The first example of heterogeneous oxidation of secondary amines by tungstate-exchanged Mg-Al layered double hydroxides: a green protocol†

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Tungstate exchanged Mg-Al layered double hydroxides as a recyclable heterogenised catalyst along with H_2O_2 as an oxidant for the oxidation of *sec*-amines to nitrones is developed for the first time, Reactions proceed at a fast rate in aqueous media in a single step at room temperature in good to excellent yields. The heterogenised catalyst showed higher activity (TOF) over their homogeneous analogues and other heterogeneous catalysts reported so far. The obtained catalysts were well characterised by various instrumental techniques such as FT-IR spectroscopy, thermal analysis (TGA and DTA), powder XRD and chemical analysis. The catalyst can be reused for six cycles with consistent activity and selectivity.

Introduction

Oxidation of amines is of interest in view of metabolism of amines *in vivo*. Nitrones, which are prepared by oxidation of secondary amines, are highly valuable synthetic intermediates[1] and excellent spin trapping reagents.[2] In particular nitrones are excellent 1,3 dipoles[3] for the preparation of various nitrogen containing biologically active compounds such as antibiotics, alkaloids, aminosugars and β-lactams. The direct oxidation of secondary amines is highly preferable to the classical methods of preparation by condensation of carbonyl compounds with N-monosubstituted hydroxylamines and oxidation of N, N-disubstituted hydroxylamines[4] as the preparation of the starting hydroxylamines is generally very tedious. Consequently several oxidising systems such as R_2CuO_2,[5] $Na_2WO_4 + H_2O_2$,[6] SeO_2,[7] tetra-*n*-propylammonium perruthenate (TPAP) + *N*-methyl-morpholine *N*-oxide (NMO),[8] and urea hydrogen peroxide (UHP-M, M = Mo, W),[9] methyltrioxorhenium (MTO) + H_2O_2,[10,11] flavin 4*a*-hydroperoxyflavin (4*a*-FlEtOOH)[12] have been reported to provide nitrones under homogeneous conditions. Either stoichiomolar or catalytic quantities are employed in these homogeneous oxidising systems to coax the oxidation of secondary amines to nitrones to completion. Homogeneous catalytic reactions are preferred over the reactions that use stoichiomolar quantities, since the latter are not only relatively expensive, but they also generate copious amounts of heavy-metal waste. However, an ideal system for such reactions would involve the use of a solid catalyst conducted under heterogeneous conditions, which allows easy separation of the catalyst from the reaction mixture and adoptability in large-scale production to conform to the class of 'greener' technologies. Another issue that worries environmentalists is the use of undesirable organic solvents, methanol and chlorinated hydrocarbons in such homogeneous reactions discussed above. Heterogeneous catalysts *viz.* titanium silicates conceived and employed for the oxidation of secondary amines in an effort to reduce pollution, has the limited scope of utility only to smaller molecules. Moreover in this process organic solvents such as methanol were used to obtain higher yields.[13]

In continued search for cleaner ('greener') technologies, there is a definite need for catalytic oxidations that use dioxygen (O_2) or hydrogen peroxide as the stoichiometric oxidant[14] in conjunction with water as a solvent. Aqueous hydrogen peroxide (30%) is an ideal oxidant in view of its high effective-oxygen content, and cleanliness producing only water as by-product, safety in storage and operation, and low cost of production and transportation.[15] Besides this, reactions performed in water are safer, cheaper, and more environmentally friendly so as to meet stringent environmental specifications. With an ever-increasing level of global competition and environmental consciousness, there is thus an incentive to find new and strategically important processes with higher atom utilisation preferably close to theoretical values to eventually minimise pollution levels using greener ingredients.

The layered double hydroxides (LDH)[16] which include hydrotalcites and hydrotalcite like compounds have recently received much attention in view of their potential usefulness as adsorbents, anion exchangers and most importantly as catalysts.[17] The hydrophilicity of LDHs makes any hosted oxidation catalyst water compatible so that reactions can be conducted using water as the solvent. Recently we reported the catalytic N-oxidation of tertiary amines by tungstate exchanged Mg-Al-LDH catalyst in quantitative yields at faster rates in aqueous

Green Context

Like so may other oxidations, the oxidation of secondary amines provides highly valuable synthetic intermediates. Nitrones can be used to make important compounds including alkaloids, antibiotics, aminosugars and β-lactams. Unfortunately, and again like so many other oxidations, traditional methods present many environmental, toxicity and efficiency problems. Here we see the first reported example of the oxidation of secondary amines using a solid tungstate catalyst based on Mg-Al layered double hydroxides. The oxidant (hydrogen peroxide) and solvent (water) add to the environmental credentials of this new process. Indeed, remarkably, water proves to be the best solvent of several tested. *JHC*

† IICT Communication No: 020213.

media.[18] In this article, we report an efficient and heterogeneous tungstate-exchanged layered double hydroxide (LDH-WO$_4$) for the oxidation of secondary amines using H$_2$O$_2$ as an oxidant in water with good to excellent yields (Scheme 1). The present catalyst has been shown to have good efficiency as reflected by its high turnover frequency (TOF) and retention of catalytic activity for several cycles. In addition, this is the first report on oxidation of secondary amines using an LDH-derived catalyst.
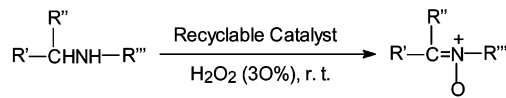
Scheme 1 The oxidation of *sec*-amines to nitrones catalysed by tungstate-exchanged Mg-Al-LDH.

Results and discussion

The structure of LDH consists of brucite [Mg(OH)$_2$] type octahedral layers in which a part of the M(II) cations are isomorphously substituted by Al(III) cations. The excess positive charge of the octahedral layers resulting from this substitution is compensated by interstitial layers built of anions such as carbonates, nitrates, chlorides or cyanides as well as containing water of crystallization. Redox properties in hydrotalcites can be imparted and tuned according to the requirement. This can be done in different ways: one is by incorporating redox-active divalent or trivalent transition metal ions (or both). A second option is to vary the ratios of the redox metal ions chosen for the preparation of a specific catalyst. Yet another manner in which the redox property of the LDH is tuned or introduced is by incorporating transition metal oxides as anions to neutralise positive charge developed as a result of isomorphous substitution of Mg in the main framework of brucite as discussed above. These hydrotalcite like materials (LDHs) are thus represented by the general formula [M$^{II}_{1-x}$M$^{III}_{x}$.(OH)$_2$]$^{x+}$[(A^{y-})$_{x/y}$·nH$_2$O]$^{x-}$ where M^{II} is a divalent cation such as Mg, Cu, Ni, Co, Mn, Fe, Zn; M^{III} is a trivalent cation such as Al, Fe, Cr, V, Ru, Rh, Ga, In; A^{n-} is an interlayer anion such as OH$^-$, Cl$^-$, CO$_3$$^{2-}$, NO$_3$$^-$, SO$_4$$^{2-}$ and the value of x is in the range of 0.1–0.33.

Small hexagonal LDH crystals with composition Mg$_{1-x}$Al$_x$(OH)$_2$Cl$_x$·zH$_2$O were synthesized following existing procedures (here, x = 0.25). The anionic species tungstate, molybdate, vanadate and {PO$_4$[WO(O$_2$)]$_4$}$^{2-}$ were exchanged on to LDH-Cl to give a series of LDH oxidation catalysts, LDH-WO$_4$ (cat **1**) (Fig. 1),[17e] LDH-MoO$_4$ (cat **2**) LDH-VO$_3$ (cat **3**) and LDH-{PO$_4$[WO(O$_2$)]$_4$} (cat **4**),[19] respectively. All these

catalysts are fully characterized by XRD, TGA–DTA and chemical analysis.

X-Ray powder diffraction

The X-ray diffraction patterns of the powdered samples were measured and LDH exchanged catalysts such as LDH-WO$_4$ (cat **1**), LDH-MoO$_4$ (cat **2**), LDH-VO$_3$ (cat **3**) and LDH-{PO$_4$[WO(O$_2$)]$_4$} show characteristic patterns of LDH (Fig. 2).[20] No new significant peaks in the XRD pattern corresponding to an insoluble Mg or Al salt to indicate the formation of new phases are observed. The X-ray powder diffraction patterns of the initial LDH materials and of the anion-exchanged LDH (cat **1–4**) hardly differ in the range 2θ = 3–65°. The d_{003} reflection corresponds to the interlamellar distance plus the thickness of mineral sheet (4.8 Å). In the case of the LDH chloride precursor (Fig. 2(e)) and cat **1–4**, no change in the interlamellar distance is observed. These data clearly demonstrate that the anion is not intercalated but present at edge-on positions of the LDH in the solid catalyst.[17e]
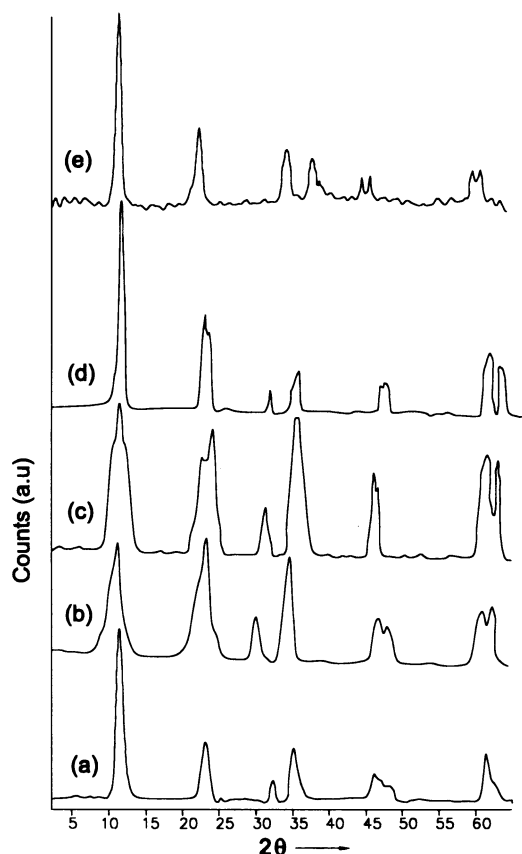
Fig. 2 X-Ray powder-diffraction patterns of various anion-exchanged LDH catalysts and their precursor: (a) LDH-WO$_4$, (b) LDH-MoO$_4$, (c) LDH-VO$_3$, (d) LDH-{PO$_4$[WO(O$_2$)]$_4$}, (e) Mg-Al-Cl LDH.

Thermal analysis

The results of thermogravimetric analysis and corresponding DTG profiles (Fig. 3) of solid catalysts (cat **1–4**) and their precursor, Mg-Al-Cl LDH, are summarised in Table 1. The DTG shows two sets of endothermic peaks, a characteristic pattern of LDH structure. The first endotherm of DTG below 280 °C corresponds to the release of surface (physically absorbed) and interlayer water of the brucite. The second endotherm in the range 280–535 °C is attributed to structural
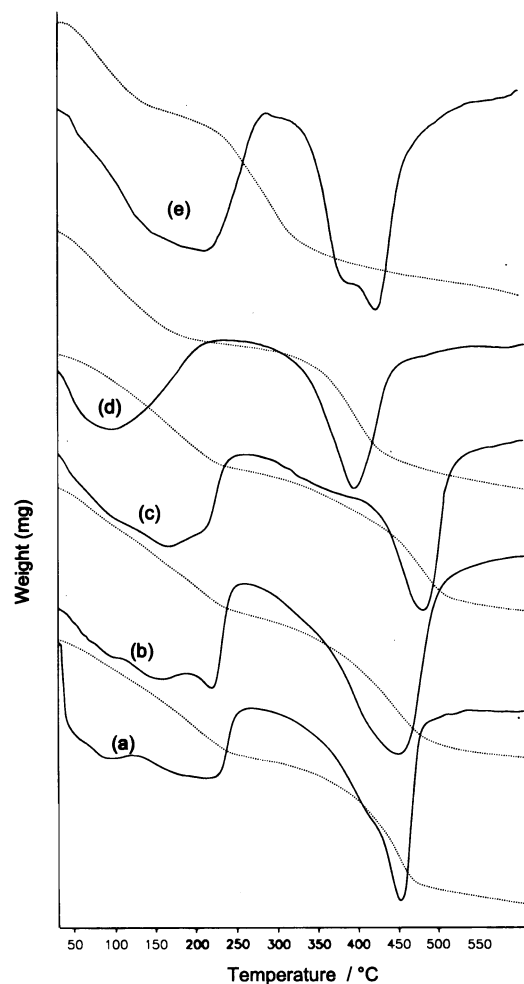
Fig. 1 Schematic representation of LDH-WO$_4$.

Fig. 3 TG (dotted lines) and DTA (solid lines) of various anion-exchanged LDH catalysts and their precursor: (a) LDH-WO$_4$, (b) LDH-MoO$_4$, (c) LDH-VO$_3$, (d) LDH-{PO$_4$[WO(O$_2$)]$_4$}, (e) Mg-Al-Cl LDH.

Fig. 4 FT-IR spectra of various anion-exchanged LDH catalysts and their precursor: (a) LDH-VO$_3$, (b) LDH-{PO$_4$[WO(O$_2$)]$_4$}, (c) LDH-MoO$_4$, (d) LDH-WO$_4$, (e) Mg-Al-Cl LDH.

dehydroxylation and decomposition of Cl$^-$. In general the weight loss above 410 °C in the TG curves may be assigned to the elimination of unexchanged Cl$^-$.[21] These results clearly indicate that there is no structural disorder even after the ion-exchange.

tested.[22] These FT-IR results also suggest that there is no structural disorder even after the ion-exchange.

FT-IR Spectroscopy

The obtained solids (cat **1**–**4**) were studied by using FT-IR spectroscopy to probe structural modifications before (Mg-Al-Cl LDH) and after the anion-exchange process of the catalysts (Fig. 4). All the catalysts cat **1**–**4** showed broad absorption bands around 3400–3600 cm^{-1} which are typical to that of OH hydroxy stretching vibrations of brucite, whereas for interlayer or physically adsorbed water the corresponding deformation mode of OH appeared around 1630 cm^{-1} in all the samples
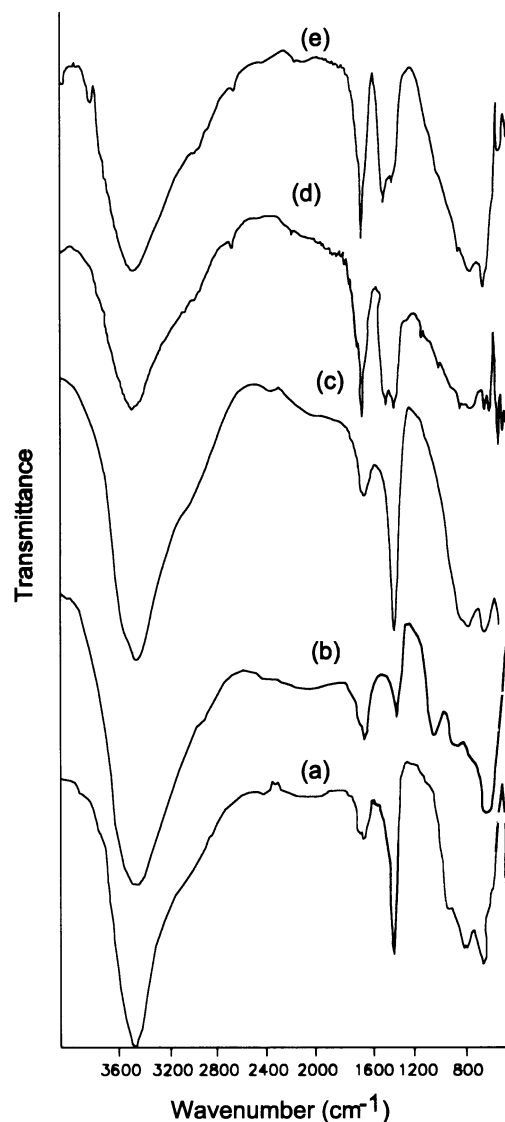
Chemical analysis

The chemical analysis of the catalysts showed the weight percentage of tungstate in cat **1** = 11.3 and cat **4** = 21, molybdate in cat **2** = 9.9, and vanadate in cat **3** = 7.8. The chemical analysis of precursor material, Mg-Al-Cl LDH showed a weight percentage of chloride = 11.2.

The exchanged LDH catalysts (cat **1**–**4**) and their homogeneous analogues were evaluated in the oxidation of dibutylamine using 3 molar equivalents H$_2$O$_2$ per mole of the substrate

Table 1 Thermogravimetric analyses of cat **1-4** and their precursor (Mg-Al-Cl LDH)

Sample no.	Catalyst	Step I/°C	Assignment	Wt%	Step II/°C	Assignment	Wt%
1	**1**	< 280	−H$_2$O	15.35	280–535	−H$_2$O, Cl$^-$	19.37
2	**2**	< 280	−H$_2$O	18.85	280–535	−H$_2$O, Cl$^-$	19.66
3	**3**	< 280	−H$_2$O	15.04	280–535	−H$_2$O, Cl$^-$	16.99
4	**4**	< 280	−H$_2$O	14.40	280–535	−H$_2$O, Cl$^-$	18.68
5	Mg-Al-Cl LDH	< 280	−H$_2$O	21.20	280–535	−H$_2$O, Cl$^-$	27.29

and water as solvent in order to identify the best catalyst in the oxidation of *sec*-amines to the corresponding N-oxides (Table 2). The order of the activity of LDH exchanged catalysts is: cat **1** > cat **2** > cat **4** > cat **3**. Essentially, there was no reaction with Mg-Al-Cl LDH, the precursor for the above catalysts (Table 2, entry 8). The heterogeneous catalysts displayed superior activity over their homogeneous counterparts. The efficacy of the catalyst is well established as is evident from the Table 2. LDH-WO$_4$ (cat **1**) exhibited the highest turnover frequency (TOF) of 21.7 h^{-1} over the other exchanged LDH catalysts. Furthermore, the exchanged LDH oxidant catalysts showed 2–5 fold activity over their analogues homogeneous catalytic systems. Thus, LDH-WO$_4$ (cat **1**) is found to be the best catalyst among the various exchanged LDH catalysts and their homogeneous analogues for the oxidation of *sec*-amines. No reaction occurred without catalyst in the oxidation of dibutylamine (Table 2, entry 9). Aqueous H$_2$O$_2$ is found to be the best oxidant among the oxidants, *tert*-butyl hydroperoxide (TBHP) and molecular oxygen, used in the oxidation of *sec*-amines. The oxidant TBHP gave very poor results, while the reaction employing molecular oxygen did not proceed. Thus H$_2$O$_2$ is an ideal and environment-friendly oxidant, in terms of its price, availability and gives only water as by-product. The solvent effect was also studied in the oxidation of dibutylamine using LDH-WO$_4$ catalyst: the activity is found to be in the following order: H$_2$O $\cong$ CH$_3$OH > CHCl$_3$ > CH$_3$CN > CH$_2$Cl$_2$. Thus water gave the best results among the solvents examined in the N-oxidation of secondary amines. The hydrophilic character of LDH, which render the catalyst water compatible is believed to promote the reaction with high yields. The high surface enrichment of secondary amines on LDH and ready formation of peroxide with LDH-WO$_4$ facilitates the higher throughput in the oxidation of secondary amines.

Table 2 The N-oxidation of dibutylamine using various anion-exchanged LDH catalysts and their homogeneous analogues[a]

Sample no.	Catalyst	Time/h	Yield[b] (%)	TOF[c]
1	LDH-WO$_4$ (cat **1**)	1.0	96	21.8
2	LDH-MoO$_4$ (cat **2**)	3.5	90	4.2
3	LDH-VO$_3$ (cat **3**)	3.5	40	1.4
4	LDH-{PO$_4$[WO(O$_2$)]$_4$} (cat **4**)	3.5	40	7.6
5	Na$_2$WO$_4$	3.5	75	13.9
6	NaVO$_3$	3.5	15	0.5
7	Na$_2$MoO$_4$	3.5	48	2.2
8	Mg-Al-Cl LDH	24	No reaction	—
9	None	24	No reaction	—

[a] All reactions were carried out using (2 mmol) of substrate with 200 mg of catalyst in 10 mL of water and 6.6 mL (6 mmol) of aqueous hydrogen peroxide (30% w/w). [b] Isolated yields. [c] TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.

In an effort to understand the scope of the reaction, several other amines having different R groups attached to the secondary nitrogen atom were subjected for the oxidation using the LDH-WO$_4$/H$_2$O$_2$ system. (Table 3). The results are summarised in Table 2. Acyclic and cyclic amines were generally converted into the corresponding nitrones in good to excellent yields. The oxidation of dibenzyl amine **3a** afforded N-benzylidenebenzylamine N-oxide **3b**, a useful precursor for N-benzylhydroxylamines. Oxidation of diisopropylamine **4a** and dibutylamine **2a** provided N-(1-methylethylidene)isopropylamine N-oxide **4b** and N-butylidenebutylamine N-oxide **2b**, respectively, in 92–96% yield.

Furthermore the reusability was checked for several cycles with the best catalyst cat **1** which showed consistent activity and selectivity for six cycles as detailed in the Table 3, entry 2. Reaction did not proceed when the process was conducted with the filtrate obtained after the separation of the solid catalyst, which indicates the active ingredient is not leached out of the

Table 3 Oxidation of *sec*-amines catalysed by LDH-WO$_4$ (cat **1**)[a]

Entry	Amine (**a**)	Nitrone (**b**)	t/h	Yield[b] (%)
1			3	96
2			3	97 (96)[c]
3			5	60
4			3	92
5			4	93
6			3	92
7			3	95

[a] Reaction conditions are as exemplified in Table 2 in footnote a. [b] Isolated yields and all the products are characterised using ^{1}H NMR, FT-IR and mass spectrometry. [c] Yield after 6th recycle.
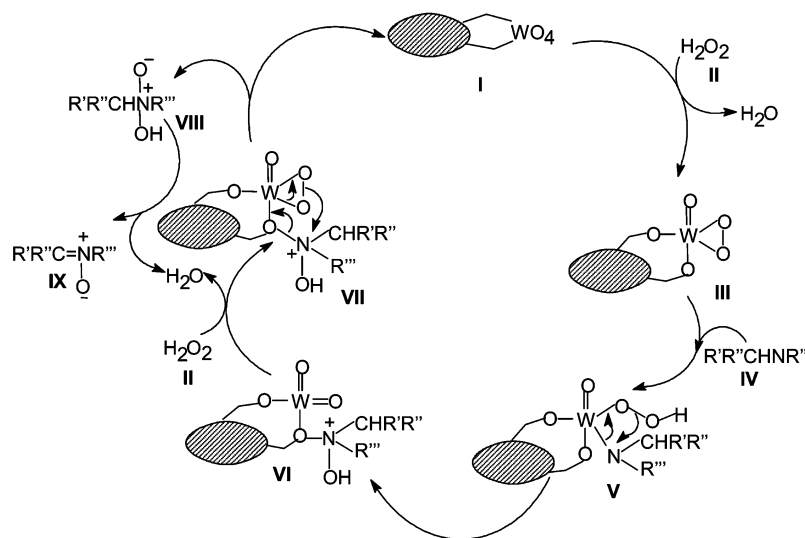
solid catalyst during the reaction. Thus, the catalyst is expected to be long-lived and stable for several cycles.

Mechanism

The plausible catalytic cycle in the N-oxidation of *sec*-amines to nitrones as described in Scheme 2 involves the formation of a peroxotungstate (oxo-bridged complex) species **III** on inter-action of tungstate LDH **I** with hydrogen peroxide **II**.[17e] A shift of λ_{max} from 250 in LDH (**I**) to 325 nm (**III**) by UV-DRS spectroscopy confirms the formation of peroxotungstate species. These peroxy species will act as active species for the oxidation of secondary amines as described by Murahashi *et al.*, for the Na$_2$WO$_4$ catalysed oxidation of secondary amines by hydrogen peroxide.[6] The secondary amine **IV** undergoes nucleophilic reaction with peroxotungstate **III** species derived from tungstate and hydrogen peroxide, to give hydroxylamine **VI** *via* intermediate **V**. Further oxidation of **VI** followed by dehydration gives nitrones **IX**, thus completing the catalytic cycle.

Conclusion

In conclusion, the present study represents the sole example wherein a recyclable heterogenised tungstate-based Mg-Al LDH is used in catalytic amounts for the N-oxidation of secondary amines to nitrones in excellent yields. The attractive feature is the accomplishment of the reaction using water as a solvent to conform not only to present environmental specifica-tions but also future restrictions. Other advantages include the use of environmentally benign H$_2$O$_2$ as an oxidant, easy separation of the catalyst and high throughput, which makes the process highly attractive in comparison to the present process.

Scheme 2 A plausible catalytic cycle for the N-oxidation of *sec*-amines to nitrones by tungstate-exchanged Mg-Al LDH.

Experimental

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Gemini Varian at 200 MHz, as solutions in CDCl$_3$ at 25 °C; δ values were in ppm downfield from tetramethylsilane (TMS). Mass spectra were obtained at an ionization potential of 70 eV, scanned on a VG 70–70H (micro mass); only selected ions are reported here. IR spectra were recorded on a Nicolet 740 FT-IR spectrometer either as neat liquids or KBr pellets. Thin layer chromatography was performed on silica gel 60F$_{254}$ plates procured from E. Merck. ACME silica gel (60–120 mesh) was used for column chromatography. Starting materials and metal salts were purchased from Aldrich, Fluka and Lancaster or prepared by known methods. Solvents purchased from commercial sources were purified prior to use. Thermogravimetric (TG) and differential thermogravimetric (DT) analysis of thermal decomposition of catalysts were studied by means of a TG-DTA Mettler Toledo Star system using open aluminium crucibles with a sample weight of about 8–10 mg and nitrogen as purge gas at a linear heating rate of 10 K min^{-1} for all measurements. X-Ray diffraction patterns were determined on a Siemens D-5000 powder X-ray diffractometer (diffraction geometry; θ–2θ, in the range 5–65°), using a sealed Cu tube (2.2 kW). CHN analysis was performed on a Vario EL analyser.

Preparation of catalysts

Mg-Al-chloride LDH[23]. Mg-Al-Cl LDH (3 : 1) was prepared as follows: a mixture of a solution of AlCl$_3$·9H$_2$O (12.07 g, 0.25 mol l^{-1}) and MgCl$_2$·6H$_2$O (30.49 g, 0.75 mol l^{-1}) in deionised and decarbonated water (200 mL) and an aqueous solution of sodium hydroxide (16 g, 2 mol l^{-1}) in deionised and decarbonated water (200 mL) were added simultaneously dropwise from the respective burettes into a round bottomed flask. The pH of the reaction mixture was maintained constant (10.00–10.2) by the continuous addition of NaOH solution. The suspension thus obtained was stirred for 2 h under a nitrogen atmosphere. The solid product was isolated by filtration, washed thoroughly with deionised and decarbonated water, and dried at 70 °C for 15 h.

Mg-Al-LDH tungstate (cat 1)[17e]. To a solution of sodium tungstate (1.87 mM, 0.616 g) in water (100 mL) Mg-Al-Cl LDH (1.0 g) was added and stirred at 293 K for 24 h. The solid

catalyst was filtered off, washed with deionised and decarbonated water and lyophilized to dryness.

Mg-Al-LDH molybdate (cat 2). To a solution of sodium molybdate (1.87 mM, 0.452 g) in water (100 mL) Mg-Al-Cl LDH (1.0g) was added and stirred at 293 K for 24 h. The solid catalyst was filtered off, washed with deionised and decarbonated water and lyophilized to dryness.

Mg-Al-LDH vanadate (cat 3). To a solution of sodium vanadate (1.87 mM, 0.228 g) in water (100 mL) Mg-Al-Cl LDH (1.0 g) was added and stirred at 293 K for 24 h. The solid catalyst was filtered off, washed with deionised and decarbonated water and lyophilized to dryness.

Mg-Al-LDH-{PO$_4$WO(O$_2$)]$_4$} (cat 4). The preparation of (NBu$^n_4$)$_3${PO$_4$[WO(O$_2$)$_2$]$_4$} was carried out according to the literature procedure.[19] To a solution of isolated (NBu$^n_4$)$_3${PO$_4$[WO(O$_2$)$_2$]$_4$} (0.46 mmol) in acetone (3 ml) was added an aqueous solution of 30% (w/w) H$_2$O$_2$ (1 ml) and Mg-Al-Cl LDH (1 g) and the mixture was stirred for 16 h at room temperature. The obtained material (cat **4**) was treated consecutively with water–acetone (1 : 1) and acetone.

General procedure for the oxidation of secondary amines

To the stirred solution of catalyst (200 mg, 0.088 mmol of WO$_4$$^{2-}$) and *sec*-amine (2 mmol) in water (10 mL) was added an aqueous solution of 30% (w/w) hydrogen peroxide (6.6 mL, 6 mmol) in two to three portions at room temperature. The reaction was allowed to stir at room temperature. After completion of the reaction (followed by TLC), the catalyst was filtered off and a small amount of MnO$_2$ was added to decompose the unreacted hydrogen peroxide. The treated reaction mixture was filtered to remove solid MnO$_2$, and the product was extracted with ethyl acetate, dried over Na$_2$SO$_4$ and evaporated *in vacuo* to afford the corresponding amine oxide (nitrone). Analytically pure compound was obtained after column chromatography (silica gel, hexane/ethyl acetate).

The products were characterised by ^{1}H NMR, mass and IR spectroscopy and elemental analysis. These data for the N-oxidation of *sec*-amines are presented below in order of the products in Table 3.

N-Ethylideneethylamine N-oxide (1b)[13]. Starting from **1a** (0.207 mL, 2 mmol), **1b** was obtained. Yield 96% (0.167 g). ^{1}H

NMR (200 MHz, CDCl$_3$): δ 0.95 (t, 3H, J = 5.2 Hz), 1.5 (q, 3H, J = 5.2 Hz), 3.4 (q, 2H, J = 4.7), 6.5 (t, 1H, J = 4.7 Hz); IR (neat) cm^{-1}: 1596 (C=N), 1180 (NO) ; MS (EI, 70 eV), m/z: 87 (M$^+$, 85), 72 (9), 70 (28), 59 (65), 55 (100). Anal. Calc. for C$_4$H$_9$NO: C, 55.17; H, 10.34; N, 16.09. Found: C, 55.16; H, 10.56; N, 16.23%.

N-Butylidenebutylamine N-oxide (2b)[6]. Starting from **2a** (0.33 mL, 2 mmol), **2b** was obtained. Yield 97% (0.277 g). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.94 (t, 3H, J = 7.6 Hz), 0.97 (t, 3H, J = 7.6 Hz), 1.15–2.21 (m, 6H), 2.47 (m, 2H), 3.73 (t, 2H, J = 7.6 Hz) 6.64 (t, 1H, J = 6.15 Hz); IR (neat) cm^{-1}: 2960, 2880, 1603 (C=N), 1477, 1425, 1383, 1190 (NO), 1120, 1065, 941; MS (EI, 70 eV), m/z: 143 (M$^+$, 5), 128 (9), 100 (100), 84 (25), 72 (26), 57 (27), 41 (48). Anal. Calc. for C$_8$H$_{17}$NO: C, 67.13; H, 11.88; N, 9.79. Found: C, 67.08; H, 11.66; N, 9.83%.

N-Benzylidenebenzylamine N-oxide (3b)[6]. Starting from **3a** (0.384 mL, 2 mmol), **3b** was obtained. Yield 60% (0.253 g). ^{1}H NMR (200 MHz, CDCl$_3$): δ 5.06 (s, 2H), 7.2–7.5 (m, 9H), 8.1–8.2 (m, 2H); IR (neat) cm^{-1}: 3058, 1580 (C=N), 1561, 1496, 1457, 1350, 1320, 1209, 1152 (NO), 1076, 1025, 944, 920, 857, 821, 749, 711, 691; MS (EI, 70 eV), m/z: 213 (M^{2+}, 2), 196 (5), 106 (36), 91 (100), 65 (12). Anal. Calc. for C$_{14}$H$_{13}$NO: C, 79.6; H, 6.16; N, 6.63. Found: C, 79.83; H, 6.36; N, 6.68%.

N-(1-Methylethylidene)-1-methylethylamine N-oxide (4b)[6]. Starting from **4a** (0.282 mL, 2 mmol), **4b** was obtained. Yield 92% (0.211 g). ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.38 (d, 6H, J = 6.4 Hz), 2.15 (s, 6H), 4.48 (hept, 1H, J = 6.4 Hz); IR (neat) cm^{-1}: 2983, 1590 (C=N), 1480, 1455, 1398, 1190 (NO), 1134, 1050, 958, 763; MS (EI, 70 eV), m/z: 115 (M$^+$, 36) 73 (77), 58 (59), 43 (100). Anal. Calc. for C$_6$H$_{13}$NO: C, 62.60; H, 11.30; N, 12.17. Found: C, 62.68; H, 11.16; N, 12.3%.

N-(Phenylmethylene)phenylamine N-oxide (5b). Starting from **5a** (0.366 g, 2 mmol), **5b** was obtained. Yield 93% (0.366 g). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.4–7.5 (m, 6H), 7.75–7.8 (m, 2H), 7.9 (s, 1H), 8.3–8.4 (m, 2H); IR (neat) cm^{-1}: 2990, 1595 (C=N), 1559, 1550, 1495, 1451, 1350, 1150 (NO), 1077, 1028, 920, 752, 699; MS (EI, 70 eV), m/z: 197 (M$^+$, 13), 105 (10), 91 (100), 77 (30), 64 (7), 51 (9). Anal. Calc. for C$_{13}$H$_{11}$NO: C, 79.18; H, 5.58; N, 7.10. Found: C, 79.22; H, 5.68; N, 7.23%.

2,3,4,5-Tetrahydropyridine N-oxide (6b)[6]. Starting from **6a** (0.196 mL, 2 mmol), **6b** was obtained. Yield 92% (0.182 g). ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.5–1.9 (m, 2H), 1.9–2.2 (m, 2H) 2.4–2.5 (m, 2H) 3.7–3.9 (m, 2H), 7.1–7.3 (m, 1H); IR (neat) cm^{-1}: 2925, 2853, 1653, 1559 (C=N), 1453, 1375, 1190 (NO), 1165, 1100, 988, 926, 850, 795, 748; MS (EI, 70 eV), m/z: 99 (M$^+$, 100), 84 (51), 69 (58), 55 (80). Anal. Calc. for C$_5$H$_9$NO: C, 60.60; H, 9.09; N, 14.14. Found: C, 60.59; H, 9.07; N, 14.32%.

6-Methyl-2,3,4,5-tetrahydropyridine N-oxide (7b)[6]. Starting from **7a** (0.235 mL, 2 mmol), **7b** was obtained. Yield 95%

(0.214 g). ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.64–1.88 (m, 2H), 1.94–2.0 (m, 2H) 2.12 (m, 3H), 2.45 (m, 2H), 3.81 (m, 2H); IR (neat) cm^{-1}: 2928, 1616 (C=N), 1450, 1190 (NO), 1168, 968, 928, 865, 748; MS (EI, 70 eV), m/z: 113 (M$^+$, 100), 83 (14), 55 (64), 41 (80). Anal. Calc. for C$_7$H$_8$SO$_2$: C, 53.09; H, 9.73; S, 12.3. Found: C, 53.22; H, 9.64; N, 12.23%.

Acknowledgments

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