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Ru(II) Phenanthroline Complex As Catalyst for Chemoselective Hydrogenation of Nitro-Aryls in a Green Process

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Ru(II) Phenanthroline [Ru(II)(Phen)_n where $n = 1, 2, 3$] complexes were used as highly chemoselective catalysts for hydrogenation of nitro aryls using molecular hydrogen in an aqueous media. Water, universal solvent, was used as a reaction mixture for hydrogenation of nitro-aryls to make the process green. The chemoselectivity in hydrogenation of substituted nitrobenzene to substituted aniline was obtained as high as >99% at about complete conversion of substituted nitrobenzene. The parametric effects, including effect of solvent, effect of ligand, effect of metal to ligand ratio, effect of temperature and pressure, were studied in detail to obtain the best results. The Ru(Phen)_n was characterized by FTIR, UV–vis, and XPS.

1. Introduction

The selective synthesis of amines from the hydrogenation of nitro compounds is commonly used to manufacture important intermediates for dyes, urethanes, agrochemicals, and pharmaceuticals. Aniline is mainly used for the production of methylene diphenyl diisocyanate (MDI), as an additive for rubber process, as an intermediate for the synthesis of dyes and pigments, pesticides, and herbicides. About 85% of global aniline is produced by catalytic hydrogenation of nitrobenzene. The hydrogenation of nitrobenzene to produce aniline can be carried out in the vapor or liquid phase using supported metal catalysts and organic solvents such as alcohols, acetone, benzene, ethyl acetate, or aqueous acidic solutions.¹ The use of these solvents has several drawbacks owing to their toxicity, flammability, and environmental hazards. Therefore the choice of an environmentally benevolent solvent has become an important factor, which can be overcome by the use of a green solvent like water for contemporary chemical processes.

The conventional process for reduction of nitro compounds (commonly known as Béchamp process) employed stoichiometric amounts of Fe-acid as the reducing agent producing an almost equivalent amount of Fe-FeO sludge as a byproduct.² Apart from the serious waste disposal problems, the Béchamp process also suffered from the difficulties in the separation of desired products from the reaction mass and use of corrosive reagents such as acids. The catalytic hydrogenation using supported metal catalysts (gas–liquid–solid multiphase catalytic reactions) has emerged as a cleaner alternative to the conventional Béchamp process with better selectivity and yield.^{3,4}

Metal nanoclusters are also used for the hydrogenation of nitro compounds exhibiting high activity and selectivity. Carbon nanotubes are used as support for the deposition of metal nanoparticles. Dai and co-workers have reported the use of various metal nanoparticles deposited on carbon nanotubes.⁵ About 3 wt % Pt on carbon nanotubes showed very high activity for nitrobenzene hydrogenation at ambient temperature and atmospheric pressure.⁶ Xu et al. investigated the Pd-macromol-

ecule supported on copolymer for the hydrogenation of 4-nitrophenol.⁷ Hydrogenation of nitrobenzene halides was carried out using platinum on carbon.^{8,9} Heterogenized rhodium metal on zinc aluminate spinel has been studied for chemoselective hydrogenation of nitro compounds.¹⁰ Pt and Pd clusters supported on ordered mesoporous carbon molecular sieve showed high catalytic activity toward the hydrogenation of nitro compounds.¹¹ The use of supercritical carbondioxide has also been investigated for the hydrogenation of nitrobenzene.^{12–15} Gold nanoparticles supported on titanium oxide were found to be a highly chemoselective catalyst for the hydrogenation of nitrostyrene.^{16,17} Ruthenium stabilized in polymer matrix is utilized for the chemoselective hydrogenation of chloro-nitrobenzene to chloro-aniline.¹⁸ Toti et al. showed that ruthenium phosphorus complex is active for the hydrogenation of nitrobenzene.¹⁹ Deshpande et al. reported the hydrogenation of substituted nitrobenzene using water-soluble iron complex catalyst under biphasic reaction conditions to achieve 98% selectivity toward aniline.²⁰

However, use of water as reaction medium has not been reported to our knowledge for hydrogenation of nitro-aromatics to corresponding amine. Similarly RuII(Phen)_x complexes have also not been used for such reaction. The present study deals with utilization of water as a reaction medium to overcome the drawbacks of organic volatile solvents for the hydrogenation of nitro aryls. The study also reflects that the heterogenized metal catalyst gets dissolved during the reaction.

The ruthenium metal, owing to it is 4D⁷5S¹ electron configuration, has wide range of possible oxidation states²¹ and thereby can stabilize various coordination geometries in each electron configuration. Particularly, the lower oxidation states of ruthenium complexes normally prefer trigonal–bipyramidal and octahedral structures; such variety of structural geometry of ruthenium complex has great potential in selective hydrogenation reactions.

2. Experimental Section

The metal complexes were synthesized by addition of ethanolic solution of ligand to the aqueous solution of anhydrous ruthenium trichloride. The resulting mixture was stirred overnight to get the desired product. Using the same procedure, different complexes with different metal to ligand ratios [1:1,

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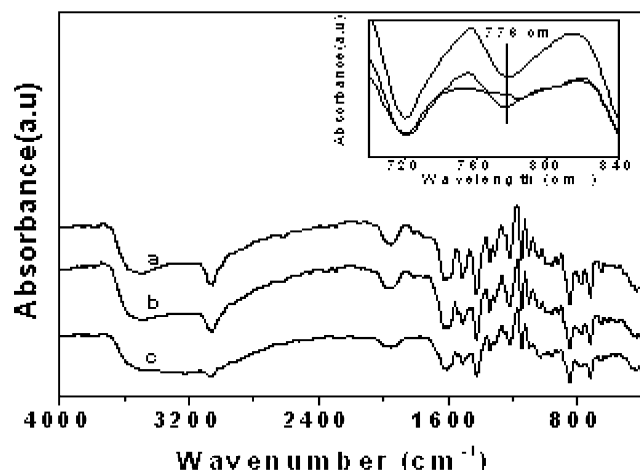


Figure 1. FT-IR spectra of the neat complex (a) Ru-Phen-1, (b) Ru-Phen-2, (c) Ru-Phen-3.

1:2, 1:3 metal/ligand (mole ratio)] where synthesized (abbreviated as Ru-Phen-1, Ru-Phen-2, and Ru-Phen-3). The hydrogenation of nitrobenzene was carried out in a 100-cm³ high-pressure and high-temperature autoclave equipped with magnetic stirrer, at different pressure (1.37–2.75 MPa) and at different temperature (120–180 °C) using water as reaction medium. The effect of different metal-to-ligand ratios and different types of substrates (substituted nitro-aryls) at 160 °C, at 2.75 MPa pressure was studied. The effect of different organic solvent was also tested at 160 °C at 2.75 MPa pressure for comparative purpose. The reaction mixture was extracted using dichloromethane and analyzed by GC on a capillary column with FID detector. The products were confirmed by GCMS.

3. Results and Discussion

3.1. Characterization of Catalyst. 3.1.1. FT-IR Spectra.

FT-IR spectra of all the neat ruthenium phenanthroline complexes with different metal-to-ligand ratios are depicted in Figure 1. 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 (Figure 1 inset) characteristic of the cis confirmation of complex which is due to the out-of-plane C–H deformation of the ligand.^{22,23}

3.1.2. UV–visible Spectra. The UV–visible spectra of six-coordinate [Ru(phen)₂]²⁺ complexes are shown in Figure 2. The absorbance spectra for these complexes in acetonitrile are characterized by the presence of intense π – π^* phenanthroline intraligand transitions in the UV-vis region and metal-to-ligand charge-transfer (MLCT) bands at 500–530 nm along with a second band of lesser intensity between 340–390 nm.²⁴ 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.²⁵ 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.

3.1.3. X-ray Photoelectron Spectra. X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of ruthenium in the neat and immobilized complex before and after reactions. Table 1 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.²⁶ The binding energy of Ru 3d_{5/2}

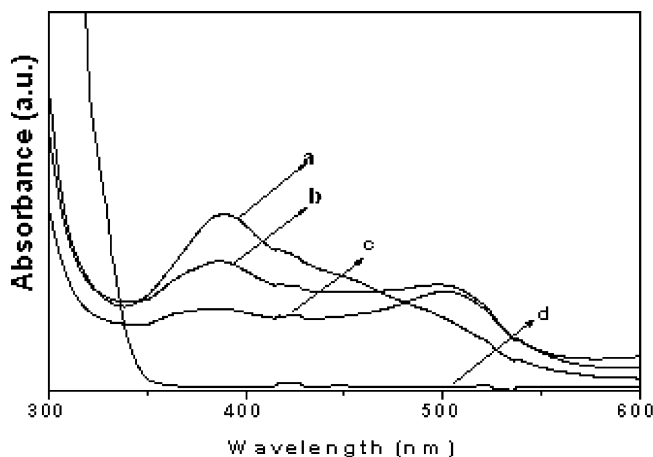


Figure 2. UV–visible spectra of the neat complex (a) Ru-Phen-1, (b) Ru-Phen-2, (c) Ru-Phen-3, (d) Phen.

Table 1. 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

Table 2. Hydrogenation of Nitrobenzene with Different Ruthenium Metal Complexes^a

sr. no.	catalyst	% conversion	% selectivity ^b	TOF (h ⁻¹) ^c
1	RuCl ₃	100	92	168
2	Ru-PY-2	100	96	113
3	Ru-BP-2	99	97	112
4	Ru-Phen-2	99	99.5	123
5	Ru-Phen-2-NH-MCM-41	98	99	109

^a Reaction conditions: nitrobenzene = 1 g, nitrobenzene/Ru-Phen-2 = 500, pressure = 2.75 MPa, temperature = 160 °C, water 30 cm³, 0.1 g K^tBuO. ^b Remaining is phenyl hydroxylamine and azobenzene. ^c TOF = number of moles of amino product formed per moles of ruthenium per hour.

in complexes decreases from top to bottom through Table 1, which is attributed to the increase in the number of electrons in the outermost shell of the ruthenium metal donated by the nitrogen atom from the ligand (as metal-to-ligand ratio increases). As the number of electrons in outermost shell increases, the ionization 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.

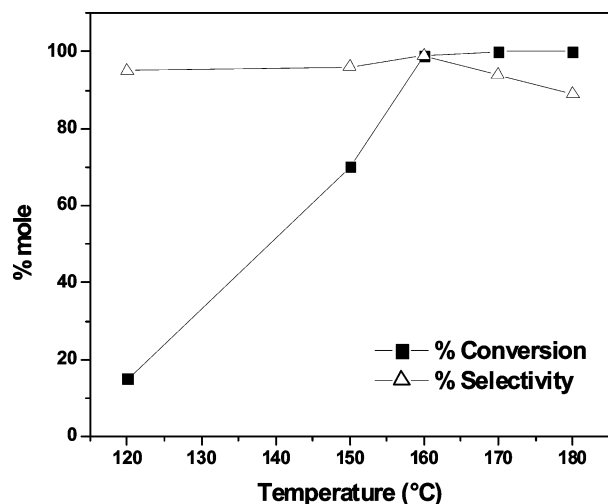
3.2. Catalytic Hydrogenation Reactions. 3.2.1. Effect of Different Ligand. The effect of ligand (pyridine as a mono or bipyridine and phenanthroline as a bidentate) on the activity and selectivity in the hydrogenation reaction of nitrobenzene to aniline was studied. The reaction was carried out over Ru(II)L₂ type complexes, [where L = pyridine (PY), bipyridyl (BP), and phenanthroline (Phen)], 160 °C and 2.75 MPa using water as a reaction medium. The results are given in Table 2, which depicts that nearly complete conversion was obtained over all the catalysts studied with ca. 92–99% selectivity toward aniline. However, the selectivity toward aniline followed the order RuCl₃ < Ru-Py-2 < Ru-Bp-2 ≈ Ru-Phen-2.

3.3. Effect of Metal-to-Ligand Ratio. To study the performance of metal-to-ligand ratio, three different catalysts with ruthenium-to-phenanthroline ratios 1, 2, and 3 were used for

Table 3. Effect of Metal-to-Ligand Ratio in Hydrogenation of Nitrobenzene^a

entry	catalyst	conv.	aniline selectivity ^b	TOF (h ⁻¹) ^c
1	RuCl ₃	100	92	168
2	Ru-Phen-1	100	96	111
3	Ru-Phen-2	99	99.5	112
4	Ru-Phen-3	80	98	91

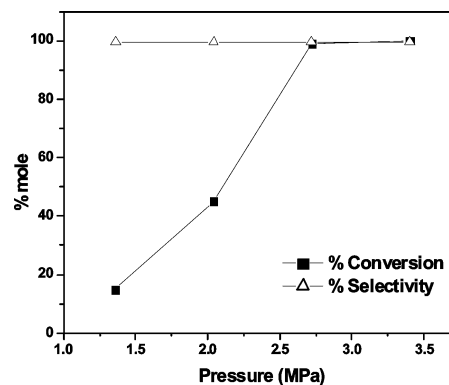
^a Reaction conditions: nitrobenzene = 1 g, nitrobenzene/Ru-Phen-2 = 500, pressure = 2.75 MPa, temperature = 160 °C, water 30 cm³, K^tBuO = 0.1 g. ^b Remaining is phenyl hydroxylamine and azobenzene. ^c TOF = number of moles of amino product formed per moles of ruthenium per hour.

**Figure 3.** Effect of temperature on the hydrogenation of nitrobenzene over Ru-Phen-2.

hydrogenation of nitrobenzene at 160 °C and 2.75 MPa (Table 3). Although, RuCl₃ shows faster reaction, the aniline selectivity was lower (92%) compared to Ru-L₂ complex (>99%). The reaction was relatively sluggish over Ru-Phen-3, mainly due to bulkiness of ligand around metal leading to steric constraints, thereby restricting the approach of reactant molecule toward reactive metal center in complex.

3.4. Effect of Temperature. Figure 3 shows the effect of temperature on activity and selectivity on catalytic hydrogenation of nitrobenzene. It was observed that with increase in temperature from 120 to 180 °C the nitrobenzene conversion increases, whereas selectivity passes through a maximum at 160 °C. The highest selectivity and conversion (>99%) was observed at reaction temperature 160 °C. The slightly lower selectivity of aniline at temperature lower than 160 °C was due to the formation of hydroxylamine as an intermediate. However, aniline selectivity decreases at reaction temperature higher than 160 °C due to the formation of condensed products (azoxybenzene). Thus, the optimized temperature for getting highest selectivity toward aniline by hydrogenation of nitrobenzene using water as a solvent was 160 °C.

3.5. Effect of Pressure. Figure 4 depicts the effect of pressure on nitrobenzene conversion and aniline selectivity at 160 °C over Ru-Phen-2 catalyst. The hydrogen pressure shows pronounced effect over conversion, as expected. The conversion increased with increasing hydrogen pressure. There were no changes observed in conversion after 2.75 MPa pressure. There was also no change in the selectivity of aniline with increase in hydrogen pressure. Thus, for all the studies the reaction temperature was maintained at 160 °C and hydrogen pressure was 2.75 MPa.

**Figure 4.** Effect of pressure on the hydrogenation of nitrobenzene over Ru-Phen-2.**Table 4. Effect of Solvent on Selectivity and Conversion for Hydrogenation of Nitrobenzene^a**

sr. no.	solvent	conversion (mole %)	aniline selectivity (mole %)	TOF (h ⁻¹) ^b
1	methanol	65	97	66
2	<i>n</i> -butanol	70	98	71
3	iso-propanol	90	98	92
4	water	99	99.5	124

^a Reaction conditions: nitrobenzene = 1 g, nitrobenzene/Ru-Phen-2 = 500, temperature = 160 °C, solvent = 30 cm³, K^tBuO = 0.1 g. ^b TOF = number of moles of amino product formed per moles of ruthenium per hour.

3.6. Effect of Solvent. 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 abstracts a proton from dissolved H₂ in solvent to form the protonated ground-state species, relaxing to the starting material in the process. In protic 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.^{27–29} 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. In Table 4 the effect of organic solvents and water on the conversion and selectivity is reported. Although complete conversion and selectivity (>99%) was obtained in the presence of water as a reaction medium for the hydrogenation of nitrobenzene, the conversion followed the order methanol < *n*-butanol < iso-propanol < water. However, the aniline selectivity ranged between 97 and 99.5%. Use of water as a solvent in reaction was found most effective in the hydrogenation of nitrobenzene compared to the other solvents (*n*-butanol, methanol, and iso-propanol). The reaction system behaves biphasic in initial stage as nitro-compounds and catalyst are not soluble in water at room temperature, but after the completion of the reaction, the reaction mixture behaves as homogeneous.

3.7. Effect of Substitution on the Aromatic Ring. The effect of different substrates having different substituted groups is shown in Table 5. The hydrogenation of 4-nitrobenzaldehyde and 4-nitrobenzoic acid gave corresponding amino derivatives without affecting the other functional group, which shows the chemoselective nature of the catalyst. The hydrogenation of chloro-nitrobenzene also showed high yield of 4-chloro-aniline without any dehalogenation of 4-chloro-nitrobenzene. The variation in the activity observed for the hydrogenation of the

Table 5. Effect of Substitution on Hydrogenation in Biphasic Medium^a

sr. no.	substrate	product	conv. (mole %)	amine selectivity (mole %)	TOF ^b (h ⁻¹)
1	Ph-NO ₂	Ph-NH ₂	>99	100	110
2	4-CH ₃ - Ph-NO ₂	4-CH ₃ - Ph-NH ₂	99	100	83
3	4-OCH ₃ - Ph-NO ₂	4-OCH ₃ - Ph-NH ₂	98	100	124
4	4-OH- Ph-NO ₂	4-OH- Ph-NH ₂	99	100	106
5	3,4-OH- Ph-NO ₂	3,4-OH- Ph-NH ₂	98	100	88
6	4-Cl- Ph-NO ₂	4-Cl- Ph-NH ₂	99	100	103
7	4-NH ₂ - Ph-NO ₂	4-NH ₂ - Ph-NH ₂	99	100	106
8	4-COOH- Ph-NO ₂	4-COOH- Ph-NH ₂	85	99	67
9	4-CHO- Ph-NO ₂	4-CHO- Ph-NH ₂	99	100	89

^a Reaction conditions: substrate = 1 g, temperature = 160 °C, pressure = 2.75 MPa, water = 20 cm³, K^tBuO = 0.1 g. ^b TOF = Mole of product formed per moles of ruthenium per hour.

different compounds could be attributed to the influence of the substituent on the ring as well as the solubility of the substrate in water. The limited solubility of the substrate in water maintains sufficient productivity. The turnover frequency of the present catalyst is much higher (10 times higher) than the reported catalytic systems^{18,19} for the hydrogenation of nitrobenzene.

3.8. Recycle Study. The recyclability of the catalyst was investigated by immobilizing Ru(Phen)₂ complex in amino functionalized MCM-41 (abbreviated as Ru-Phen-2-NH-MCM-41) using the reported method.³⁰ The hydrogenation of nitrobenzene was performed at the best reaction condition to achieve maximum conversion and selectivity. After reaction, the immobilized catalyst was subjected for XRD and the mother liquor was analyzed by AAS to determine the phase stability of MCM-41 and leaching of ruthenium into mother liquor. The XRD pattern showed very weak intensity for 100 peak ($2\theta = 2.1^\circ$) whereas no other characteristic peaks ($2\theta = 3.7^\circ$, 4.3° , and 5.6°) of MCM-41 were observed. AAS showed almost complete leaching of ruthenium metal, clearly indicating that under the reaction conditions particularly in the presence of aniline and water the MCM-41 disintegrates and therefore results in the leaching of metal complex from solid. Hence, all the further experiments were conducted using neat metal complex.

4. Conclusion

The successful use of water as a reaction medium has shown great promise in eliminating the necessity of using organic solvent, thereby making the process more eco-friendly. The highly selective hydrogenation of nitro aryl in biphasic aqueous medium using ruthenium metal complexes has been shown for the first time. The simplicity of the catalyst preparation, and the low cost, coupled the prospect of solvent-free operations. Due to the leaching of ruthenium metal and breaking of MCM-41 structure, this heterogenized catalyst cannot be used as it follows the homogeneous path.

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