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Solid-supported ruthenium(0): an efficient heterogeneous catalyst for hydration of nitriles to amides under microwave irradiation† ‡

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Solid-supported ruthenium(0) was synthesized by the reduction deposition method and used as a heterogeneous catalyst for the hydration of nitriles to amides under microwave irradiation. A wide range of aromatic, α,β-unsaturated and aliphatic nitriles were efficiently converted to their corresponding primary amides under milder conditions. The catalyst was found to be very stable under moisture and microwave irradiation, easily separable from the reaction mixture, to cause negligible metal contamination of the product and was recyclable up to ten times without significant loss of catalytic activity.

The hydration of organonitriles to amides in water[1] is one of the most important functional group transformations in academia and industry because of their usefulness as chemical intermediates in organic synthesis,[2] pharmaceutical molecules[3] and functional polymers.[4] Transition metal catalyzed processes are more prevalent and selective than traditional acid base approaches.[5] A variety of homogeneous transition-metal complexes of ruthenium,[6] rhodium,[7] palladium,[8] platinum[9] and gold[10] have been developed for this purpose. But the special handling of sensitive metal complexes, difficulty of product–catalyst separation and no reusability in most cases limits the use of these homogeneous metal complexes. In this context, heterogeneous transition metal catalysts have gained enormous interest due to easy handling, excellent stability, easy recovery and reusability compared to homogeneous catalysts. Much effort has been given to the synthesis of $Ru(OH)_x$ based catalysts, such as $Ru(OH)_x/Al_2O_3$,[11] nanoferrite-$Ru(OH)_x$[12] and nano-Fe@$SiO_2Ru(OH)_x$[13] synthesized under strong basic conditions using NaOH or NH_4OH. The $Ru(OH)_x/Al_2O_3$[11] catalyst was also recharged in NaOH for its reuse. Although the hydration reactions have been carried out in aqueous media under neutral conditions, the role of catalytically bound OH^- in $Ru(OH)_x$ cannot be ignored. So far, the totally base free hydration of organonitriles has been difficult except for the use of ligands with ruthenium metal.[14] Recently, a Nafion–Ru nanoparticle system has been developed that catalyzes the reaction of aromatic and heterocyclic organonitriles under base free conditions,[15] but the hydration of less reactive aliphatic nitriles has not been attempted. Further, the long reaction time (12 h) and high temperature (175 °C) also limits this methodology.

In continuation of our previous work on solid supported transition metal nanoparticles,[16] herein we report solid supported ruthenium(0) nanoparticles that efficiently catalyze the hydration of aromatic, heterocyclic, α,β-unsaturated and aliphatic nitriles in base free conditions under microwave irradiation.

Solid supported nanoparticles of ruthenium(0) (SS-Ru) were synthesized by a reduction deposition approach. Amberlite IRA 900 chloride form resin, selected as the solid support, was treated with a catalytic quantity of $NaBH_4$ to partially exchange chloride ions for BH_4^- ions and then treated with $RuCl_3\cdot H_2O$ in DMF at 100 °C for 1 h. The white solid surface of the resin was soon found to be turned grey/blackish after complete impregnation of Ru(0) (Fig. 1).

After complete immobilization of Ru over the solid surface, the resin was washed with water, then with acetone and dried

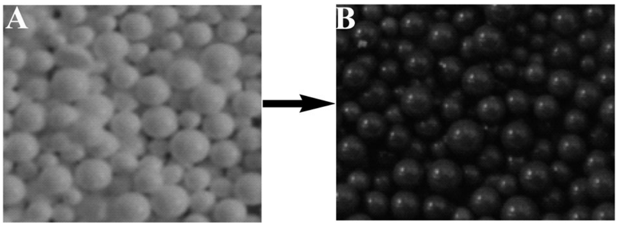

Fig. 1 (A) The polymeric polystyrene resin as a solid support; (B) the solid supported Ru(0) catalyst.

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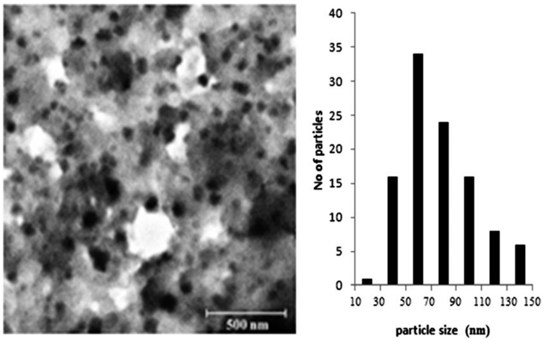


Fig. 2 A transmission electron microscopy (TEM) image of SS-Ru nanoparticles and a histogram representing particle size distribution.

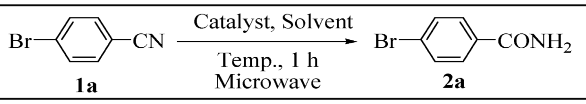
under reduced pressure. The conversion of Ru(III) to Ru(0) was monitored by UV-Vis spectroscopy[17] and confirmed by energy dispersive X-ray (EDX) and X-ray diffraction (XRD) analysis, as mentioned in our earlier report.[18]

The impregnation and distribution of nanoparticles of Ru(0) over the solid matrix was determined by transmission electron microscopy (TEM) and represented by a histogram (Fig. 2).

In an attempt to find the best reaction conditions, the hydration of *p*-bromobenzonitrile as a model substrate with homogeneous Ru(III) and heterogeneous SS-Ru catalysts in different solvents was monitored by GCMS. The use of homogeneous $RuCl_3{\cdot}H_2O$ catalyst afforded 76% of product **2a** under the reaction conditions but the catalyst is not recoverable and recyclable. The reaction under conventional heating and unpressurized conditions using SS-Ru (2–3 mol%) gave poor conversion of **1a** (Table 1, entries 4 and 5). Among different catalysts and conditions, SS-Ru (2 mol% Ru) in water at 130 °C (80 psi, 100 W) yielded the best results (Table 1, entry 3) and was selected as the optimum conditions for the hydration of substituted nitriles to the corresponding amides in water.

The less soluble amides, like *p*-bromobenzamide, crystallized in the water and can be separated by decanting. In the cases of

Table 1 Optimization of reaction conditions for the microwave assisted hydration of *p*-bromobenzonitrile

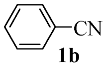
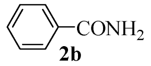
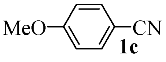
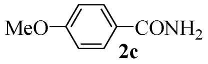
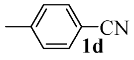
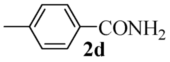
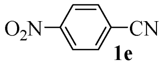
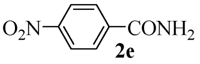
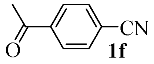
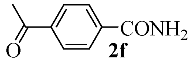
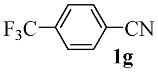
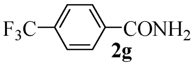
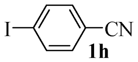
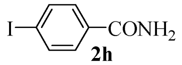
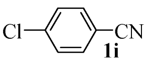
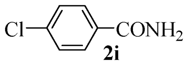
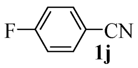
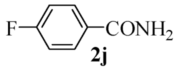
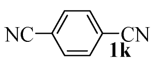
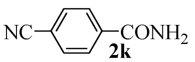
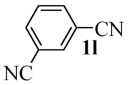
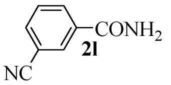
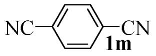
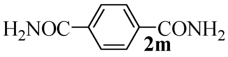
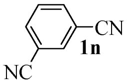
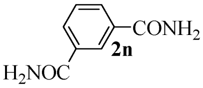
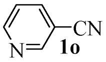
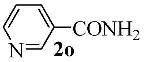
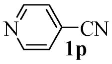
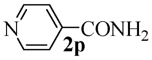
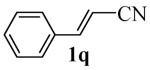
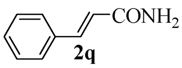
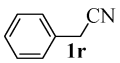
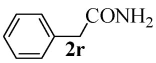
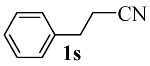
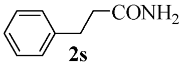


Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Yield[a] (%)
1	SS-Ru (3)	H_2O	100	35
2	SS-Ru (3)	H_2O	130	>99
3	**SS-Ru (2)**	**H_2O**	**130**	**>99 (85)**
4[b]	SS-Ru (3)	H_2O	130	10
5[b]	SS-Ru (2)	H_2O	130	8
6	SS-Ru (1)	H_2O	130	60
7	$RuCl_3{\cdot}H_2O$ (2)	H_2O	130	76
8	—	H_2O	130	nr
9	SS-Ru (2)	DMF	130	nr
10	SS-Ru (2)	THF	130	nr
11	SS-Ru (2)	EtOH	130	nr

Isolated yield in parenthesis; nr = no reaction. [a] GCMS yield. [b] Reaction carried out under conventional heating for 3 h.

Table 2 SS-Ru catalyzed hydration of substituted nitriles under microwave irradiation

$$\text{R-CN} \xrightarrow[\text{Microwave, 130 °C}]{\text{SS-Ru, H}_2\text{O}} \text{R-CONH}_2$$

Entry	Substrate	Time (min)	Product	Yield[a] (%)
1	 **1b**	60	 **2b**	86 (>99)
2[b]	 **1c**	120	 **2c**	83 (>99)
3[b]	 **1d**	120	 **2d**	84 (>99)
4	 **1e**	60	 **2e**	88 (>99)
5	 **1f**	60	 **2f**	79 (>99)
6	 **1g**	60	 **2g**	85 (>99)
7	 **1h**	60	 **2h**	84
8	 **1i**	60	 **2i**	83 (>99)
9	 **1j**	60	 **2j**	86 (>99)
10	 **1k**	30	 **2k**	77
11	 **1l**	30	 **2l**	73
12[c]	 **1m**	120	 **2m**	80
13[c]	 **1n**	120	 **2n**	82
14	 **1o**	60	 **2o**	84 (>99)
15	 **1p**	60	 **2p**	88 (>99)
16	 **1q**	60	 **2q**	80 (>97)
17	 **1r**	60	 **2r**	86 (>99)
18	 **1s**	120	 **2s**	72 (>80)
19	CH_3CH_2CN **1t**	120	$CH_3CH_2CONH_2$ **2t**	60

[a] Isolated yields. GCMS yield in parentheses. [b] SS-Ru (3 mol%) was used. [c] Reactions carried out at 150 °C.

products that are not crystallized, the crude reaction mixture was extracted with ethyl acetate and further purified by column chromatography.

The scope of this transformation was explored using a variety of substrates, including aromatic, heterocyclic, α,β-unsaturated and aliphatic nitriles. The reaction of benzonitrile **1b** under the optimized reaction conditions afforded benzamide in good yield. Different aromatic nitriles containing electron donating substituents, like methyl, methoxy **1c** and **1d**, and electron withdrawing nitro, acetyl and trifluoromethyl **1e–g** groups gave the desired products in good yields (Table 2, entries 2–9). In the case of electron donating aromatic nitriles, the reaction proceeded slowly at the optimized catalyst concentration. Increasing the catalyst loading to 3 mol% and reaction time to 2 h afforded the corresponding products in good yields. The slow reaction rate observed might be due to the fact that electron donating groups deactivate the eletrophilicity of nitrile carbon atom, making it less susceptible to attack from the nucleophilic water molecule. The halo substituted benzonitriles, such as iodo, chloro, fluoro **1h–j**, smoothly yielded the corresponding products in good yields without any dehalogenation. Further, 1,3-benzodinitriles and 1,4-benzodinitrile, **1k–n**, were selectively hydrated to mono- and di-amides by controlling the reaction parameters, such as time and temperature. The mono-amides were selectively obtained in 73–77% yields by shortening the reaction time to 30 minutes, while diamides were obtained by increasing the reaction time to 2 hours at 150 °C. Heterocyclic nitriles were also efficiently converted to nicotinamide, a part of the vitamin B group and isonicotinamide from 3-cyanopyridine and 4-cyanopyridine, respectively **1o–p**. The α,β-unsaturated cinnamonitrile **1q** yielded the cinnamide in good yield and no hydration of the carbon–carbon double bond was observed. The less active aliphatic nitriles also yielded the corresponding amides in moderate to good yield. Phenylacetonitrile **1r** was found to be reactive under similar conditions and produced the corresponding amide **2r** in quantitative yield (>99% GCMS) while phenylpropionitrile **1s** was found to be slightly less reactive and the reaction took 2 hours to give a good yield of the corresponding amide **2s** (72%). The low molecular weight propionitrile **1t** similarly participated in the hydration reaction to give the corresponding amide **2t** in moderate yield (60%).

The reaction may be following the mechanism of activation of the nitrile moiety by coordination of ruthenium metal to the nitrogen atom and then the nucleophilic attack of water on the electrophilic carbon to yield the amide.

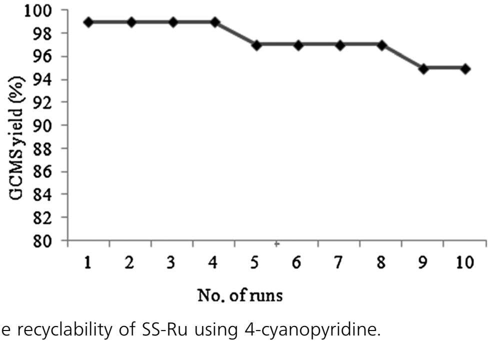


Fig. 3 The recyclability of SS-Ru using 4-cyanopyridine.

The catalyst is easily recoverable and recyclable. The recyclability experiments of SS-Ru were conducted by using 4-cyanopyridine as a test substrate. After completion of the reaction, the product was extracted using ethyl acetate. The catalyst was washed with water and acetone then dried. The catalyst was used ten times without significant loss of catalytic activity (Fig. 3).

Conclusions

In conclusion, we have developed air and moisture stable solid supported Ru(0) nanoparticles as a heterogeneous catalyst that efficiently catalyzed the base free hydration of a wide range of nitriles to their corresponding amides under microwave irradiation. The catalyst was easy to handle, recoverable and reusable up to several runs and no significant loss of catalytic activity was observed.

Acknowledgements

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