Catal Lett (2008) 120:257–260
DOI 10.1007/s10562-007-9278-3

Highly Chemoselective Catalytic System for Hydrogenation of Diketones to Ketols: An Environmentally Benevolent System

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Received: 29 December 2006 / Accepted: 13 September 2007 / Published online: 10 October 2007

Abstract Ru(Phen)$_2$Cl$_2$ [Phen = Phenanthroline] anchored in organo-functionalized MCM-41 [Ru(Phen)$_2$Cl-NH-MCM-41] efficiently catalyzes highly chemoselective hydrogenation of diketones to ketols (Sel. ~99%) under environmentally benign tri-phasic (solid–liquid–liquid) reaction condition in aqueous medium.

Keywords Chemoselective · Hydrogenation · Ruthenium phenanthroline · Water · Dione · Ketol

1 Introduction

Ketols are of immense importance for the synthesis of fine chemicals [1], as they provide two different functionalities in the same molecule ready for manipulation. Several attempts have been made to hydrogenate diketones over cinchonidine [2–6], BINAP [7] and cyclooctadine [8] metal complexes in organic solvents. However, significant formation of diol or condensed by-product reduces the chemoselectivity towards ketol formation. Therefore, to develop highly chemoselective catalytic system for hydrogenation of diketone to selectively produce corresponding ketols is quite desirable. Generally, liquid phase hydrogenation of organic substrate is carried in the presence of organic solvents, which can significantly influence the course of reaction. Solvent is mainly used to remove the phase boundaries, if any, and facilitate the heat and mass transfer. However, the use of organic solvent also poses down stream work up problem including solvent removal and recycle as well as low space–time-yield of the product. Further, the use of organic solvent is against the principles of green chemistry as they are detrimental to environment.

Now, the present article reports, for the first time, excellent chemoselective hydrogenation of diketones to ketols using heterogenized ruthenium phenanthroline metal complex anchored in organo-functionalized MCM-41 [Ru(Phen)$_2$Cl-NH-MCM-41] as catalytic system under tri-phasic system using water as reaction medium (Scheme 1).

2 Experimental

The [Ru(Phen)$_2$]Cl$_2$ metal complex was synthesized according to the classical procedure [9]. The synthesis of Si-MCM-41 and organo-functionalization of MCM-41 was carried out using the reported procedure [10, 11]. The grafted ruthenium phenanthroline complex was obtained by taking 1 g functionalized NH-MCM-41 (aminopropyl-MCM-41) in acetonitrile. To this solution 0.03 g of pre-dissolved complex in 10 mL of acetonitrile and *N,N*-dimethyl-formamide (9:1 ratio) was added [12]. The solid was stirred for 12 h under nitrogen atmosphere, filtered and dried at 70 °C.

Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Rigaku Mini-Flex instrument using Cu K_α radiation ($l = 1.5404$ Å), in the 2θ range 1.5–10° at scan rate of 1°/min. FTIR spectra of samples were taken in the range of 4,000–400 cm^{-1} on a Shimadzu FTIR 8201 instrument. XPS analyses of the catalysts were recorded on a VG Microtech ESCA 3000 spectrometer using Mg K_α radiation (photon energy = 1253.6 eV) at a pressure better than 0.133 μPa, pass energy of 50 eV and

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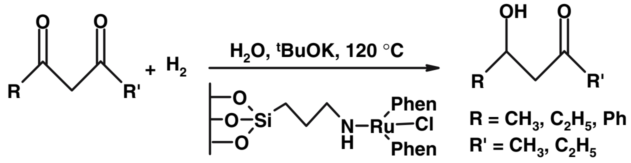


Scheme 1 Reaction scheme for the hydrogenation of diketone

electron take-off at angle of 60°. ^{13}C magic angle spinning nuclear magnetic resonance (^{13}C MAS NMR) spectra were recorded in a Bruker DRX-500 FT NMR spectrophotometer. The reactants and products were extracted with dichloromethane and analyzed on GC and GC–MS using HP-5 column.

3 Results and Discussion

In Fig. 1, the powder XRD pattern of calcined Si-MCM-41 (curve a), organo-functionalized NH-MCM-41 (post synthesis method) (curve b) and [Ru(Phen)$_2$Cl-NH-MCM-41] (curve c) are shown. The XRD pattern of Si-MCM-41 shows characteristic four distinct low angle (100), (110), (200) and (210) reflections at 2θ = 2.6°, 4.5°, 5.1°, and 6.7°, respectively. The XRD patterns indicate high degree of orderness amongst the hexagonal mesophases of Si-MCM-41 [13–15]. The decrease in the peak intensities was observed in the case of Ru-complex loaded samples, which might be due to the partial filling of Ru-complex inside the mesoporous MCM-41.

Figure 2 shows the FTIR spectra of (a) pure complex (b) NH-MCM-41 (c) [Ru(Phen)$_2$Cl-NH-MCM-41]. Spectrum of functionalized NH-MCM-41 (Fig. 2b) shows characteristic bands at 1,080, 796 and 452 cm^{-1}. Bands at similar wave number in the spectra of the crystalline and amorphous SiO$_2$ have been assigned to characteristic vibrations of Si–O–Si bridges cross-linking the silicate network [16, 17]. In the case of amino functionalized MCM-41 (NH-MCM-41) the peak at 3,305 cm^{-1} corresponds to –NH$_2$ group. The transmission bands at 2,935 and 2,841 cm^{-1} correspond to the asymmetric and symmetric vibrations of –CH$_2$ group of the propyl chain, which indicate successful anchoring of amine moieties in the mesoporous MCM-41. The Ru(Phen)$_2$Cl$_2$ complex shows, peak at 1,547 cm^{-1} due to the vibration of C=C in ligand (Fig. 2a).

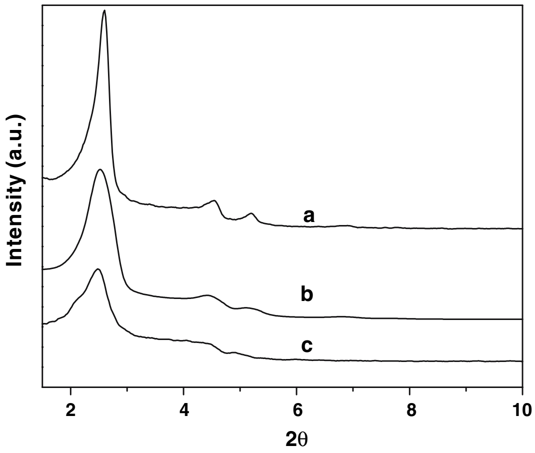


Fig. 1 XRD pattern for (a) calcined Si-MCM-41 and (b) NH-MCM-41, (c) Ru-Phen-2-NH-MCM-41

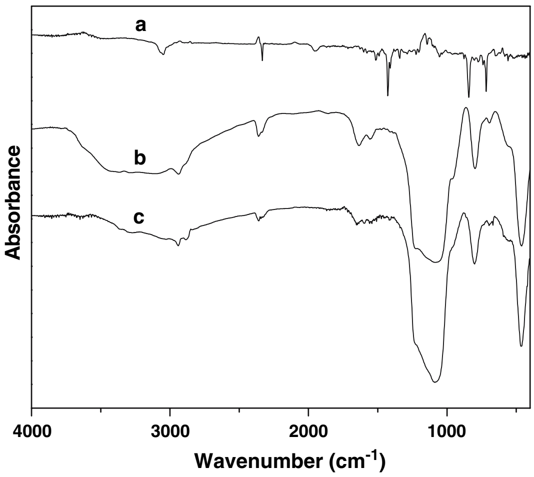


Fig. 2 FTIR spectra for (a) neat complex (b) amine functionalized MCM-41 and (c) heterogenized ruthenium phenanthroline complex on NH-MCM-41

To find out the oxidation state of ruthenium in the neat and immobilized complex before and after reactions, X-ray photoelectron spectroscopy (XPS) was performed. It is evident from XPS data that Ru 3d$_{5/2}$ and Ru 3p$_{3/2}$ BE values of 280 and 465 eV, due to the presence of Ru^{II} species [18].

The ^{13}C MAS NMR spectrum of the NH-MCM-41 sample shows three distinct ^{13}C signals at $\delta \approx$ 13, 29 and 49 ppm as usual, which can be assigned to C$_1$, C$_2$,and C$_3$ in amino-propyl MCM-41, respectively [19] further supporting the successful functionalization of MCM-41.

Figure 3 shows time profile data for the hydrogenation of acetylacetone over neat and heterogenized [Ru(Phen)$_2$ Cl-NH-MCM-41] complex at 120 °C and 2.0 MPa H$_2$ pressure using water as solvent. For the reaction involving homogeneous Ru(Phen)$_2$Cl$_2$ catalyst, the substrate was almost completely hydrogenated in 8 h, while in the case of heterogenized metal complex the reaction took 10 h for completion, probably due to relatively restricted mass transfer and thereby slower interaction between reactant molecule and active metal center under heterogenized condition. However, the slightly higher chemoselectivity towards ketol formation in heterogeneous catalyst (99%) as compared to homogeneous catalyst (96%) was observed. When RuCl$_3$ was used as catalyst under homogeneous

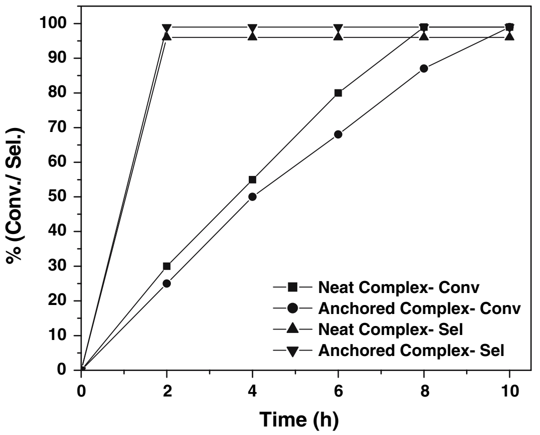


Fig. 3 Effect of time on profile on rate of reaction and chemoselectivity in reduction of acetyl acetone using neat complex and heterogenized complex

condition (Table 1, entry 1) quite low selectivity towards ketol formation (51%) was observed compared to $Ru(Phen)_2Cl_2$ complex (96%) clearly indicating that steric hindrance around metal center plays important role in obtaining higher ketol selectivity. To find out whether the reaction is truly heterogenized, we carried out reaction of aqueous layer obtained after hot filtration followed by-product extraction in dichloromethane (Table 1, entry 4). No reaction was observed. However, when the reaction was carried out using the mother liquor, obtained after hot filtration, as such without extraction very insignificant conversion (ca. 3%) was obtained (Table 1, entry 5). Further, the filtered mother liquor was analyzed by AAS and the Ru contents were found be less than 0.9 wt% of the total Ru present in the solid catalyst. These results show the reaction that reaction is truly heterogenized. The encapsulated catalyst can be effectively recovered by filtration and reused for the hydrogenation reaction (Table 1, entries 5–7). The catalyst showed slightly lower yield at the time of third recycle, which is due to the partial leaching of ruthenium from the complex as was confirmed by chemical analysis of aqueous layer obtained after work-up.

Table 1 Acetylacetone hydrogenation over various catalysts systems

Entry	Catalyst	Conversion%	Ketol selectivity[a]	TOF (h^{-1})[b]
1	Rucl$_3$	87	51	50
2	Ru-phen-2	98	96	245
3[c]	Ru-phen-2-MCM-41	99	99	184
4[d]	Aqueous layer of entry 3	0	0	0
5[e]	Hot filtered mother liquor	3	98	–
6[f]	Ru-phen-2-MCM-41-1	97	98	181
7[f]	Ru-phen-2-MCM-41-2	98	95	174
8[f]	Ru-phen-2-MCM-41-3	89	95	158

Temp = 120 °C, PH_2 = 2.04 MPa, Base = 10 wt% of the substrate

[a] Remaining is diol

[b] TOF = Turn over frequency = mole of product formed/Mole of Ru per hour

[c] Fresh catalyst

[d] Aqueous layer after hot filtration and extraction in DCM

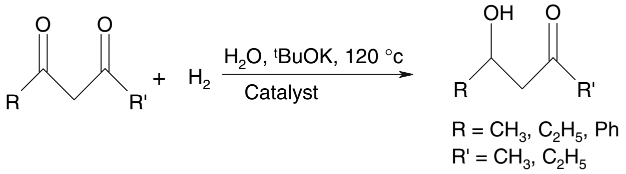
[e] Aqueous layer after hot filtration with out extraction. This filtered mother liquor was analyzed by AAS and the Ru contents were found be 0.9 wt% of the total Ru present in the solid catalyst

[f] Recycled catalyst

To find out the generality of our catalyst system, different diketones, including the cyclicdione were used as substrate for hydrogenation (Table 2). It is clear that all the substrates show very high conversion (>99%) over $Ru(Phen)_2Cl_2$ and $[Ru(Phen)_2Cl\text{-}NH\text{-}MCM\text{-}41]$. Use of water as solvent in reaction was found most effective in the hydrogenation of unsaturated ketone compare to the other solvents (*n*-butanol, methanol and iso-propanol) as the solubility of gaseous H_2 is more in water as compare to other organic solvent [20].

The selectivity of ketol was observed quite high (98–99%) in all the cases. The diketone is first hydrogenated to corresponding ketol and because of weaker absorption property of ketol at metal site, compared to that of diketone, the further hydrogenation to diol is avoided and thereby resulting in very high chemoselectivity of ketol. It may also be noted that the adsorption of reactant and all intermediates occurs in competition with solvent or

Table 2 Effect of different substrate on catalytic activity of Ru-Phen-2,



Catalyst	Substrate	Ketol selectivity[a]	TOF (h^{-1})[b]
Ru-Phen-2	R and $R^1 = CH_3$, $n = 1$	96	240
	$R = C_3H_7$, $R^1 = CH_3$, $n = 1$	96	219
	R = Ph, $R^1 = CH_3$, $n = 0$	95	197
	R = Ph, $R^1 = CH_3$, $n = 1$	93	197
	1,3-cyclopentanedione	95	163
Ru-Phen-2-NH-MCM-41	R and $R^1 = CH_3$, $n = 1$	99	186
	$R = C_3H_7$, $R^1 = CH_3$, $n = 1$	98	133
	R = Ph, $R^1 = CH_3$, $n = 0$	98	105
	R = Ph, $R^1 = CH_3$, $n = 1$	98	105
	1,3-Cyclopentanedione	98	143

[a] Remaining is diol

[b] TOF = Turn over frequency = mole of product formed/Mole of Ru per hour

reaction medium. Since unlikely diketone, facilitated under present reaction conditions, where water is used as reaction medium, thereby avoiding further hydrogenation of ketol to diol [21].

4 Conclusion

In summary, we successfully demonstrate the 99% chemoselective hydrogenation of diketone to ketol over [Ru(Phen)$_2$Cl-NH-MCM-41] using water as reaction medium. The weaker adsorption property of ketol on catalyst surface and solubility of ketol in water plays a vital role in obtaining highly selective formation of ketol.

Acknowledgment Amit Deshmukh acknowledges Council of Scientific and Industrial Research (CSIR), Govt. of India for research fellowship.

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