3.1.1 Ru-based oxidation catalysis

Ru-based oxidation catalysis is a powerful and extremely versatile synthetic tool to afford selectively oxygenated products both in homogeneous and in heterogeneous conversions. Numerous RuNPs can selectively catalyze a large variety of hydrogenation transformations, the oxidative dehydrogenation of alcohols to carbonyls, dehydrogenation of diamine-borane, methanlosis of borane, oxidation of anilines and alkenes and hydrogen storage materials.

Zeolite confined nanostructured dinuclear ruthenium clusters (ZC-Ru) have been used for the aerobic oxidation of alcohols under mild conditions (Scheme 3.1.1).

![Scheme 3.1.1 ZC-Ru catalyzed aerobic oxidation of 1-phenylethanol to acetophenone at 160°C under molecular oxygen.](image)

Nanosized Pt-Ru/C catalysts and their superior catalytic activities for methanol, and ethanol oxidation and Pt-Ru catalyst for formic acid oxidation are reported. Mizuno et al. have used alumina supported ruthenium (Ru/Al₂O₃) catalyst for the oxidation of primary and secondary benzylic alcohols quantitatively to the corresponding benzaldehydes and ketones in solvent-free conditions (Scheme 3.1.2).

![Scheme 3.1.2 Oxidation of various alcohols catalyzed by Ru/Al₂O₃ with molecular oxygen.](image)

Ru/Al₂O₃ catalyzes the dehydrogenation of alcohols using acetone as hydrogen acceptor to yield carbonyl compounds Scheme 3.1.3.
Scheme 3.1.3 Dehydrogenation of alcohols using Ru/Al$_2$O$_3$.

It is also an active catalyst for aerobic oxidation of various amines to the corresponding nitriles or imines (Scheme 3.1.4).$^{39d}$

Scheme 3.1.4 Ru/Al$_2$O$_3$ catalyzed oxidation aromatic amines.

Chang et al.$^{40}$ developed a highly efficient, user-friendly, reusable, and external ligand-free heterogeneous ruthenium catalyst (Ru/Al$_2$O$_3$) for Suzuki, Heck and Sonogashira coupling reactions (Scheme 3.1.5).

Scheme 3.1.5 Ruthenium-catalyzed Suzuki, Heck and Sonogashira coupling reactions.
3.1.2 Ru-based hydrogenation catalysis

Ruthenium as a catalyst for hydrogenation reactions, have been widely used in the chemical, petrochemical, food, and pharmaceutical industries, and in energy conversion technologies. The scope of homogeneous Ru catalysts has been well illustrated recently (Scheme 3.1.6).

Scheme 3.1.6 Hydrogenation of benzaldehyde on supported Ru catalyst.

Ruthenium(0) nanoclusters supported on hydroxyapatite and PVP-Ru micro reactor systems provide high activity and reusability in the complete hydrogenation of aromatics under mild conditions. It serves as the highly active, reusable and green catalyst in the hydrogenation of aromatics under mild conditions (Scheme 3.1.7).

Scheme 3.1.7 Ru catalyzed hydrogenation of aromatics in cyclohexane under mild conditions.

Supported RuNPs are also used for the hydrogenation of D-glucose, cellobiose and cellulose (Scheme 3.1.8).
Scheme 3.1.8 Conversion of cellobiose to sorbitol using a RuNPs.

Efficient and controlled chemoselectivities are obtained in the hydrogenation of arene derivatives by the methylated cyclodextrins (Me-CDs) and HEA16Cl (N,N-dimethyl-N-cetyl-N-(2-hydroxyethyl)ammonium chloride) stabilized ruthenium nanoparticles.\textsuperscript{45} The hydrogenation of \( \alpha \)- and \( \beta \)-pinenes leads to the major formation of \textit{cis}-pinanes, interesting synthons for fine chemistry, with high diastereoisomeric excesses (Scheme 3.1.9).

Scheme 3.1.9 Hydrogenation of \( \alpha \)- and \( \beta \)-pinenes using ruthenium nanocatalyst.

3.1.3 Sulfoxidation using nanocatalysts

The development of the highly efficient catalytic systems for the oxidation of sulfides to sulfoxides and sulfones has received much attention because they are important as intermediates of biologically significant molecules,\textsuperscript{22-28,46,47} ligands in asymmetric catalysis,\textsuperscript{48} and oxo-transfer reagents.\textsuperscript{49} In addition, the oxidative desulfurization is a promising method for the removal of sulfur compounds from fuels and industrial effluents.\textsuperscript{50,51}
Recently, nanomaterials have been a topic of interest as heterogeneous catalysts since they have extraordinary properties relative to their corresponding bulk materials.

Sreedhar et al.\textsuperscript{29,52} developed the synthesis of nanostructured polyaniline (PANI) and vanadium-doped PANI and used for the application for sulfoxidation reactions in water (Scheme 3.1.10).

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\includegraphics[width=\linewidth]{scheme3.1.10.png}};
\end{tikzpicture}
\end{center}

\textit{Scheme 3.1.10} Oxidation of 4-bromothioanisole with 30\% $\text{H}_2\text{O}_2$ in water using different undoped and doped PANI catalysts.

The enhancement of selectivity and efficiency of the nano-sized TiO$_2$ for oxidation of sulfides into their corresponding sulfoxides has been reported by supporting of Preyssler heteropoly acid ($\left[\text{NaP}_5\text{W}_{30}\text{O}_{110}\right]^{14-}$) on TiO$_2$ nanoparticles (Scheme 3.1.11).\textsuperscript{53}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\includegraphics[width=\linewidth]{scheme3.1.11.png}};
\end{tikzpicture}
\end{center}

\textit{Scheme 3.1.11} Oxidation of sulfides by supporting of Preyssler heteropoly acid on TiO$_2$ nanoparticles.

Nanobiocatalysts\textsuperscript{54} and nanosized WO$_3$ particles supported on MCM-48 work as highly efficient and selective heterogeneous catalysts for the oxidation of olefins, sulfides, and cyclic ketones using hydrogen peroxide or peracetic acid (Scheme 3.1.12).\textsuperscript{55}

The catalytic activity is turned out to be dependent on the nature of the supporting materials and particle size of the metal oxide. In this chapter we report a novel and simple method for the oxidative conversion of sulfides to sulfoxides using H$_2$O$_2$ as the oxidant and RuNPs loaded on $\gamma$-Al$_2$O$_3$ as the catalyst I, (Ru(PVP)/$\gamma$-Al$_2$O$_3$). H$_2$O$_2$, an environmentally benign oxidant, is frequently used by many researchers. However, H$_2$O$_2$ alone has to be used in a controlled manner to reduce the possibility of an over-oxidation reaction. Therefore, there is a need to improve the utility of H$_2$O$_2$ for the selective conversion of sulfides to sulfoxides. The title reaction is represented in (Scheme 3.1.13).

Scheme 3.1.13 Oxidation of sulfides using Ru(PVP)/$\gamma$-Al$_2$O$_3$.

3.2 Experimental section
3.2.1 Synthesis of Ru(PVP)/$\gamma$-Al$_2$O$_3$ catalyst

Metal colloids dispersed liquid medium can be divided into four categories, solvent stabilized$^{56}$, surfactant-stabilized$^{57}$, ligand-stabilized$^{58}$ and polymer stabilized$^{59}$. Metal colloids of the first three categories are usually unstable when they are used as catalysts even when the reaction is conducted in ambient conditions. Thus, the polymer-stabilized metal colloids are the most useful catalytic systems for
organic transformation. Very stable PVP-capped RuNPs were synthesized by reduction of Ru$^{3+}$ with 1,2-propanediol in the presence of PVP according to Chen et al.$^{60}$ Briefly, RuCl$_3$ (0.1434 g, 5.25×10$^{-4}$ M), and PVP (0.5828 g, 5.25×10$^{-3}$ M, as monomeric unit) were dissolved in 1,2-propanediol (100 mL) under stirring to form a dark red solution and refluxed. The color of the solution changed from dark red to yellow and then turned to deep green and finally to dark brown. The dark brown colored solution was then left to cool to room temperature.

**Scheme 3.1.14** illustrates the two-step process that we have used for the synthesis of the RuNPs supported on the alumina: (i) synthesis of the ruthenium colloids, and (ii) impregnation of the RuNPs onto the alumina nano surface using PVP as the stabilizer. The 1,2-propanediol was removed later by diluting the suspension with 450mL of 0.3 M NaNO$_3$ aqueous solution. The black solid was collected by filtration, washed with distilled water to remove the Na$^+$ and Cl$^-$ ions, dried under vacuum at RT and calcinated at 500°C for 8 h and stored in a closed container. The details of the synthesis of the catalyst I are given **Scheme 3.1.14**.

**Scheme 3.1.14 Two-step process for the synthesis of catalyst I.**

The catalyst support, γ-Al$_2$O$_3$, was dried at 120°C overnight prior to impregnation and surface area >40m$^2$/g (BET) is the property which makes γ-Al$_2$O$_3$
appealing as a catalyst support. The $\gamma$-alumina supplied by Sigma-Aldrich with an average particle size of $<50$ nm (TEM) is used as the support in this study.

### 3.2.2 Catalytic reaction

The selective oxidation of organic sulfide to sulfoxide is an important reaction particularly because sulfoxides are used as the starting materials in the synthesis of organic drug molecules. The general procedure for the sulfoxidation reactions is as follows: Catalyst I (1 wt %, 0.5-2 mmol) and 1 mmol sulfide were dissolved in CH$_3$CN (3.0 mL) at 298 K. To the mixture, 30% H$_2$O$_2$ (1.0 mmol) was added dropwise slowly. The mixture was stirred for 1-2 h in room temperature. The resulting solution was diluted with CHCl$_3$ and washed with water and then with saturated brine solution. The organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (2:1) as eluent. The solvent was evaporated and the product was analyzed using $^1$H-NMR and FT-IR techniques.

**Table 3.1 Oxidation of various sulfides by H$_2$O$_2$ catalyzed by catalyst I$^{[a]}$**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time (min)</th>
<th>Conversion (%)$^{[b]}$</th>
<th>Yield (%)$^{[b],[c]}$</th>
<th>Selectivity (%)$^{[b],[c]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Substrate 1" /></td>
<td>120</td>
<td>100</td>
<td>$98,92^b,98^c$</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Substrate 2" /></td>
<td>150</td>
<td>98</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Substrate 3" /></td>
<td>150</td>
<td>98</td>
<td>97</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Substrate 4" /></td>
<td>150</td>
<td>99</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5" alt="Substrate 5" /></td>
<td>180</td>
<td>99</td>
<td>90</td>
<td>95</td>
</tr>
</tbody>
</table>
3.3 Results and discussion

3.3.1 XRD results

The X-ray diffraction pattern of the catalyst I is shown in Figure 3.1. For the metallic ruthenium, the diffraction peak is around $2\theta = 44^\circ$ which is exactly consistent with the d value (2.11 Å) of standard ruthenium metal data file (JCPDS No. 06-0663). The pattern of the catalyst I (Figure 3.1) contains reflections from...
γ-Al₂O₃, Ru, and RuO₂ and these were detected by XRD. Figure 3.1 also indicates a very little aggregation on the catalyst surface. Minor ruthenium reflection peaks emerging from catalyst I indicate that Ru forms very small particles dispersed on the support.⁶¹

Figure 3.1 The XRD patterns of the catalyst I. The catalyst is calcinated at 500 °C in air for 8 h. Fresh catalyst (black line), and used catalyst (red line). (●), Ru; (■), RuO₂; (○), γ-Al₂O₃.

The Ru colloids show a diffuse peak which is separated into three independent peaks located at 2θ = 38.5°, 42.8° and 44° stand for Ru [100], [002] and [101] respectively.⁶²,⁶³ The average crystal size of the RuNPs calculated by the Scherrer formula is in agreement with the average diameter (5-6 nm) determined by HRTEM. (vide infra)

3.3.2 HRTEM results

Representative HRTEM micrographs of the catalyst I (Figures 3.2a and 3.2b) show the presence of numerous dark and well-dispersed nanoparticles on the alumina support. It reveals that these spots correspond to the RuNPs. It can be seen that individual RuNPs have clear edge and are quite uniform in size as shown in Figure 3.2c.
Figure 3.2 HRTEM photographs of ruthenium catalyst I. a, b, c, and d correspond to the different images and electron diffraction pattern of the representative RuNPs is also shown in inset d. The bars represent (a, b) 50 nm, (c) 20 nm, and (d) 5 nm.

It reveals that the RuNPs are crystalline and observed lattice fringes are shown in Figure 3.2d. The average diameter of RuNPs estimated from Gaussian fit of the particle size distribution histograms is about 5-6 nm, and it corresponds well to the average size of the supported catalyst I.

Selected-area electron diffraction (SAED) analysis confirmed that the particles corresponded to ruthenium with an average diameter of about 5-6 nm. At low magnification all particles appear as smooth-surfaced and perfect spheres (Figure 3.2a) but on higher magnification, with appropriately clean surfaces, they are observed to be covered with relatively complicated patterns of steps (Figure 3.2d) which can be correlated with lattice planes. At higher magnification, it is seen that the particles are single crystals exhibiting lattice fringes characteristic of
RuNPs. The electron diffraction pattern of the representative ruthenium nanoparticle is also shown in Figure 3.2d, inset; it exhibits bright spot with rings with the d-spacings of hcp ruthenium metal. Considerable broadening of the diffraction rings suggests that the particles are very small and of high crystallinity. These results are in good agreement with corresponding XRD data.\textsuperscript{61} When high-energy X-ray diffraction is used for the characterization of RuNPs they are only 5 nm in size and are heavily disordered.\textsuperscript{60} Calcination at 500°C for 8 h caused some broadening of the particle size distribution and the particles have better developed crystal faces with no evidence of any amorphous surface layer shown in Figure 3.2d. Bedford \textit{et al.}\textsuperscript{64} showed, by calcination at higher temperatures 600 and 700°C, significant broadening of the particle shape with increasing particle size from round ones (small particles) to flat, elongated ones (large particles). It has high thermal stability up to 700°C and some migration and coalescence of small RuNPs are reported.\textsuperscript{62}

### 3.3.3 BET surface area studies

The N\textsubscript{2} adsorption and desorption isotherms for γ-Al\textsubscript{2}O\textsubscript{3} and catalyst I were measured at 77 K. Prior to the adsorption measurement, the samples were pretreated under helium gas flow at 300°C for 4 h. Total surface areas were calculated according to the BET and Langmuir methods.\textsuperscript{65,66} Alumina exhibited a Brunauer-Emmett-Teller (BET) surface area of 26.5 m\textsuperscript{2}/g, including micropore area of 0.19 m\textsuperscript{2}/g and external surface area of 29.2 m\textsuperscript{2}/g. The catalyst I gave a BET surface area of 24.2 m\textsuperscript{2}/g, average micropore area of 0.14 m\textsuperscript{2}/g and external surface area of 26.3 m\textsuperscript{2}/g. The decrease in surface area is mainly due to the reduction of micropore surface area. The results help us to conclude that the RuNPs were impregnated on the surface of the γ-Al\textsubscript{2}O\textsubscript{3}. The RuNPs were well dispersed on the outside surface and no obvious aggregation was observed, whereas unsupported RuNPs were likely to aggregate immediately.
Figure 3.3 Adsorption-desorption isotherm for (a) γ-Al₂O₃ and (b) catalyst I.

From the measurements, the BET surface area, Langmuir surface area, pore volume and average pore diameter were calculated and the data given in Table 3.2.

Table 3.2 Physicochemical properties of the γ-Al₂O₃ and catalyst I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ru content (wt%)</th>
<th>BET Surface area (m²/g)</th>
<th>Langmuir surface area (m²/g)</th>
<th>t-Plot Micropore area (m²/g)</th>
<th>Average pore diameter (nm)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>-</td>
<td>26.5</td>
<td>42.4</td>
<td>0.19</td>
<td>33</td>
<td>0.13</td>
</tr>
<tr>
<td>Catalyst I</td>
<td>1.0</td>
<td>24.2</td>
<td>40.0</td>
<td>0.14</td>
<td>20</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The change in textural property of γ-Al₂O₃ and RuNPs impregnated on γ-Al₂O₃ (catalyst I) are given Table 3.2. A sharp inflection of the adsorption and desorption isotherms, in particular around P/P₀ = 0.9712 (for N₂ at 77 K), indicates a forced closure of the hysteresis loop. In Figure 3.3a the inset figure shows the details of the isotherm in the P/P₀ range 0.8-1.0 (dotted square) emphasizing the TSE (Tensile strength effect) at P/P₀ = 0.97. The (4V/A) term used in the estimation of pore average sizes corresponds to the assumed cylindrical model of pores. However, this assumption of cylindrical model of pores is also cited in BJH estimates of pore volume and surface area distributions. Figure 3.3b shows the adsorption and desorption isotherm value of catalyst I at P/P₀ = 0.9711. However, pores with
diameters smaller than 4 nm show no hysteresis and are completely filled and emptied at similar pressures, resulting in a reversible adsorption and desorption isotherm.\textsuperscript{67} The results may point to localization of the RuNPs mainly at the outer surface of the $\gamma$-Al$_2$O$_3$ and only some of them may be present inside the $\gamma$-Al$_2$O$_3$ pores. The average pore diameter, pore volume and surface area of the $\gamma$-Al$_2$O$_3$ decrease after impregnation with RuNPs (Table 3.2). Okal \textit{et al.}\textsuperscript{68} reported that the impregnation of $\gamma$-Al$_2$O$_3$ with an aqueous solution of RuCl$_3$ caused a 25\% decrease in BET surface area and some drop of the pore volume. Mieth and Schwarz\textsuperscript{69} pointed out that the partial dissolution of the support during impregnation may have significant consequences on the catalyst activity. Similar effect was observed with other systems such as Pd/Al$_2$O$_3$\textsuperscript{70} and Pt/Al$_2$O$_3$.\textsuperscript{71} The adsorption studies help us to conclude that due to impregnation of RuNPs on $\gamma$-Al$_2$O$_3$ the surface area, pore diameter and pore volume of catalyst \textbf{I} decreased.

\textbf{3.3.4 Hydrogen chemisorption studies}

Figure 3.4 presents the hydrogen chemisorption on catalyst \textbf{I} carried out at 77 K using Micromeritics 2020 equipment with use of glass volumetric adsorption system described elsewhere.\textsuperscript{72} This study provides hydrogen/metal (H/M) data. (H/M is the ratio of the number of adsorbed hydrogen atoms to the total number of metal atoms multiplied by 100\%). Each measurement was performed three times and the average value $H/M = 1:1$ was used. The total amount of adsorbed hydrogen was obtained by extrapolating the linear high-pressure part of the isotherm to zero pressure. H$_2$ chemisorption at 77 K is helpful to determine the percent dispersion and average Ru particle size to be 17\% and 5.1 nm respectively. The equilibrium adsorption measurements were made for equilibrium pressures of 0-850 mmHg range. Average RuNPs size was estimated using the relation $l_{(chem)} = 5/Sd$, where $S$ is the metal surface area and $d$ is the density of ruthenium.\textsuperscript{73,74}
Chapter IIIA

The reversible hydrogen isotherms (Figure 3.4) show a linear dependence on pressure in the 200-850 mm Hg range but the uptake decreased slowly at 200 mm Hg. Sayari et al.\textsuperscript{75} found that at room temperature reversible $\text{H}_2$ chemisorption occurs in appreciable amounts on the Ru crystallites with sizes within the limited range of 5-6 nm. Zupanc et al.\textsuperscript{76} explained this finding by a modification in the surface energetics of the Ru crystallites with the change of their size. However, only very small change in the mean size of RuNPs was detected by the hydrogen chemisorption.

3.3.5 SEM-EDX observations

SEM-EDX shows typical results of catalyst I powder deposited on a carbon strip by means of SEM. Figure 3.5a represents the view of the sample at 40 K× magnification which stands for examining the area of 9.6×9.6 mm$^2$ surface. These objects consist of tiny particles, as can be proved by SEM results gathered on one of the particles. The above results are shown in Figure 3.5b 9.6×9.6 mm$^2$ area, magnification 100 K× with high roughness surface area is better for a catalyst.
Figure 3.5 SEM pictures of catalyst I: (a) 40 K× magnification, (b) 100 K× magnification and (c) EDX analysis of catalyst I.

Analysis through energy dispersive X-ray (EDX) spectrometers confirmed the presence of elemental ruthenium and aluminum signals from the catalyst I as confirmed in Figure 3.5. The vertical axis displays the number of X-ray counts whilst the horizontal axis displays energy in KeV. Identification lines for the major emission energies for aluminum (Al) are displayed and these correspond with peaks in the spectrum, thus giving confidence that ruthenium has been correctly identified.

3.3.6 UV-vis absorption spectral analysis

UV-visible absorption spectroscopy was used to establish quantitatively the reduction of Ru$^{3+}$ to Ru$^0$ state. The Ru$^{3+}$ is mixed with PVP in 1, 2-propanediol and warmed up to the indicated temperatures as displayed in Scheme 3.1.15. The color changes showed that Ru$^{3+}$ (dark red) was reduced, step by step, to Ru$^0$ (dark brown) during the reaction; (a) the reaction mixture at the beginning of the reaction, (b) reaction solution obtained almost immediately at the beginning of warming,
yellow color is brightened at approximately 20 min of the reaction. (c) at approximately 30 min. (d, e) solutions, at approximately 50 min. (f) at the end of the reaction.

Scheme 3.1.15 Color changes of the reaction solution during the course of the ruthenium nano colloids formation with 1, 2-propanediol taken as solvent.

The UV-visible absorption spectra of the solutions are displayed in Figure 3.6 and color changes with the change of temperature in Scheme 3.1.15.

Figure 3.6 UV-vis absorption spectra of the PVP-Ru in a 1, 2-propanediol solution at different stages.
One of the well-known reduction methods for the preparation of metal colloid is by employing 1, 2-propanediol as a solvent and reducing agent, and the polymer like PVP as the stabilizing agent. The standard reduction potential of Ru$^{3+}$ to Ru(0) is relatively high ($\varphi^0$ 0.3862 V). The redox properties of 1, 2-propanediol is superior to 1, 2-ethanediol but it is less toxic.

Table 3.3 Relationship between the oxidation states of Ru in the Ru-PVP in 1, 2-propanediol with the absorbance data.

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Temp (°C)</th>
<th>Color</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$^{3+}$</td>
<td>RT</td>
<td>Dark red</td>
<td>391</td>
</tr>
<tr>
<td>Ru$^{2+}$</td>
<td>80-120</td>
<td>Yellow</td>
<td>345</td>
</tr>
<tr>
<td>Ru$^+$</td>
<td>120-180</td>
<td>Green</td>
<td>328</td>
</tr>
<tr>
<td>Ru$^0$</td>
<td>&gt;200</td>
<td>Dark brown</td>
<td>No characteristic peak</td>
</tr>
</tbody>
</table>

The UV-vis spectrum of the freshly prepared Ru$^{3+}$ solution in 1, 2-propanediol exhibited a broad absorption with maximum at 391 nm. It is well known that colloidal dispersion of metals exhibit broad regions of absorption in the UV-visible range. These are due to the excitation of plasma resonances or interband transitions, and they are thus a very characteristic property of the metallic nature of the particles Figure 3.6b. This peak is shifted to a shorter wavelength, 345 nm, after 20 min of reduction Figure 3.6c. At this reduction time the solution turned to light yellow color. The intensity of the peak decreases at 328 nm and the solution turned dark green by further heating. After about 110 min, the absorption peak disappeared completely, which indicated that Ru$^{3+}$ was entirely reduced to Ru$^0$ (Figures 3.6f and 3.6g). The increasing scattering absorbance at wavelengths between 300 and 800 nm with time revealed the formation of ruthenium colloids. Each color change represents a change in the oxidation state of ruthenium and reduction takes place stepwise from Ru$^{3+}$ state to Ru$^0$ state and the details are collected in Table 3.2.
3.3.7 AFM analysis

AFM provides real topographical image of sample surface. Since ruthenium nanocatalysts exhibit physical properties different from bulk ruthenium and the properties largely dependent on their size and structure, a good structural characterization becomes possible. A good dispersion of the nanoparticles is possible to image them individually using AFM. Further, this technique enables measuring the size of the particle, considering the particle height rather than its width because the particle may be distorted by the AFM tip geometry. Figure 3.7 provides three-dimensional structural information, which is not available with conventional light-scattering measurements. Figures 3.7a and 3.7b show three-dimensional overview of the fresh catalyst I in a scan size of 1.7 × 1.7 µm.

![AFM Image](image)

**Figure 3.7** (a) AFM image of catalyst I in 2D and (b) the 3D representation.

The nanoparticles have an average size of 50-100 nm and are separated from each other. The particle size of nanoruthenium was determined using HRTEM as shown in Figure 3.2.

3.3.8 FT-IR analysis

The γ-alumina is chemically inert in 1, 2-propanediol under the conditions used in this study and thus used as a support for Ru catalyst. The catalyst I is characterized using FT-IR spectroscopy and the spectrum is shown in Figure 3.8. The FT-IR fingerprints of the PVP indicate that the polymer is present on the surface of the RuNPs serving as a good stabilizing agent. Compared to the spectrum of PVP,
the resonance peak of C=O of PVP coordinated to RuNPs was shifted from 1656 cm\(^{-1}\) to 1644 cm\(^{-1}\) while the C-N peaks at (1014 cm\(^{-1}\) and 1074 cm\(^{-1}\)) were not changed. These changes suggest that the coordination of nitrogen-containing heterocyclic ring of the PVP to the RuNPs surface may be weaker compared to the carbonyl group.\(^{59}\)

![FT-IR spectra](image)

**Figure 3.8 FT-IR spectra of (a) PVP (b) \(\gamma\)-Al\(_2\)O\(_3\) and (c) catalyst I after treatment at 500\(^{\circ}\)C.**

Such PVP coordination to the surface of the RuNPs was also proposed by Bonet *et al.*\(^{83}\) The spectrum also exhibits an O-H stretching mode, associated with water and hydroxide species centered at \(\sim\)3470 cm\(^{-1}\) and \(\sim\)1620 cm\(^{-1}\) respectively. Though the signal obtained for the FT-IR spectrum is predominantly from the RuNPs there is some contribution from the surface of \(\gamma\)-alumina as shown in **Figure 3.8.**

### 3.3.9 Selective oxidation of sulfides to sulfoxides

In this study, 14 organic sulfides are oxidized to sulfoxides by using H\(_2\)O\(_2\) and catalyst I (Table 3.1). After the completion of the reaction, the catalyst was
extracted with CHCl₃. The oxidation process was repeated for three consecutive cycles with little loss of activity (entry 1).

The data collected in Table 3.1 show that the rate of oxidation of aromatic sulfides varied with the nature of substituents on the phenyl ring (entries 2-7). The presence of electron withdrawing substituents on the phenyl ring required slightly longer reaction times when compared to electron donating substituents.

Selectivity towards the formation of sulfoxide is higher than 90% in all cases and in most of the cases it is close to 100%. The other product expected is the corresponding sulfone but the yield of sulfone is negligible here. However, with increase in time and H₂O₂, the formation of sulfone (i.e. overoxidation) has been observed. As far as diphenyl sulfide (DPS) is concerned MeOH seems to be better solvent than CH₃CN. The alkyl sulfides are more reactive than aryl sulfides and the reaction is little sensitive to steric effect. The values of selectivity for the obtained products are presented in Table 3.1. Notably, the use of catalyst 1 at 1 wt% resulted in the quantitative conversion of sulfides to the corresponding sulfoxides with 1 mmol of 30% H₂O₂.

3.3.10 Product analysis

The H₂O₂ oxidation of sulfides in the presence of the catalyst 1 was monitored via ¹H-NMR to identity the products of the reaction. The ¹H-NMR spectra for the products obtained during the course of the reaction (entry 1, 5, 8, 10 and 13 in Table 3.) are shown in Section 3.5.

CDCl₃ is used as the solvent and TMS as an internal standard. The peak appeared as a singlet at δ 2.73 ppm corresponds to methyl proton. The aromatic region is also informative as the aromatic protons of sulfoxide appear as multiplets centered at δ values 7.4-7.6 ppm. The FT-IR spectrum of the product obtained from the oxidation of MPS shows S=O stretching frequency at 1043 cm⁻¹ and no stretching frequency at 1150 cm⁻¹ corresponding to the formation of sulfone is seen. The interesting aspect of this work is that the substrate to H₂O₂ molar ratio of 1:1 was sufficient enough to give 98% conversion within 2 h. Increasing the amount of oxidant to 2:1 (oxidant: substrate) molar ratio causes the formation of a mixture of
-sulfoxide and sulfone which is confirmed using $^1$H-NMR and FT-IR spectroscopy. The aqueous layer containing the catalyst is washed with acetone three times, dried in vacuum and preserved for the next run to check their catalytic activity. This product analysis study demonstrates that sulfoxide is the only product formed under the present reaction conditions.

### 3.3.11 Influence of different solvents on the oxidation reaction

We first investigated the oxidation reaction with MPS as model substrate by using 30% H$_2$O$_2$ (1.0 mmol) as an oxidant. To a solution of 3.0 mL of MPS (1.0 mmol) and catalyst I (1.0 mmol) taken in a solvent (the reaction was carried out in different solvents) the oxidant was added at room temperature. The results given in Table 3.4 show that the reaction is sensitive to the change of solvent.

#### Table 3.4 Oxidation of MPS by H$_2$O$_2$ in the presence of catalyst I$^\text{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Conversion (%)$^\text{[b]}$</th>
<th>Yield (%)$^\text{[b, c]}$</th>
<th>Selectivity (%)$^\text{[d]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>80</td>
<td>52</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$O:CH$_3$CN</td>
<td>80</td>
<td>75</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>MeOH</td>
<td>90</td>
<td>82</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>EtOH</td>
<td>95</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>CH$_3$CN</td>
<td>98</td>
<td>97</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>CHCl$_3$</td>
<td>72</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>CH$_2$Cl$_2$</td>
<td>75</td>
<td>60</td>
<td>85</td>
</tr>
<tr>
<td>8</td>
<td>1,4-Dioxane</td>
<td>88</td>
<td>71</td>
<td>86</td>
</tr>
<tr>
<td>9</td>
<td>MeOH</td>
<td>99</td>
<td>98</td>
<td>98$^\text{[e]}$</td>
</tr>
</tbody>
</table>

$^\text{[a]}$Reaction conditions: 3.0 mL of solvent; 1.0 mmol of MPS; 1 mmol, H$_2$O$_2$; 0.5 mmol (catalyst I); RT with stirring.

$^\text{[b]}$Determined by GC on the crude reaction mixture.

$^\text{[c]}$Yield = No. of moles of sulfoxide/No. of moles of sulfide.

$^\text{[d]}$Selectivity = Sulfoxide/(Sulfoxide + Sulfone).

$^\text{[e]}$The substrate used was DPS.
Generally sulfides are insoluble in water, but when a mixed solvent (H₂O:CH₃CN) 1:1 (v/v) is used for oxidation the yield is 75%. As far as the oxidation of MPS is concerned CH₃CN is the best solvent. On the other hand CH₃OH seems to be the better solvent for the oxidation of DPS and it provides the highest yield (99%) and selectivity is 98%. The data collected in Table 3.4 show that of all the solvents, the selectivity and yields are better in CH₃CN but lower in the mixed solvent H₂O:CH₃CN (1:1) because the substrates are poorly soluble in water specifically.

### 3.3.12 Influence of reaction time with MPS oxidation

The influence of the reaction time is investigated with catalyst I and MPS as the substrate at RT and the results are summarized in Table 3.5.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (min)</th>
<th>Conversion (%)&lt;sup&gt;[b]&lt;/sup&gt;</th>
<th>Yield (%)&lt;sup&gt;[b,c]&lt;/sup&gt;</th>
<th>Selectivity (%)&lt;sup&gt;[d]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>73</td>
<td>60</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>89</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>92</td>
<td>85</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>120</td>
<td>98</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>98</td>
<td>98</td>
<td>98</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 3.0 mL of solvent, 1.0 mmol of MPS, 1.0 mmol, H₂O₂, 0.5 mmol (catalyst I); RT with stirring.

<sup>b</sup>Determined by GC on the crude reaction mixture.

<sup>c</sup>Yield = No.of moles of sulfoxide/No.of moles of sulfide.

<sup>d</sup>Selectivity = Sulfoxide/(Sulfoxide + Sulfone).

Initially the oxidation reaction is slow till 60 min but the reaction is completed in 120 min (Table 3.5). When the progress of the oxidation reaction is monitored for 30 min, the yield is 60% but the maximum yield is obtained in 120
min. But the increase in the selectivity is also significant, from 85% to 98%, compared with the results obtained in 30 min (Table 3.5, entry 1 vs. entry 4). If the reaction time is increased to 150 min there is no change in selectivity as well as in yield.

### 3.3.13 Comparison with other catalyst systems

In order to evaluate the efficiency of the catalyst, we have compiled the data available on the H$_2$O$_2$ oxidation of MPS in the presence of other catalysts in Table 3.6.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Size (nm)</th>
<th>Mol (%)</th>
<th>Time (h)</th>
<th>Solvent</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH-WO$_2$$_4$</td>
<td>-</td>
<td>4.4</td>
<td>0.5</td>
<td>H$_2$O</td>
<td>94</td>
<td>88</td>
</tr>
<tr>
<td>SiO$_2$@WO$_2$$_4$</td>
<td>50-60</td>
<td>2.0</td>
<td>1.5</td>
<td>CH$_2$Cl$_2$;CH$_3$OH</td>
<td>100</td>
<td>82</td>
</tr>
<tr>
<td>WO$_3$/MCM-48</td>
<td>30-100</td>
<td>1.0</td>
<td>4.0</td>
<td>CH$_3$OH</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Nanobiocatalyst$^{[54]}$</td>
<td>90</td>
<td>5</td>
<td>10 min</td>
<td>-</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>6-8</td>
<td>1.25</td>
<td>3.0</td>
<td>CH$_3$CN</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$</td>
<td>&lt;50</td>
<td>0.5</td>
<td>5.0</td>
<td>CH$_3$CN</td>
<td>60</td>
<td>50$^{[b]}$</td>
</tr>
<tr>
<td>Catalyst I</td>
<td>5-6</td>
<td>0.5</td>
<td>2.0</td>
<td>CH$_3$CN</td>
<td>100</td>
<td>98$^{[c]}$</td>
</tr>
<tr>
<td>RuCl$_3$</td>
<td>-</td>
<td>0.5</td>
<td>5.0</td>
<td>CH$_3$CN</td>
<td>50</td>
<td>Trace$^{[d]}$</td>
</tr>
</tbody>
</table>

$^{[a]}$References

$^{[b]}$,$^{[c]}$,$^{[d]}$ Reaction conditions as exemplified in the experimental procedure.

It is clear from the data collected in Table 3.6 that although the yields are similar, and mol% and the size of catalyst I used in the present case are smallest, the selectivity is better than the other systems. The additional advantage with the present system is that the reaction is conducted at room temperature.
To investigate the effect of size on the catalytic activity, different supported catalysts used so far for the oxidation of organic sulfides are collected in Table 3.6. In the present work when catalyst I is used for the oxidation of MPS (as illustrated in Table 3.3) the reaction is carried out using 0.5 mol% of catalyst I and 1.0 mmol of 30% H$_2$O$_2$. The data in Table 3.6 clearly indicate that the catalyst I has the smallest size but exhibits comparable efficiency and selectivity with SiO$_2$@WO$_4^{2-}$ and nanocatalyst systems. The novelty of this catalyst is that less quantity of catalyst (0.5 mol %) is needed during the sulfoxidation reaction compared to other catalysts (Table 3.6). Therefore, the catalytic activity is influenced by the nature and size of the nanocatalyst. Thus, ruthenium catalyst (0.5 mol %) in combination with H$_2$O$_2$ provided the complete conversion of MPS to MPSO (98% yield), indicating a very good catalytic performance in sulfoxidation reactions.

The major problem with the nanobiocatalyst (chloroperoxidase-coated magnetic nanoparticles) is the unsatisfied catalyst stability during operation and the recycling process and the dramatically reduced activity in comparison with catalyst I.

### 3.3.14 Mechanism for the oxidation of organic sulfides to sulfoxides

Generally, thiols (-SH) interact strongly with RuNPs. Here we presume that organic sulfides also bind fairly well with Ru surface. A possible reaction mechanism for the H$_2$O$_2$ oxidation of sulfides to sulfoxides using catalyst I is proposed in Scheme 3.1.16. Initially, the sulfur atom of the substrate is likely to attach with the surface of the ruthenium nanoparticles. It is proposed that the interaction between the metal and sulfur is due to metal-to-sulfur charge transfer as the result of thiol-metal bonds at the surface of the particles.
It is known that organic sulfides are oxidised by $\text{H}_2\text{O}_2$ in a heterolytic process involving the nucleophilic attack of the sulfur atom on the oxygen according to Scheme 3.1.17.

The rate of the oxidation of substrates increases with the increased nucleophilicity on the sulfur atom. The oxygen atoms of the $\text{H}_2\text{O}_2$ molecule bound on the surface of Ru(0) can interact with sulfide to form an intermediate which readily forms the corresponding sulfoxide and water as the products. Aqueous $\text{H}_2\text{O}_2$ is an ideal oxidant owing to its high effective-oxygen content, cleanliness (it produces only water as by-product), and enough safety in storage and operation.
Therefore, the importance of H$_2$O$_2$ as a “green” oxidizing agent has grown considerably.\textsuperscript{91b,c} The progress of the reaction is monitored using TLC and yield of products analyzed by using GC method. Also, the catalyst I was reused up to three times (entry 1 in Table 3.3) and the catalytic activity decreased only slightly.

## 3.4 Conclusions

This work provides important insight into the heterogeneous catalysis on the H$_2$O$_2$ oxidation of sulfides in the presence of catalyst I, which is one of the most convenient, cheap and green methods for the synthesis of various sulfoxides. The vital role of catalyst is surface binding and the surface binding facilitates the interaction of substrate (thioether) with the oxidant (H$_2$O$_2$) resulting in the efficient formation of the selective oxidized products. The synthesized catalyst I is characterized using XRD, HRTEM, BET, H$_2$ chemisorption, SEM-EDX, AFM, FT-IR, and UV-vis spectral techniques and the characterization of products is done by $^1$H-NMR, FT-IR, and GC analysis. This nanocatalyst may prove useful in the development of selective oxidation catalyst for the oxidation of other organic substrates.
3.5 Spectral analysis

3.5.1 NMR data of products

**Methylphenyl sulfoxide** (Table 3.3, entry 1): Colorless liquid\(^{92}\) \(^1\)H-NMR (300 MHz, CDCl\(_3\)): δ 2.73 (s, 3H, Me), 7.49-7.66 (m, 5H, Ar-H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): 43.7, 123.3, 129.2, 130.9, 145.4; FT-IR (KBr, cm\(^{-1}\)): ν 1043, 752, 694.

**Methylphenyl sulfone** (Table 3.3, entry 1): White solid\(^{92}\) \(^1\)H-NMR (300 MHz, CDCl\(_3\)): δ 3.06 (s, 3H), 7.58-7.65 (m, 3H), 7.93-7.97 (m, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): 44.4, 127.2, 129.2, 133.6, 140.5; FT-IR (KBr, cm\(^{-1}\)): ν 1311, 1157.

**4-Chlorophenyl methyl sulfoxide** (Table 3.3, entry 2): Colourless oil,\(^{92}\) \(^1\)H-NMR (300 MHz, CDCl\(_3\)), δ 2.75 (s, 3H, Me), 7.52 (d, \(J = 7.2\text{Hz}, 2\text{H}\)), 7.59 (d, \(J = 7.2\text{Hz}, 2\text{H}\)); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)), δ 43.9, 124.9, 129.8, 137.5, 144.6.

**4-Bromophenyl methyl sulfoxide** (Table 3.3, entry 3): Colourless oil,\(^{92}\) \(^1\)H-NMR (300 MHz, CDCl\(_3\)), δ 2.75 (s, 3H), 7.66 (d, \(J = 7.5\text{Hz}, 2\text{H}\)), 7.69 (d, \(J = 7.5\text{Hz}, 2\text{H}\)), \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)), δ 44.0, 124.6, 129.9, 137.8, 144.9. FT-IR (CHCl\(_3\), cm\(^{-1}\)): ν 3003, 1042, 741

**4-Fluorophenyl methyl sulfoxide** (Table 3.3, entry 4): Colourless oil,\(^{92}\) \(^1\)H-NMR (300 MHz, CDCl\(_3\)): δ = 2.65 (s, 3H), 7.31 (d, \(J = 7.2\text{Hz}, 2\text{H}\)), 7.71 (d, \(J = 7.2\text{Hz}, 2\text{H}\)).
4-Nitrophenyl methysulfoxide (Table 3.3, entry 5): Pale yellow solid,\textsuperscript{92} \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 2.56 (s, 3H, Me), 7.84 (d, \(J = 7.8\)Hz, 2H), 8.34 (d, \(J = 7.8\)Hz, 2H); \textsuperscript{13}C-NMR (75MHz, CDCl\textsubscript{3}): 47.7, 124.5, 132.5, 149.3, 153.1; FT-IR (KBr, cm\textsuperscript{-1}): v 1524, 1345, 1049, 852.

4-Toly methyl sulfoxide (Table 3.3, entry 6): Pale White solid,\textsuperscript{92} \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}), \(\delta\) 2.41 (s, 3H), 2.70 (s, 3H), 7.34 (d, \(J = 7.2\)Hz, 2H), 7.52 (d, \(J = 7.2\)Hz, 2H); \textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}), \(\delta\) 21.5, 43.9, 123.4, 130.4, 141.2, 142.8. FT-IR (KBr, cm\textsuperscript{-1}): 3010, 1590, 1495, 1088, 1043.

4-Methoxy phenyl methyl sulfoxide (Table 3.3, entry 7): Colourless sticky oil,\textsuperscript{92} \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}), \(\delta\) 2.68 (s, 3H), 3.85 (s, 3H), 7.01 (d, \(J = 7.8\)Hz, 2H), 7.56 (d, \(J = 7.8\)Hz, 2H); \textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}), \(\delta\) 43.9, 55.4, 114.5, 125.6, 136.9, 161.5.

Diphenyl sulfoxide (Table 3.3, entry 8): Colorless crystals,\textsuperscript{94} \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 7.43-7.66 (m, 10H, Ph); \textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): 124.7, 129.2, 130.9, 145.5; FT-IR (KBr, cm\textsuperscript{-1}): v 3047, 1473, 1436, 1087, 1037, 734.

Phenyl ethyl sulfoxide (Table 3.3, entry 9): Colourless oil,\textsuperscript{92} \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}), \(\delta\) 1.19 (t, \(J = 6.6\)Hz, 3H), 2.70-2.80 (m, 1H), 2.81-2.96 (m, 1H), 7.47-7.54 (m, 3H), 7.59-7.62 (m, 2H); \textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}), \(\delta\) 5.7, 50.4, 123.9, 128.6, 130.5, 143.1.
Tetramethylene sulfoxide (Table 3.3, entry 10): Colorless oil,\(^{92}\) \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta \) 2.05-2.07 (m, 2H), 2.45-2.98 (m, 6H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): 24.8, 53.7; FT-IR (KBr, cm\(^{-1}\)): ν 1446, 1269, 1022, 877.

Diethyl sulfoxide (Table 3.3, Entry 11) Colorless oil,\(^{92}\) FT-IR (KBr, cm\(^{-1}\)): 2925, 1051.

Dibutyl sulfoxide (Table 3.3, entry 12): Yellow liquid,\(^{97}\) \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta \) 0.99 (m, 6H), 1.81-1.49 (m, 8H), 2.69 (t, \(J = 6.6\)Hz, 4H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): 13.4, 21.7, 24.3, 51.8; FT-IR (KBr, cm\(^{-1}\)): ν 1078, 1026, 919, 732.
3.5.2. NMR spectra of products

Figure 3.5.1 $^1$H-NMR spectrum of MPSO (Table 3.3 Entry 1).

Figure 3.5.2 $^{13}$C-NMR spectrum of MPSO (Table 3.3 Entry 1).
Figure 3.5.3 $^1$H-NMR spectrum of 4-NO$_2$-MPSO (Table 3.3 Entry 5).

Figure 3.5.4 $^{13}$C-NMR spectrum of 4-NO$_2$-MPSO (Table 3.3 Entry 5).
Figure 3.5.5 $^1$H-NMR spectrum of DPSO (Table 3.3 Entry 8).

Figure 3.5.6 $^{13}$C-NMR spectrum of DPSO (Table 3.3 Entry 8).
Figure 3.5.7 $^1$H-NMR spectrum of TMSO (Table 3.3 Entry 10).

Figure 3.5.8 $^1$H-NMR spectrum of TMSO (Table 3.3 Entry 10).
Figure 3.5.9 $^1$H-NMR spectrum of DBSO (Table 3.3 Entry 12).

Figure 3.5.10 $^{13}$C-NMR spectrum of DBSO (Table 3.3 Entry 12).
Figure 3.5.11 $^1$H-NMR spectrum of MPSO2 (Table 3.3 Entry 1).

Figure 3.5.12 $^{13}$C-NMR spectrum of MPSO2 (Table 3.3 Entry 1).
3.5.3. FTIR spectra of some sulfoxide and sulfone products

Figure 3.5.13 FT-IR spectrum of MPSO (Table 3.3, Entry 1).

Figure 3.5.14 FT-IR spectrum of MPSO2 (Table 3.3, Entry 1).
Figure 3.5.15 FT-IR spectrum of DPSO (Table 3.3, Entry 8).

Figure 3.5.16 FT-IR spectrum of TMSO (Table 3.3, Entry 10).
3.6 References


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2003, 59, 3613.
3.7 Introduction

In recent years, nanoparticles particularly supported nanocatalysts, have proven to be efficient and selective oxidation catalysts for a variety of oxidation reactions of organic compounds.\textsuperscript{1} Oxidation is one of the most fundamental reactions in organic synthesis.\textsuperscript{2} The oxidation of organo nitrogen compounds opens up an access to a multitude of versatile building blocks for organic synthesis as well as good oxidants.\textsuperscript{3a} N-oxides are oxidation products of tertiary amines. They were detected as a new class of chemical compounds before 1900 and later found to occur as constituents of living matter.\textsuperscript{3b} In recent years an increasing number of studies by biomedical scientists has been devoted to N-oxides.\textsuperscript{4}

The natural occurrence of N-oxides in plant and animal tissues has posed interesting problems as to the biochemistry and function of these compounds in biological systems. In several cases N-oxides are more active than their corresponding tertiary amines. Hence several N-oxides are important as pharmacological or toxicological agents, \textit{e.g.}, in the groups of alkaloids, chemotherapeutics, antibiotics, psychotropic drugs, methemoglobin forming compounds, and carcinogenic agents.\textsuperscript{4b}

Very recently, several literature reports concerning the preparation and catalytic activity of the metal nanoparticles on supported metal oxides such as TiO\textsubscript{2}, SiO\textsubscript{2}, MgO and SBA-15 have been published.\textsuperscript{5,6} The synthesis of the $\gamma$-Al\textsubscript{2}O\textsubscript{3} supported Ru catalysts from the Ru colloid and its catalytic activity have been reported.\textsuperscript{7-10} Silica supported vanadium,\textsuperscript{11} titanium molecular sieves (TiMCM-41 and TiZSM-5(30)),\textsuperscript{12} Mg-Al-OtBu hydrotalcite (HT-OtBu),\textsuperscript{13} tungstate-exchanged layered double hydroxide (LDH-WO\textsubscript{4}),\textsuperscript{14} titanium silicalite (TS-1),\textsuperscript{15} vanadium-silicate molecular sieve materials,\textsuperscript{16} were used as catalysts for the oxidation of heterocyclic nitrogen compounds to their N-oxides by using H\textsubscript{2}O\textsubscript{2} as an oxidant. Some oxides of metals Cu,\textsuperscript{17} Pt,\textsuperscript{18} Re,\textsuperscript{19,20} Fe,\textsuperscript{21} Co(II) Schiff base complexes and heteropolyacids Preyssler’s anion $[\text{NaP}_{5}\text{W}_{30}\text{O}_{110}]^{14-}$ and Mg\textsubscript{10}Al\textsubscript{2}(OH)\textsubscript{24}CO\textsubscript{3} were used as catalyst for oxidation of tertiary amines.\textsuperscript{22-24}

More powerful oxygen transfer agents $m$-CPBA,\textsuperscript{25} KHSO\textsubscript{5},\textsuperscript{26} oxaziridines or dioxiranes,\textsuperscript{27} H\textsubscript{2}SO\textsubscript{5} (Caro’s acid),\textsuperscript{28} ozone,\textsuperscript{29} peroxymonocarbonate ion (HCO\textsubscript{4}\textsuperscript{-}).\textsuperscript{30}
urea-hydrogen peroxide (UHP),\textsuperscript{31} HOF.CH\textsubscript{3}CN,\textsuperscript{32,33} aqueous chlorine,\textsuperscript{34} carbon-based solid acid,\textsuperscript{35} and flavin\textsuperscript{36} were also acting as an oxygen transfer catalysts in the formation of N-oxides. Most of these reagents are not only expensive, but also generate large amounts of effluent during the reaction process and demand a laborious work-up procedure. Aqueous H\textsubscript{2}O\textsubscript{2} is an ideal oxidant in view of its high effective oxygen content, and greener reagent producing only water as the by-product, safety in storage and operation, and low cost of production and transportation. Ruthenium catalyzed oxidation of tertiary nitrogen compounds to N-oxides with molecular oxygen as the sole oxidant has been reported.\textsuperscript{37-40}

3.7.1 Oxidation of tertiary amines with different catalysts

It is known that all types of amines are easily oxidized using appropriate reagents. The course of the reaction is quite variable and depends very much on the structure of the amine but, in general, hydrogen peroxide converts the primary amines into nitro compounds, whereas the secondary amines are oxidized to hydroxylamines. Tertiary amines are converted by hydrogen peroxide into the relative hydrated N-oxides which are transformed to N-oxides by heating or stirring under vacuum. Due to the widest scope of oxidation states among the transition metals, ruthenium has proved to be the most versatile catalyst for organic transformations and has been used for epoxidation of alkenes, oxidation of alkanes and alcohols with molecular oxygen as oxidant.\textsuperscript{41} The oxidation of tertiary amines is simple compared to the oxidation of primary and secondary amines since the only possible products are N-oxides. The metal-salen complexes (metal = Mn, Cr, Fe, Ru, Co, V and Ti) find widespread use as efficient catalysts for the selective oxygenation of organic aromatic amines. The active oxidant can be generated from the metal-salen ion using PhIO, H\textsubscript{2}O\textsubscript{2}, \textit{t}-BuO\textsubscript{2}H and ClO\textsuperscript{-} as the oxygen source.\textsuperscript{41e}

Sain \textit{et al.}\textsuperscript{38,40} have developed this transformation and it has been found recently that RuCl\textsubscript{3}.nH\textsubscript{2}O catalyzes this reaction under aerobic conditions (Scheme 3.7.1).
Scheme 3.7.1 Tertiary nitrogen compounds are efficiently oxidized to N-oxides with molecular oxygen in the presence of ruthenium trichloride.

The vanadium containing silica ($V_xSi_{4x}O_{6-4x}$) is recyclable and catalyzes efficiently the oxidation of tertiary amines to the corresponding N-oxides with 30% H$_2$O$_2$ in high yields (Scheme 3.7.2). Aromatic as well as aliphatic amines could be oxidized to the corresponding N-oxides.$^{11}$

Scheme 3.7.2 Catalytic oxidation of aliphatic and aromatic tertiary amines to N-oxides.

Alumina supported MoO$_3$ serve as an efficient and recyclable catalyst for selective oxidation of tertiary nitrogen compounds to N-oxides using anhydrous TBHP (t-BOOH) as oxidant under mild reaction conditions (Scheme 3.7.3)$^{42}$

Scheme 3.7.3 Oxidation of tertiary nitrogen compounds to N-oxides with the use of alumina-supported MoO$_3$ catalyst.

Recently vanadium-substituted polyoxometalate of K$_6$[PW$_9$V$_3$O$_{40}$]·4H$_2$O has been reported as an effective and recyclable catalyst for the oxidation of pyridines in water at room temperature.$^{43}$ The process is outlined in Scheme 3.7.4.
After reaction, the products were separated from the aqueous phase by extraction, and the aqueous solution containing the catalyst could be used for the next cycle.

Among the primary oxidants employed for N-oxides production, oxygen\(^4^4\) and hydrogen peroxide\(^4^5\) are the most interesting species because of their high atom efficiency,\(^4^6\) safe handling and low cost. Moreover water is the only by-product of their reduction, and this makes their use very attractive for the development of “green” oxidation processes. Employment of \(O_2\) for N-oxides production has been reported,\(^4^7\) while \(H_2O_2\) has been investigated mainly with heterogeneous catalysts.\(^1^1,1^2,1^6,4^8\) The N-oxides play significant role as an important target in anticancer chemotherapy,\(^4^9\) DNA cleavage,\(^5^0\) anti-cancer activity.\(^5^1\) Similarly phenazine-5,10- dioxide (PDO) and their derivatives find major application in the field of antitumor effect and selective hypoxic cytotoxins.\(^5^2-5^3\)

In continuation to our oxidation studies (previous chapter),\(^9\) here we applied the catalyst \(I\) for the oxidation of tertiary amines to the corresponding N-oxides with 30\% \(H_2O_2\) in high yields. The title reaction is represented in Scheme 3.7.5.

---

**Scheme 3.7.4 Catalytic oxidation of pyridines to N-oxides.**

**Scheme 3.7.5 N-oxidation of amines using catalyst I.**

To the best of our knowledge, there is no literature report on the oxidation of tertiary nitrogen compounds to N-oxides using ruthenium nanoparticles (RuNPs).
3.8. Experimental

3.8.1 Synthesis and characterization of Catalyst I

In our recent report, we have shown the synthetic procedure for the catalyst I as given in detail in the previous chapter. Briefly, RuCl$_3$ (0.1434 g, 5.25×10$^{-4}$ M), and PVP (0.5828 g, 5.25×10$^{-3}$ M, as monomeric unit) were dissolved in 1,2-propanediol (100 mL) under stirring to form a dark red solution and refluxed. The color of the solution changed from dark red to yellow and then turned to deep green and finally to dark brown. The dark brown colored (RuNPs) solution was then left to cool to room temperature. After impregnation of the RuNPs onto the alumina nano surface, a black solid (Catalyst I) was collected and dried under vacuum at room temperature and calcinated at 500 °C for 8 h and stored in a closed container.

3.8.2. General procedure for the oxidation of amines using $\text{H}_2\text{O}_2$

A typical procedure for the oxidation of tertiary nitrogen compounds to its N-oxide is as follows: Catalyst I (1.0 wt%, 0.5-2.0 mmol) and amine (2.0 mmol) were dissolved in CH$_3$CN (3.0 mL) at 298K. To this mixture, 30% H$_2$O$_2$ (2.0 mmol) is added dropwise slowly, then the temperature is raised to 70-80°C and the reaction continued. The progress of reaction is monitored by TLC (SiO$_2$). At the end of reaction, the catalyst is removed by filtration and dried over MgSO$_4$ to afford the product and the reaction mixture thus obtained is purified by passing through a column of silica gel using dichloromethane/MeOH (90:10) as eluent. Similarly other N-oxides are prepared and the reaction times required and yields obtained are shown in Table 3.1. The products are identified by comparing their physical and spectral data given in the Section 3.5.

3.9 Results and discussion

The catalyst I was prepared in our laboratory as given in the experimental section and it is well characterized by XRD, HRTEM, BET, H$_2$ chemisorption, SEM-EDX, AFM, FT-IR and UV-vis spectral techniques as discussed in our previous Chapter 3A.
3.9.1 Oxidation of tertiary amines

A wide variety of tertiary nitrogen compounds were oxidized to their corresponding N-oxides in near quantitative yields and results are summarized in Table 3.7. In our studies it is observed that pyridines having electron donating substituent groups such as -CH₃ are oxidized rapidly in a single step to yield the corresponding N-oxides as the exclusive oxidation product when the substrate is treated with 30% of H₂O₂.

Table 3.7 Oxidation of tertiary amines to N-oxides with H₂O₂ catalyzed by catalyst 1[^a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Products</th>
<th>Time (h)</th>
<th>Yield (%)[^b][^c][^d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>3</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>3</td>
<td>94, 96, 96, 95, 85</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>2.5</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>3</td>
<td>95[^d]</td>
</tr>
<tr>
<td>6</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td>3</td>
<td>97[^d]</td>
</tr>
</tbody>
</table>
Reaction conditions: 3.0 mL of solvent, 2.0 mmol of amines, 6.0 mmol of 30% H$_2$O$_2$ and 0.5 mmol (catalyst I) were stirred at 80°C.

Determined by TLC and NMR method.

Yield = No. of moles of N-oxide/No. of moles of amine.

The substrate used was pyridine.

Lower activity is observed with pyridine unless aromatic substitution changes markedly the electronic properties of the heteroatom (Table 3.7, entries 1 and 2) due to their intrinsic lower basicity and nucleophilicity. The catalyst I is used as catalyst for the oxidation of pyridine, DMA, substituted DMA and quinoline (Table 3.7, entries 1-5). The reaction required 3.0 mmol of H$_2$O$_2$ for the oxidation whereas the oxidation of pyrazine, phenazine, quinoxaline, 2,2'-bipy, and 4,4'-bipy (Table 3.7, entries 6-10) required 6.0 mmol of H$_2$O$_2$ for the oxidation and their products are obtained in quantitative yields at 3h. The catalyst I is recycled used to 2$^{nd}$, 3$^{rd}$ and 4$^{th}$ the yields of the PDO decreases 95, 90 and 87 respectively.

DMA containing electron donating group (-CH$_3$) is found to react faster and required lower reaction times, whereas (DMA) bearing electron withdrawing group (-COOH,-Br and-CN) requires longer reaction times for their oxidation and gives low yield compared to others. The oxidation process is repeated for three consecutive cycles with little loss of activity (Table 3.7, entry 8). The mixture of mono-and di
N-oxides are obtained by treating the substrates (Table 1, entries 9 and 10), the crude mixture was filtered and the solvent removed *in vacuo*. The resulting brown solid was extracted with hot water and water was removed to give a light tan colored solid which was further extracted with a mixture of EtOAc and MeOH (9:1) to yield pure corresponding di-N-oxides as major products.

Our choice of H$_2$O$_2$ rests on several advantages it naturally possesses right from being considered a “green” oxidizing agent by virtue of eliminating H$_2$O as a byproduct to being cheap and also atom efficient in carrying out the oxidation reactions.

**3.9.2. Product analysis**

We have used FT-IR and NMR techniques for the analysis of the products obtained during the course of the reaction. The FT-IR spectral analysis of orange-red crystals PDO shows a strong N-O absorption band at 1348 cm$^{-1}$ and the absorption band corresponding to the formation of N-oxide are shown in Figure 3.9. The PDO has absorption maximum at 277, 392, 435, 462 and 480 nm in CH$_2$Cl$_2$.

![Figure 3.9 The absorption spectrum of PDO in CH$_2$Cl$_2$ solvent.](image)
This product analysis demonstrates that N-oxide is the only product formed under the present reaction conditions. The \(^1\)H-NMR data also confirmed the formation of the PDO. Peaks between 7.82-8.76 ppm are consistent with the presence of signals for aromatic protons.

### 3.9.3 Influence of different solvents on amine oxidation

The effect of varying the solvent is also studied for this reaction and the results are presented in Table 3.8. The PDO is extensively used as an antibacterial activity compound. So we first investigated the oxidation reaction with phenazine as model substrate by using 30% H\(_2\)O\(_2\) (4.0 mmol) as an oxidant. Without any solvent the reaction required long time and only a trace amount product is observed.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Conversion (%)(^b)</th>
<th>Yield (%)(^b,)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>42</td>
<td>40</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>H(_2)O</td>
<td>12</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>MeOH</td>
<td>3</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>EtOH</td>
<td>3</td>
<td>85</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>H(_2)O:CH(_3)CN</td>
<td>12</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>CH(_3)CN</td>
<td>1</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>CHCl(_3)</td>
<td>4</td>
<td>80</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>CH(_2)Cl(_2)</td>
<td>3</td>
<td>85</td>
<td>80</td>
</tr>
<tr>
<td>9</td>
<td>1,4-Dioxane</td>
<td>10</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>Acetic acid</td>
<td>8</td>
<td>92</td>
<td>98(^d)</td>
</tr>
</tbody>
</table>

\(^{[a]}\)Experimental conditions: Amine (2.0 mmol), H\(_2\)O\(_2\) (3.0 mmol), catalyst I (1 wt%, 0.5-2 mmol) and acetonitrile (CH\(_3\)CN, 3.0 mL) were stirred at 80°C.

\(^{[b]}\)Yield of isolated product.

\(^{[c]}\)Determined by TLC and NMR; Yield = No. of moles of N-oxide/No. of moles of amine.

\(^{[d]}\)6.0 mmol of 30% H\(_2\)O\(_2\) used;\(^{[e]}\)^{[f]}\(^{[g]}\)The catalyst is reused repeatedly.
Chapter IIIB

The reaction in different solvents is carried out at 80°C and the observed results given in Table 3.8 show that the reaction is sensitive to the change of solvent. Generally tertiary amines are insoluble in water, but when a mixed solvent (H$_2$O:CH$_3$CN) 1:1 (v/v) is used for oxidation the yield is 70%. As far as the oxidation of phenazine is concerned CH$_3$CN is the best solvent. Acetic acid also seems to be the good solvent particularly for the oxidation of pyridine and it provides the (98%) yield. The data collected in Table 3.8 show that of all the solvents, the yields are best in CH$_3$CN but lower in the mixed solvent H$_2$O:CH$_3$CN (1:1) because the substrates are poorly soluble in water specifically.

3.9.4. Influence of different reaction time

The effect of varying the reaction temperature and time for the oxidation of phenazine is studied and the results are presented in Table 3.9. Initially the oxidation reaction is slow till 30 min but the reaction is completed in 80 min (Table 3.9).

Table 3.9 Oxidation of phenazine DMA: variation of reaction temperature.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>Conversion (%)$^{[b]}$</th>
<th>Yield (%)$^{[b],[c]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RT</td>
<td>15</td>
<td>30</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>30</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>45</td>
<td>90</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>60</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>100</td>
<td>98</td>
<td>99</td>
</tr>
</tbody>
</table>

$^{[a]}$Reaction conditions: 3.0 mL of solvent, 2.0 mmol of phenazine, 6.0 mmol, H$_2$O$_2$ and 0.5 mmol of catalyst I.

$^{[b]}$Determined by TLC and NMR method.

$^{[c]}$Yield = No. of moles of N-oxide/No. of moles of amine.

RT= Room temperature.
The progress of the oxidation reaction is monitored from RT to 100°C. The yield is 50% in 30 min but the maximum yield is obtained in 60 min (99%). But the further increase in the reaction time from 60 to 100 min has no significant effect in the yield compared with the results obtained in 30 min (Table 3.9, entry 2 vs. entry 4).

3.9.5 Oxygen transfer reactions

The reaction of triphenylphosphine with some aromatic amine oxides were previously reported. The catalyst I also catalyzes oxygen transfer from tertiary amine oxides to triphenylphosphine, forming the amine and triphenylphosphine oxide. This reaction also occurs at 80°C under nitrogen atmosphere. This reaction is investigated by using 'H-NMR, 'C-NMR and FT-IR for N,N’-dimethylaniline N-oxide (Scheme 3.8.5).

Scheme 3.8.5 Oxygen transfer mechanism of amine oxides.

The triphenylphosphine acts as a deoxygenating agent, oxygen atom is transferred from the N-oxides to phosphines. Although triphenylphosphine is substantially stable in air, it is attacked by a wide variety of oxygen-containing compounds with the formation of triphenylphosphine oxide given in the Scheme 3.8.5.

3.9.6 Mechanism for the oxidation of amines to N-oxides

Generally, amines(-NH₂) interact strongly with transition metal nanoparticles. Here we presume that amines also bind fairly well with
A possible reaction mechanism for the H$_2$O$_2$ oxidation of amines to N-oxides using catalyst I is proposed in **Scheme 3.9**.

**Scheme 3.9 Mechanism for the oxidation of tertiary amines using catalyst I.**

In **step I**, the nitrogen atom of the substrate is likely to attach with the surface of the ruthenium nanoparticles **Scheme 3.9**. It is proposed that the interaction between the metal and nitrogen is due to metal-to-nitrogen charge transfer as the result of nitrogen-metal bonds at the surface of the particles (**step II**). A stronger and favorable interaction between the amines and RuNPs could be proposed in **Scheme 3.10**.

**Scheme 3.10 Representation of binding orientations of amines (a) pyridine, (b) 2,2'-bipy and (c) 4,4'-bipy onto surface of RuNPs.**
Organic ligands stabilize the metal nanoparticles Au, Pd and Rh NPs. It has been proposed, that ligands bind to the surface of these nanoparticles in a perpendicular orientation via the lone pair of electrons on the endocyclic nitrogen atom.\textsuperscript{64,68,69} It is believed that electron delocalization places a formal negative charge on the endocyclic nitrogen atom, which is highly favorable for bonding to the metal nanoparticles while concomitantly placing a formal positive charge on the exocyclic nitrogen atom. A similar weak noncovalent interaction may be expected for the pyridine with RuNPs reported here (see Scheme 3.10). In this mechanism \textbf{step II} involves the added H\textsubscript{2}O\textsubscript{2} is also bound on the Ru surface. Finally, nitrogen atom of amine is oxidized by H\textsubscript{2}O\textsubscript{2} in a heterotypic process involving the nucleophilic attack of the nitrogen atom on the oxygen in the \textbf{step IV}. The progress of the reaction is monitored using TLC and products analyzed by using NMR, FT-IR techniques. Also, the catalyst I is reused up to three times (entry 8 in \textbf{Table 3.7}) and the catalytic activity decreased only slightly.

\textbf{3.9.7 Comparison with other molecular catalyst systems}

Previous research has shown that transition metal based materials are effective catalysts for the oxidation of amines when using hydrogen peroxide as an oxidant.\textsuperscript{43,70-74} In order to evaluate the efficiency of the catalyst, we have compiled the data available on the H\textsubscript{2}O\textsubscript{2} oxidation of pyridine in the presence of other catalysts systems in \textbf{Table 3.10}. 

Table 3.10 Oxidation of pyridine using 30% H$_2$O$_2$ using different catalysts.

<table>
<thead>
<tr>
<th>Catalyst $^{[a]}$</th>
<th>Size (nm)</th>
<th>Mol (%)</th>
<th>Time (h)</th>
<th>Temp (°C)</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$<em>3$Si$</em>{4x}$O$_{6-4x}$ $^{[13]}$</td>
<td>37.2</td>
<td>3.7</td>
<td>3.0</td>
<td>80</td>
<td>CH$_3$CN</td>
<td>79</td>
</tr>
<tr>
<td>Mg$_{10}$Al$<em>2$(OH)$</em>{24}$CO$_3$ $^{[26]}$</td>
<td>-</td>
<td>0.05 g</td>
<td>24.0</td>
<td>60</td>
<td>CH$_3$CN</td>
<td>80</td>
</tr>
<tr>
<td>Carbon-based solid acid $^{[58]}$</td>
<td>-</td>
<td>0.2 g</td>
<td>75 min</td>
<td></td>
<td>ClCH$_2$CH$_2$Cl</td>
<td>85</td>
</tr>
<tr>
<td>RuCl$_3$ $^{[40]}$</td>
<td>-</td>
<td>5.0</td>
<td>8.0</td>
<td>20</td>
<td>ClCH$_2$CH$_2$Cl</td>
<td>85</td>
</tr>
<tr>
<td>[TBA]$_2$[W$<em>6$O$</em>{19}$] $^{[76]}$</td>
<td>-</td>
<td>0.5</td>
<td>5.0</td>
<td>90</td>
<td>CH$_3$CN</td>
<td>74</td>
</tr>
<tr>
<td>RuCl$_3$/Bromamine- T $^{[40]}$</td>
<td>0.5</td>
<td>3.0</td>
<td>80</td>
<td>CH$_3$CN: H$_2$O (1:1)</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Au/Al$_2$O$_3$ $^{[75]}$</td>
<td>3.4</td>
<td>1.0</td>
<td>2.0</td>
<td>90</td>
<td>-</td>
<td>100$^{[b]}$</td>
</tr>
<tr>
<td>[(C$_1$H$_4$)$_2$(CH$_3$)$<em>2$N]$<em>3$[PW$</em>{11}$O$</em>{39}$] $^{[72]}$</td>
<td>8.0$^{[c]}$</td>
<td>3.0</td>
<td>65</td>
<td>1,4-dioxane</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>K$_6$[PW$_9$V$<em>5$O$</em>{49}$]·4H$_2$O $^{[43]}$</td>
<td>-</td>
<td>14.0$^{[d]}$</td>
<td>8.0</td>
<td>RT</td>
<td>H$_2$O</td>
<td>84</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$</td>
<td>&lt;50</td>
<td>0.5</td>
<td>5.0</td>
<td>80</td>
<td>CH$_3$CN</td>
<td>40$^{[d]}$</td>
</tr>
<tr>
<td>Catalyst I $^{[13]}$</td>
<td>5-6</td>
<td>0.5</td>
<td>3.0</td>
<td>80</td>
<td>CH$_3$CN</td>
<td>98$^{[d]}$</td>
</tr>
<tr>
<td>RuCl$_3$</td>
<td>-</td>
<td>0.5</td>
<td>8.0</td>
<td>80</td>
<td>CH$_3$CN</td>
<td>75$^{[d]}$</td>
</tr>
</tbody>
</table>

[a] References.

[b] Using molecular oxygen (O$_2$, 2 atm) and selectivity (100%) as a sum of the free N-oxide and its hydrated form.

[c] Where µmol amount of catalyst was used.

[d] Reaction conditions as exemplified in the experimental procedure.

RT = Room temperature.

The N-oxidation of tertiary amines by using V$_3$Si$_{4x}$O$_{6-4x}$ in the presence of 30% H$_2$O$_2$ gives lower yield (79%) compared to catalyst I. The scanning electron microscopic (SEM) and high resolution optical microscopic (OM) analysis of the V$_3$Si$_{4x}$O$_{6-4x}$ particles show an average size of 37.24 µm. The presence of catalyst I enhances the extent of N-oxidation which is essentially complete in the case of pyridine after 3 h (Table 3.10). The HRTEM images reveals that the size of RuNPs is in the range of 5-6 nm. Pyridine is smoothly oxidized by molecular oxygen (O$_2$) in the presence of Au/Al$_2$O$_3$ as a catalyst in 100% yield. $^{75}$
Temperature-controlled phase transfer catalyst \([\text{[(C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]]_0[\text{PW}_{11}\text{O}_{39}]\) has been developed for the oxidation of pyridine with \(\text{H}_2\text{O}_2\) in 1,4-dioxane to afford pyridine N-oxide 99% at 65°C. At the beginning of the reaction the catalyst was insoluble in 1,4-dioxane at room temperature. When the oxidation is carried out with heating, the catalyst dissolved in the system gradually. After the reaction is completed with the temperature dropped, the system gradually changed from clear to turbid and the catalyst precipitated itself from the system.\(^7\) 

\(\text{K}_6[\text{PW}_{9}\text{V}_3\text{O}_{40}]\cdot4\text{H}_2\text{O}\) have utilized to the oxidation of pyridine 84% of yield was obtained within 8 h. When the reaction time proceeded to 12 h, the yield of pyridine N-oxide reached up to 91%.\(^4\)

The major problem with the \(\text{RuCl}_3\) and \(\text{RuCl}_3/\text{Bromamine-T}\) is that the catalyst is not a recycling catalyst in comparison with catalyst I. Finally, the N-oxidation reaction using catalyst I, has the following advantages: (i) simple work-up procedures and reusable catalysts, (ii) use of nonpolluting catalysts, and (iii) use of stable oxygenation system (\(\text{CH}_3\text{CN}\) and \(\text{H}_2\text{O}_2\)) and (iv) \(\text{H}_2\text{O}_2\) is a powerful reagent for the preparation of N-oxide with fast and high yielding reaction conditions (Table 3.7).

3.10 Conclusions

In this work, we have reported a new and highly efficient methodology for the oxidation of tertiary amines to N-oxides with aqueous hydrogen peroxide in the presence of catalytic amounts of catalyst I. The simplicity of the system, easy separation of the catalyst I, simple workup and excellent yields make this method an attractive, environmentally acceptable synthetic tool for the oxidation of tertiary nitrogen compounds to their corresponding N-oxides. The cheapness and the availability of the reagents, easy and clean work-up, and good to high yields make this method attractive for the large-scale operations.
3.11 Spectral analysis

3.11.1 NMR data of products

**Pyridine N-oxide** (Table 3.1 entry 1): Colorless solid, which becomes liquid by exposing in atmosphere\(^7\); \(^1\)H-NMR (300 Hz, CDCl\(_3\)): δ 7.32-7.45 (m, 3H), 8.23-8.36 (m, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) δ 125.9, 125.9, 139.0

**4-Picoline N-oxide** (Table 3.1 entry 2): White solid\(^7\); \(^1\)H-NMR (300 MHz, D\(_2\)O): δ 2.31 (s, 3H), 7.44 (d, \(J = 6.9\)Hz, 2H), 8.14 (d, \(J = 6.9\)Hz, 2H); FT-IR (KBr, cm\(^{-1}\)) 2941, 1432-1490, 1180-1248, 1046, 859, 758.

**N,N-Dimethyl aniline N-oxide** (Table 3.1 entry 3): Yellow colored hygroscopic solid\(^7\); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): δ 3.32 (s, 6H), 7.18-7.21 (m, 3H), 7.55-7.59 (m, 2H); FT-IR (KBr, cm\(^{-1}\)) 2941, 1587, 1492, 1351, 1219, 1190, 1162, 1063, 1030, 1000, 943, 746, 689.

**Quinoline N-oxide** (Table 3.1 entry 4): Colorless solid\(^7\); \(^1\)H-NMR (300 MHz, D\(_2\)O): δ 7.12-7.83 (m, 4H), 8.11-8.15 (m, 2H), 8.5 (d, \(J = 7.2\)Hz, 1H); FT-IR (KBr, cm\(^{-1}\)) 3448, 3030, 1492, 1428, 1388, 1298, 1265, 1219, 1204, 1176, 1136, 1086, 1052, 1010, 877, 826, 763, 722.
**Pyrazine N,N-dioxide.** (Table 3.1 entry 5): Colorless solid\(^7\); \(^1\)H-NMR (300MHz, D\(_2\)O): \(\delta\) 8.52 (s, 4H); FT-IR (KBr, cm\(^{-1}\)) 3028, 1652, 1599, 1441, 1391, 1315, 1221, 1042, 1002, 864, 801.

**Quinoxaline N-oxide** (Table 3.1, entry 6): Yellow crystals \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.74-7.87 (m, 2H), 8.12 (d, \(J\) = 6.9Hz, 1H), 8.87 (s, 2H), \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta\) 118.9, 130.2, 137.4, 145.9.

**Phenazine-5,10-dioxide** (Table 3.1, entry 8): Red orange crystals\(^5\); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm 7.82-7.87 (m, 4H), 8.70 (d, \(J\) = 7.2Hz, 4H) \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta\) 120.1, 131.1, 136.0.

**2,2'-bipyridine N-dioxide** (Table 3.1, entry 9): Light grey white solid\(^7\); FT-IR (KBr, cm\(^{-1}\)): 1250.

**4,4'-bipyridine N-dioxide** (Table 3.1, entry10): Grey white solid\(^7\); \(^1\)H-NMR (300 MHz, D\(_2\)O): \(\delta\) 7.60 (d, \(J\) = 7.8Hz, 4H). 8.52 (d, \(J\) = 7.8Hz, 4H).

**Triphenylphosphine oxide.** Colorless solid\(^7\)^; \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.43- 7.68 (m, 15H).
3.11.2 NMR spectra of products

Figure 3.11.1 $^1$H-NMR spectrum of pyridine N-oxide (Table 3.1, entry 1).

Figure 3.11.2 $^{13}$C-NMR spectrum of pyridine N-oxide (Table 3.1, entry 1).
Figure 3.11.3 $^1$H-NMR spectrum of quinoxaline N-oxide (Table 3.1, entry 6).

Figure 3.11.4 $^{13}$C-NMR spectrum of quinoxaline N-oxide (Table 3.1, entry 6).
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Figure 3.11.5 $^1$H-NMR spectrum of phenazine-5,10-dioxide (Table 3.1, entry 8).

Figure 3.11.6 $^{13}$C-NMR spectrum of phenazine-5,10-dioxide (Table 3.1, entry 8).
3.11.3. FT-IR spectra of some N-oxide products

Figure 3.11.7 FT-IR spectrum of pyridine-N-oxide (Table 3.1, entry 1).

Figure 3.11.8 FT-IR spectrum of quinoline-N-oxide (Table 3.1, entry 4).
Figure 3.11.9 FT-IR spectrum of quinoxaline-1,4-dioxide (Table 3.1, entry 6).

Figure 3.11.10 FT-IR spectrum of triphenyl amine-N-oxide (Table 3.1, entry 7).
Figure 3.11.11 FT-IR spectrum of phenazine 5,10-dioxide (Table 3.1, entry 8).
3.12 References


