Heterogeneous Oxidation of Pyrimidine and Alkyl Thioethers in Ionic Liquids over Mesoporous Ti or Ti/Ge Catalysts

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Abstract: Heterogeneous catalytic oxidation of a series of thioethers (2-thiomethylpyrimidine, 2-thiomethyl-4,6-dimethyl-pyrimidine, 2-thiobenzylpyrimidine, 2-thiobenzyl-4,6-dimethylpyrimidine, thioanisole, and *n*-heptyl methyl sulfide) was performed in ionic liquids by using MCM-41 and UVM-type mesoporous catalysts containing Ti, or Ti and Ge. A range of triflate, tetrafluoroborate, trifluoroacetate, lactate and bis(trifluoromethanesulfonyl)imide-based ionic liquids were used. The oxidations were carried out by using anhydrous hydrogen peroxide or the urea–hydrogen peroxide adduct and showed that ionic liquids are very effective solvents, achieving greater reactivity and selectivity than reactions performed in dioxane. The effects of halide and acid impurities on the reactions were also investigated. Recycling experiments on catalysts were carried out in order to evaluate Ti leaching and its effect on activity and selectivity.

Keywords: heterogeneous catalysis • ionic liquids • mesoporous materials • sulfoxidation • thioether

Introduction

The oxidation of thioethers provides straightforward access to two classes of compounds: sulfoxides and sulfones (Figure 1). Both are used extensively in the pharmaceutical and fine-chemical industries, for example, the sulfoxide radical is present in one of the highest selling drugs, the proton-pump inhibitor Omeprazole,[1] and also in the pesticide Fipronil. The sulfone moiety is found in Vioxx (Rofecoxib), a new FDA-approved inhibitor of cyclooxygenase-2.[2]

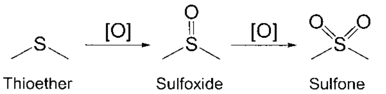

Figure 1. Schematic showing the oxidation of a thioether to sulfoxide and then to sulfone.

Liquid-phase oxidation of thioethers using heterogeneous catalysts, in particular the extensive use of titanium-based catalysts, has already been reported.[3–9] For example, Reddy et al. used molecular sieves containing titanium to achieve chemoselectivities of between 75 and 97% for dialkyl and alkyl–aryl thioethers.[5] Hulea et al. also reported the selective oxidation of dialkyl thioethers over various zeolites.[6] Robinson et al. investigated the rates of sulfoxide and sulfone formation following the oxidation of alkyl and allyl thioethers using TS-1/H_2O_2 and demonstrated that shape-selective catalysis could occur for the more bulky thioethers studied.[7] Enantioselective oxidations have also been reported. Iwamoto et al. showed that *ee*'s of 30% were obtained for the oxidation of methyl 4-methylphenyl sulfide using Ti-MCM-41 modified with (*R*,*R*)-tartaric acid.[8] In many of these studies, the properties of the solvent used were found to be important, for example, a strong correlation between molar transition energy $\varepsilon_T(30)$ and initial oxidation rate was observed.[5] In all these reactions the foremost criterion is that the oxidation is selective, with the rate of reaction being of secondary importance. It has recently been shown that ionic liquids can provide a medium in which to perform reactions without over-oxidation,[10] and therefore the effect of ionic liquids on the selective oxidation of thioethers was investigated.

Ionic liquids are a possible replacement for conventional organic solvents in which to perform synthetic reactions. They exhibit low volatility and have a wide liquid tempera-

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ture range. This combination, together with their ability to dissolve a wide range of organic and inorganic materials, makes them versatile engineering solvents.[11,12] The ionic environment can lead to dramatic changes in selectivity and rate, when compared with molecular solvents, and has been used extensively to immobilise homogeneous catalysts so that they may be recycled easily.[13] To date, there has been little attention given to heterogeneously catalysed reactions. These have been limited to hydrogenation reactions,[14,15] Heck coupling,[16] Friedel–Crafts[17] and cyclisation reactions.[18] The ionic liquid can have a significant effect on the reaction, for example, in the hydrogenation of α,β-unsaturated aldehydes, much higher selectivities were achieved in ionic liquids relative to conventional organic solvents.[15] The present study is part of an ongoing investigation into the use of combined ionic-liquid/heterogeneous-catalyst systems.

The aim of this study was to investigate the oxidation of thioethers in a range of ionic liquids by using mesoporous catalysts containing Ti, or Ti and Ge combined with hydrogen peroxide as the oxidant. The selectivity behaviour of these catalysts in the ionic liquids was compared with molecular solvents with a view to maximising the selectivity towards the sulfoxide. In addition, the combination of a benign oxidant, such as hydrogen peroxide, and an ionic-liquid/heterogeneous-catalyst system provides a green route for production of fine chemicals.[1,19] Figure 2 illustrates the substrates investigated in this study.

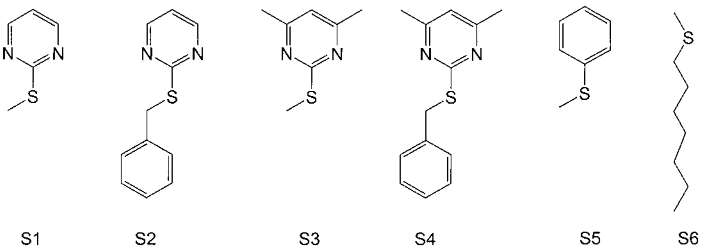

Figure 2. Substrates used: 2-thiomethylpyrimidine (**S1**), 2-thiomethyl-4,6-dimethylpyrimidine (**S2**), 2-thiobenzylpyrimidine (**S3**), 2-thiobenzyl-4,6-dimethylpyrimidine (**S4**), thioanisole (**S5**) and *n*-heptyl methyl sulfide (**S6**).

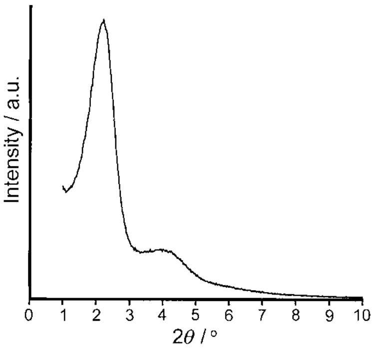

Figure 3. X-ray powder diffraction pattern of Ti-UVM-7.

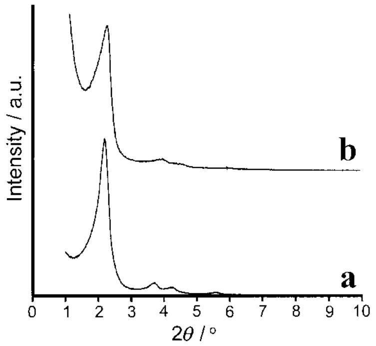

Figure 4. X-ray powder diffraction patterns of Ge-Ti-MCM-41 materials a) GeTiSi10 and b) GeTiSi15.

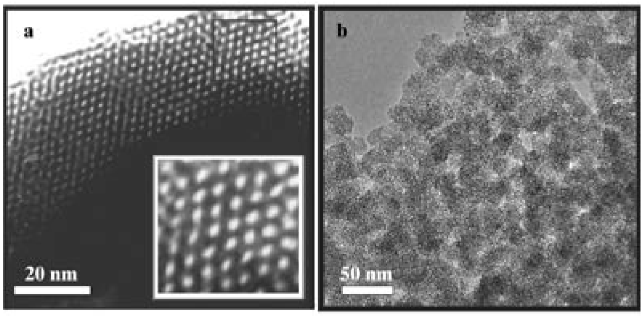

Figure 5. TEM images of a) GeTiSi15 and b) Ti-UVM-7.

Results

Catalyst characterisation: Table 1 summarises the details of the chemical composition and the textural parameters of the catalysts investigated. Figures 3, 4 and 5 show the XRD patterns and TEM pictures for the catalysts used. The catalysts show features typical for mesoporous solids, indicating that the incorporation of Ti and Ge into the silica lattice causes no significant alteration to the structure, as expected.

Effect of ionic liquid: Table 2 summarises the percentage conversion and selectivity data for the sulfoxidation of 2-thiobenzylpyrimidine (**S3**) over the range of ionic liquids studied, with GeTiSi15 as catalyst and hydrogen peroxide dissolved in dioxane (HPD) as the oxidant. For all the ionic liquids studied, the reaction proceeded with high selectivity towards the desired sulfoxide product—greater than 85 % and generally greater than 90 % for all conversions. Much lower selectivi-

Table 1. The chemical composition and textural parameters of the catalysts investigated.

Catalyst	Si/Ti (molar ratios)	Si/Ge (molar ratios)	S (BET) [M^{2}g^{-1}]	Pore vol. [cm^{3}g^{-1}]	Pore (BJH) [nm]
Ti-Ge-MCM-41 (GeTiSi10)	43	85	954	0.97	2.98
Ti-Ge-MCM-41 (GeTiSi15)	41	62	998	1.10	3.04
Ti-UVM-7 (TiSi68)	68	–	1125	2.61	3.16 (small pore) 57.2 (large pore)

Table 2. Percentage conversion and selectivity towards sulfoxide for the sulfoxidation of **S3** in a range of ionic liquids using GeTiSi15 and HPD.

Solvent	% Selectivity to SO[a]	% Conversion[a]	% Selectivity to SO[b]	% Conversion[b]
[emim][BF$_4$]	100	26	95	77
[bmim][BF$_4$]	100	22	96	73
[C$_8$mim][BF$_4$]	100	7	100	27
[C$_6$Py][BF$_4$]	100	10	100	41
[C$_8$Py][BF$_4$]	100	11	99	44
[bmim][PF$_6$]	100	24	94	75
[bmim][NTf$_2$]	100	23	97	70
[C$_4$Py][NTf$_2$]	100	15	96	57
[bdmim][NTf$_2$]	100	15	96	61
[N$_{8,8,8,1}$][NTf$_2$]	100	3	95	10
[bmpyr][NTf$_2$]	100	2	100	9
[emim][EtOSO$_3$]	100	7	100	25
[bmim][OMs]	100	3	100	9
[emim][OTf]	100	12	98	49
[bmim][OTf]	100	14	96	53
[bmim][Tfa]	100	41	91	86
[bmim][Lac]	100	2	100	8
dioxane	95	19	80	41

[a] After 30 min. [b] After 120 min.

ties were found using dioxane as the solvent and, relative to most of the reactions performed in an ionic liquid, lower reaction rates were also observed. Figure 6 compares the reaction data with respect to time for [emim][NTf$_2$], [bmim][BF$_4$] and dioxane (emim = 1-ethyl-3-methylimidazolium, bmim = 1-butyl-3-methylimidazolium, NTf$_2$ = bis(trifluoromethanesulfonyl)imide). Similar profiles were found for each system studied.

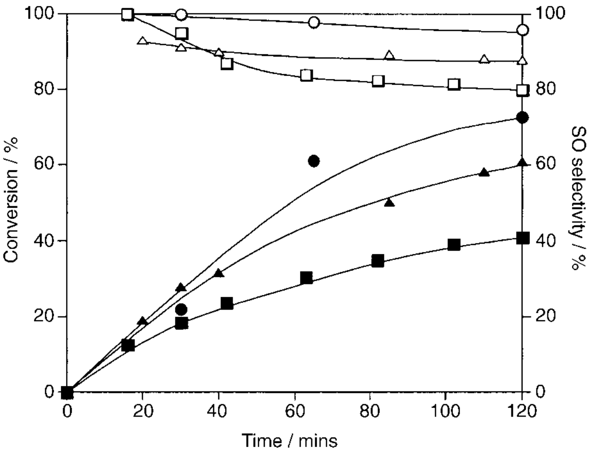

Figure 6. Variation of percentage conversion (closed symbols) and selectivity towards sulfoxide (open symbols) with respect to time for the sulfoxidation of **S3** using GeTiSi15 and HPD in [emim][NTf$_2$] (triangle), [bmim][BF$_4$] (circle) and dioxane (square).

It is clear that the solvent strongly influences the rate of reaction. For both [BF$_4$]$^-$-and [NTf$_2$]$^-$-based ionic liquids, the rate was found to decrease with increasing chain length and cation size. This may simply be related to the viscosity of the ionic liquid,[20] with the most viscous ionic liquids exhibiting the lowest rates. However, since the catalysts are mesoporous materials, the lower rate may reflect how the increasing cation size limits access to the active sites within the catalyst's pores.

The anion effect is more complex. For a common cation, for example, [bmim]$^+$, the rate was found to follow the order: [Tfa]$^-$ > [BF$_4$]$^-$ ~ [PF$_6$]$^-$ ~ [NTf$_2$]$^-$ > [OTf]$^-$ > [OMs]$^-$ ~ [Lac]$^-$ (Tfa = trifluoroacetate, OTf = triflate, OMs = mesylate, Lac = lactate). In this case, neither the viscosity nor the size of the anion is the only controlling factor. For example, [bmim][BF$_4$] has a smaller anion than [bmim][PF$_6$] and a much higher viscosity than [bmim][NTf$_2$], yet the rates are similar. Furthermore, [emim][EtOSO$_3$] has an anomalously low activity in comparison with the equivalent [OTf]$^-$- and [NTf$_2$]$^-$-based ionic liquids. To understand the anion-dependence, it is necessary to also consider the interaction of the ionic liquid with the catalyst's active sites. For example, in [emim][EtOSO$_3$], the sulphate can coordinate strongly to the titanium ions on the catalyst and block the active site. A similar effect may explain the low activity found in [bmim][Lac], although it should be noted that the latter is also bulky and highly viscous.

The high viscosity of the ionic liquid will reduce the diffusion coefficient in the ionic-liquid media relative to organic solvents. This can affect the mass-transfer rate both within the pores of the catalyst as well as in the bulk solution. However, as described above, the transport within the pores is suspected to be rate-limiting, which is consistent with the weak dependence of the rate on stirring speed. Changing the stirring speed from 60 to 1000 rpm caused only a 20% increase in the rate.

The rate may be further complicated by the possible presence of adventitious acid, from either the ionic-liquid preparation or from HF generated by hydrolysis of the [PF$_6$]$^-$ and [BF$_4$]$^-$ ions. Hydrolysis is known for all [PF$_6$]$^-$ and [BF$_4$]$^-$ salts; however, these are normally at low levels (<20 ppm), unless the ionic liquids have been exposed to high temperatures. Although the sulfoxidation is normally considered as a Lewis acid catalysed process, Brønsted acids may also catalyse the reaction. Blank reactions without the catalyst present were performed in each of the ionic liquids used. In these reactions, less than 0.5% conversion was found for **S3** after 30 minutes, irrespective of the ionic liquid used. From Table 2 it is also evident that reactions performed in 1,3-dialkylimidazolium-based ionic liquids show increased activity relative to either 1,2,3-trialkylimidazolium ionic liquids (i.e., C2-protected imidazolium) or those based on pyridine. The blank reactions show that this cannot be due to the acidic hydrogen at the C2 position acting as a Brønsted acid. Whilst the increased rate may be due to a decrease in viscosity or the size of the cation, as described above, the ionic liquid may also form hydrogen bonds with the peroxy species, resulting in an increased rate (see discussion).

Effect of catalyst: Table 3 summarises the data obtained using GeTiSi15, GeTiSi10 and TiSi68 in [emim][OTf] and [emim][NTf$_2$]. Although it is clear that the rate increases with increasing germanium concentration in the catalyst in both [emim][OTf] and [emim][NTf$_2$], it is also true that the selectivity drops with greater germanium content. These re-

Table 3. Percentage conversion and selectivity towards sulfoxide for the sulfoxidation of **S3** over different catalysts after 30 minutes using HPD.

Catalyst	Ionic liquid	% Selectivity to SO	% Conversion
GeTiSi15	[emim][OTf]	100	12
GeTiSi15	[emim][NTf_2]	91	28
GeTiSi10	[emim][OTf]	100	11
GeTiSi10	[emim][NTf_2]	95	28
TiSi68	[emim][OTf]	100	8
TiSi68	[emim][NTf_2]	100	12

sults are in accordance with previous studies concerning the liquid oxidation of alkanes; these showed that Ge faujasites were efficient oxidation catalysts.[21]

It should also be noted that these catalysts show a high hydrogen peroxide efficiency of 92–98 % for the reactions studied in both ionic liquids and molecular solvents.

Effect of oxidant: In all the above cases, oxidation was performed by using HPD, which forms a homogeneous mixture with the ionic liquid. Comparison with oxidation using the urea–hydrogen peroxide (UHP) complex dissolved directly in the ionic liquid shows a reduced reaction rate. For example, GeTiSi10 in [emim][BF_4] gave 26 % conversion after 30 minutes with HPD, whilst only 7 % was obtained with UHP. Addition of a co-solvent, such as dioxane, is known to significantly decrease the viscosity of the ionic liquid,[22] and therefore the difference in rate observed between the two oxidants may be due to increased mass transfer in the mixed-solvent system.

Effect of substrate: The relative reactivity and selectivity of a range of 2-thiopyrimidine derivatives and aromatic/aliphatic thioethers were studied with the GeTiSi15 catalyst. The results, summarised in Table 4, show that there are significant differences in the reactivity of the substrates; however, the order of reactivity is not affected by the nature of the ionic liquid. The least active substrates are based on the 2-pyrimidyl moiety, and the aromatic substrates are less reactive than the aliphatic thioether. Within the 2-thiopyrimidine derivatives, the reactivity of **S1**–**S4** may be easily explained by the molecular size and shape of each substrate. It is clear that increasing the bulkiness of either the aromatic ring or the sulfur atom decreases the reactivity of the substrate. Comparing the rates for **S1** with **S2** and **S3** shows that the more the steric hindrance reduces access to the sulfur atom, the greater the decrease in the rate, that is, the ability of the molecule to penetrate the mesoporous structure is, as expected, of secondary importance relative to the adsorption geometry of the sulfur within the active site.

Table 4. The effect of substrate on percentage conversion and selectivity towards sulfoxide after 30 minutes using GeTiSi15 and HPD.

Thioether	Ionic liquid	% Selectivity to SO	% Conversion
S1	[emim][BF_4]	100	32
S2	[emim][BF_4]	100	18
S3	[emim][BF_4]	100	26
S4	[emim][BF_4]	100	12
S5	[emim][BF_4]	90	47
S6	[emim][BF_4]	54	100
S1	[bmim][NTf_2]	100	29
S2	[bmim][NTf_2]	100	16
S3	[bmim][NTf_2]	100	22
S4	[bmim][NTf_2]	100	10
S5	[bmim][NTf_2]	97	41
S6	[bmim][NTf_2]	72	98

For both ionic liquids studied, the more easily oxidised substrates **S5** and **S6** also showed the lowest sulfoxide selectivities.

The effect of impurities: Ionic liquids are generally synthesised by using a two-step process: An organic halide salt is formed through alkylation of a phosphine, amine, pyridine or azole by using a haloalkane. This halide salt is then converted to the ionic liquid of choice by either a metathesis reaction using an alkali metal salt (e.g., $NaBF_4$ to produce the tetrafluoroborate ionic liquid), or by anion exchange using acid addition (e.g., trifluoromethanesulfonic acid to form the corresponding triflate ionic liquid). This second step results in halide impurities, which can be minimised by washing the ionic liquid with water. However, as the removal of halide is labour-intensive and time-consuming, and the large-scale production of ultra-pure ionic liquids expensive, it is important to know the effect of halide impurities in the ionic liquid on the reaction. Clearly, if less pure solvents can be used this will be advantageous for large-scale application.

Reactions were performed in [bmim][BF_4] in the presence of known amounts of chloride determined by ion chromatography.[23] No significant change in reaction rate was observed between 1.5 ppm Cl^-, present in the original ionic liquid, and 700 ppm Cl^-, obtained by doping the ionic liquid with [bmim]Cl. A small increase in sulfoxide selectivity, from 79 % at 1.5 ppm to 88 % at 700 ppm, was observed. The increased selectivity may be due to the halide preferentially coordinating to the active sites for the oxidation of sulfoxide to the sulfone.

As well as halide impurities, the ionic liquids may also contain traces of acid. As noted above, the sulfoxidation can be catalysed by Brønsted acids as well as Lewis acids. For example, using GeTiSi10 for the oxidation of **S3** in dioxane, the addition of 2×10^{-3} M triflic acid increased the conversion after 1 h from 15 % to 44 %. Given the significant effect of the acid, reactions were compared in [bmim][OTf] synthesised from HOTf and NaOTf, with conversions of 52 % and 10 %, respectively, observed after 1 h. This clearly shows the strong effect of a low concentration of acid impurities on the rate of reaction in ionic liquids.

Catalyst stability and recycling experiments: After the reaction was completed, the ionic liquid was examined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), which showed the presence of titanium in solution. Figure 7 shows how recycling the catalyst in fresh ionic liquid affected the conversion and selectivity, as well as the titanium leached from the GeTiSi15 catalyst found in solution after each recycle. There is a strong correlation between

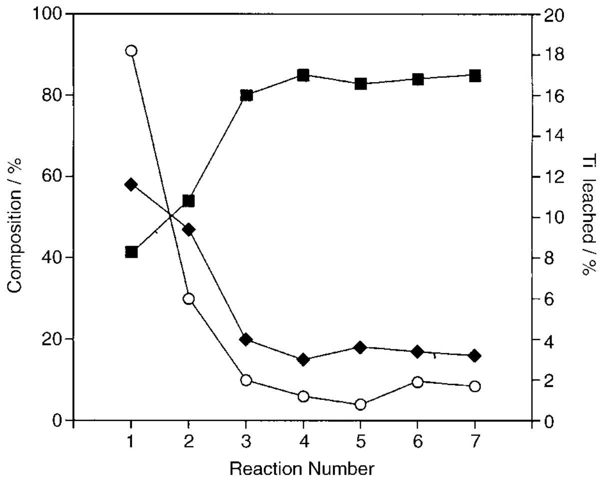

Figure 7. Percentage composition with respect to thioether **S3** (square) and sulfoxide (diamond) in the reaction mixture, and %Ti leaching with respect to the original catalyst (circle), as a function of catalyst recycling using GeTiSi15 and HPD in [emim][BF_4].

the decrease in the thioether sulfoxidation activity and the loss of titanium; however, if the rate per titanium is calculated for each reaction, taking the leaching into account, this remains constant. After two reactions, the leaching represents a loss of 24 % of the original Ti in the catalyst; however, in subsequent reactions the leaching is not significant.[24] The leaching may be associated with dissolution of Ti aggregates from the catalyst, that is, weakly bound material rather than framework titanium within the oxide. Significantly more leaching is found in organic solvents than in ionic liquids. For example, after one reaction, approximately 40 % of the titanium present in the catalyst is lost in ethanol or dioxane, whereas only 18 % is removed in [emim][BF_4].

Leaching was found in the ionic liquid only in the presence of the oxidant, even in the absence of the substrate, indicating that the Ti dissolution does not originate from the sulfoxidation reaction as such, but rather as a result of interactions of the peroxy species with the catalyst. It should be noted that the leached titanium is very active in the oxidation reaction, albeit to a lesser degree than when the heterogeneous catalyst is present. For example, after stirring 5 mg of GeTiSi15 catalyst for 1 h with 0.44 mmol of HPD in 0.8 cm^3 [bmim][BF_4], the catalyst was removed from the ionic liquid and **S3** was added. Under these conditions, 34 % conversion (100 % selectivity) was achieved after 420 minutes, compared with 3 % conversion in the absence of the catalyst. Similar results were obtained with [bmim][OTf] (acid free) and [bmim][NTf_2].

Discussion

Compared with many thioethers, the substrates employed in this study normally show low reactivity towards oxidation. For example, by using hydrogen peroxide in ethanol, 40 % conversion of diethyl thioether in 120 minutes at 30 °C is observed,[25] whereas only 1.3 % conversion is found after 180 minutes at 40 °C for **S3**. In addition, the oxidation products of 2-pyrimidine thioethers are not stable towards hydrolysis, especially in acidic media, when 2-pyrimidones are formed.[26] The rates observed when employing ionic liquids with mesoporous Ti or Ti/Ge catalysts are higher than those for organic media, in which only sulfoxide and sulfone reaction products are observed.

It has been proposed that the oxidation of thioether with hydrogen peroxide on these catalysts occurs through the formation of a peroxotitanium or perhaps a peroxogermanium species.[27,28] Subsequently, nucleophilic attack of the sulfur atom in the thioether on the peroxo species takes place. This mechanism explains the relative reactivities of **S1**–**S4** versus **S5**–**S6**. The substituents on the sulfur control the electron density of this atom. In the case of **S1**–**S4**, the electron density of the sulfur atom is reduced by the electron-withdrawing effect of the pyrimidine ring, making these thioethers less reactive towards electrophiles.[26] As found in other studies [25], aromatic thioethers are less reactive than aliphatic thioethers, due to the delocalisation of the electron density on the sulfur. Hence **S6** is more reactive than **S5**.

A further observation was that the more protic the ionic liquid, the higher the rate of reaction, that is, $[bmim]^+ > [bdmim]^+ \sim [C_6Py]^+$. However, as noted above, despite the fact that the presence of Brønsted acid also significantly increases the rate, the ionic liquids do not catalyse the reaction in the absence of the catalyst. Although the variation according to cation may result from differences in cation viscosity and size, which consequently alter the accessibility of the mesopores, the solvent can also interact with the peroxy species (Figure 8), which increases the electrophilicity of the oxygen. A similar mechanism has been proposed for the enhanced rate observed for protic organic solvents (alcohols in general), relative to aprotic solvents (acetonitrile and ethers).[29] The anion may also interact with the active site; however, the activity in the ionic liquid is highest when the anion's ability to coordinate is reduced.[30] This interaction must be weak, since the presence of small amounts of chloride impurities has no significant effect on the rate. It should be noted that competitive, radical processes cannot be ruled out in the ionic liquids. For example, radicals have

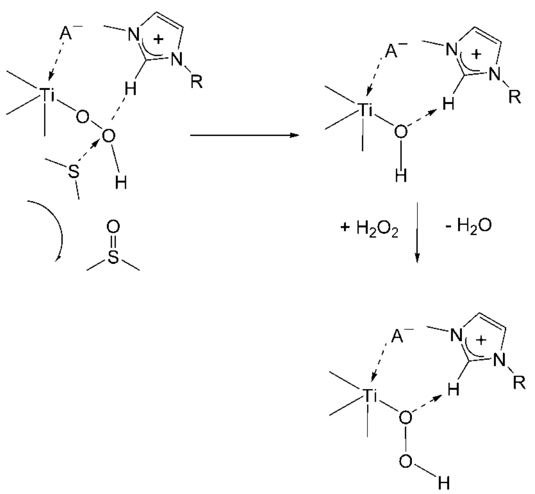

Figure 8. Proposed mechanism for Ti-catalysed oxidation of thioethers in the presence of 1,3-dialkylimidazolium-based ionic liquids.

been shown to be stable in ionic liquids for polymerisations,[31] and the sulfoxidation mechanism in the ionic liquid is currently under further investigation. However, Kholdeeva et al. have shown that the sulfoxidation of thioethers over titanium-containing polyoxometalate catalysts is unaffected by light, oxygen or hydroquinone, indicating that radical processes are not significant.[32]

Access to the pores of the catalyst may also be affected by the interfacial tension between the catalyst surface and the ionic liquid. For all the reactions performed with oxide-based catalysts in our laboratory, including the present study, the solid shows a high degree of stability with respect to particle agglomeration, and remains dispersed/suspended in ionic liquid for days. This indicates good wetting of the catalyst surface with the ionic liquid. In addition, spin-coating of ionic liquids on silicon wafers coated with an SiO_2 overlayer also showed good wetting and a strong interaction between the surface and the charged portions of the ionic liquid, that is, not the alkyl chains, as expected.[33] This is consistent with the view that the rates are most significantly affected by the viscosity/size of the ionic liquid, which prevents good transport into/within the pores of the catalyst, and not by the ability of the ionic liquid to wet the surface of the catalyst.

Despite the higher viscosity and size of the ionic liquid relative to dioxane, the ionic environment leads to a higher rate and sulfoxide selectivity. This may be due to the almost total absence of Brønsted acidity, demonstrated by the very high hydrogen peroxide efficiency measured with these catalysts. On et al. showed that Brønsted acids cause a nonselective decomposition of hydrogen peroxide.[34]

Conclusion

Titanium/silica-based mesoporous catalysts are effective systems for selective sulfoxidation of aromatic/aliphatic thioethers, including pyrimidine thioethers. Ionic liquid solvents gave higher rates and sulfoxide selectivity than dioxane. The addition of Ge to Ti was found to increase the rate of oxidation, but reduced the selectivity towards the sulfoxide. Although some titanium leaching was observed during the oxidations performed with ionic liquids, this was much less than that seen with a pure organic medium. Also of interest was the very high hydrogen peroxide efficiency when using these systems.

Experimental Section

Substituted 2-thiopyrimidines (**S1**, **S2**, **S3**, **S4**) were prepared using the method described by Hunt et al.[35] Thioanisole (**S5**) and *n*-heptyl methyl sulfide (**S6**) were obtained from Aldrich and used as received.

Ti-Ge-MCM-41 catalysts were prepared by a one-pot, surfactant-assisted procedure, known as the "atrane route".[36,37] This procedure is based on the use of a cationic surfactant as a structural directing agent (in this case cetyltrimethylammonium bromide), and a complexing polyalcohol (2,2′,2″-nitriletriethanol), capable of matching the hydrolysis and co-condensation reaction rates of the different heteroelements, as well as the self-assembly processes between the inorganic precursors and the surfactant micelles.

Ti-UVM-7 catalysts were prepared by a modified atrane route. This method has been recently applied to the preparation of bimodal mesoporous silicas, and procedural details are described elsewhere.[38,39]

Adsorption and desorption isotherms of N_2 at 77 K were obtained using a Micromeritics ASAP 2000 apparatus following degassing of the samples at 150 °C for 12 h under vacuum. Electron probe microanalysis (EPMA) was performed using a Philips SEM-515 instrument. Si/Ti and Si/Ge molar ratio values averaged from EPMA data corresponded to about 50 different particles. X-ray powder diffraction (XRD) data was recorded on a Seifert 3000 θ-θ diffractometer using $\mathrm{Cu}_{\mathrm{K}\alpha}$ radiation. Patterns were collected in steps of 0.02°(2θ) over the angular range 1–10°(2θ) for 25 s per step. TEM micrographs and electron diffraction patterns were obtained using a Hitachi H9000NAR electron microscope operating at 300 kV, giving a point-to-point resolution of 0.18 nm. Samples were gently ground in butanol, and microcrystals were deposited on a porous carbon film supported on a Cu grid.

1-Butyl-3-methylimidazolium triflate ([bmim][OTf]), 1-ethyl-3-methylimidazolium triflate ([emim][OTf]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF_4]), 1-hexylpyridinium tetrafluoroborate ([C_6Py][BF_4]), 1-octylpyridinium tetrafluoroborate ([C_8Py][BF_4]), 1-butyl-3-methylimidazolium trifluoroacetate ([bmim][Tfa]), 1-butyl-3-methylimidazolium mesylate ([bmim][OMs]), 1-ethyl-3-methylimidazolium ethylsulfate ([emim][$EtOSO_3$]), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([bmim][NTf_2]), 1-butylpyridinium bis(trifluoromethanesulfonyl)imide ([C_4Py][NTf_2]), 1-butyl-1-methylpyrolidinium bis(trifluoromethanesulfonyl)amide ([bmpyr][NTf_2]), 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ([bdmim][NTf_2]), methyltrioctylammonium bis(trifluoromethanesulfonyl)imide ([$N_{8,8,8,1}$][NTf_2]) and 1-butyl-3-methylimidazolium lactate ([bmim][Lac]) were prepared in-house using standard literature methods.[40–42]

All the catalytic sulfoxidation experiments were carried out at 40 °C in sealed, 25 cm^3 flat-bottomed flasks using solvent (0.8 cm^3), catalyst (5 mg), substrate (0.15 mmol) and peroxide (0.30 mmol), and stirred at 1000 rpm, unless otherwise stated. The oxidations were performed by using either 2 M anhydrous HPD or the solid UHP complex.

The reaction products were analysed by HPLC, and ^1H and ^{13}C NMR spectroscopy. NMR spectra were obtained by using a Bruker Avance DRX spectrometer, operating at 300 MHz for ^1H and 75 MHz for ^{13}C. In each case, the NMR and HPLC analysis showed comparable results. HPLC analysis was performed on an Agilent 1200 at 1 $cm^3 min^{-1}$ with a C8 (Eclipse-XDC8) column, an eluent containing acetonitrile/water (1:1) and a detector wavelength of 254 nm. All the conversion data presented have an associated error of ±3 % due to difficulties in the measurement of the small catalyst weights. The hydrogen peroxide content in the reaction mixture was measured by using standard iodometric titration methods.[43] Solvent extraction with 5×3 cm^3 of diethyl ether was used to separate the products and starting material from the ionic liquid. The extraction procedure was found to result in a mass balance of >95 % for the extracted material.

During the recycling experiments, the catalyst was separated from the solvent by centrifugation at 2500 rpm for 5 min with a BTL bench centrifuge. After separation, the catalyst was stirred for 2 min with 2 cm^3 HPLC-grade acetone, then separated again by centrifugation. This procedure was repeated three times. The mother liquor following reaction was analysed by ICP-AES in order to check for titanium leaching. After washing and drying the catalyst for 2 h at 120 °C, fresh reagents and solvent were stirred with the catalyst and the reaction repeated.

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