



Immobilization of Ru(III) complex on silica: a heterogenized catalyst for selective oxidation of alcohols in water at room temperature



S. Ganesamoorthy^{a,b}, M. Muthu Tamizh^{a,c}, K. Shanmugasundaram^b, R. Karvembu^{a,*}

^a Department of Chemistry, National Institute of Technology, Tiruchirappalli 620015, Tamil Nadu, India

^b Synthetic Chemistry, Syngene International Limited, Biocon Park, Bangalore 560099, Karnataka, India

^c Interdisciplinary School of Indian System of Medicine (ISISM), SRM University, Kattankulathur 603203, Tamil Nadu, India

ARTICLE INFO

Article history:

Received 9 August 2013

Revised 10 October 2013

Accepted 15 October 2013

Available online 22 October 2013

Keywords:

Oxidation

Alcohols

Ruthenium(III)

Water solvent

ABSTRACT

We have developed a heterogenized catalyst ('SiO₂'-NH₂-Ru^{III}) by the immobilization of [Ru(acac)₂(CH₃CN)₂]PF₆ on SiO₂. The catalyst was characterized by SEM, solid state NMR, EPR, FT-IR, ICP, and BET surface area analyses. 'SiO₂'-NH₂-Ru^{III} catalyzed the selective oxidation of alcohols with periodic acid in water at room temperature. This protocol was applicable to the controlled oxidation of structurally diverse primary and secondary alcohols. The catalyst could be quantitatively recovered and reused up to six cycles without significant loss of catalytic activity.

© 2013 Elsevier Ltd. All rights reserved.

The aldehydes and ketones are being recognized as important starting materials for multitude of carbon–carbon or carbon–heteroatom bond formation reactions. The scarce stability and commercial availability of these compounds made the selective oxidation of alcohols as an instant synthetic tool for laboratory and industrial processes.^{1–5} The noncatalytic methods with stoichiometric oxidants like dichromate and permanganate produce a tremendous amount of metal salts as waste.^{6,7} Among several metal based oxidation methods, selective oxidation of alcohols to the corresponding carbonyl compounds in the presence of catalytic amount of a transition metal in water is very attractive in terms of environmental and economic stand points.^{8,9} The reason is that aqueous H₂O₂ or gaseous O₂ can be used as a stoichiometric oxidant.^{10–14} However these oxidants are often employed under an elevated temperature and high pressure, respectively, to influence their reactivity. Moreover, it is difficult to control the consumption of gaseous O₂ added as an oxidant. In contrast, H₅IO₆ as an oxidant offers several advantages, including solubility in water, stability, simple handling, controllable addition, safe operation, cost effectiveness, and nontoxic nature,¹⁵ even though H₂O₂ and O₂ are environmentally benign. Recently, heterogenized metal acetylacetonate complexes have been found more effective and selective than their homogeneous counterparts.^{16–18} During the course of our study, we proved [Ru(acac)₂(CH₃CN)₂]PF₆ as an effective catalyst for the controlled oxidation of alcohols in water

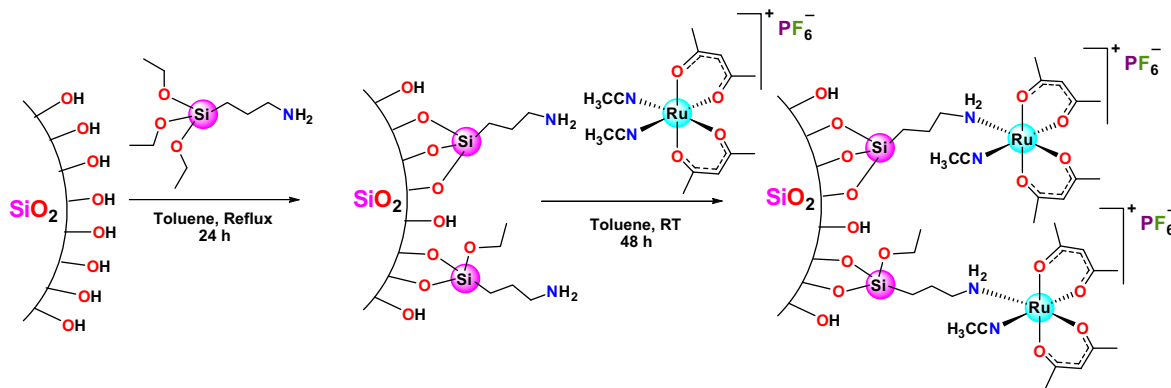
medium.¹⁹ This catalyst was immobilized onto silica by replacing one of the weakly coordinated acetonitrile molecules with amine functionalized silica to form 'SiO₂'-NH₂-Ru^{III}. The newly developed heterogenized Ru(III) catalyst in water with H₅IO₆ as oxidant showed the highest selectivity; it avoids carboxylic acid formation. This is an inexpensive, mild protocol for the selective oxidation of alcohols. Advantageously the catalyst has several benefits including high stability, ease of use, leach proof, and reusability.

Fumed silica (1 g, surface area 225 m²/g) was dispersed in dry toluene under N₂ atmosphere. To this 3-aminopropyl-1-triethoxysilane (12 mL) was added slowly and refluxed overnight under stirring. The reaction mixture was cooled down to room temperature, 1.5 N HCl was added slowly and stirred for an hour. The mixture was filtered and the resulting solid was washed with acetone several times. The solid was dried at 100 °C under vacuum for 6 h to get 'SiO₂'-NH₂.

[Ru(acac)₂(CH₃CN)₂]PF₆ was prepared according to the literature method.²⁰ [Ru(acac)₂(CH₃CN)₂]PF₆ (0.2 g) and 'SiO₂'-NH₂ (1 g) were stirred at room temperature in dry toluene (20 mL) for 48 h. The reaction mixture was filtered and washed several times with CH₂Cl₂. The obtained solid was subjected to the Soxhlet extraction using CH₂Cl₂ for two days to ensure leaching out of all unbound Ru(III). The filtration gives a solid which was dried at 100 °C under vacuum for 6 h to give a pale brown powder (1.1 g, 0.066 wt % of Ru, surface area 209 m²/g) (Scheme 1). The Ru content was estimated by ICP-OES analysis using a Perkin Elmer Optima 5300 DV instrument. The SEM image (Fig. S1 in Supplementary data) of the catalyst was obtained using a JEOL JSM-6701F FE-SEM

* Corresponding author. Tel.: +91 431 2503631; fax: +91 431 2500133.

E-mail address: kar@nitt.edu (R. Karvembu).



Scheme 1. Preparation of 'SiO₂'-NH₂-Ru^{III}.

microscope. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer as KBr pellet in the frequency range of 400–4000 cm⁻¹. The BET surface area was found using a ASAP 2020 surface area and porosimetry system. ²⁹Si CP-MAS solid state NMR spectrum was recorded using a Bruker DSSX-300 solid state NMR spectrometer.

Catalyst (0.06 mol %) and H₅IO₆ (1 mmol) were stirred with 10 mL of H₂O taken in a round bottom flask. The alcohol (1 mmol) was added slowly to the stirring solution. Stirring was continued for the required time at room temperature. After the requisite time, the catalyst was separated by centrifugation. The product was extracted from the centrifugate with diethyl ether. The ether extract was evaporated to get the product which was dissolved in dry acetone and then analyzed by GC. Authentic samples of both reactant and product were used to verify the retention times and to confirm the product formation. The ether extract was concentrated and chromatographed on a silica gel column with *n*-hexane:ethyl acetate (4:1) as the eluent to give carbonyl product. The used catalyst was washed with diethyl ether, dried and then it was reused for the subsequent oxidation of alcohol for testing the catalyst reusability.

Shimadzu GC-2010 gas chromatograph (GC) with a 60 m × 0.32 mm Restek Rtx[®]-5 column and a flame ionization detector (FID) was used to monitor the catalytic reactions. The initial column temperature was increased from 60 to 150 °C at the rate of 10 °C/min and then to 220 °C at the rate of 40 °C/min. N₂ was used as a carrier gas. The temperatures of the injection port and FID were kept constant at 150 and 250 °C, respectively, during product analyses.

The new catalyst ('SiO₂'-NH₂-Ru^{III}) was characterized by using different analytical techniques. The ²⁹Si CP-MAS NMR spectrum showed two peaks that indicate the presence of two different silicon atoms in the catalyst (Fig. 1). The peaks at -109 and -67 ppm are the characteristic of Q type [Si(O-)₄] and T type [R-Si-(O-)₃] silicates, respectively.²¹ The later one confirms the amino propyl group bound to the support. The observed split in the peak at -67 ppm refers to unreacted ethoxy groups of 3-aminopropyl-1-triethoxysilane during the grafting process (Scheme 1). The EPR spectrum of the catalyst had a signal with the 'g' value of 2.2, which has been assigned to Ru³⁺ with a low-spin d⁵ configuration, consistent with the reported literature value (Fig. 2).²² The FT-IR spectrum of the catalyst showed bands at 1095, 1629, and 2925 cm⁻¹, indicating the presence of Si-O, C=O, and NH₂ groups in the catalyst (Fig. S2 in Supplementary data).²³ These spectral observations confirm Ru(III) loading on SiO₂.

Among different solvents studied, water proved to be propitious. Hence, we preferred to use water as reaction medium for optimizing the reaction variables such as oxidant and catalyst

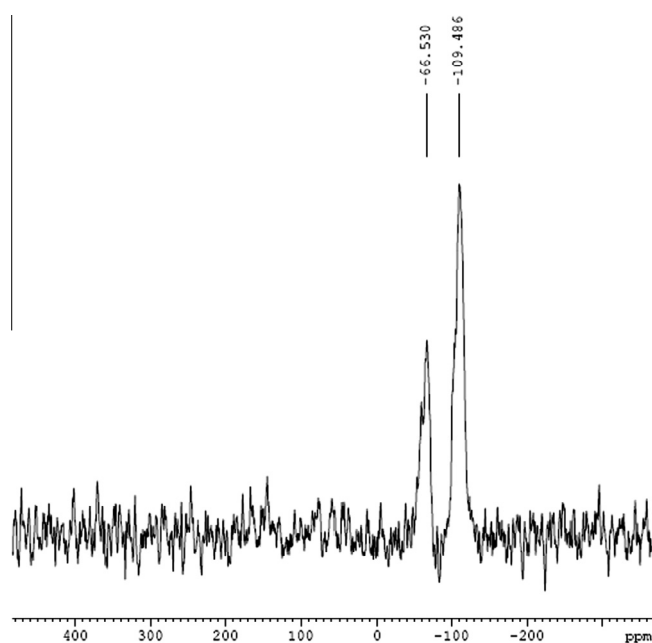


Figure 1. ²⁹Si CP-MAS NMR spectrum of 'SiO₂'-NH₂-Ru^{III}.

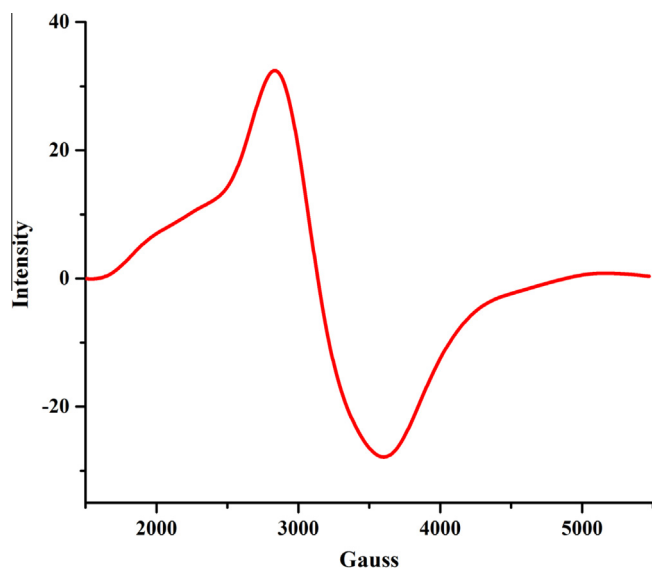


Figure 2. EPR spectrum of 'SiO₂'-NH₂-Ru^{III}.

Download English Version:

<https://daneshyari.com/en/article/5262708>

Download Persian Version:

<https://daneshyari.com/article/5262708>

[Daneshyari.com](https://daneshyari.com)