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An efficient heterogeneous catalytic system for chemoselective hydrogenation of unsaturated ketones in aqueous medium

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ABSTRACT

A highly chemoselective and green heterogeneous catalytic system of immobilized Ru(II)–phenanthroline complexes on amino functionalised MCM-41 material for the chemoselective hydrogenation of unsaturated ketones to unsaturated alcohols is demonstrated using water as a solvent. The XRD and FTIR spectra show the highly ordered hexagonal nature of the MCM-41, even after encapsulation of the ruthenium complex. The complex retains its configuration after anchoring, as was confirmed by FTIR and UV–Vis analysis. The detailed reaction parametric effect was studied for the hydrogenation of 3-methylpent-3-en-2-one to achieve complete conversion up to >99% chemoselectivity of 3-methylpent-3-en-2-ol. The anchored heterogeneous catalysts were recycled effectively and reused five times with marginal changes in activity and selectivity. The use of water as a solvent not only afforded high activity for the hydrogenation reaction compared to organic solvents, but also afforded a green process.

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1. Introduction

 α , β -Unsaturated alcohols are of great commercial importance as they are widely used in fragrances, pharmaceutical industries, intermediates in fine chemicals syntheses etc [1]. The chemoselective hydrogenation of α , β -unsaturated ketones to the corresponding unsaturated alcohols using molecular hydrogen is quite challenging because of the higher reactivity of the C=C bond compared with that of the C=O group [2], i.e. the favorable thermodynamics for hydrogenation of the C=C bond compared to the C=O bond by ca. 35 kJ/mol [3]. Hence, the challenge is to achieve unsaturated alcohols via selective reduction of unsaturated ketones. In addition, the product formed in the reaction may isomerize to the corresponding saturated ketones, resulting in lower unsaturated alcohol selectivity [4].

The reduction of unsaturated aldehydes or ketones has been reported using various transition metal catalysts in the form of homogeneous metal complexes, viz. diamine(ether-phosphine) ruthenium(II) [5], η^6 -*p*-cymene ruthenium(II) [6] and phenyldimethylphosphine copper (I) complexes [7]. Supported metals like Ir or Ru on H- β zeolite [8], immobilized Zr and Hf alkoxide on mesoporous materials [9], gold supported on Fe₂O₃ [10,11] and gold

supported on polymers [12] and MgO [13] have been reported as heterogeneous catalysts for selective hydrogenation. Cinchonidine metal complexes have also been used for the hydrogenation of unsaturated ketones to saturated ketones [14]. In all the above reactions, relatively low to moderate chemoselectivity towards unsaturated alcohols was obtained. Several attempts have been made to develop suitable heterogeneous catalysts for the chemoselective hydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenation of the C=O group in α , β -unsaturated aldehydrogenat

Ruthenium metal, owing to its 4d⁷5s¹ electron configuration, has a wide range of possible oxidation states [16] and thereby can stabilize various coordination geometries in each electronic configuration. In particular, the lower oxidation states of ruthenium complexes normally prefer trigonal-bipyramidal and octahedral structures, such a variety of structural geometries of ruthenium complexes has great potential in selective hydrogenation reactions.

The use of nitrogen containing metal complexes for hydrogenation of unsaturated carbonyl compounds to unsaturated alcohols has not been extensively studied to date. Also due to increasing environmental concern in recent years for eco-friendly catalytic systems, the use of water as a reaction medium has become an important factor. The present study details with chemoselective hydrogenation of α , β -unsaturated ketones with particular emphasis on 3-methylpent-3-en-2-one over homogeneous Ru–Phen-2 as well as the heterogenized Ru–Phen-2-NH-MCM-41 catalyst in aqueous medium.



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2. Material and methods

2.1. Synthesis and functionalization of MCM-41

The synthesis of the mesoporous material was carried out hydrothermally as described earlier [17] in an autoclave under autogenous pressure. In a typical synthesis procedure, 3 g fumed silica (Aldrich) was added to a solution containing 0.64 g NaOH (Merck) in 25 mL deionized H₂O and stirred for 45 min. To this mixture, a solution of 3.64 g CTABr (Loba Chemie) in 50 mL deionized H₂O was added dropwise under stirring, and the stirring was continued for another 45 min. Finally, 37 mL deionized H₂O was added to the final synthesis gel, stirred further for 30 min and then autoclaved at 100 °C for 36 h. The resultant molar gel composition was 1 SiO₂:0.32 NaOH:0.2 CTABr:125 H₂O. The solid product thus obtained after hydrothermal synthesis was filtered, washed thoroughly with distilled water and acetone, and dried at 70 °C under vacuum for 12 h. After drying, the product was calcined at 540 °C for 8 h. The solid product after calcination was characterized by XRD for structure confirmation.

Before grafting the metal complex in MCM-41, the MCM-41 was organo-functionalized by 3-aminopropyltrimethoxysilane (3APTS). In the procedure, 1.0 g of calcined Si-MCM-41 was taken in 25 mL *dry* toluene and stirred. To this stirred suspension, 0.60 g of diluted APTS in 25 mL of *dry* toluene was added slowly under a N₂ atmosphere at room temperature. After complete addition of APTS, the mixture was refluxed at 80 °C for 24 h in N₂ atmosphere. The product thus obtained was filtered, washed with *dry* toluene followed by acetone and dried at 70 °C under vacuum. The functionalised (NH-MCM-41) thus obtained was confirmed by elemental analysis.

2.2. Synthesis of the metal complexes

The ruthenium metal complexes were prepared according to the procedure available in literature [18]. In the complex synthesis, an ethanolic solution of the phenanthroline ligand was added to an aqueous solution of ruthenium under stirring conditions, and kept overnight. The solid precipitate of the ruthenium phenanthroline complex (abbreviated as Ru–Phen) was filtrated, washed with ethanol and dried at 70 °C for 12 h. Various metal complexes with different metal to ligand ratios (metal:ligand = 1–3) (Scheme 1) were synthesized using the same methodology. Similarly ruthenium bipyridine and pyridine complexes were also synthesized by the same procedure with a metal to ligand ratio of 1:2, abbreviated as Ru–Py and Ru–Bipy respectively. The complexes thus obtained were characterized by UV–Vis and FTIR spectroscopy.

2.3. Grafting of metal complexes on to organo-functionalised MCM-41

The grafted ruthenium phenanthroline complexes (Scheme 2) were obtained by taking 1 g of functionalized NH-MCM-41 in acetonitrile. To this solution, 0.03 g of the predissolved complex in



Scheme 1. Schematic representation of the ruthenium metal complexes.

10 mL of acetonitrile and *N*,*N*-di-methyl-formamide (9:1 ratio) were added as described earlier [19]. The mixture was then stirred at room temperature for 12 h under a nitrogen atmosphere. The solid product was filtered and washed with ethanol. Finally the solid product was dried under vacuum at 80 °C. The grafted metal complex in organo-functionalised NH-MCM-41 was confirmed by FTIR and UV–Vis. The retained structure of MCM-41 was also confirmed by XRD and TEM.

2.4. Catalytic hydrogenation reactions

The catalytic hydrogenation of 3-methylpent-3-en-2-one was performed in a 100 mL high-pressure and high temperature autoclave at temperatures between 80 and 150 °C, at different H₂ pressures (1.37–2.75 MPa). In a typical reaction, 0.1 g of catalyst, 10% (wt%) of potassium *ter*-butoxide (^tBuOK) with respect to substrate and 30 mL water as a solvent were used. The catalyst was recovered by centrifugation and recycled for the same substrate under identical reaction parameters.

The reaction mixtures were analyzed by an Agilent 6890 series gas chromatograph (GC) containing a capillary column (30 m \times 0.32 mm \times 0.25 µm film thickness) and flame ionization detector. The products were also confirmed by GC–IR and GC–MS.

3. Results and discussion

3.1. Characterization of the catalyst

The powder XRD patterns recorded on a Rigaku-Mini-Flex instrument of calcined Si-MCM-41 (Fig. 1 curve (a)), organofunctionalized NH-MCM-41-P (post synthesis method) (Fig. 1 curve (b)) and Ru-Phen-2-NH-MCM-41 (Fig. 1 curve (c)), are shown. The XRD pattern of Si-MCM-41 shows four distinct characteristic low angle reflections for the strong (100) reflection and feeble (110), (200) and (210) reflections at $2\theta = 2.5^{\circ}$, 4.2° , 4.9° and 6.2°, respectively. The XRD patterns of each sample indicate a high degree of order amongst the hexagonal mesophases of Si-MCM-41. as reported earlier [20-22]. The XRD results show a decrease in the peak intensity after functionalization and loading of the Ru complex, which is due to the partial filling of mesopores by the functional group and the Ru complex. This result was also supported by a surface area and pore volume measurement study, given in Table 1. Calcined MCM-41 shows the highest surface area $(1322 \text{ m}^2/\text{g})$, which decreased by 15–20% and 22–28% by amine surface modification and ruthenium phenanthroline complex loading. The decrease in pore volume also confirms the anchoring of the Ru metal complex in mesoporous MCM-41.

The TEM images of Ru–Phen-NH-MCM-41 materials, shows a clear hexagonal pattern of lattice fringes along the pore direction (Fig. 2(A)). Parallel fringes due to the side-on view of the long pores were also observed. The equidistant parallel fringes in the images show the unique feature of separate layers and the addition of the layers one after the other results in the formation of bunch of layers.

The selected area electron diffraction (SAED) pattern of the sample (Ru–Phen-2-NH-MCM-41) is given in Fig. 2(B). The TEM images and SAED patterns are well consistent with the regular hexagonal mesophases of MCM-41, with the homogeneity in the patterns indicating the retention of the ordered patterns of MCM-41 after anchoring of the above mentioned Ru–Phen complexes. These results corroborate the XRD results presented earlier (Fig. 1).

The effect of surface modification on the specific surface area, pore volume and pore diameter values, estimated from N_2 adsorption–desorption isotherms, is given in Table 1. Fig. 3 shows the N_2 adsorption–desorption isotherm and pore size distribution curve



Scheme 2. Immobilization of the Ru(Phen)_nCl₂ complex onto functionalised MCM-41.



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

Table 1

Physical characteristics of various surface modified MCM-41 materials before and after immobilization of metal complexes.

Material	Pore diameter (Å)	Pore volume $(cm^3 g^{-1})$	Surface area $(m^2 g^{-1})$
Si-MCM-41 NH ₂ -MCM-41 Ru-Phen-1-NH-MCM-41 Ru-Phen-2-NH-MCM-41	22.54 18.49 18.11 17.93	0.70 0.55 0.55 0.54	1322 1113 1104 1093
Ru–Phen-3-NH-MCM-41	17.80	0.54	893

(inset). All the samples showed similar type IV isotherms, having inflections around $P/P_0 = 0.35-0.8$, characteristic of MCM-41 type ordered mesoporous material. Calcined MCM-41 shows the highest surface area, which decreases after surface modification for NH-MCM-41 and Ru-(Phen)_n-MCM-41 (n = 1-3), as expected. These results indicate that partial filling of the mesopores occurred by the aforesaid coordination of the ruthenium compounds, which are anchored inside the pores of the mesoporous material.

FTIR spectra of all the neat ruthenium phenanthroline complexes with different metal to ligand ratios are depicted in Fig. 4(A). The peaks observed between wavenumbers 1000 and 1600 cm⁻¹ were attributed to bands for the framework-stretching mode of the phenanthroline ligands. The absorption at ~776 cm⁻¹ is characteristic of the *cis* confirmation of these complexes due to the out of plane C–H deformation of the ligand [23].

Fig. 4(B) shows the FTIR spectra (a) NH-MCM-41 and (b) Ru– Phen-2-NH-MCM-41 between 3200 and 400 cm⁻¹. The spectra (Fig. 4(A and B)) obtained from template-free –NH-MCM-41 shows characteristic bands at 1080, 796 and 452 cm⁻¹. Bands at similar wavenumbers in the spectra of the crystalline and amorphous SiO₂ have been assigned to characteristic vibrations of Si–O–Si



Fig. 2. TEM images recorded from (A) Ru-NH-MCM-41 and (B) SAED patterns.

bridges cross-linking the silicate network [18]. In the case of NH-MCM-41 with $-(CH_2)_3NH_2$ (NH-MCM-41), the peak at 3305 and 3428 cm⁻¹ corresponds to the $-NH_2$ group, whereas the transmission bands at 2935 and 2841 cm⁻¹, from the asymmetric and symmetric vibrations of the $-CH_2$ group of the propyl chain of the silylating agent, were indicative of successful anchoring of amine moieties in the mesoporous material. The pore volume, average pore diameters and BET surface area values of all the siliceous and organo-functionalized MCM-41 samples are summarized in Table 1. After grafting of the $-NH_2$ functional group of the MCM-41 materials, a decrease in surface areas, pore volumes and pore diameters by ca. 15–20%, 6–11% and 22–28% respectively were observed. All these results strongly indicate that the organic functional groups are mainly located inside the channels.

The UV–Vis spectra of different metal to ligand ratios $[Ru(Phen)_n]^{2+}$ complexes are shown in Fig. 5. The absorbance spectra for these complexes in acetonitrile shows intense π – π^* phenanthroline intra-ligand transitions in the UV–Vis band at



Fig. 3. $N_{\rm 2}$ adsorption–desorption isotherms and corresponding pore size distribution curves (inset) for Si-MCM-41.



Fig. 4. FTIR spectra of (A) neat complex (a) Ru–Phen-1, (b) Ru–Phen-2, (c) Ru–Phen-3; and (B) (a) NH-MCM-41, (b) Ru–Phen-2-NH-MCM-41.

500–530 nm and a second band of lesser intensity for metal-to-ligand charge-transfer (MLCT) transitions is between 340 and 390 nm [24]. The complexes also show a blue shift in the range 510–530 nm and which is characteristic of a *cis* configuration [25]. The bathochromic shift for the *cis*-conformation is due to the destabilization of the ruthenium t_{2g} orbital because of electron donation from the two anionic chloride ligands to the ruthenium center. The UV–Vis patterns in the case of the immobilized metal



Fig. 5. UV–Vis spectra of the (A) neat complex (a) Ru–Phen-1, (b) Ru–Phen-2, (c) Ru–Phen-3, (d) Phen; and (B) immobilized metal complex (a) Ru–Phen-1-NH-MCM-41, (b) Ru–Phen-2-NH-MCM-41, (c) Ru–Phen-3-NH-MCM-41.

complex in functionalised MCM-41 shows a characteristic band at 510–530 nm, indicating successful anchoring of the complex without any change in the configuration of the complex.

To find out the oxidation state of ruthenium before and after immobilization, X-ray photoelectron spectroscopy (XPS) was performed and the results are shown in Table 2. The Ru $3d_{5/2}$ and Ru $3p_{3/2}$ BE values at ca. 280 and ca. 465 eV are evident for a Ru^{II} species in the catalysts [26]. With increasing metal to ligand ratio, the binding energy (Ru $3d_{5/2}$) of the complexes decreases, which is attributed to the increase in the number of electrons in the outermost shell of the ruthenium metal, donated by the nitrogen atom of the ligand. It is well known that as the number of electrons in the outermost shell increases, the ionization energy decreases (shielding effect), and as a result a decrease in the binding energy was observed.

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Core level binding energies (in eV) of various elements present in the catalyst precursors and anchored catalysts.

Material	Ru 3d _{5/2}	Ru 3p _{3/2}	N 1s	Si 2p
Ru-Phen-1	280.4	465.1	401.5	-
Ru-Phen-2	280.3	465.0	401.6	-
Ru–Phen-3	279.8	464.8	401.5	-
Ru-Phen-1-NH-MCM-41	280.5	465.2	401.5	103.4
Ru-Phen-2-NH-MCM-41	280.3	465.1	401.5	103.4
Ru-Phen-3-NH-MCM-41	279.8	465.0	401.6	103.5

3.2. Catalytic hydrogenation reactions

3.2.1. Effect of metal to ligand ratio

To understand the performance of the metal to ligand ratio, different complexes with ruthenium to phenanthroline ratios were studied at 100 °C, 2.0 MPa and using water as a reaction medium, and the results are shown in Fig. 6. RuCl₃ as well as RuCl₃-NH-MCM-41 were also included in the studies for a comparative purpose. Under homogeneous conditions, RuCl₃ showed complete conversion but lower selectivity compared to RuCl₃ on MCM-41, which clearly support the above conclusion that the accessibility of the reactant molecule to metal is higher in RuCl₃, while the conversion remains comparable except for Ru–Phen-3. The selectivity of the unsaturated alcohol goes on increasing in both cases (homogeneous and heterogeneous conditions) as the ruthenium to phenanthroline ratio increases from one to three. The increase in the selectivity for metal to ligand ratios of 2 and 3 (compared to 1) is because of the steric effect of the ligand around active metal centre, but the rate of reaction decreases in the case of a metal to ligand ratio of 3, leading to a slower reaction over Ru-Phen-3 and Ru-Phen-3-NH-MCM-41 catalyst. Therefore, further work was carried out using Ru-Phen-2 and the Ru-Phen-2-NH-MCM-41 catalyst as the best results were obtained with these catalysts. The reaction of two equivalents of phenanthroline with RuCl₃ provides the octahedral [(phen)₂RuCl₂] complex containing *cis*-chlorides. In this complex the two chloride ions can be displaced from the coordination environment by reaction with another phenanthroline ligand to provide the cationic [(phen)₃Ru]Cl₂ complex [27]. Reaction with one equivalent of phenanthroline, however, provides the polymeric [(phen)RuCl₂]_n.

For the catalytic transfer hydrogenation, an easily hydrolysable ligand is necessary to initiate a $Ru-H_2$ functionality [28]. Ru-Cl has been recognized as an easily hydrolysable ligand in the literature. Since the phenanthroline ligand in $[(phen)_3Ru]^{2+}$ is bound more strongly than the Cl ligand, it follows that the reactivity of this complex is lower than that of the $[(phen)_2RuCl_2]$ complex. Similarly, the bridging chloride ions in $[(phen)RuCl_2]_n$ are more difficult to hydrolyse, resulting in a lower rate.

3.2.2. Effect of different ligands

The effect of ligand (pyridine as a monodentate ligand or 2,2'bipyridyl and 1,10-phenanthroline as bidentate ligands) on the activity and selectivity in the hydrogenation reaction of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol was studied. The reactions were carried out using Ru-Py-2, Ru-Phen-2 and Ru-Bipy-2 as



Fig. 6. Effect of metal to ligand ratio on the conversion and selectivity of the hydrogenation of 3-methylpent-3-en-2-one.



Fig. 7. Effect of ligand on the conversion and selectivity of the hydrogenation of 3methylpent-3-en-2-one.

homogeneous catalysts. The same metal complexes, anchored in NH-MCM-41 were used as heterogeneous catalysts. The reactions were carried out at 100 °C and at 2.0 MPa using water as a reaction medium and the results are given in Fig. 7.

The conversion exhibited by the Ru-complexes using all three ligands was more or less comparable, ramping between 96% and 100%, whereas Ru–Phen-2 gave nearly quantitative conversion. However, the selectivity for the unsaturated alcohol was lower when the monodentate pyridine ligand was used, due to the formation of 3-methylpentane-2-ol. This is due to more sites being available for the reactant molecule to interact with the active metal of the complex. Although the conversions using homogeneous as well as heterogeneous catalyst systems were comparable, the selectivity towards 3-methylpent-3-en-2-ol was slightly higher in the case of the heterogeneous catalysts, in accordance with the trend observed in the case of ketone hydrogenations.

3.2.3. Effect of solvent

Table 3 depicts the effect of different solvents for the hydrogenation of 3-methylpent-3-en-2-one using Ru–Phen-2 and Ru– Phen-2-NH-MCM-41 as catalysts. Except in *n*-butanol, almost complete conversion was obtained in the other solvents (methanol and iso-propanol) or reaction medium (water). It is quite interesting that in spite of being biphasic (in the case of the homogeneous catalytic system) or tri-phasic (in the case of the heterogeneous catalytic system), the reaction was complete in the presence of water. However, the selectivity for the primary product (unsaturated

Table 3

Effect of solvent on the selectivity and conversion of the hydrogenation of 3-methylpent-3-en-2-one^a.

S. No.	Catalyst	Solvent	Conversion (mole %)	>C=O selectivity (mole %)
1	Ru-Phen-2	n-Butanol	81	69
2	Ru-Phen-2-NH-MCM-41		80	75
3	Ru–Phen-2	Methanol	100	79
4	Ru-Phen-2-NH-MCM-41		100	87
5	Ru–Phen-2	Iso-propanol	100	86
6	Ru-Phen-2-NH-MCM-41		99	92
7	Ru-Phen-2	Water	100	95
8	Ru-Phen-2-NH-MCM-41		99	99

^a Reaction conditions: substrate = 1 g, neat catalyst = 0.005 g (Ru-Phen-2), solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), agitation = 300 rpm, substrate:base = 10 (wt/wt), temperature = 100 °C, pressure = 2.04 MPa, reaction medium = 30 mL water.

alcohol) was significantly lower in the case of organic solvents visà-vis water. In fact, the selectivity trend follows the order: *n*-butanol < methanol < iso-propanol < water. This may be due to the high cohesive energy density of water over other organic solvents used during the reaction and the availability of hydrogen during the reaction, as the solubility of hydrogen is less in water as compared to other solvents [29].

3.2.4. Effect of temperature

Fig. 8 shows the effect of temperature on the activity and selectivity of the catalytic hydrogenation of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol. As the conversion temperature was increased from 80 to 100 °C, the yield of the unsaturated alcohol increased sharply from ca. 75% to 99%. However, a further increase in temperature resulted in a decrease in selectivity towards the unsaturated alcohol. This is quite expected, as at higher temperatures, saturated alcohols will also be formed due to further hydrogenation.

3.2.5. Effect of pressure

Fig. 9 depicts the effect of pressure on the conversion of 3methylpent-3-en-2-ol at 100 °C using water as a reaction medium over Ru–Phen-2 catalyst. The hydrogen pressure shows a pronounced effect on the conversion. There is a decrease in the selectivity of 3-methylpentane-2-ol with an increase in hydrogen pressure. At higher hydrogen pressures, further hydrogenation of 3-methylpent-3-en-2-ol to 3-methylpentane-2-ol may be possible and as a result the selectivity decreases.

3.2.6. Effect of time

Fig. 10 shows a typical time profile for the hydrogenation of 3methylpent-3-en-2-one over Ru–Phen-2 and heterogenized Ru– Phen-2-NH-MCM-41 catalysts at 100 °C, 2 Mpa pressure. In both cases the conversion increases with reaction time, up to 4 h, whereas the selectivity remains comparable throughout the reaction. The reaction is faster in the case of the homogeneous catalyst compared to the heterogeneous catalyst, as there is no diffusion barrier/transport limitation for the reactant to adsorb on the surface of the catalyst in the case of the homogeneous catalyst system. The conversion after 4 h is almost 100%, however, the selectivity for the heterogeneous catalyst (99%) was found to be slightly higher compared to the homogeneous catalyst (96%). A decrease in



Fig. 8. Effect of temperature on the conversion and selectivity of the hydrogenation of 3-methylpent-3-en-2-one.



Fig. 9. Effect of pressure on the conversion and selectivity of the hydrogenation of 3-methylpent-3-en-2-one.



Fig. 10. Effect of time on the conversion and selectivity of the hydrogenation of 3-methylpent-3-en-2-one.

selectivity was observed when the reaction was prolonged, which is due to the further hydrogenation of the unsaturated alcohol.

3.2.7. Catalyst recycling studies

The solid anchored catalyst was filtered and recycled three times with a slight decrease in the activity and selectivity (Table 4). The decrease in conversion is due to the partial leaching of ruthenium (ca. 11 ppm of ruthenium) from the total ruthenium present in the solid catalyst. However, there is a very minor de-

Table 4

Recycling studies of the heterogeneous catalysts for the hydrogenation of 3-methylpent-3-en-2one^a.

No. of cycle	Conversion (mole %)	>C=O Selectivity (%)
Fresh catalyst	98	99
Recycle 1	98	97
Recycle 2	95	97
Recycle 3	92	97

^a Reaction conditions: substrate = 1 g, neat catalyst = 0.005 g (mole/mole) (Ru-Phen-2), solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), agitation = 300 rpm, substrate:base = 10 (wt/wt), temperature = 100 °C, pressure = 2.04 MPa, water = 30 mL, time = 6 h.

Table 5

Effect of different substrates on the catalytic activity.^a



Catalysts	Substrate	Conversion (%)	>C=O selectivity (%)	TOF $(h^{-1})^b$
Ru–Phen-2	$R_1 = C_2 H_5, R_2 = C H_3$	99	95	246
Ru-Phen-2-NH-MCM-41		99	99	212
Ru–Phen-2	$R_1 = C_5 H_{11}, R_2 = C H_3$	100	98	241
Ru-Phen-2-NH-MCM-41		98	>99	201
Ru–Phen-2	$R_1 = Ph, R_2 = CH_3$	99	96	257
Ru-Phen-2-NH-MCM-41		99	98	247
Ru–Phen-2	Cyclohex-2-ene-one	100	94	363
Ru-Phen-2-NH-MCM-41	-	97	97	339

^a Reaction conditions: substrate = 1 g, substrate: base = 10 (wt/wt), neat catalyst = 0.005 g (Ru-Phen-2), solid catalyst = 0.1 g (Ru-Phen-2-NH-MCM-41), temperature = 100 °C, pressure = 2.04 MPa, agitation speed = 300 rpm, and water = 30 mL.

^b TOF = turn over frequency = mole of product formed/mole of Ru per hour.

crease in selectivity using the recycled catalyst. The fresh reaction was performed using the mother liquor and it was observed that the conversion was around 9%. This takes the process towards a green chemistry route in which a non-environmental pollutant solvent and an easily separable and recyclable catalyst are used.

3.2.8. Effect of substrate

Table 5 shows the hydrogenation of unsaturated ketones with the substitution of C=C by pentane or phenyl. The increase in the turn over frequency (TOF) value in the case of the phenyl substituted compound is attributed to the lower steric hindrance as compared to that of pentane, as the phenyl ring always remains in one plane. However, in both the cases the selectivity remains unaffected. This indicates that only the functional group (C=O) is reduced over the catalyst and the double bond remains protected, giving very high selectivity towards the unsaturated alcohol. An increase in selectivity and decrease in TOF was observed in the case of the heterogenized metal complex due to the diffusion barrier as compared to the homogeneous catalytic system.

4. Conclusion

The synthesis and catalytic activity of Ru(phen)₂ immobilized on MCM-41 has been successfully investigated. The rate of reaction under homogeneous conditions is higher as compare to heterogeneous conditions, and the selectivity is lower. The heterogenization of a homogeneous catalyst gives a higher selectivity for the product compared to the reaction under homogeneous conditions for the same conversion, as the rate of reaction is lower in the case of the heterogeneous catalyst. The heterogeneous catalyst can be recycled and reused. Bidentated ligands show higher activity and selectivity for the product in the hydrogenation of 3-methylpent-3-en-2-one to 3-methylpent-3-en-2-ol because these reduce the accessibility of reactant molecules towards the metal center, resulting in a lower rate of reaction. The most important aspect of this publication is the utilization of water as a reaction medium, which makes this process green.

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References

- [1] Ullmann's Encyclopedia of Technical Chemistry, sixth ed., Wiley-VCH, 2000.
- [2] V. Ponec, Appl. Catal. A: Gen. 149 (1997) 27.
- [3] P. Claus, Appl. Catal. A: Gen. 291 (2005) 222.
- [4] M.G. Musolino, P. de Maio, A. Donato, R. Pietropaolo, J. Mol. Catal. A: Chem. 208 (2004) 219.
- [5] (a) E. Linder, A. Ghanem, I. Warad, K. Eichele, H.A. Mayer, V. Schurig, Tetrahedron Asymmetry 14 (2003) 1045;
 (b) E. Lindner, I. Warad, K. Eichele, H.A. Mayer, Inorg. Chim. Acta 350 (2003) 49
- [6] P. Peach, D.J. Cross, J.A. Kenny, I. Mann, I. Houson, L. Campbell, T. Walsgrove, M. Wills. Tetrahedron 62 (2006) 1864.
- [7] J.X. Chen, J.F. Daeuble, D.M. Brestensky, J.M. Stryker, Tetrahedron 56 (2000) 2153.
- [8] M. De bruyn, S. Coman, R.R. Bota, V.I. Parvulescu, D.E. De Vos, P.A. Jacobs, Angew. Chem., Int. Ed. 42 (2003) 5333.
- [9] M. De bruyn, M. Limbourg, J. Denayer, G.V. Baron, V. Parvulescu, P.J. Grobet, D.E. De Vos, P.A. Jacobs, Appl. Catal. A: Gen. 254 (2003) 189.
- [10] C. Milone, R. Ingoglia, M.L. Tropeano, G. Neri, S. Galvagno, Chem. Commun. (2003) 868.
- [11] C. Milone, R. Ingoglia, L. Schipilliti, C. Crisafulli, G. Neri, S. Galvagno, J. Catal. 236 (2005) 80.
- [12] P.G.N. Mertens, P. Vandezande, X. Ye, H. Poelman, I.F.J. Vankelecom, D.E. De Vos, Appl. Catal. A: Gen. 355 (2009) 176.
- [13] G. Szollosi, M. Bartok, J. Mol. Catal. A: Chem. 148 (1999) 265.
- 14] G. Fogassy, A. Tungler, A. Levai, J. Mol. Catal. A: Chem. 192 (2003) 189.
- [15] T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 117 (1995) 2675.
- [16] E.A. Seddon, K.R. Seddon, The Chemistry of Ruthenium, Elsevier, Amsterdam, 1984.
- [17] S.C. Laha, P. Mukherjee, S.R. Sainkar, R. Kumar, J. Catal. 207 (2002) 213.
- [18] (a) R.A. Krause, Inorg. Chim. Acta 22 (1977) 209;
- (b) S. Sen, S. Mitra, P. Kundu, M.K. Saha, C. Kruger, J. Bruckmann, Polyhedron 16 (1977) 2475.
- [19] M. Eswaramoorthy, Chem. Commun. (1998) 615.
- [20] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
- [21] C.Y. Chen, H.X. Li, M.E. Davis, Microporous Mater. 2 (1993) 17.
- [22] J. Xu, Z. Luan, H. He, W. Zhou, L. Kevan, Chem. Mater. 10 (1998) 3690.
- [23] (a) M.R. Almeida, C.G. Pantano, J. Appl. Phys. 68 (1990) 4225;
- (b) E.I. Kamitsos, A.P. Patsis, G. Kordas, Phys. Rev. B. 48 (1993) 12499.
- [24] R.J. Staniewicz, R.F. Sympson, D.G. Hendricker, Inorg. Chem. 16 (1977) 2166.
- [25] S. Zakeeruddin, Md.K. Nazeeruddin, R. Humphry-Baker, M. Grätzel, Inorg. Chim. Acta 296 (1999) 250.
- [26] J.W. Robinson (Ed.), Practical Handbook of Spectroscopy, CRC Press, Florida, 1991. p. 183.
- [27] S. Rau, B. Schäfer, A. Grüßing, S. Schebesta, K. Lamm, J. Vieth, H. Görls, D. Walther, M. Rudolph, U.W. Grummt, E. Birkner, Inorg. Chim. Acta 357 (2004) 4496.
- [28] P. Štěpnička, J. Ludvík, J. Canivet, G. Süss-Fink, Inorg. Chim. Acta 359 (2006) 2369.
- [29] (a) T.E. Crozier, S. Yamamoto, J. Chem. Eng. Data 19 (1974) 242;
 (b) T. Katayama, T. Nitta, J. Chem. Eng. Data 21 (1976) 194.