[13] herein a new and efficient strategy was introduced for the oxidation of styrene to acetophenone by a $PdCl_2/Fe_3O_4$ nanoparticles (Fe_3O_4 NPs)/dimethylacetamide (DMA) catalytic system with H_2O_2 as a green oxidant in H_2O as a green solvent (Scheme 1). This methodology is extremely simple, and the oxidation proceeds efficiently without any by-product. Interestingly, the addition of Fe_3O_4 NPs instead of Cu(II) increases the catalytic activity of the palladium and directed the reaction conditions to green chemistry.



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Scheme 1 Oxidation of styrene to acetophenone

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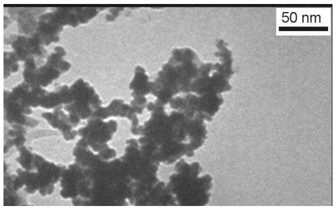

Fig. 1 The TEM image of Fe_3O_4 NPs

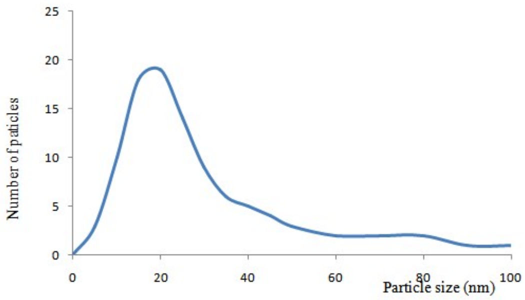

Fig. 2 The size distribution diagram of Fe_3O_4 NPs

Fe_3O_4 NPs was prepared from Fe(II) and Fe(III) in basic media and characterized with TEM (Fig. 1). The TEM image revealed that a large number of Fe_3O_4 NPs were formed with the particle size between 10-30 nm (Fig. 2).

A new copper free catalytic system was introduced for the oxidation of styrene to acetophenone using Pd(II)/ Fe_3O_4 NPs/DMA. In this system Pd(II) acted as a main catalyst for the oxidation reaction and DMA as a ligand activated Pd(II). Reduced Pd(0) atoms were oxidized into Pd(II) with the reduction of Fe(III) to Fe(II) and H_2O_2 oxidized Fe(II) to Fe(III). So, the oxidation of styrene (**1**) with H_2O_2 was investigated for optimization of the reaction conditions. It was found that 5 mol% $PdCl_2$, 10 mol% Fe_3O_4 NPs and 5 mol% DMA in H_2O with 3 equivalents of H_2O_2 at 100 °C is the best reaction conditions for the oxidation of styrene. Oxidation of styrene proceeded to give acetophenone (**2**) as the sole product in 94% yield in short reaction duration (2h) without isomerization or chlorination of styrene (Table 1, entry 1). The reaction needs long time for high yields in the absence of Fe_3O_4 NPs (Table 1, entries 2 and 3). However, performing of the reaction in the absence of Fe_3O_4 NPs show that oxidation of Pd(0) to Pd(II) can be carried out with H_2O_2, but in long time and low efficiency. Use of Fe_3O_4 NPs accelerate the reaction and increases the yield. The ligand is a necessary component for the oxidation reaction and the reaction did not perform in the absence of DMA (Table 1, entry 4). After screening a variety of solvents, H_2O and EtOH were determined to be the best solvents which H_2O was selected due to accordance with the green chemistry principles (Table 1, entries 6-9). It is important to note, the reaction in organic solvents needs H_2O (3 mmol) for afford high yield (Table 1, entries 5 and 6). Also, in the absence of Fe_3O_4 NPs the reaction in EtOH as the solvent gave higher yields compare to the reaction in H_2O as the solvent (Table 1, entry 10 compared to entry 3). Temperature is an important factor for this reaction and the yield was decreased in low temperatures (Table 1, entries 11 and 12). Among the palladium compounds tested, $PdCl_2$ was effective as the catalyst (Table 1, entries 13 and 14). The low activity of $Pd(OAc)_2$ may be attributed to the absence of chloride ion. It should be mentioned that the reaction in the presence of Fe_3O_4 with the particle size <5µm was carried out in 4h with 92% yield (Table 1, entry 15).

Table 1. Optimization of the reaction conditions for oxidation of styrene[a]

Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	$PdCl_2$	H_2O	100	2	94
2[c]	$PdCl_2$	H_2O	100	2	26
3[c]	$PdCl_2$	H_2O	100	12	73
4[d]	$PdCl_2$	H_2O	100	12	0
5	$PdCl_2$	DMA	100	4	61
6[e]	$PdCl_2$	DMA	100	4	87
7[e]	$PdCl_2$	-	100	2	28
8[e]	$PdCl_2$	MeCN	Reflux	3	85
9[e]	$PdCl_2$	EtOH	Reflux	2	94
10[c,e]	$PdCl_2$	EtOH	Reflux	12	86
11	$PdCl_2$	H_2O	90	4	82
12	$PdCl_2$	H_2O	80	4	59
13	$Pd(OAc)_2$	H_2O	100	2	37
14	$[PdCl_2(NH_3)_4]$	H_2O	100	2	84
15	$PdCl_2$	H_2O	100	2.5	92

[a] Reaction conditions: styrene (1 mmol), Fe_3O_4 NPs (10 mol%), DMA (5 mol%) H_2O_2 (3 mmol), Pd(II) (5 mol%), solvent (5 mL). [b] Isolated yield. [c] Without Fe_3O_4. [d] Whitout DMA. [e] H_2O (3 mmol) was added.

While the oxidation reaction in the solvents used in Table 1 gave acetophenone selectively, the Wacker oxidation of styrene in toluene and DMSO afforded two products including acetophenone (yields: 57% in toluene, 54% in DMSO) and 2-phenyl acetaldehyde (yields: 11% in toluene, 8% in DMSO).

Also, the reaction was examined under an oxygen atmosphere created with a balloon instead of H_2O_2 which the reaction was performed in long duration (36 h) with 83% yield. Therefore, the presence of ready oxygen in the reaction media afforded with H_2O_2 was accelerated the oxidation process. More importantly, the oxidation reaction of Fe(II) to Fe(III) needs an oxidant such as H_2O_2 or O_2 which H_2O_2 due to liquid nature is more effective.

Finally, the catalyst amount was evaluated for the oxidation reaction of styrene. For this propose 5 mL of styrene, 0.05 mmol $PdCl_2$, 0.10 mmol Fe_3O_4 NPs and 0.05 mmol DMA were added to 15 mL H_2O. The reaction was stirred at 100 °C and 1.5 mL H_2O_2 added dropwise to the reaction mixture. After 24h, the GC monitoring showed that the reaction was stopped. So, the product was isolated from the reaction mixture with column chromatography in 11% yield. This result shows that our catalytic system was deactivated after conversion of 4.7 mmol of styrene to acetophenone.

The results of our catalyst are compared with previously reports about oxidation of styrene with respect to their catalytic system, oxidant, solvent, reaction duration, temperature, yield and selectivity (Table 2). Pd(0) supported on Fe_3O_4[9] (entry 1) has some advantages such use of O_2 as a cheap oxidant and relatively milder reaction conditions compared to our report. Therefore, copper free oxidation reaction, greener solvent and short reaction duration are advantages of our report.

Table 2 Comparasion of the results obtained for oxidation of styrene to acetophenone.

Entry	Catalytic system	Oxidant	Solvent	Time (h)	Temp. (°C)	Isolated yield (%) (I) or GC yield (%) (G)	Selectivity
1	$Pd@Fe_3O_4/CuCl$[9]	O_2 (balloon)	$EtOH:H_2O$ (4:1)	36	75	94 (I)	100
2	$Au\text{-}Pd@Al_2O_3$ [10]	H_2O_2	Supercritical CO_2 (9 MPa)	3	120	68 (G)	87
3	$PdCl_2/NaOAc$ [11]	O_2 (10 atm)	Ethylene carbonate	12	80	61 (I)	100
4[a]	$PdCl_2$ [14]	H_2O_2	Ionic liquids	3	60	100 (G)	62
5[b]	$PdCl_2$ [14]	H_2O_2	Ionic liquids	3	60	80 (G)	95
6	$PdCl_2/Fe_3O_4$ NPs	H_2O_2	H_2O	2	100	94 (I)	100

[a] Best yield for this report. [b] Best selectivity for this report.

Also, the introduced catalytic oxidation reaction is a reoxidant chloride free system which has other advantages including: good selectivity (compared to entries 2, 4 and 5), high yield (compared to entries 2, 3 and 5) and no need to high pressure (compared to entries 2 and 3).

Conclusions

In conclusion, we have demonstrated the Fe_3O_4 NPs assisted reoxidant chloride free Wacker oxidation of styrene into acetophenone in the presence of $PdCl_2$/DMA as a catalyst. High yield of acetophenone was obtained selectively in the copper free conditions in short reaction duration. H_2O as a green solvent, H_2O_2 as a green oxidant and development an organic solvent-free approach are other advantages of this report.

Experimental

All of the chemical compounds were purchased from sigmaaldrich.

For preparation of Fe_3O_4 NPs, $FeCl_3.6H_2O$ (20 mmol) and $FeCl_2.4H_2O$ (10 mmol) were added to 30 mL distilled water. The salt mixture drop wise was added to 120 mL ammonia solution under nitrogen atmosphere at 70 °C. The solution was stirred mechanically under vigorous stirring for 30 min. Black precipitate was decanted by a permanent magnet and washed by distilled water three times and dried under vacuum at 50 °C

For oxidation of styrene, styrene (0.10 g, 1.00 mmol) was added to a round bottom flask containing colloidal of $PdCl_2$ (0.009 g, 0.05 mmol), Fe_3O_4 NPs (0.023 g, 0.10 mmol), DMA (0.004 g, 0.05 mmol) and H_2O (5 mL). H_2O_2 (30%) (30 µL, 3.00 mmol) was added dropwise to the reaction mixture and the mixture was stirred at 100 °C for 2h. Upon completion, the mixtures were cooled to room temperature and the product extracted with diethyl ether (3 × 5 mL). The combined extracts were then washed with water, dried with $MgSO_4$, and analyzed by GC-MS and NMR spectroscopy. For avoiding from organic solvents, the reaction was repeated with 10.00 mmol styrene, $PdCl_2$ (0.09 g, 0.50 mmol), Fe_3O_4 NPs (0.23 g, 1.00 mmol), DMA (0.04 g, 0.50 mmol), H_2O_2 (30%) (0.30 mL, 30.00 mmol) and H_2O (50 mL) and after completion of the reaction during 2h, Fe_3O_4 was isolated with a magnet and the solvent and DMA were evaporated with rotary. Then, $MgSO_4$ was added to the vessel, the solid separated with filtration and pure acetophenone obtained in 93% yield.

Acknowledgements

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