



Heterogenized Ru(II) phenanthroline complex for chemoselective hydrogenation of diketones under biphasic aqueous medium

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ABSTRACT

The chemoselective hydrogenation of acetylacetone to 4-hydroxypentan-2-one over immobilized ruthenium phenanthroline metal complexes in amino functionalized MCM-41 in biphasic aqueous reaction medium was investigated. The catalyst was characterized by XRD, TEM, surface analysis, FT-IR and UV–vis to understand the morphology, complex geometry, and XPS such that the oxidation state of the metal complex inside the MCM-41 framework could be understood. The use of water as a solvent, not only gives high activity and selectivity for hydrogenation of acetylacetone, but also gives a path for an environmentally safer process. The optimizations of ligand, metal to ligand ratio, the choice of solvent and other reaction parameters were studied in detail. The heterogeneous catalytic system gave a higher degree of chemoselectivity (99%) towards 4-hydroxypentan-2-one as compared to homogeneous catalyst when hydrogenation was carried out using water as a solvent. The immobilized ruthenium–phenanthroline complex was easily separated and reused.

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1. Introduction

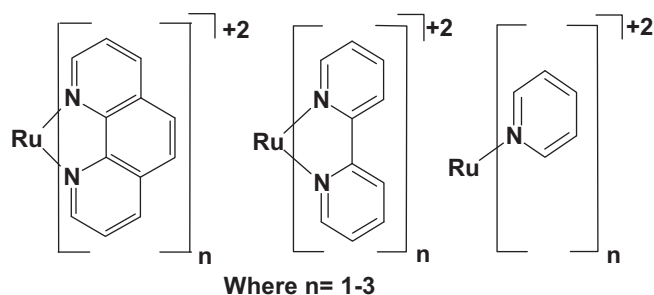
Ketols are of immense importance for the synthesis of fine chemicals [1], as they provide two different functional groups in the same molecule that are ready for manipulation, one hydroxyl and other carbonyl. For example, 4-hydroxypentan-2-one is used as flavoring agent. Several attempts have been made to hydrogenate diketones over cinchonidine [2–6], BINAP [7] and cyclooctadine [8] metal complexes to diols. In all above studies significant formation of the diol was obtained resulting in low chemoselectivity towards ketol formation. Transition metal complexes of ruthenium, rhodium, palladium and platinum containing nitrogen ligand viz. phenanthroline and bipyridyl have also been utilized for the transfer hydrogenation of carbonyl compounds [9]. Ruthenium metal is getting more and more attention because of it is low cost, activity, availability, etc. It is worth recalling that among the other transition metals Ru has $4d^7 5s^1$ electronic configuration and hence it has wide range of oxidation states from -2 to $+8$. Therefore, it forms various coordination geometries in each electronic configuration.

It also has great potential for exploitation of novel catalytic reactions and variety of Ru complexes are prepared and used for various reactions. In the case of bipyridyl or phenanthroline complexes, the steric hindrance caused by the interaction between hydrogen atoms of aromatic rings causes the Ru(II) complexes to possess the *cis* geometrical conformation [10]. Therefore, it is interesting to utilize these complexes for the hydrogenation of acetylacetone to 4-hydroxypentan-2-one. To the best of our knowledge this is the first reported case in which a phenanthroline metal complex is used for diketone hydrogenation.

The increased environmental concerns in recent years advocate the replacement of organic solvents by water for environmentally benign catalytic systems and also to use easily separable and recyclable catalyst in the reaction. The present study is extension of our earlier work [11] which focused on the catalytic activity of Ru–Phen-2 (number 2 indicates ruthenium: phenanthroline = 1:2) and heterogenized Ru–Phen-2–NH–MCM-41 (Ru–Phen-2 encapsulated in amino functionalized MCM-41) for chemoselective hydrogenation of acetylacetone to 4-hydroxypentan-2-one using water as the preferred reaction medium. Initially the system behavior is triphasic, but after completion, the reaction behavior is biphasic due to the fact that the ketol formed during the reaction is soluble in water. Some other biphasic systems and different diketone hydrogenation results are also reported for the comparison.

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Scheme 1. Schematic representation of ruthenium metal complexes.

2. Experimental

2.1. Synthesis of metal complexes

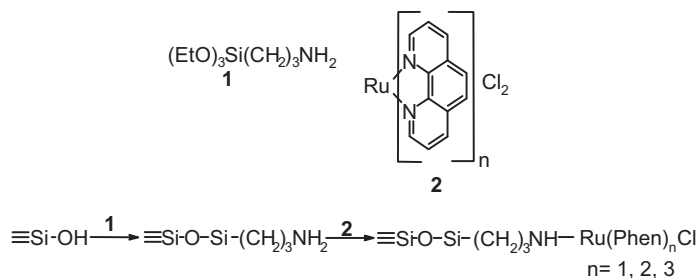
Ruthenium metal complexes were prepared according to the procedure available in literature [12]. In a typical complex synthesis, ethanolic solution of the phenanthroline ligand was added to the aqueous solution of ruthenium under stirring conditions and kept overnight. The solid precipitate was filtered, washed with ethanol, and dried at 70 °C for 12 h. Similarly, ruthenium bipyridine and pyridine complexes were also synthesized by the same procedure with a metal to ligand ratio of 1:2. The complexes thus obtained were characterized by UV–vis and FT-IR spectroscopy.

2.2. Synthesis of MCM-41 mesoporous material

The synthesis of a mesoporous material was carried out hydrothermally as described earlier [13] in an autoclave under autogeneous pressure. 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 then dried at 70 °C temperature under vacuum for 12 h. After drying the product was calcined at 540 °C for 8 h. The structure of MCM-41 was confirmed by XRD. The MCM-41 was then amino-functionalized by 3-aminopropyltrimethoxy-silane (APTS). In this procedure, 0.60 g of diluted APTS in 25 mL of dry toluene was added slowly under an N₂ atmosphere at room temperature to a suspension of 1.0 g of calcined Si-MCM-41 in 25 mL dry toluene. After complete addition of APTS, the mixture was refluxed at 80 °C for 12 h in N₂ atmosphere. The product thus obtained was filtered, washed with dry toluene followed by acetone and then dried at 70 °C under vacuum. The amino functionalized (NH-MCM-41) material thus obtained was confirmed by elemental analysis, FT-IR, UV–vis spectroscopy.

2.3. Grafting of metal complexes on to amino-functionalized MCM-41

The grafted ruthenium phenanthroline complex (Scheme 1) was obtained by first taking 1 g NH-MCM-41 in acetonitrile. To this solution 0.03 g of the pre-dissolved complex in 10 mL of acetonitrile and N,N-di-methyl-formamide (9:1 ratio) was added as described earlier [14]. The mixture was then stirred at room temperature for 12 h under a nitrogen atmosphere (Scheme 2). 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 amino-functionalized MCM-41 was confirmed by FT-IR and UV–vis spectroscopy. The retained structure of MCM-41 was also confirmed by XRD.



Scheme 2.

2.4. Catalytic hydrogenation reactions

In a typical reaction, 0.1 g of catalyst in the case of heterogenized complex system is used. In homogeneous complex system, the substrate to metal ratio was 1000. In both the cases, 10% of potassium *tert*-butoxide (*t*BuOK) with respect to the substrate as a base and 30 mL water as a solvent was placed in a 100 mL high pressure autoclave. The catalytic hydrogenation of acetylacetone was performed at different temperatures (100–150 °C), at different H₂ pressures (1.37–2.75 MPa) and at stirring at 300 rpm, using water as a solvent. The reaction mixtures were analyzed on an Agilent 6890 series gas chromatograph (GC) containing 10% β-cyclodextrin capillary column (30 m × 0.32 mm × 0.25 μm film thickness) and flame ionization detector. The products were also confirmed by GC–MS. After reaction the catalyst was separated by centrifugation and recycled for the same substrate under identical reaction parameters.

3. Results and discussion

3.1. Characterization of catalyst

3.1.1. Powder X-ray diffraction

The XRD (powder) pattern (Fig. 1) of calcined Si-MCM-41 (curve (a)), organofunctionalized NH-MCM-41-P (post synthesis method) (curve (b)), Ru-Phen-2-NH-MCM-41 (curve (c)) are shown. The XRD pattern of Si-MCM-41 shows four characteristic low angle reflections [strong 100 reflection and weak (1 1 0), (2 0 0) and (2 1 0) reflections] at $2\theta = 2.1^\circ, 3.7^\circ, 4.3^\circ$ and 5.6° respectively. The XRD patterns indicate high degree of order-ness amongst the hexagonal (*p6mm*) mesophases of Si-MCM-41 [15–17]. The results indicate an ordered mesoporous material even after immobilization of metal complex. However, a slight decrease in the peak intensities were observed in the case of Ru-complexes containing samples, which

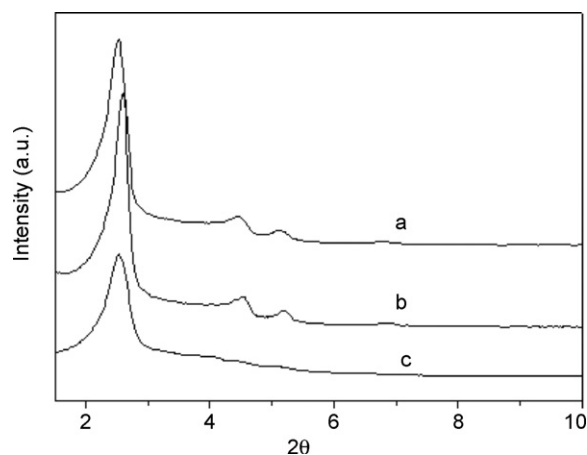


Fig. 1. XRD pattern for (a) calcined Si-MCM-41, (b) NH-MCM-41 and (c) Ru-Phen-2-NH-MCM-41.

Table 1
Physical characteristics of various surface modified MCM-41 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	22.54	0.70	1322
NH-MCM-41	18.49	0.55	1113
Ru-Phen-1-NH-MCM-41	18.11	0.55	1104
Ru-Phen-2-NH-MCM-41	17.93	0.54	1093
Ru-Phen-3-NH-MCM-41	17.80	0.51	893

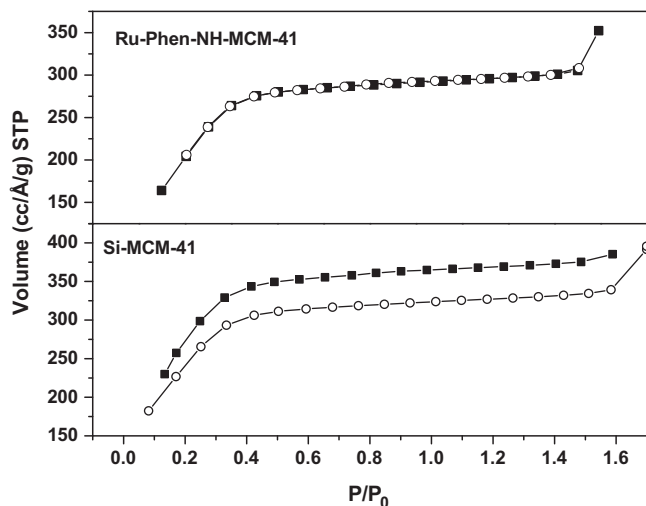


Fig. 2. N₂ adsorption–desorption isotherms and corresponding pore size distribution curves (inset) for Si-MCM-41 and Ru-Phen-NH-MCM-41.

might be due to the partial filling of Ru-complexes inside the mesopores. The *d* spacing and unit cell parameters of the samples are given in Table 1.

3.1.2. Specific surface area

Table 1 depicts the effect of surface modification on the specific surface area, pore volume and pore diameter values as estimated from N₂ adsorption–desorption isotherms. Fig. 2 shows the N₂ adsorption–desorption isotherm and pore size distribution curve (inset). All the samples showed a similar type IV isotherm having inflection around $P/P_0 = 0.35\text{--}0.8$ which is characteristic of MCM-41 type ordered mesoporous materials. Calcined MCM-41 showed highest surface area, which goes on decreasing after surface modification for NH-MCM-41 and Ru-(Phen)_{*n*}-MCM-41 (*n* = 1, 2, 3), as expected. These results indicate that partial filling of mesopores occurred by the aforesaid coordination of compounds, which are anchored inside the pores of 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 –NH₂ 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 of the support.

3.1.3. FT-IR spectra

FT-IR spectra of all the neat ruthenium–phenanthroline complexes with different metal to ligand ratios are depicted in Fig. 3(A). The peaks observed between wavenumber 1000 and 1600 cm⁻¹ were attributed to bands for the framework-stretching mode of the phenanthroline ligand. The band at ~776 cm⁻¹ (Fig. 3(A) inset) characteristic of the *Cis* confirmation of complex which is due to the out-of-plane C–H deformation of the ligand [18].

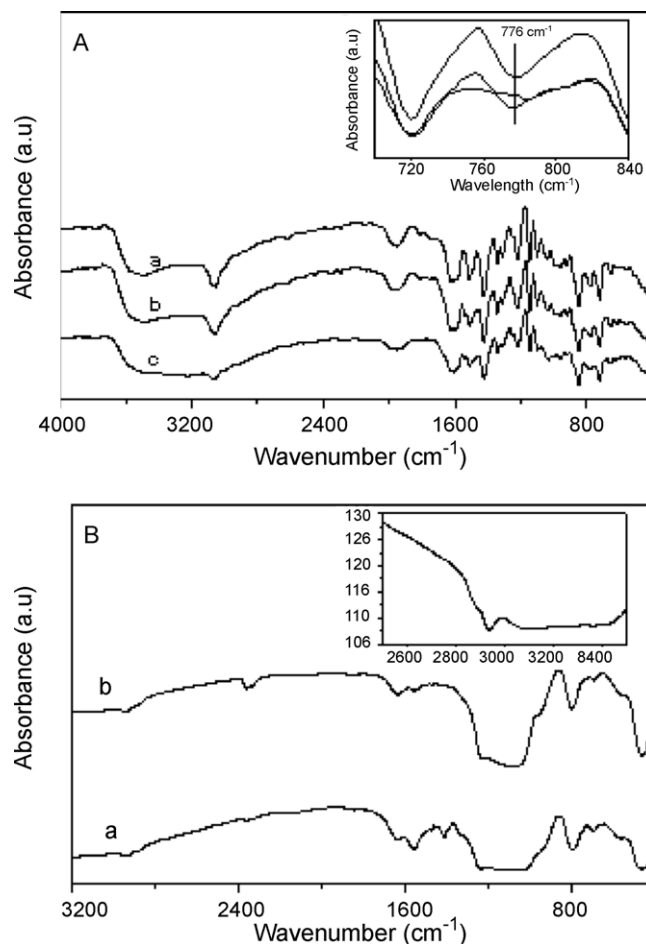


Fig. 3. FT-IR spectra of the (A) neat complex (a) Ru-Phen-1 and (b) Ru-Phen-2, (c) Ru-Phen-3; and (B) (a) NH-MCM-41 (b) Ru-Phen-2-NH-MCM-41.

Fig. 3(B) shows the FT-IR spectra (a) NH-MCM-41 and (b) Ru-Phen-2-NH-MCM-41 between 3200 and 400 cm⁻¹. Spectrum (Fig. 3(A) and (B)) obtained from template-free –NH-MCM-41 shows characteristic bands at 1080, 796 and 452 cm⁻¹. Bands at similar wavenumber in the spectra of the crystalline and amorphous SiO₂ have been assigned to characteristic vibrations of Si–O–Si bridges cross-linking the silicate network [19]. In the case of NH-MCM-41 with –(CH₂)₃NH₂ (NH-MCM-41), the peak at 3305 and 3428 cm⁻¹ corresponds to the –NH₂ group, whereas the transmission bands at 2935 and 2841 cm⁻¹ from the asymmetric and symmetric vibrations of –CH₂ group of the propyl chain of the silylating agent were indicative of successful anchoring of amine moieties in the mesoporous material.

3.1.4. UV-vis spectra

The UV-vis spectra of six-coordinate [Ru(phen)₂]²⁺ complexes are shown in Fig. 4. The absorbance spectra for these complexes in acetonitrile are characterized by the presence of intense $\pi\text{--}\pi^*$ phenanthroline intraligand transitions in the UV-vis region

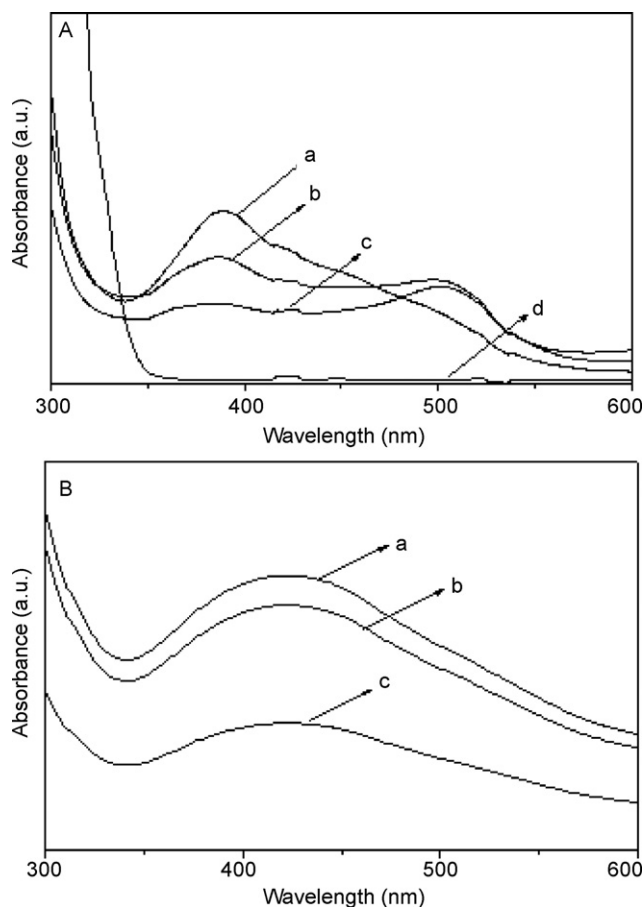


Fig. 4. UV-vis spectra of the (A) neat complex (a) Ru-Phen-1, (b) Ru-Phen-2, (c) Ru-Phen-3 and (d) Phen; and (B) immobilized metal complex (a) Ru-Phen-1-NH-MCM-41, (b) Ru-Phen-2-NH-MCM-41 and (c) Ru-Phen-3-NH-MCM-41.

and metal-to-ligand charge-transfer (MLCT) bands at 500–530 nm along, with a second band of lesser intensity between 340 and 390 nm [20]. Interestingly the complexes show a blue shift in the range of 510–530 nm which is characteristic of the *Cis* configuration and is attributed to the electron donating chlorine group [21]. The bathochromic shift in *cis*-conformation is due to the destabilization of the ruthenium t_{2g} orbital because of electron donation from the two anionic chloride ligands to ruthenium center.

The UV-vis patterns observed in the case of immobilized metal complexes on surface modified MCM-41 are shown in Fig. 4(B). Curves a–c represents Ru-Phen-1-NH-MCM-41, Ru-Phen-2-NH-MCM-41, Ru-Phen-3-NH-MCM-41 samples respectively. The band at 510–530 nm clearly indicates the anchoring of the complex in the surface modified MCM-41 without change in the configuration of the complex.

3.1.5. X-ray photoelectron spectra

X-ray photoelectron spectroscopy (XPS) was used to find out the oxidation state of ruthenium in the neat and immobilized complex before and after reactions. Table 2 represents the Ru 3d_{5/2}, Ru 3p_{3/2} and N 1s core level binding energy (BE) obtained from XPS analysis. BE values for Ru 3d_{5/2} and Ru 3p_{3/2} were ca. 280 and 465 eV respectively, making it evident that the ruthenium in the catalysts was present as Ru^{II} species [22]. The binding energy of Ru 3d_{5/2} in complexes goes on decreasing from top to bottom through Table 2, which is attributed to the increase in the number of electrons in the outer most shell of the ruthenium metal donated by the nitrogen atom from the ligand (as metal to ligand ratio goes on increasing). As the number of electrons in outer most shell increases, the ion-

Table 2

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

ization energy decreases (shielding effect) and as a result the bond strength between the metal and the ligand decreases, which in turn decreases the binding energy.

3.1.6. Transmission electron microscopy

Fig. 5(A) represents the TEM images of Ru-Phen-NH-MCM-41 materials, showing a clear hexagonal pattern of lattice fringes along the pore direction. 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 other results in the formation of a bunch of layers.

The selected area electron diffraction (SAED) pattern of the sample (Ru-Phen-2-NH-MCM-41) is given in Fig. 5(B). The TEM images

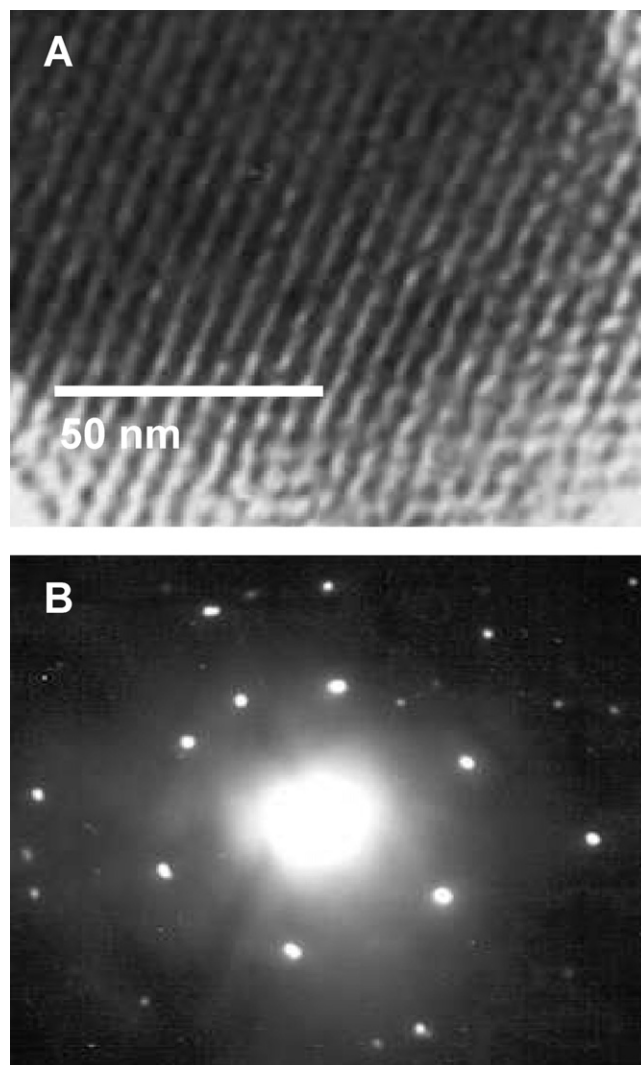


Fig. 5. TEM images recorded from (A) Ru-NH-MCM-41 and (B) SAED patterns.

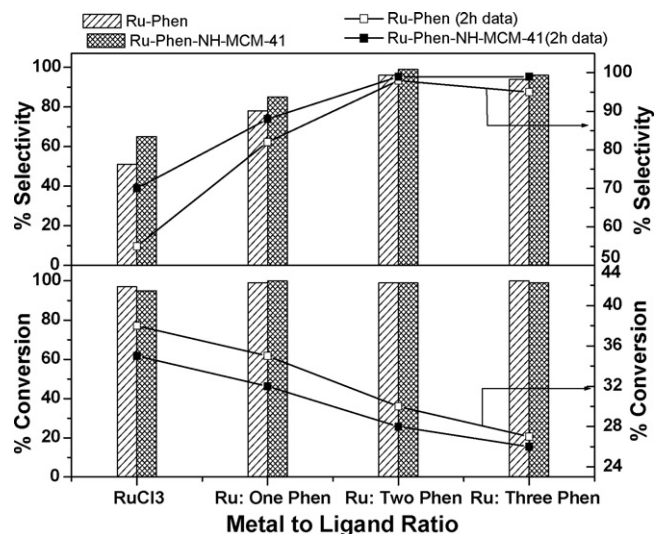


Fig. 6. Effect of metal to ligand ratio on conversion and selectivity in hydrogenation of acetylacetone to 4-hydroxypentan-2-one over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41.

and SAED patterns are well consistent with the regular hexagonal mesophases of MCM-41, with homogeneity in patterns indicating the retention of the ordered patterns of MCM-41 after anchoring of the abovementioned Ru-Phen complexes. These results corroborate the XRD results presented earlier (Fig. 1).

3.2. Catalytic hydrogenation reactions

3.2.1. Effect of metal to ligand ratio

The effect of metal to ligand ratio was investigated to achieve the maximum selectivity which is shown in Fig. 6. Different complexes with different ruthenium to phenanthroline ratios were studied at the 120 °C, 2.0 MPa and using water as a solvent. Although, comparable conversions were obtained in the case of homogeneous as well as heterogeneous conditions, the heterogenized metal complex showed an increase in selectivity, which is due to the diffusion barrier for the reactant. The selectivity of 4-hydroxypentan-2-one, in both homogeneous and heterogeneous conditions, increased as the ruthenium to phenanthroline ratio decreased from one to three. This may be attributed the steric effect of ligand molecule, which controls the approach of the reactant molecule towards the reactive metal center in complex.

3.2.2. Effect of different ligand

The effect of ligand (pyridine as a mono or 2,2'-bipyridyl and 1,10-phenanthroline as a bi-dentate) on the activity and selectivity of the catalyst in the hydrogenation reaction of acetylacetone to 4-hydroxypentan-2-one is shown in Fig. 7. The reactions were carried out using Ru-Py-2, Ru-Phen-2 and Ru-Bipy-2 as a homogeneous catalysts. The same metal complexes were also anchored in NH-MCM-41 and were used as heterogeneous catalyst. The reactions were carried out at 120 °C and at 2.0 MPa using water as a reaction medium and the results are given in Fig. 7.

The conversion exhibited by Ru-complexes using all the three ligands is comparable. However, there was significant loss of selectivity towards alcohol (due to the formation of 2,4-dihydroxypentane), when mono-dentate ligand pyridine was used. The cause of this is may be the less steric hindrance around the active metal center (as compared to bi-dentate ligand), which facilitates ketol to interact and further hydrogenate to diol. Although, the conversions using homogeneous as well as heterogeneous catalyst systems were comparable, the selectivity for 4-hydroxy-

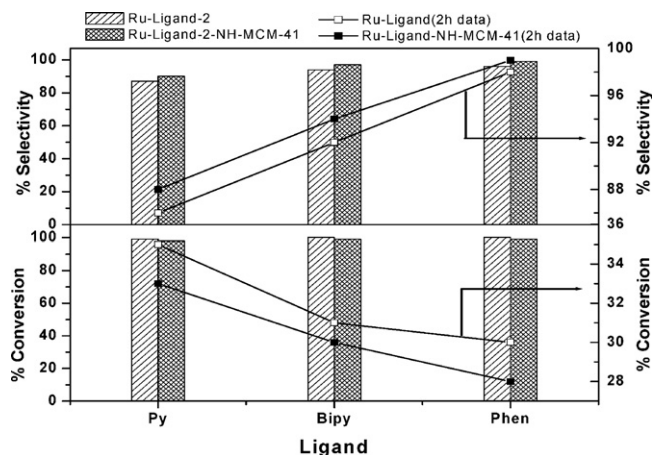


Fig. 7. Effect of different ligand on conversion and selectivity in hydrogenation of acetylacetone to 4-hydroxypentan-2-one over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41.

pentan-2-one was slightly higher in case of the heterogeneous catalyst.

3.2.3. Effect of solvent

To find out the suitable reaction medium for the hydrogenation of acetylacetone, the reactions were carried out using Ru-Phen-2 and Ru-Phen-2-NH-MCM-41 catalysts with different solvents (Table 3). Both, homogeneous and heterogeneous conditions, the conversions are found comparable, however, the selectivity of 4-hydroxypentan-2-one was lower in case of homogeneous condition as compared to heterogeneous condition. The uses of water as a solvent gave higher conversion and selectivity compared to different alcohols, as the solubility of hydrogen is higher in alcohol as compared to water therefore reaction tended towards total hydrogenation. Therefore, for further studies water, a universal and environmentally benign solvent was used. In aqueous solution the Ru-(Phen)₂Cl₂ complex shows metal-to-ligand charge transfer in the excited state. The increased electron density in the phenanthroline ligand system has the effect of turning the excited state of nitrogen in the ligand into a stronger basic group. In water, this group abstract a proton from dissolved H₂ in solvent to form the protonated ground-state species, relaxing to the starting material in the process. In protonic solvents this protonated pathway is precluded and the charge-transfer state is in equilibrium with the excited metal species that then collapses to the ground state with emission of proton [23–25]. This type of activation of molecular splitting of hydrogen by Ru-(Phen)₂Cl₂ complex in aqueous media leads the higher rate of hydrogenation reactions in aqueous medium than in alcoholic medium

Table 3

Effect of different solvents on conversion and selectivity for hydrogenation of acetylacetone^a.

Sl.no.	Catalyst	Solvent	% Conv.	Ketol Sel. (%)
1	Ru-Phen-2	n-Butanol	85	75
2	Ru-Phen-2-NH-MCM-41		80	79
3	Ru-Phen-2	Methanol	90	82
4	Ru-Phen-2-NH-MCM-41		88	85
5	Ru-Phen-2	Iso-propanol	100	87
6	Ru-Phen-2-NH-MCM-41		98	92
7	Ru-Phen-2	Water	100	99
8	Ru-Phen-2-NH-MCM-41		100	99

^aReaction conditions: substrate = 1 g, substrate:base = 10 (w/w), substrate:catalysis = 1000 (mole/mole) (Ru-Phen-2), in case of Ru-Phen-2-NH-MCM-41 = 0.1 g, temp. = 120 °C, pressure = 2.04 MPa, agitation speed = 300 rpm, 30 mL water.

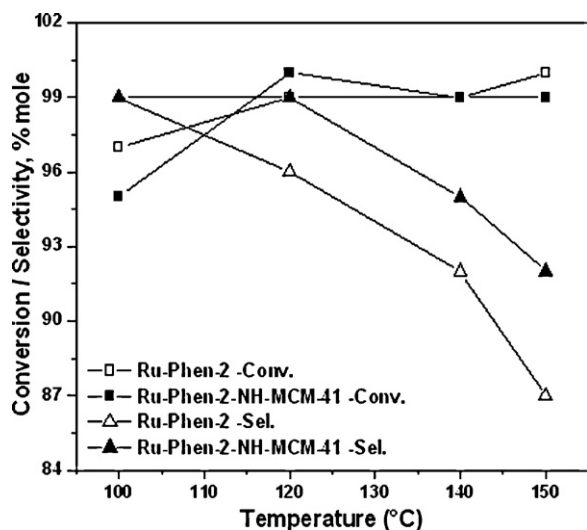


Fig. 8. Effect of temperature on conversion and selectivity in hydrogenation of acetylacetone to 4-hydroxypentan-2-one over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41.

3.2.4. Effect of temperature

To find out the optimum reaction temperature for the hydrogenation of acetylacetone, reactions were carried out at various temperatures and the results are shown in Fig. 8. It was observed in both the homogeneous as well as heterogeneous cases that, with increase in temperature from 100 to 150 °C the conversion increases and selectivity of 4-hydroxypentan-2-one decreases. The highest selectivity (99%) was observed at 120 °C reaction temperature. However, the selectivity decreases from 120 °C onwards due to further hydrogenation of acetylacetone to form 2,4-pentane-diol. In heterogeneous condition the selectivity of 4-hydroxypentan-2-one is higher compared to that of homogeneous condition at all the temperatures.

3.2.5. Effect of pressure

Fig. 9 depicts the effect of pressure on chemoselectivity of 4-hydroxypentan-2-one at 120 °C using water as a solvent. The hydrogen pressure shows a pronounced effect on the conversion and selectivity. As expected, the high conversion and low selectivity

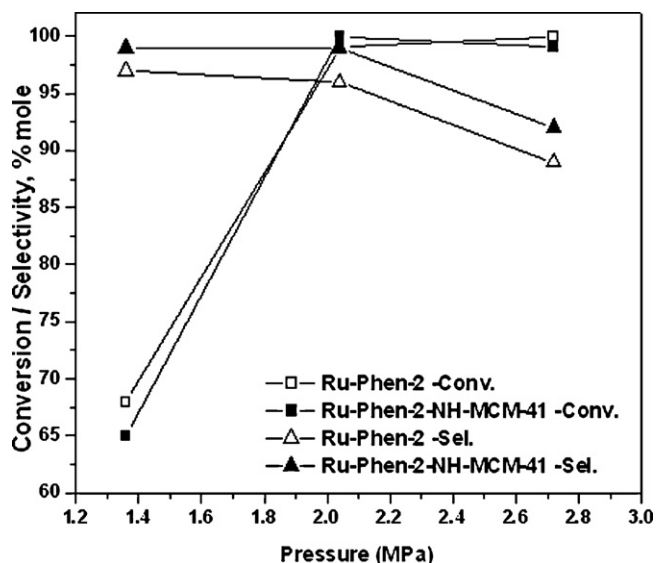


Fig. 9. Effect of pressure on conversion and selectivity in hydrogenation of acetylacetone to 4-hydroxypentan-2-one over Ru-Phen-2 and Ru-Phen-2-NH-MCM-41.

Table 4

Recycle studies of the heterogeneous catalysts for hydrogenation of acetylacetone.

Entry	Catalyst	% Conv.	Ketol Sel. (%)	TON ^a
1	Ru-Phen-2-NH-MCM-41	98	99	1921
2	Ru-Phen-2-NH-MCM-41-R1	97	98	1902
3	Ru-Phen-2-NH-MCM-41-R2	98	95	1745
4	Ru-Phen-2-NH-MCM-41-R3	89	95	1504

^a Reaction conditions: substrate = 1 g, substrate:base = 10 (w/w), 0.05 g (Ru-Phen-2), in case of Ru-Phen-2-NH-MCM-41 = 0.1 g, temp. = 120 °C, pressure = 2.04 MPa, agitation speed = 300 rpm, 30 mL water.

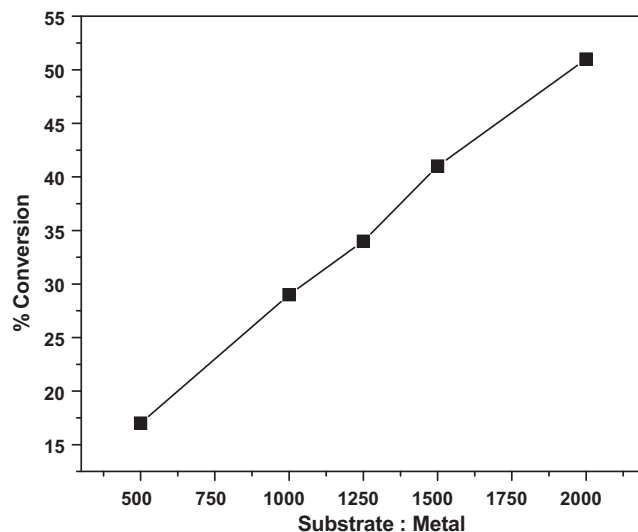


Fig. 10. Effect of catalyst loading on conversion of acetylacetone.

was obtained at higher pressure of hydrogen in both homogeneous and heterogeneous reaction conditions. There is a decrease in the selectivity of 4-hydroxypentan-2-one as H₂ pressure increases from 1.36 to 2.72 MPa as more hydrogen is available to further hydrogenate 4-hydroxypentan-2-one to diol. The heterogeneous catalyst shows higher chemoselectivity than the homogeneous catalyst although the conversion is higher for homogeneous catalyst.

3.2.6. Recycle studies

Table 4 depicts the recyclability of the heterogenized catalyst. The heterogenized catalyst can be recycled three times. The selectivity and conversion decreases to 95% and 89%, respectively, at the time of third recycle. The decrease in the conversion and selectivity is attributed to the partial leaching of ruthenium (0.9% of total ruthenium loaded) from the catalyst and break down of metal complex respectively. A fresh reaction was performed using mother liquor of previous reaction and around 10% conversion was observed which is due to the partial leaching of ruthenium.

3.2.7. Effect of agitation

The effect of agitation speed was performed (200–1000 rpm) to ascertain the liquid–solid mass transfer effect. The data obtained showed that there is no effect of agitation on the selectivity pattern, indicating that the reaction is not dependent on liquid–solid mass transfer barrier.

3.2.8. Effect of catalyst loading

Effect of catalyst loading on the conversion of acetylacetone was investigated for substrate to metal ratio in the range of 500–2000 and the results are shown in Fig. 10. The conversion was observed to increase linearly dependent on the amount of catalyst loading, indicating the absence of external liquid–solid mass transfer.

4. Conclusion

In general, the rate of the reaction in homogeneous condition is higher as compared to heterogeneous condition and the selectivity is lower. The heterogenization of homogeneous catalyst gives higher selectivity (99%) of the product compared to the reaction in homogeneous condition (%96) at the same conversion. The *cis* geometry of the metal complex was retained even after immobilization of metal complex in MCM-41. The heterogeneous catalyst can be recycled for three times with slight decrease in the activity which is due to the leaching of 0.9% of ruthenium with respect to the total amount of ruthenium loaded. Bi-dented ligands show higher activity and selectivity of the product in hydrogenation of acetylacetone to 4-hydroxypentan-2-one because of reducing the accessibility of reactant molecule towards the metal center, thus lowering the rate of the reaction. The use of water gives another benefit of green chemistry and higher selectivity to 4-hydroxypentan-2-one for the hydrogenation of acetylacetone.

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