

Ru/Al<sub>2</sub>O<sub>3</sub> catalyzed N-oxidation of tertiary amines by using H<sub>2</sub>O<sub>2</sub><sup>†</sup>Pitchaimani Veerakumar,<sup>a</sup> Subramanian Balakumar,<sup>b</sup> Murugesan Velayudham,<sup>c</sup> Kuang-Lieh Lu<sup>c</sup> and Seenivasan Rajagopal<sup>\*a</sup>

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Synthesis of several aromatic heterocyclic N-oxides using nano-ruthenium (Ru(PVP)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, catalyst I) in the presence of 30% H<sub>2</sub>O<sub>2</sub> as the oxidant is presented. Catalyst I shows good catalytic activity in N-oxidation reactions. Aqueous H<sub>2</sub>O<sub>2</sub> as a cheap and clean oxidant with active catalyst I has been developed to minimize waste production and meet the requirements of green chemistry. A variety of aromatic tertiary nitrogen compounds have been efficiently oxidized to their corresponding N-oxides in excellent yields.

## Introduction

In recent years nanoparticles, particularly supported nano-catalysts, have proven to be efficient and selective oxidation catalysts for a variety of oxidation reactions of organic compounds.<sup>1</sup> Oxidation is one of the most fundamental reactions in organic synthesis.<sup>2</sup> 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.<sup>3</sup> Very recently, several literature reports concerning the preparation and catalytic activity of the metal nanoparticles on supported metal oxides such as TiO<sub>2</sub>, SiO<sub>2</sub>, MgO and SBA-15 have appeared.<sup>4</sup> Heterocyclic N-oxides have novel applications in the field of chemistry because of their wide usefulness in inorganic and organic chemistry.<sup>5</sup> Pyridine N-oxide derivatives are interesting compounds and have been widely used as protecting groups, auxiliary agents, oxidants, catalysts, surrogates for heterocyclic boronic acids and ligands in metal complexes.<sup>6</sup> Ruthenium nanoparticles (RuNPs) supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> have been found to display high catalytic activity in organic reactions.<sup>7</sup> Silica supported vanadium,<sup>8</sup> titanium molecular sieves (TiMCM-41 and TiZSM-5(30)),<sup>9</sup> Mg–Al–O'Bu hydrotalcite (HT–O'Bu),<sup>10</sup> tungstate-exchanged layered double hydroxide (LDH–WO<sub>4</sub>),<sup>11</sup> titanium silicalite (TS-1),<sup>12a</sup> vanadium-silicate molecular sieve materials<sup>12b</sup> were

used as catalysts for the oxidation of heterocyclic nitrogen compounds to their N-oxides by using H<sub>2</sub>O<sub>2</sub> as an oxidant.

For the past decade, our research has been focused on ruthenium and it has been used as a sensitizer, for electron transfer reactions and in catalysis.<sup>13</sup> Some oxides of metals such as Cu,<sup>14a</sup> Re,<sup>14b</sup> Fe,<sup>14c</sup> oxo-salen complexes of Co, Cr, Fe, Mn<sup>15a</sup> and heteropolyacids Preyssler's anion<sup>15b</sup> [NaP<sub>3</sub>W<sub>30</sub>O<sub>110</sub>]<sup>14–</sup> and Mg<sub>10</sub>Al<sub>2</sub>(OH)<sub>24</sub>CO<sub>3</sub><sup>15c</sup> were used as catalysts for the oxidation of tertiary amines.<sup>15d, e</sup>

More powerful oxygen transfer agents such as *m*-CPBA,<sup>16</sup> KHSO<sub>5</sub>,<sup>17</sup> oxaziridines or dioxiranes,<sup>18</sup> H<sub>2</sub>SO<sub>5</sub> (Caro's acid),<sup>19</sup> ozone,<sup>20</sup> peroxymonocarbonate ions, HCO<sub>4</sub><sup>–</sup>,<sup>21</sup> urea–hydrogen peroxide (UHP),<sup>22</sup> HOF·CH<sub>3</sub>CN,<sup>23</sup> aqueous chlorine,<sup>24</sup> and carbon-based solid acids<sup>25</sup> were also used as oxygen transfer reagents in the formation of N-oxides. Most of these reagents generate large amounts of effluent during the reaction process and demand a laborious work-up procedure.

Compared to the above powerful oxygen transfer reagents flavins are more important and greener reagents for oxygen transfer in many biologically important redox reactions.<sup>26</sup> The oxidation reactions of various sulfur and nitrogen containing heterocyclic compounds have been exemplified by the mild and highly efficient oxidant H<sub>2</sub>O<sub>2</sub> as described in a recent review article.<sup>26a</sup> Biomimetic manganese porphyrin or methyltrioxorhenium(vii) were also employed as a catalyst, in the presence of H<sub>2</sub>O<sub>2</sub>, for the oxidation of aromatic N-heterocyclic compounds to their corresponding N-oxides.<sup>26c,d</sup>

Aqueous H<sub>2</sub>O<sub>2</sub> is an ideal oxidant in view of its high effective oxygen content, safety in storage and operation, low cost of production and transportation, and is also a greener reagent producing only water as the by-product.

The oxidation process followed in this work is a clean process and Ru(PVP)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (catalyst I) is recyclable with very little decrease in its activity. Ruthenium catalyzed oxidation of tertiary nitrogen compounds to N-oxides with molecular oxygen as the sole oxidant has been reported.<sup>27a–d</sup>

In our previous work, we found that the catalyst RuNPs immobilized on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> worked well for the selective oxidation of organic sulfides to the corresponding sulfoxides.<sup>7c</sup> In continuation of our previous study, here we applied catalyst I for the oxidation of tertiary amines with 30% H<sub>2</sub>O<sub>2</sub> to the corresponding N-oxides in high yields. The details of oxidation of amine in CH<sub>3</sub>CN at 80 °C using catalyst I are outlined in Scheme 1.

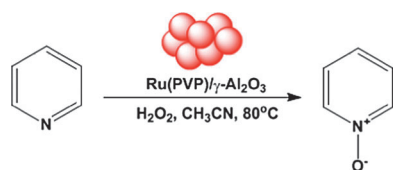
To the best of our knowledge, there is no literature report on the oxidation of tertiary nitrogen compounds to N-oxides using ruthenium nanoparticles (RuNPs).

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<sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedures as well as the characterization of the N-oxides (NMR and FT-IR and UV-vis), HRTEM images of catalyst I after the third cycle and HRTEM, SEM-EDX spectra. See DOI: 10.1039/c2cy20047c



**Scheme 1** Oxidation of aromatic amines using 30%  $\text{H}_2\text{O}_2$  in the presence of catalyst **I**.

## Results and discussion

Catalyst **I** is prepared in our laboratory as given in the experimental section and it is well characterized by XRD, HRTEM, BET,  $\text{H}_2$  chemisorption, SEM-EDX, AFM, FT-IR, and UV-vis spectral techniques as discussed in our earlier report.<sup>7c</sup> The average diameter of alumina supported RuNPs (catalyst **I**) estimated from the Gaussian fit of the particle size distribution histograms and also confirmed by SAED (Selective Area Electron Diffraction) analysis is about 5–6 nm.<sup>7c</sup>

## Oxidation of tertiary amines

The reactions employed in this study are heterogeneous for the catalytic N-oxidations using hydrogen peroxide as the oxidant. Catalyst **I** is the catalyst used, which is totally insoluble in the employed solvents. A wide variety of tertiary nitrogen compounds are oxidized to their corresponding N-oxides in near quantitative yields and results are summarized in Table 1.

In our studies it is observed that pyridines having electron donating substituent groups such as  $-\text{CH}_3$  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  $\text{H}_2\text{O}_2$ .

Higher activity (95%) is observed with pyridine unless aromatic substitution changes markedly the electronic properties of the heteroatom (Table 1, entries 1 and 2) due to their intrinsic basicity and nucleophilicity. Catalyst **I** is used as the catalyst for the oxidation of pyridine, DMA (*N,N'*-dimethyl aniline), substituted DMA and quinoline (Table 1, entries 1–5). The reaction required 3.0 mmol of  $\text{H}_2\text{O}_2$  for the oxidation whereas the oxidation of pyrazine, phenazine, quinoxaline, 2,2'-Bipy and 4,4'-Bipy (Table 1, entries 6–10) required 6.0 mmol of  $\text{H}_2\text{O}_2$  and their products are obtained in quantitative yields at 3 h. When catalyst **I** is recycled in the 1st, 2nd and 3rd cycle the yield of the product decreases to 95%, 90% and 87%, respectively, as given in ESL†

DMA containing a methyl group ( $-\text{CH}_3$ ) is found to react faster and required shorter reaction times, whereas DMA bearing other groups ( $-\text{COOH}$ ,  $-\text{Br}$  and  $-\text{CN}$ ) required longer reaction times for their oxidation and affords low yield compared to the parent compound. The oxidation process is repeated for three consecutive cycles with little loss of activity (Table 1, entry 8).

The mixture of mono- and di-N-oxides is obtained on treating the substrates (Table 1, entries 9 and 10). The crude mixture is filtered and the solvent removed *in vacuo*. The resulting brown solid is extracted with hot water and the water removed to give a light tan colored solid which is further extracted with a mixture of EtOAc and MeOH (9:1) to yield pure corresponding di-N-oxides as major products.

Nearly quantitative amounts of catalyst **I** (up to 97–98%) could be recovered from each run. In a test of the third cycle,

**Table 1** Oxidation of tertiary amines to N-oxides with  $\text{H}_2\text{O}_2$  catalyzed by catalyst **I**<sup>a</sup>

Entry	Substrate	Products	Time/h	Yield <sup>b,c</sup> (%)
1			3	95
2			2	98
3			3	94,96,96,95,85
	(R = H, $\text{CH}_3$ , Br, CN, COOH)			
4			2.5	90
5			3	95 <sup>d</sup>
6			3	97 <sup>d</sup>
7			5	92
8			3	98 <sup>d</sup>
9			3	95 <sup>d</sup>
10			3	98 <sup>d</sup>

<sup>a</sup> Reaction conditions: 3.0 mL of solvent, 2.0 mmol of amines, 6.0 mmol of 30%  $\text{H}_2\text{O}_2$  and 0.25 mol% (catalyst **I**) are stirred at 80 °C.

<sup>b</sup> Determined by TLC and NMR. <sup>c</sup> Yield = no. of moles of N-oxide/no. of moles of amine. <sup>d</sup> Pyridine is used.

the catalyst could be reused without significant loss of catalytic activity. The slight reduction in yield is probably due to the loss of some catalyst at the time of filtration. The recovered catalyst **I** after the third run had no obvious change in structure according to the HRTEM images in comparison with the fresh catalyst **I** (Fig. S5, see ESI†). The low activity of catalyst **I** may be due to low Ru dispersion on the surface of Al<sub>2</sub>O<sub>3</sub> after recovery from the third cycle. The HRTEM images also reveal that catalyst **I** is very stable and capable of producing catalytic activity. These results indicate that the present catalyst on an Al<sub>2</sub>O<sub>3</sub> support (catalyst **I**) is good for N-oxidation.

### 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 2. Bearing in mind that the CH<sub>3</sub>CN–H<sub>2</sub>O<sub>2</sub> system is stable for a long time it has been used in a large number of oxidation reactions.<sup>7c,28a–c</sup> So we first investigated the oxidation reaction with phenazine as a model substrate by using 30% H<sub>2</sub>O<sub>2</sub> (4.0 mmol) as an oxidant. In the absence of solvent the reaction required a long time and only a trace amount of product is observed.

The reaction in different solvents is carried out at 80 °C and the observed results presented in Table 2 show that the reaction is sensitive to the change of solvent. Generally tertiary amines are insoluble in water, but when a mixed solvent (H<sub>2</sub>O : CH<sub>3</sub>CN, 1 : 1 (v/v)) is used for the oxidation the yield is 70%. As far as the oxidation of phenazine is concerned CH<sub>3</sub>CN is the best solvent. Acetic acid also seems to be a good solvent particularly for the oxidation of pyridine and it provides 98% yield. The data collected in Table 2 show that of all the solvents, the yields are best in CH<sub>3</sub>CN but lower in the mixed solvent H<sub>2</sub>O : CH<sub>3</sub>CN (1 : 1) because the substrates are poorly soluble in water specifically.

### Influence of 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. Initially the oxidation reaction is slow till 30 min but the reaction is completed in 80 min (Table 3).

**Table 2** Effect of changing solvent on the oxidation of phenazine by H<sub>2</sub>O<sub>2</sub> in the presence of catalyst **I**<sup>a</sup>

Entry	Solvent	Reaction time/h	Conversion <sup>b</sup> (%)	Yield <sup>b,c</sup> (%)
1	—	42	40	Trace
2	H <sub>2</sub> O	12	60	50
3	MeOH	3	80	70
4	EtOH	3	85	65
5	H <sub>2</sub> O : CH <sub>3</sub> CN	12	75	70
6	CH <sub>3</sub> CN	1	98	99
7	CHCl <sub>3</sub>	4	80	75
8	CH <sub>2</sub> Cl <sub>2</sub>	3	85	80
9	1,4-Dioxane	10	60	50
10	Acetic acid	8	92	98 <sup>d</sup>

<sup>a</sup> Experimental conditions: amine (2.0 mmol), H<sub>2</sub>O<sub>2</sub> (3.0 mmol), catalyst **I** (0.25 mol%), acetonitrile (CH<sub>3</sub>CN, 3.0 mL) were stirred at 80 °C. <sup>b</sup> Yield of isolated product. <sup>c</sup> Determined by TLC and NMR; yield = no. of moles of N-oxide/no. of moles of amine. <sup>d</sup> About 6 mmol of 30% H<sub>2</sub>O<sub>2</sub> was used.

**Table 3** Temperature and time dependence of oxidation of phenazine DMA<sup>a</sup>

Entry	Temp/°C	Time/min	Conversion <sup>b</sup> (%)	Yield <sup>b,c</sup> (%)
1	RT	15	30	Trace
2	40	30	60	50
3	60	45	90	85
4	80	60	98	99
5	80	100	98	99

<sup>a</sup> Reaction conditions: phenazine (2.0 mmol), solvent (3.0 mL), H<sub>2</sub>O<sub>2</sub> (6.0 mmol) and catalyst **I** (0.25 mol%). <sup>b</sup> Determined by TLC and NMR. <sup>c</sup> Yield = no. of moles of N-oxide/no. of moles of amine; RT = room temperature.

The progress of the oxidation reaction is monitored from room temperature (RT) to 80 °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 on the yield (Table 3, entry 4 vs. entry 5).

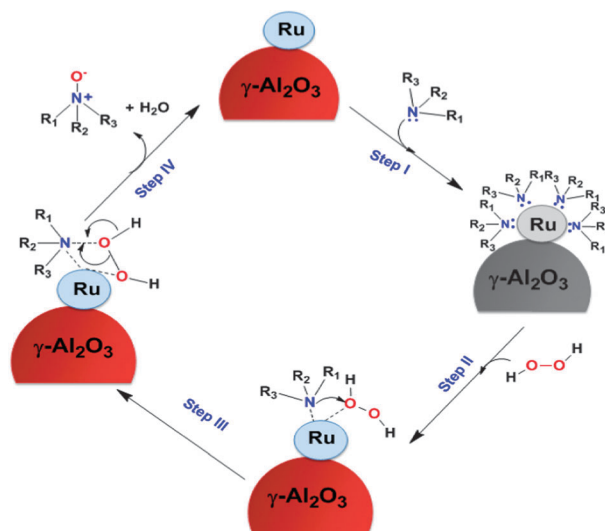
### Oxygen transfer reactions of N-oxides

The reaction of triphenylphosphine with some aromatic amine oxides was previously reported.<sup>29a,b</sup> 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 a nitrogen atmosphere. This reaction is investigated by using <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and FT-IR for *N,N'*-dimethylaniline N-oxide (see ESI†).

Triphenylphosphine acts as a deoxygenating agent, oxygen atoms are 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 (see ESI†).

### Mechanism for the oxidation of amines to N-oxides

Generally, amines (–NH<sub>2</sub>) interact strongly with transition metal nanoparticles.<sup>27d,28–31</sup> Here also we presume that amines bind fairly well to the Ru surface.<sup>32a,b</sup> A possible reaction



**Scheme 2** Mechanism for the oxidation of tertiary amines using catalyst **I** in CH<sub>3</sub>CN.

**Table 4** Comparison of the present system with other catalytic systems

Entry	Catalyst <sup>a</sup>	Size/nm	Mol. (%)	Time/h	Temp/°C	Solvent	Yield (%)
1	V <sub>x</sub> Si <sub>4x</sub> O <sub>6.4x</sub> <sup>8</sup>	37.2 (μm)	3.7	3.0	80	CH <sub>3</sub> CN	79
2	Mg <sub>10</sub> Al <sub>2</sub> (OH) <sub>24</sub> CO <sub>3</sub> <sup>15c</sup>	—	0.05 g	24.0	60	CH <sub>3</sub> CN	80
3	Carbon-based solid acid <sup>35</sup>	—	0.2 g	75 min		ClCH <sub>2</sub> CH <sub>2</sub> Cl	85
4	RuCl <sub>3</sub> <sup>27a</sup>	—	5.0	8.0	20	ClCH <sub>2</sub> CH <sub>2</sub> Cl	85
5	[TBA] <sub>2</sub> [W <sub>6</sub> O <sub>19</sub> ] <sup>40</sup>	—	0.5	5.0	90	CH <sub>3</sub> CN	74
6	RuCl <sub>3</sub> /Bromamine-T <sup>27d</sup>	—	0.5	3.0	80	CH <sub>3</sub> CN : H <sub>2</sub> O (1 : 1)	75
7	Au–Al <sub>2</sub> O <sub>3</sub> <sup>39</sup>	3.4	1.0	2.0	90	—	100 <sup>b</sup>
8	[(C <sub>18</sub> H <sub>37</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> N] <sub>7</sub> [PW <sub>11</sub> O <sub>39</sub> ] <sup>37</sup>	—	8.0 <sup>c</sup>	3.0	65	1,4-dioxane	99
9	K <sub>6</sub> [PW <sub>9</sub> V <sub>3</sub> O <sub>40</sub> ]·4H <sub>2</sub> O <sup>36b</sup>	—	14.0 <sup>c</sup>	8.0	RT	H <sub>2</sub> O	84
10	γ-Al <sub>2</sub> O <sub>3</sub>	<50	0.25	5.0	80	CH <sub>3</sub> CN	40 <sup>d</sup>
11	Catalyst I <sup>7c</sup>	5–6	0.25	3.0	80	CH <sub>3</sub> CN	98 <sup>d</sup>
12	RuCl <sub>3</sub>	—	0.25	8.0	80	CH <sub>3</sub> CN	75 <sup>d</sup>
13	—	—	—	24.0	80	CH <sub>3</sub> CN	Trace <sup>e,d</sup>
14	Catalyst I <sup>7c</sup>	5–6	0.20	3.0	80	CH <sub>3</sub> CN	70–75 <sup>f</sup>
15	Catalyst I <sup>7c</sup>	5–6	0.15	3.0	80	CH <sub>3</sub> CN	50–60 <sup>f</sup>
16	Catalyst I <sup>7c</sup>	5–6	0.10	3.0	80	CH <sub>3</sub> CN	25–30 <sup>f</sup>

<sup>a</sup> References. <sup>b</sup> Using molecular oxygen (O<sub>2</sub>, 2 atm) and selectivity (100%) as a sum of the free N-oxide and its hydrated form. <sup>c</sup> Where μmol amount of catalyst is used. <sup>d</sup> Reaction conditions as exemplified in the experimental procedure; RT = room temperature. <sup>e</sup> Absence of catalyst I. <sup>f</sup> Different amounts of catalyst I were used.

mechanism for the H<sub>2</sub>O<sub>2</sub> oxidation of amines to N-oxides using catalyst I is proposed in Scheme 2.

In step I, the nitrogen atom of the substrate is likely to attach to the surface of the ruthenium nanoparticles (Scheme 2). It is proposed that the interaction between the metal and nitrogen is due to charge transfer as the result of nitrogen–metal bonds at the surface of the particles (step II).<sup>33a,b</sup>

Organic ligands stabilize the Au, Pd and Rh metal nanoparticles.<sup>34a–c</sup> It has been proposed that the ligands bind to the surface of these nanoparticles in a perpendicular orientation *via* the lone pair of electrons on the endocyclic nitrogen atom.<sup>32a,35a,b</sup> 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 non-covalent interaction may be expected for pyridine with RuNPs as reported here (see Scheme 2). In this mechanism step II indicates that the added H<sub>2</sub>O<sub>2</sub> is also bound to the Ru surface. Finally, the nitrogen atom of amine is oxidized by H<sub>2</sub>O<sub>2</sub> in a heterolytic process involving the nucleophilic attack of the nitrogen atom on the oxygen in step IV. The progress of the reaction is monitored using TLC and products analyzed by using NMR and FT-IR techniques. Also, catalyst I is reused up to three times (entry 8 in Table 1) and the catalytic activity decreased only slightly.

## Comparison with other molecular catalyst systems

Previous research has shown that transition metal based materials are effective catalysts for the oxidation of amines when hydrogen peroxide is used as the oxidant.<sup>36–39</sup> In order to evaluate the efficiency of the catalyst, we have compiled the data available on the H<sub>2</sub>O<sub>2</sub> oxidation of pyridine in the presence of other catalysts systems in Table 4.

The N-oxidation of tertiary amines using V<sub>x</sub>Si<sub>4x</sub>O<sub>6.4x</sub> in the presence of 30% H<sub>2</sub>O<sub>2</sub> leads to lower yield (79%) compared to catalyst I. The scanning electron microscopic (SEM) and high resolution optical microscopic (OM) analysis of the V<sub>x</sub>Si<sub>4x</sub>O<sub>6.4x</sub> particles show an average size of 37.24 μm.<sup>8</sup>

The presence of catalyst I enhances the extent of N-oxidation which is essentially complete in the case of pyridine after 3 h (Table 4). The HRTEM images reveal that the size of RuNPs is in the range of 5–6 nm.<sup>7c</sup> Pyridine is smoothly oxidized by molecular oxygen (O<sub>2</sub>) in the presence of Au/Al<sub>2</sub>O<sub>3</sub> as a catalyst in 100% yield.<sup>39</sup>

Temperature-controlled phase transfer catalyst [(C<sub>18</sub>H<sub>37</sub>)<sub>2</sub>-(CH<sub>3</sub>)<sub>2</sub>N]<sub>0</sub>[PW<sub>11</sub>O<sub>39</sub>] has been developed for the oxidation of pyridine with H<sub>2</sub>O<sub>2</sub> in 1,4-dioxane to afford 99% pyridine N-oxide at 65 °C, see Table 4, entry 8. At the beginning of the reaction the catalyst is insoluble in 1,4-dioxane at room temperature. When the oxidation is carried out with heating, the catalyst is dissolved in the system gradually. After the completion of the reaction the temperature is dropped, the system gradually changed from clear to turbid and the catalyst precipitated from the system.<sup>37</sup> K<sub>6</sub>[PW<sub>9</sub>V<sub>3</sub>O<sub>40</sub>]·4H<sub>2</sub>O has been utilized for the oxidation of pyridine and 84% of yield of the product is obtained within 8 h (see Table 4, entry 9). When the reaction time is increased to 12 h, the yield of pyridine N-oxide reached 91%.<sup>36b</sup> We checked without using catalyst I and oxidant (Table 4, entry 13) under similar experimental conditions. A trace amount of product was identified using the TLC method.

The major problem with RuCl<sub>3</sub><sup>27a</sup> and RuCl<sub>3</sub>-Bromamine-T<sup>27d</sup> (Table 4, entries 4 and 6) is that it is not a recycling catalyst in comparison with catalyst I. Finally, the N-oxidation reaction using catalyst I has the following advantages: (i) a simple work-up procedure and reusability of the catalyst, (ii) it is a green catalytic system, and (iii) use of a stable oxygenation system (CH<sub>3</sub>CN and H<sub>2</sub>O<sub>2</sub>). Thus it is clearly shown that H<sub>2</sub>O<sub>2</sub> is a powerful reagent for the preparation of N-oxide in a fast and high yielding reaction (Table 1).

## 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 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 large-scale operations.

## Experimental section

### Materials and reagents

Pyridine, *N,N'*-dimethyl aniline (DMA), *para*-substituted *N,N'*-dimethyl anilines (*p*-methyl, *p*-cyano, *p*-bromo and *p*-carboxy), quinoline, phenazine, quinoxaline, pyrazine, morpholine, triphenylamine, 2,2'-bipyridine (2,2'-Bipy) and 4,4'-bipyridine (4,4'-Bipy) were purchased from Aldrich and used as such. Dichloromethane (Merck), HPLC grade acetonitrile and 30% H<sub>2</sub>O<sub>2</sub> were used as received.

### General procedure for the oxidation of amines using H<sub>2</sub>O<sub>2</sub>

A typical procedure for the oxidation of tertiary nitrogen compounds to their N-oxides is as follows: a 50 mL two neck round bottom flask is charged with amine (2.0 mmol) and catalyst **I** (0.25 mol%) dissolved in CH<sub>3</sub>CN (3.0 mL) at 298 K. To this mixture, 30% H<sub>2</sub>O<sub>2</sub> (2.0 mmol) is added dropwise slowly, then the temperature is raised to 70–80 °C and the reaction continued. The progress of the reaction is monitored by TLC (SiO<sub>2</sub>). At the end of the reaction, the catalyst is removed by filtration, dried over anhydrous MgSO<sub>4</sub> 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 an eluent. Similarly other N-oxides were prepared and the reaction times required and yields obtained are presented in Table 1. The products were identified by comparing their physical and spectral data (see ESI†).

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