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Solid supported Ru(0) nanoparticles: an efficient ligand-free heterogeneous catalyst for aerobic oxidation of benzylic and allylic alcohol to carbonyl

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ABSTRACT

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Oxidation of primary and secondary alcohol to carbonyl represents an important class of compounds or intermediates presence in several pharmaceuticals, agrochemicals, perfumes, and flavoring agents.^{1–3} Successful examples for the aerobic oxidation of alcohols include both homogeneous as well as heterogeneous Ru⁴ catalyst. Most of the ruthenium catalyzed oxidation reactions have been explored either in perruthenates⁵ or ruthenium complex preferentially with salen⁶ and phosphate ligands.⁷ Further, Ru immobilized on different solid supports include Ru-hydroxyapatite (HAP),8 [RuCl₂(*p*-cymene)]₂/activated carbon,⁹ Al₂O₃,¹⁰ carbon,¹¹ zeolite¹², and MgO¹³ have been designed and developed for aerobic oxidation reactions. Polymer incarcerated Ru catalyst in a flow system,14,15 and zeolite-confined nano-RuO216 have been explored extensively but the major drawbacks of these system were the pretreatment of catalyst with costly silver salts, use of N-methylmorpholine (NMO),¹⁷ TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) which act as a co-catalyst, use of oxidants either an amine N-oxide or an iodosobenzene derivative¹⁸ and longer reaction time required for the synthesis of nano-catalyst, respectively. Solid supported Ru^{II} and Ru^{II}-Dower catalyzed reaction were also reported, but the use of harsh oxidant, NaIO₄ made it less convenient.¹⁹

In recent reports, our group described the synthesis of solid supported palladium and rhodium (SS-Pd and Rh) nano/microparticles as heterogeneous catalyst and their application in different areas of organic synthesis.²⁰

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Herein, we report a facile process for in situ generation of Ru(0) nanoparticles and their simultaneous deposition over solid matrix to produce SS-Ru and their applicability in aerobic oxidation of benzylic and allylic alcohols to their corresponding carbonyls, with excellent recyclability of catalyst up to seven cycles.

Polymer immobilized stable, spherical ruthenium nanoparticles were prepared, characterized, and acted

as a heterogeneous catalyst for the selective benzylic and allylic alcohol oxidation into the corresponding

carbonyls using molecular oxygen. The solid supported Ru(0) (SS-Ru) as a heterogeneous catalyst exhibits

good reusability and easy separation from the reaction mixture by filtration.

SS-Ru was prepared following the same strategy which has been applied for SS-Pd preparation. Amberlite IRA 900 chloride form resin was partially exchanged with $^{-}BH_4$ ion and then washed with water and acetone properly. Further it was treated with catalytic quantity of RuCl₃·H₂O in DMF solvent for 1 h at 100 °C. The







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Figure 2. A gradual appearance of transmission electron micrograph (TEM) and corresponding histogram of SS-Ru to illustrate particle size distributions.

white solid surface of resin soon turned gray after complete impregnation of Ru (Supplementary data). After complete immobilization of Ru over solid surface, the resin was washed with water, then with acetone and dried under reduced pressure. The conversion of Ru(III) to Ru(0), was monitored by UV-vis spectroscopic studies (Fig. 1).

Disappearance of the peak at 425 nm showed the conversion of Ru(III) to Ru(0)²¹ (Fig. 1). The change of oxidation state, nanoparticles formation, and metal detection were determined by UV–vis, TEM (Fig. 2), EDX (Fig. 3), and XRD (Supplementary data) analysis.

In order to optimize the reaction conditions several bases, solvents, and catalytic conditions were investigated. SS-Ru (0.05 mmol Ru), triethyl amine in toluene at 90 °C was found suitable to give the highest yield of **2a** in 90% (Table 1). With the decrease of temperature the rate of reaction as well as product yield were decreased assertively. The same reaction was also performed in open air condition in place of oxygen but no oxidized product was observed. The generality of this methodology was investigated using optimized reaction conditions with different primary and secondary benzylic as well as allylic alcohols (Table 2).

The reaction was also quite tolerant concerning the electronic nature of the functional groups on the aromatic ring and did not



Figure 3. EDX analysis of SS-Ru(0) for elemental detection of Ru.

Table 1 Optimization studies for benzylalcohol oxidation

Í	\searrow	ОН	Catalyst, Solvent	СНО
	\checkmark		Base, 90 °C	\checkmark
	ÓMe		O ₂ , 4h	ÓMe
	1a			2a
Entry		Catalyst ^b	Base/solvent	Yield ^a (%)
1		SS-Ru	Toulene	20
2		SS-Ru	Cs ₂ CO ₃ /Toulene	60
3		SS-Ru	K ₂ CO ₃ /Toulene	70
4		SS-Ru	Pyridine/Toulene	58
5		SS-Ru	Et ₃ N/Toulene	90
6		SS-Ru ^c	Et ₃ N/Toulene	51
7		SS-Ru ^d	Et ₃ N/Toulene	90
8		RuCl ₃	Et ₃ N/Toulene	65
9 ^e		SS-Ru	Et ₃ N/Toulene	89
10 ^f		SS-Ru	Et ₃ N/Toulene	70
11 ^g		SS-Ru	Et ₃ N/Toulene	no reaction

^aIsolated yield. Reaction condition: substrate (1 equiv), catalyst (0.05^b, 0.03^c and 0.06^d mmol), solvent (3 mL), base (1.5 equiv), was heated for 3 h at 90 °C; 5 h at 80 °C (entry 9); ^e9 h at 70 °C (entry 10); ^fair at 90 °C (entry 11).^g

apparently affect the efficiency of the oxidation in terms of yield and chemo-selectivity (Table 2, entries 1-20). Alcohols bearing electron donating substituents such as 2-ethoxy, 4-methyl, 4methoxy, and 2,3,4-trimethoxy readily converted into the corresponding aldehydes **2b-e** in considerably good yields. Halogen substituted benzyl alcohols afforded the corresponding aldehydes 2f-h in satisfactory yields and no dehalogenation product was observed. Generally electron deficient functional group attached to the aromatic ring causes electron deficiency on -CH₂OH group and thereby retards the rate of the oxidation process. In our study, we also observed that nitro substituted benzyl alcohols 1i-j gave lesser yields than the electron rich analogues (Table 2, entries 8 and 9). Similarly, secondary benzyl alcohols 1k-q containing both the electron rich and deficient substituents showed comparable results as primary benzylic derivatives leading to desired ketones $2k-q^{22}$. Interestingly, SS-Ru was also found to be applicable to the oxidation of heterocyclic alcohol **1r**-**s** to respective aldehydes 2r-s in high yields. Allyl alcohols 1t-v were also found to be active in our standard reaction conditions and underwent selective oxidation to give excellent yields of cinnamylaldehydes 2t-v. Oxidation reaction of geraniol 1w under the optimized condition even after 12 h ended with poor yield (20%) of the corresponding oxidized product **2w** and major unreacted geraniol was detected (Table 2).

Table 2

SS-RU CALAIVZED AEFODIC OXIDALION OF AICONOIS TO CALD

Entry	Reactant	Product	Time	Yield ^a (%)
1	OH OEt 1b	CHO OEt 2b	3	90
2	Me OH Ic	Me CHO 2c	3	80
3	MeO OH 1d	MeO CHO	3	85
4	MeO OMe OMe 1e	MeO OMe OMe	4	84
5	CI OH	CI CHO	3	92
6	Br 1g	Br CHO 2g	3	86
7	он Br 1h	CHO Br 2h	3	85
8	OH 1i NO ₂	CHO 2i NO ₂	3	87
9	O ₂ N OH 1j	O ₂ N CHO 2j	3	72
10			4	96
11		21	4	89
12	MeO 1m	McO 2m	4	87
13	MeO In OMe	MeO 2n OMe	4	85
14	OH Br 10		4	90
15			4	87
16		2q	4	85
17	CH ₂ OH 1r	CHO 2r	3	94
18		CHO S 2s	3	88

 Table 2 (continued)



Reaction condition: substrate (1 equiv), solvent (3 mL), catalyst (0.05 mol), Et_3N (1.5 equiv) were heated using O_2 at 90 °C for appropriate time. ^a Isolated yield after column chromatography.



Figure 4. Recovery and reuse of SS-Ru^{a,b}, ^a3-methoxybenzyl alcohol (1 equiv), SS-Ru (0.05 mol), Et₃N (1.5 equiv). ^bConversion was determined on the basis of GC-MS analysis.

Recovery of the catalyst was done by filtration and washing with water, acetone and then dried under reduced pressure. The catalyst so obtained could be reused without any activation. Moreover, the reused SS-Ru catalyst exhibit similar efficiency for oxidation reaction, which was confirmed by the example of oxidation of 3-methoxybenzyl alcohol (Fig. 4). Upto seven cycles, minor loss of product yields 2–5% were observed.

Also the reaction mixture showed no further conversion on removing the catalyst from the system, indicating that metal is not leaching from supports.

In summary, we have developed active and environmentally sustainable immobilized ruthenium nanoparticles (SS-Ru) as heterogeneous catalyst. This catalyst has been utilized successfully in an aerobic oxidation of benzylic and allylic alcohols to corresponding carbonyls with high efficiency, selectivity, and reusability. Use of milder base, oxygen as an inexpensive primary oxidant and water as the only by product, highlights the environmentally benign green chemical aspect of the present process.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.03. 106.

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22. Typical experimental procedure for SS-Ru catalyzed oxidation of alcohols. A mixture of 2-phenyl ethanol 1k (100 mg, 0.818 mmol) SS-Ru (914 mg, 0.05 mmol), Et₃ N (171 µl, 1.22 mmol) and 3 ml of toluene was purged with molecular oxygen and stirred at 90 °C for 4 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction was cooled, diluted with ethyl acetate, and filtered through cotton bed. The combined

organic layer was evaporated under reduced pressure and the crude residue was purified by silica gel (mesh 60–120) column chromatography (hexane/EtOH::95:5) afforded **2k** as colorless liquid (94 mg, 96%). ¹H NMR (300 MHz, CDCl₃) δ 2.36 (s, 3H), 7.31–7.37 (m, 3H), 7.74–7.77 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 25.49, 127.64 (2C), 128.25 (2C), 132.04, 136.06, 197.11.