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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 posses 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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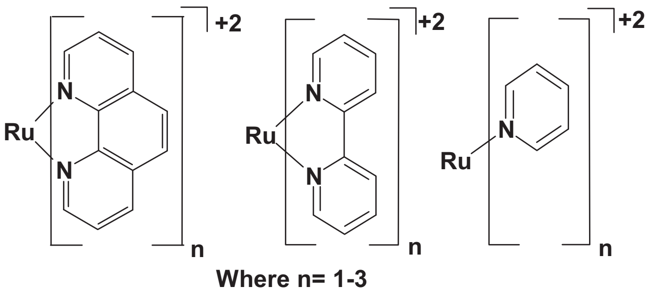


Scheme 1. Schematic representation of ruthenium metal complexes.

2. Experimental

2.1. Synthesis of metal complexes

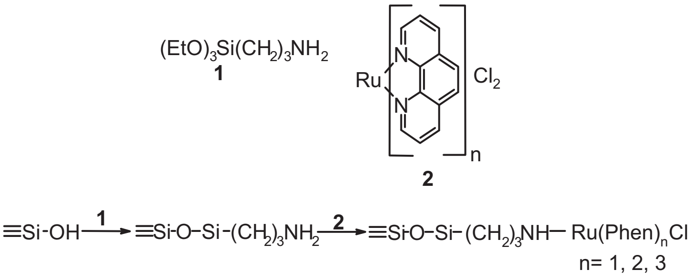
Ruthenium metal complexes were prepared according to the procedure available in literature [12]. In a typical complex synthesis, ethanolic solution of the phenanthroline ligand was added to the aqueous solution of ruthenium under stirring conditions and kept overnight. The solid precipitate was filtered, 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 SiO_2:0.32 NaOH:0.2 CTABr:125 H_2O. 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 N_2 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 N_2 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 *ter*-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 H_2 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 $2\theta = 2.1°$, $3.7°$, $4.3°$ 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

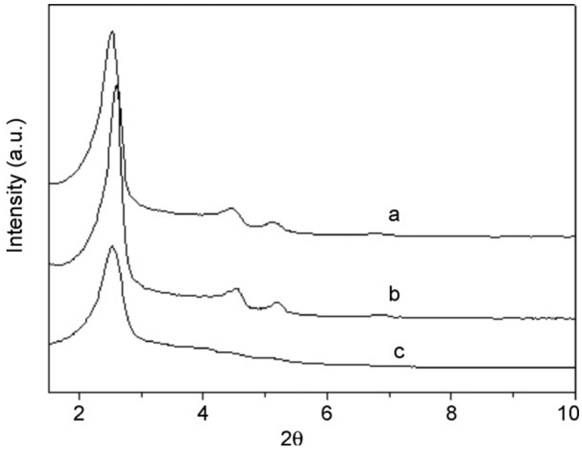


Fig. 1. XRD pattern for (a) calcined Si–MCM-41, (b) NH–MCM-41 and (c) Ru–Phen-2-NH–MCM-41.

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