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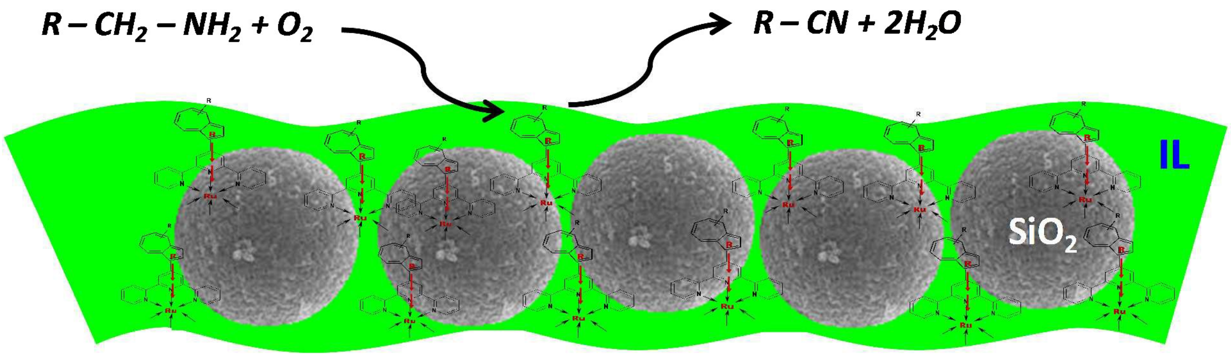
$R-CH_2-NH_2 + O_2$
$R-CN + 2H_2O$
IL
SiO_2
Ru
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PAPER

Direct oxidation of amines to nitriles in the presence of ruthenium-terpyridyl complex immobilized on ILs / SILP

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The immobilization of a ruthenium complex (Ru_2Cl_4(az-tpy)$_2$) within a range of supported ionic liquids ([C_4C_1im]Cl, [C_4C_1im][NTf_2], [C_6C_1im]Cl, [C_4C_1pyrr]Br, [C_4C_1im]Br, [C_4C_1pyrr]Cl) dispersed silica (SILP) operates as an efficient heterogeneous catalyst in oxidation of long chain linear primary amines to corresponding nitriles. This reaction follows a "green" route using a cheap and easy to handles oxidant (oxygen or air). The conversion was found to be strongly influenced by the alkyl chain length of the amine substrate and the choice of oxidant. No condensation reaction was observed between the starting amines and the selectivity to nitrile is 100%. Moving from a composition of 20 atm N_2/5 atm O_2 to 5 atm N_2/20 atm O_2 led to enhancements in the conversion (n-alkylamines) and selectivity (benzonitrile) which have been correlated with an increase of the solubilized oxygen. This was further supported by using different inert gas (nitrogen, helium, argon)/ oxygen mixtures indicating that the O_2 solubility in the SILP system, has an important effect on conversions and TOF in this reaction using SILP catalysts. Experiments performed in the presence of CO_2 led to a different behaviour due to the formation of amine-CO_2 adducts. The application of the Weisz-Prater criterion confirmed the absence of any diffusional constraints.

1. Introduction

Ionic liquids (ILs) are salts commonly in the liquid state at ambient temperatures.[1] They are considered as "green" alternatives to volatile organic solvents especially due to the low vapour pressure and high solubility of many organic and inorganic substances. ILs have several attractive properties including chemical and thermal stability, low flammability, high ionic conductivity and a wide electrochemical potential window.[2] In addition, these solvents can interact with catalysts and enhance the reactivity of the process being undertaken.[1,3] Based on these properties, over the last two decades they have been extensively employed as solvents and/or catalysts in many processes.[4-11] They have been shown to be effective in, for example, oxidation, hydrogenation, acid-catalyzed C-C and C-X bond-forming reactions, carbonyl allylation of aldehydes and ketones, Stille coupling, sulfonylation reactions of aromatics, isomerization, hydroformylation and Diels-Alder reactions.[5]

Oxidations in presence of ILs have been reported using both homogeneous organometallic complex catalysts and heterogeneous catalysts.[12] The reactions reported have used a number of different ionic liquids[5,12] and oxidants[13-16]. Molecular oxygen and air are cheap and easy to handle agents for several catalytic reactions which have also been applied with ILs. For example, the metal-catalysed selective aerobic oxidation of alcohols to the corresponding aldehydes or ketones using two-component system (VO(acac)$_2$/DABCO) has been investigated using O_2 in 1-butyl,3-methyl imidazolium hexafluorophosphate ([C_4C_1im][PF_6]).[17] Similarly, the organocatalysed Baeyer-Villiger oxidative synthesis of lactones from ketones using oxygen/benzaldehyde in a range of [C_4C_1im]$^+$ based ILs has also been successful.[18] The air oxidation of thiols to disulfide in the presence of [C_4C_1im][$SeO_2(OCH_3)$][19] or aerobic oxidation of primary and secondary alcohols to aldehydes and ketones, in the presence of an immobilizated heteropolyacid, such as molybdovanadophosphoric acid, within an ionic liquid-modified mesoporous SBA-15 silica,[20] are also good examples. However, despite these successes the use of pure ILs as reaction media can lead to product separation difficulties.

To overcome this issue, several attempts of using a supported liquid for the immobilization of the catalytically active species have been suggested.[21] After 1990, the heterogenisation of the ILs as a thin supported ionic liquid phase (SILP) has been developed.[22-28] The SILP concept combines the benefits of heterogeneous catalysis and ionic liquids, such as good solubility of the catalytically active species, ease of handling, catalyst separation and recycling.[29] When dispersed in an ionic liquid layer, the complex-metal catalyst resides close to the reaction interface and, therefore, the diffusion pathways are reduced as compared with the bulk biphasic systems.[30] Such an arrangement often leads to higher reaction rates. The preparation of SILP catalysts is typically carried out by immersion of porous solid support material in the corresponding ionic liquid containing the catalytically active species; in this case the ionic liquid is physisorbed on the support.[31] Another alternative to generate heterogeneous catalysts containing ILs is where the IL is attached to the support surface via a covalent bond, SILC.[31] This method is generally considered a more expensive and synthetically demanding approach. Therefore, the SILP system is generally preferred and a number of SILP systems have been successfully tested in industrially important catalytic reactions.[26,32]

By means of the SILP immobilization method the dissolved catalyst still acts on the molecular scale as a homogeneously dispersed complex in a uniform ionic liquid environment but macroscopically it behaves as a solid SILP material.[33] SILP catalysts have been used as heterogeneous catalysts in fixed-bed reactors for many reactions including hydroformylation,[34] methanol carbonylation,[35] hydroaminations,[36] hydrogenations[37] or ultralow temperature water-gas shift[38]. However, there are only few examples of oxidations carried out in the presence of SILP.[20,39]

Nitriles are important and versatile synthetic intermediates and can be produced by ammoxidation (whereby the corresponding arene or alkene is reacted with oxygen and ammonia),[40,41] dehydration of amides and aldoximes, conversion of alcohols, aldehydes and carboxylic acids using various reagents and direct conversion of amines.[42] Several ruthenium complexes have been used for the oxidation of amines to nitriles using molecular oxygen,[43,44] iodosylbenzene[45] and persulfate ions[46] as oxidants. However, these systems are not efficient enough for routine operation and, in addition, generate significant amounts of by-products or result in rapid deactivation of the catalyst. Recently, we reported a new ruthenium/azulene based homogenous catalyst for the selective oxidation of both aromatic and aliphatic amines to nitriles.[47]

The aim of this paper is to report the immobilization of the ruthenium complex $Ru_2Cl_4(az\text{-}tpy)_2$ via SILP methodology using different ionic liquids and SiO_2 as support. Air or molecular oxygen were used as cheap oxidizing agents. *n*-Dodecyl amine and *n*-stearyl amine were used as test molecules. *n*-Dodecane nitrile has a lemon odor while *n*-stearyl nitrile is a platform molecule for organic synthesis, resins, pesticides and asphalt emulsifiers, fungicides, colour photograph couplers, softeners, and for wetting and waterproofing, cationic grease thickening and mineral flotation agents or refining inhibitors.

2. Experimental

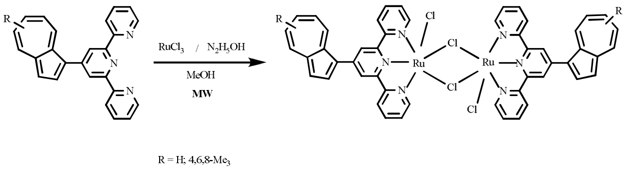
2.1. Catalysts Preparation

The dinuclear ruthenium (II) complex with 4'-azulenyl-2,2':6',2"-terpyridine was prepared using a previously reported procedure.[47] $RuCl_3$ (103.5 mg, 0.5 mmol) was mixed with hydrazine hydrate (25 mg, 0.5 mmol) in methanol (5 mL) under an inert atmosphere, at room temperature for 10 min, and the methanolic solution was mixed with a suspension of 4'-azulenyl-2,2':6',2"-terpyridine ligand, L,30 (179.5 mg, 0.5 mmol) in methanol (10 mL) and heated in a microwave system at 100 °C for 15 min, to yield a deep red solution. After removal of methanol under vacuum the obtained solid was washed with dichloromethane to remove traces of un-reacted ligand, resulting in 504 mg of dark red crystalline powder with a 95 % yield (Scheme 1).

Immobilization of the catalyst in the ionic liquid was performed in a flask with mouth evacuation by means of stirring 2 mL ionic liquid with 3 mL methanol and the Ru complex (0.0094 mmol Ru). Thereafter, the flask was connected to a vacuum pump in order to remove the organic solvent. For the SILP preparation, to the above IL immobilized complex was added SiO_2 (Silica code Si 1302 supplied by Grace, surface area 273 m^2/g, average pore diameter of 14.2 nm and an average pore volume of 0.97 cm^3/g).[25] The organic solvent was completely removed under the vacuum conditions.

1-Butyl-3-methylimidazolium chloride, $[C_4C_1im]Cl$; 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_4C_1im][NTf_2]$; 1-hexyl-3-methyl-imidazolium chloride, $[C_6C_1im]Cl$; 1-butyl-1-methylpyrrolidinium bromide, $[C_4C_1pyrr]Br$; 1-butyl-3-methyl-imidazolium bromide, $[C_4C_1im]Br$ and 1-butyl-1-methylpyrrolidinium chloride, $[C_4C_1pyrr]Cl$ were prepared using procedures previously reported.[48] All ionic liquids had >98% purity by ^1H-NMR analysis and contained <80 ppm water by KF analysis.

In order to increase the silica hydrophobicity, derivatization reagents (BSTFA/TMCS =99/1 and pyridine) were purchased from Macherey-Nagel Corp. (Duren, Germany) and Fluka (Switzerland).



Scheme 1. Scheme of dinuclear ruthenium (II) complex with 4' azulenyl-2,2':6',2"-terpyridine formation.

2.2. Catalysts characterization

Elemental analysis was performed on a EuroEA 3000 automated analyzer. The samples (<1 mg) were weighed into tin containers and were burned in a vertical reactor (oxidation tube) in the dynamic mode at 980 °C in a flow of He with the addition of O_2 (10 mL) on sample introduction. Portions of the sample in tin capsules were placed in the automated sampler, from which they were transferred to the oxidation tube at regular intervals. The concentration of each element was calculated using the Callidus program supplied with the analyzer. UV-vis spectra were taken in the range 200 – 600 nm using an Analytic Jena Specord 250 spectrometer with an integration sphere coated with MgO taken as reference. DRIFT spectra obtained from accumulation of 400 scans in the domain 500 – 4000 cm^{-1} were recorded with NICOLET 4700 spectrometer. DRIFT spectra were averaged over 600 scans.

2.3. Catalytic tests

Oxidation of *n*-dodecyl amine, *n*-stearyl amine, *n*-hexadecyl amine and benzyl amine (purchased from Sigma-Aldrich, purity >98%) with air or molecular oxygen (Linde, Purity >99.9%) to the corresponding nitriles (Scheme 2) was carried out under pressure conditions and temperature, in an autoclave (reactor 316SS, HEL Group) with a capacity of 16 mL into which the catalyst (0.0094 mmol Ru), amine (0.27 mmol) and 5 mL *n*-hexane as solvent were placed. The autoclave was sealed and heated to 100 ºC under vigorous magnetic stirring (600 rpm). The reactants and products were analysed after 5 h of reaction by GC-MS, after filtration and centrifugation, using a Trace GC 2000 system with MS detector (Thermo Electron Scientific Corporation, USA) incorporating a TR-WAX capillary column. The injection chamber was set at 200 °C and the temperature in the detector cell was 270 °C. The leaching of ruthenium was checked by induced coupled plasma analysis on an Agilent Technologies 715 ICP-OES apparatus.

$$R - CH_2 - NH_2 \frac{+O_2\ (Ru_2Cl_4(az-tpy)_2\ /ILs/SILP)}{-2H_2O,\ hexane} > R - C \equiv N$$

Scheme 2. The direct oxidation of amines with molecular oxygen.

The solubility of inert gases (N_2, He, Ar) and CO_2 and O_2 in $[C_4C_1im][NTf_2]$ was determined using the following procedure. Gas mixtures containing *X* atm *G* (*X* = 0, 5, 10, 15, 20 atm, *G* = N_2, He, Ar, CO_2) and *X*-20 atm O_2 were introduced in the presence of 2 mL of $[C_4C_1im][NTf_2]$ in a 16 mL autoclave. After stirring (1200 rpm at 70 °C) for 15 min the gas composition was analysed by a GC-TCD chromatograph Thermo Quest equipped with a Carboxen 1000 (60/80 mesh sizes) column using as eluent either N_2 or Ar. The values presented in Figure 4 were calculated as mol fractions and were deduced from the volumes of the gases solubilized in IL.

3. Results and discussion

3.1. Characterization of catalysts

The UV–Vis spectra of Ru_2Cl_4(az-tpy)$_2$ (Figure 1) showed intense absorption bands attributed to the π–π* transitions associated with the aromatic rings of the ligands, 288 nm.[47] The metal to ligand charge transfer (MLCT) transition of the ruthenium complex was observed at around 513 nm (Figure 1). UV-Vis (MeOH) [$\lambda_{max/nm}$ (log ε)]: 273 (4.68), 288 (4.70), 307 (4.71), 380 (4.12), 513 (4.30).

The UV-vis spectra of the SILP catalysts showed corresponding absorption bands of catalysts (Figure 1, *i*-samples). The recorded UV-Vis spectra did not show any significant influence of the IL since the absorption bands remained the same.

This indicates that there is no significant interaction between the ruthenium complex with the ionic liquid or silica. Therefore, this is consistent with the fact that the ruthenium is affected only by the interaction with the 4'-azulenyl-2,2':6',2"-terpyridine ligand.

The UV-Vis spectra also remained invariant following the oxidation of *n*-dodecyl amine (Figure 1, *f*-samples).

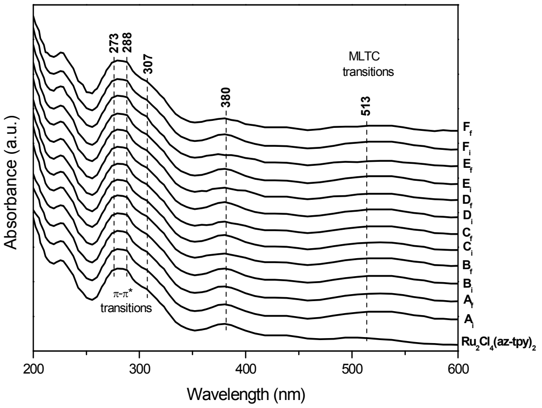


Figure 1. The UV-Vis spectra of Ru_2Cl_4(az-tpy)$_2$ and SILP before and after *n*-dodecylamine oxidation (Notation $A_{i/f}$: Ru/$[C_4C_1im]Cl/SiO_2$ before/after reaction; $B_{i/f}$: Ru/$[C_4C_1im][NTf_2]/SiO_2$; $C_{i/f}$: Ru/$[C_6C_1im]Cl/SiO_2$; $D_{i/f}$: Ru/$[C_4C_1pyrr]Br/SiO_2$; $E_{i/f}$: Ru/$[C_4C_1im]Br/SiO_2$; $F_{i/f}$: Ru/$[C_4C_1pyrr]Cl/SiO_2$).

3.2. Catalytic tests

Table 1 summarizes the activity data under homogenous reaction conditions with Ru_2Cl_4(az-tpy)$_2$ dissolved in methanol, $[C_4C_1im]Cl$ and $[C_4C_1im][NTf_2]$. The reaction in methanol resulted in yields of the corresponding nitrile of 32.8% for *n*-stearyl amine, 39.2% for *n*-hexadecyl amine and 48.9% for *n*-dodecyl amine after 5 h reaction with 100% selectivity observed in each case. No by-products, such as *n*-alkylimine were observed and no condensation between the starting amines occurred. In methanol the variation of activity vs. the length of the hydrocarbon chain is not significantly influenced by the solubility of air.[49]

Table 1. The activity of Ru_2Cl_4(az-tpy)$_2$ in ILs (5 h reaction time; 25 atm of air).

Entry	Solvent	Substrate	Conversion of amines (%)	Selectivity in corresponding nitrile (%)	TON$^{(b)}$
1	Methanol	*n*-dodecyl amine	48.9	100	14.05
2	$[C_4C_1im]Cl^{(a)}$		57.8	100	16.60
3	$[C_4C_1im][NTf_2]^{(a)}$		58.9	100	16.92
4	Methanol	*n*-hexadecyl amine	39.2	100	11.26
5	$[C_4C_1im]Cl^{(a)}$		40.9	100	11.75
6	$[C_4C_1im][NTf_2]^{(a)}$		42.6	100	12.24
7	Methanol	*n*-stearyl amine	32.8	100	9.42
8	$[C_4C_1im]Cl^{(a)}$		5.4	100	1.55
9	$[C_4C_1im][NTf_2]^{(a)}$		5.2	100	1.49

$^{(a)}$extracted with 5 mL hexane; $^{(b)}$Turnover Number: moles of product per mole of catalyst at 5 h

Regardless of the solvent, the increase in the number of carbons in the hydrocarbon chain of the starting material led to a decrease of activity. With the exception of the oxidation of *n*-stearyl amine where low yields of ~5% were obtained, the oxidations carried out in ILs led to slightly higher yields than observed using methanol as the solvent (Table 1). No significant change was observed on replacing the IL anion from Cl$^-$ with [NTf$_2$]$^-$ showing that effect of any coordination of the ionic liquid to the complex was minimal. All further experiments considered only *n*-dodecyl amine and *n*-stearyl amine as substrates.

On dispersing the complex in ILs on silica as the support (SILP), the yields decreased dramatically, from 40-60% to ≤5% for both amines (Table 2) over the same reaction time. Such behaviour is unlikely to be associated with mass transfer limitations of the substrates. In this case, the average pore size measurements of the SILP indicated only a slight decrease in the pore size and average pore volume (13.7 nm and 0.91cm^3 g^{-1} compared with 14.2 nm and 0.97 cm^3 g^{-1} for the silica prior to deposition of the IL). This is in agreement with previous studies. For example, Sievers et al.[50] reported that the ionic liquid, for imidazolium salts supported on silica, entirely filled pores with less than 9 nm radius, whereas larger pores remain unaffected, in the main. To examine this quantitatively, the Weisz-Prater criterion was used.[51] This criterion estimates the influence of pore diffusion on reaction rates in heterogeneous catalytic reactions and is expressed as:

$$N_{W\text{-}P}=\Re\cdot R_p^{\,2}/C_S\cdot D_{eff} \qquad (1)$$

where: $\Re$ is the reaction rate, R_p is the catalyst particle radius, C_S is the reactant concentration at the particle surface, D_{eff} is the effective diffusivity (calculated according to[52]). Due to the average pore radius being less than 100 nm, the diffusion was considered to occur in the Knudsen regime. Table 2 summarises the values measured for the experiments that have been carried out. Values smaller than 0.3 indicate the absence of pore diffusion limitation.[53]

In the range of small oxygen pressures the conversion (TON) increased with the O$_2$ pressure, in agreement with previous reports related to the solubility of oxygen in ionic liquids[54] (Table 3). Unexpectedly, mixing oxygen with another gas led to a change in catalytic behaviour. The effect of the dinitrogen was demonstrated by the fact that replacing air (25 atm) with molecular oxygen (5 atm) increased the conversion significantly and led to similar yields for *n*-dodecyl amine with those obtained working under homogeneous reactions conditions using ILs as solvents (Table 4). These tests also confirmed the influence of both the cation and anion in this reaction. The cation ([C$_4$C$_1$im]$^+$) led to the best results while anions Cl$^-$ and [NTf$_2$]$^-$ resulted in the highest activities observed (see entries 1 and 2, Table 4).

The effect of the N$_2$/O$_2$ composition is demonstrated by experiments carried out in the oxidation of *n*-dodecyl amine (Table 5). Changing the N$_2$/O$_2$ composition used led to significant changes in the activity of the catalyst (Table 5) for the SILP systems. In this case, a decrease in the nitrogen content corresponded to a significant increase in the conversion observed with no effect on the selectivity. For example, the conversion increased from 3% using 25 atm air to 61.6 % using a mixture of 5 atm N$_2$ - 20 atm O$_2$.

Table 2. The activity of Ru$_2$Cl$_4$(az-tpy)$_2$ complex (SILP) in oxidation of *n*-dodecyl amine and *n*-stearyl amine (5 mL hexane as solvent; 5 h reaction time; 25 atm air).

ILs	Amine	Conversion of amine (%)	Selectivity in corresponding nitrile (%)	TON$^{(a)}$	$N_{W\text{-}P}$ x 10^6
[C$_4$C$_1$im]Cl	*n*-dodecyl amine	3.0	100	0.9	2.51
[C$_4$C$_1$im][NTf$_2$]		3.7	100	1.1	3.07
[C$_6$C$_1$im]Cl		2.8	100	0.8	2.23
[C$_4$C$_1$pyrr]Br		4.0	100	1.2	3.35
[C$_4$C$_1$im]Br		3.7	100	1.1	3.07
[C$_4$C$_1$pyrr]Cl		4.0	100	1.2	3.35
[C$_4$C$_1$im]Cl	*n*-stearyl amine	5.0	100	1.4	3.91
[C$_4$C$_1$im][NTf$_2$]		3.7	100	1.1	3.07
[C$_6$C$_1$im]Cl		4.0	100	1.2	3.35
[C$_4$C$_1$pyrr]Br		3.2	100	0.9	2.51
[C$_4$C$_1$im]Br		2.3	100	0.7	1.96
[C$_4$C$_1$pyrr]Cl		3.0	100	0.9	2.51

$^{(a)}$Turnover Number, as moles of product per mole of catalyst at 5 h

Table 3. The activity of Ru$_2$Cl$_4$(az-tpy)$_2$/[C$_4$C$_1$im]Cl/SiO$_2$ (SILP) in oxidation of *n*-dodecyl amine as substrate vs. oxygen pressure (5 mL hexane as solvent; 5 h reaction time).

Entry	Oxygen pressure	Conversion of *n*-dodecyl amine (%)	Selectivity in *n*-dodecane nitrile (%)	TON$^{(a)}$
1	1	9.8	100	2.8
2	2	20.8	100	6.0
3	3	34.5	100	9.9
4	4	40.6	100	11.7
5	5	48.2	100	13.8

$^{(a)}$Turnover Number: moles of product per mole of catalyst at 5 h

Due to the unusual behaviour that there was a significant difference in conversion for the case of 5 bar total pressure of O$_2$ compared with 5 bar partial pressure of O$_2$ in a total pressure of 25 bar, i.e. the mixture containing 20 bar of N$_2$, DRIFT spectra were collected under nitrogen. According to previous reports, depending on the environment of ruthenium, the chemisorption of nitrogen can generate a band located in the range 2000-2300 cm^{-1}.[55,56] However, this is not the case with the present system and Figure 2 shows only bands assigned to the SILP catalyst irrespective of working conditions.

To probe whether the nitrogen effect may be blocking the sites, the inert gas was changed to helium and argon. In each case the trends found for the activity of SILP with respect to the partial pressure of O$_2$ were similar, albeit with higher conversions compared with the nitrogen mixtures (Figure 3). For He, Ar and N$_2$ the rate was found to increase with O$_2$ partial pressure indicating that it is dependent on the solubility of O$_2$ in the SILP. In these cases, as expected, no changes in the DRIFTS spectra of the ruthenium species were observed (Figure SI1).

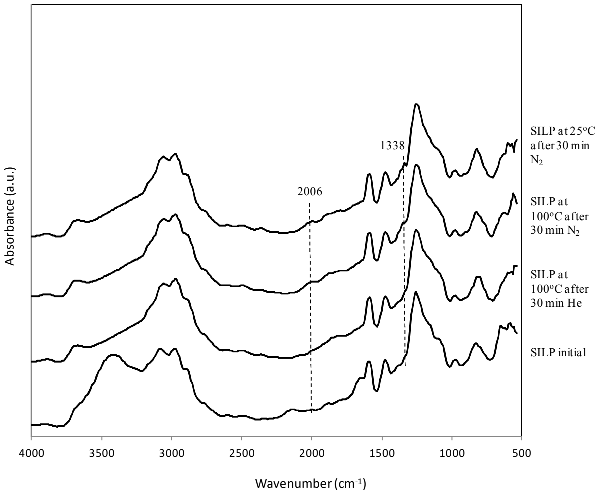


Figure 2. DRIFT spectra of Ru_2Cl_4(az-tpy)$_2$/[C_4C_1im]Cl/SiO_2 in different conditions.

Given the fact that it is thought that O_2 solubility plays an important role in the reaction rate, the change in solubility at a given partial pressure of O_2 in the presence and absence of N_2 as well as the differences between the inert molecules must be understood. Comparing the case for the 20 bar He+5 bar O_2 with 5 bar O_2 shows that the conversion increases from ~39 to ~48%. Given the low solubility of He in the ionic liquid,[57] it is not likely that the He is affecting the solubility of the O_2 directly, and therefore, we speculated that the increased total pressure results in a structural change in the SILP which affects the O_2 solubility. If this is true this does not explain why the presence of Ar results in a smaller but sizeable increase in the conversion to ~25% whereas the presence of N_2 reduces the conversion to <5% (Figure 3). It is possible that there are two competing effects, one is the structural change which increases the O_2 solubility and the second is the relative pressure dependence of the O_2 solubility compared with the inert. Literature indicated values of the solubility of N_2, O_2 and Ar in pure IL systems at 70 °C, expressed as Henry's law constant (K_H/1 atm)[58,59] of 1854 (for O_2), 3064 (for N_2) and 2707 (for Ar). However, they do not fit the dependences presented in Figure 3 and Table 5.

Figure 4 presents the variation of the gas solubility in [C_4C_1im][NTf_2] vs. gas mixture composition as it has been determined at 70 °C. A significant change in the solubility of oxygen was found with the different types of "inert" gas used. Figure 5 correlates the conversion vs. the oxygen solubility for all the gas mixtures with the exception of CO_2. A good correlation was shown indicating that the solubility of oxygen in mixture controls the rate. The small dependence of the conversion with the O_2 solubility in the case of CO_2 gas mixtures is due to the simple fact the acidic CO_2 is not innocent in this reaction interacting directly with the amine.

Table 4. The activity of Ru_2Cl_4(az-tpy)$_2$ complex (SILP) in oxidation of *n*-dodecyl amine as substrate (5 mL hexane as solvent; 5 h reaction time; 5 atm molecular oxygen).

Entry	IL	Conversion of *n*-dodecyl amine (%)	Selectivity in *n*-dodecane nitrile (%)	TON[(a)]
1	[C_4C_1im]Cl	48.2	100	13.8
2	[C_4C_1im][NTf_2]	50.8	100	14.6
3	[C_6C_1im]Cl	10.6	100	3.0
4	[C_4C_1pyrr]Br	37.1	100	10.7
5	[C_4C_1im]Br	22.6	100	6.5
6	[C_4C_1pyrr]Cl	30.3	100	8.7

[(a)] Turnover Number: moles of product per mole of catalyst at 5 h

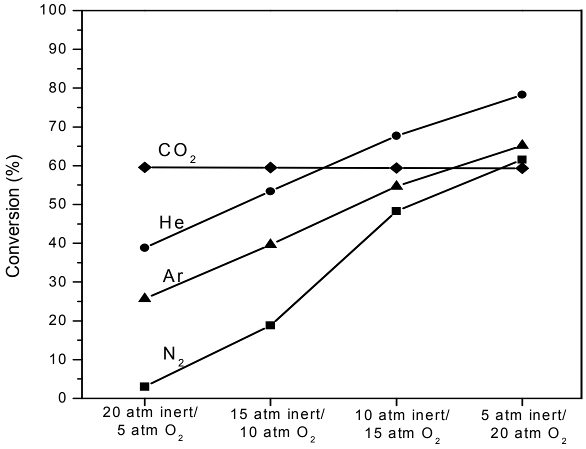


Figure 3. Variation of conversion of *n*-dodecyl amine as a function of the gas mixture composition.

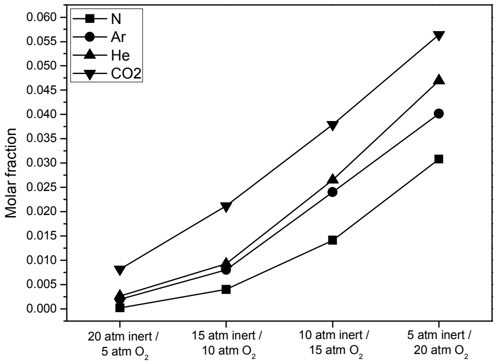


Figure 4. Variation of gas solubility in [C_4C_1im][NTf_2] vs. gas mixture composition at 70 °C.

In order to understand the effect of CO_2 on the system, the reaction of dodecylamine with CO_2 was examined using HPLC. Experiments carried out with 0.0125 g amine, 5 mL hexane and 5 atm CO_2 indicated that 45% of the amine was transformed to the corresponding ammonium carbamate. Aliphatic amines are known to react promptly with CO_2 to afford an ammonium carbamate.[61]

$$2RNH_2 + CO_2 \rightarrow RNH_3^{+-}O_2CNHR$$

At low temperatures, these slowly converts into dimeric form of the carbamic acid $(RNHCOOH)_2$. Unfortunately, once formed these carbamate/carbamic acid mixtures are quite stable by in comparison with the carbamates of diamines, for instance, which easily release CO_2 upon heating.[62] Indeed, the level of the amine conversion is ~ 60% irrespective of the CO_2/O_2 ratio indicating a high stability of the formed carbamate (~ 40%). It should also be noted, however, that the presence of CO_2 will also change the pH of the reaction mixture and this may also change the reaction rate.

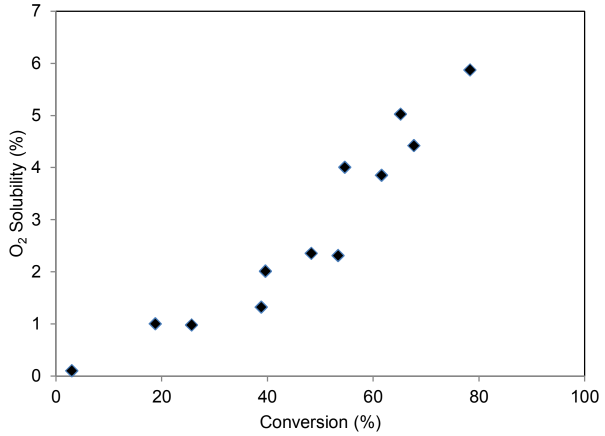


Figure 5. Correlation of conversion of *n*-dodecyl amine as a function of of O_2 solubility in $[C_4C_1im][NTf_2]$ in all the gas mixtures studied herein, except for CO_2, 70 °C.

Table 5. The activity of $Ru_2Cl_4(az\text{-}tpy)_2/[C_4C_1im]Cl/SiO_2$ (SILP) in oxidation of *n*-dodecyl amine vs. O_2/ N_2 composition (5 mL hexane as solvent; 5 h reaction time; autoclave).

Entry	N_2/O_2 composition	Conversion of *n*-dodecyl amine (%)	Selectivity in *n*-dodecane nitrile (%)	TON[(a)]
1	20 atm N_2 - 5 atm O_2	3.0	100	0.9
2	15 atm N_2 - 10 atm O_2	18.8	100	5.4
3	10 atm N_2 - 15 atm O_2	48.3	100	13.9
4	5 atm N_2 - 20 atm O_2	61.6	100	17.7

[(a)] Turnover Number as moles of product per mole of catalyst at 5 h

To determine whether the order that the gases (O_2 and CO_2) were introduced into the autoclave two reactions were compared namely 5 atm CO_2 then 20 atm O_2 *vs.* 20 atm O_2 then 5 atm CO_2 with, in each case, the first gas left for 15 min before introduction of the second gas. In the first case the conversion of dodecylamine was 56.6% with 100% selectivity in nitrile and in the second, the conversion was 59.3% showing that there was no effect of the order of addition of the gas, and the reaction of CO_2 with amine is responsible for the observed data.

3.3. Catalyst reusability

In all cases, after oxidation, the catalyst could be easily separated by simple filtration and reused. Induced coupled plasma analysis confirmed that no ruthenium was present in the filtrate showing no significant leaching of the noble metal. Compared with the as prepared catalyst, the oxidation of amine afforded the corresponding nitrile in nearly the same yield over the first two recycles and a decrease of only ~5% and ~8% after the third recycle, and ten recycles, respectively (Figure SI2). These results are supported by UV-Vis spectra of SILP after reaction, Figure 1, where no significant changes were observed. However, working under these conditions led to rather modest TONs.

3.4. Catalytic activity in benzylamine oxidation

Changing the aliphatic substrate with an aromatic one leads to low activity in corresponding nitrile even if oxygen was used as an oxidizing agent, Table 6, entry 1. The oxidation of benzylamine to the *n*-benzylidene benzylamine can occur even in the presence of air at atmospheric pressure without catalysts.[47] Increasing the reaction time led to a slight increase in conversion, Table 6, entry 3.

In order to increase the silica hydrophobicity the support was treated with BSTFA/TMCS = 99/1 and pyridine as reported previously.[63] Following the treatment, an increase of the nitrile selectivity was found but only at low conversions (Table 6, entry 5).

Table 6. The activity of $Ru_2Cl_4(az\text{-}tpy)_2/[C_4C_1im]Cl/SiO_2$ (SILP) in benzyl amine oxidation (amine 0.27 mmoles, 5 mL n-hexane as solvent, 100°C).

Entry	Conditions	Benzyl amine conversion (%)	Selectivity (%) / TON[(a)]	
			Benzo nitrile	*n*-benzyl-idene benzyl-amine
1	SiO_2 un-hydrophobised, 5 atm O_2, 5 h	18.5	15.1 / 0.8	84.9 / 4.5
2	SiO_2 un-hydrophobised, 10 atm O_2, 5 h	15.5	18.6 / 0.8	81.4 / 3.6
3	SiO_2 un-hydrophobised, 10 atm O_2, 24h	25.2	12.9 / 0.9	87.1 / 6.3
4	SiO_2 hydrophobised, 10 atm O_2, 5 h	21.7	6.5 / 0.4	93.5 / 5.8
5	SiO_2 hydrophobised, 5 atm O_2, 5 h	12.2	20.8 / 0.7	79.2 / 2.8
6	SiO_2 hydrophobised, 5 atm O_2, 5 h, water	24.7	16.5 / 1.2	83.5 / 5.9
7	SiO_2 un-hydrophobised, 20 atm N_2 - 5 atm O_2	23.2	16.6 / 1.1	83.4 / 5.6
8	SiO_2 un-hydrophobised, 15 atm N_2 - 10 atm O_2	21.8	18.9 / 1.2	81.1 / 5.1
9	SiO_2 un-hydrophobised, 10 atm N_2 - 15 atm O_2	19.6	29.8 / 1.7	70.2 / 4.0
10	SiO_2 un-hydrophobised, 5 atm N_2 - 20 atm O_2	18.7	47.9 / 2.6	52.0 / 2.8

[(a)] Turnover Number as moles of product per mole of catalyst at 5 h

The presence of a polar environment, created by the introduction of water, led to an increase in conversion but with a decrease in the nitrile selectivity. A decrease of the nitrile selectivity was also observed with the increase of the conversion in time. No extraction of IL has been found from the elemental analysis. For example, elemental analysis of the SILP catalysts containing 1-butyl-3-methylimidazolium chloride treated with water showed the same C and N content for the SILP catalyst as for found for the catalyst prior to reaction (5.38% C, 2.38% H, 4.50% SiO_2). Table 6 also indicates the influence of the N_2/O_2 composition on both the conversion of benzylamine and the selectivity to nitrile. On changing from a gas composition of 20 atm N_2/5 atm O_2 to 5 atm N_2/20 atm O_2, a decrease in the conversion of only <5% was observed; however, this change led to almost three times the selectivity to the corresponding nitrile.

4. Conclusions

The stoichiometric reaction between 4’-azulenyl-2,2’:6’,2”-terpyridine (az-tpy) with ruthenium chloride and hydrazine hydrate in methanol under microwave irradiation leads to the formation of di-nuclear species of type Ru_2Cl_4(az-tpy)$_2$. The complex can be easily immobilized in several ionic liquids ([C_4C_1im]Cl, [C_4C_1im][NTf_2], [C_6C_1im]Cl, [C_4C_1pyrr]Br, [C_4C_1im]Br, [C_4C_1pyrr]Cl) leading to results comparable or better than in methanol using air as oxidizing agent. Immobilization as SILP of the complex led to a poorer activity when air was used as the oxidizing agent. However, on changing air to oxygen the conversion approached the values found under homogeneous reaction conditions in the pure ILs. An effect of the inert gas + O_2 composition was clearly demonstrated working with *n*-dodecyl amine. A reduction in the amount of nitrogen in the gas phase led to higher conversions of the amine and it was found to correlate with the solubility of oxygen in SILP. CO_2 exhibited a different effect that was associated to its reaction with part of the amine. The selectivity to nitrile was 100% and no condensation was observed between the starting amines for aliphatic amines. Changing the aliphatic substrate with benzyl amine led to lower activities and a decreased selectivity for the nitrile with the imine found as the predominant product. The increase of the silica hydrophobicity led to a decrease of the conversion with a slight increase in the nitrile selectivity.

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Notes and references

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