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Liquid-phase oxidation of a pyrimidine thioether on Ti-SBA-15 and UL-TS-1 catalysts in ionic liquids

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Abstract

Ti-SBA-15 and UL-TS-1 catalysts with 1.0 and 1.5 at% Ti were tested for the liquid-phase sulfoxidation of 4,6-dimethyl-2-thiomethylpyrimidine in a range of water-miscible and immiscible ionic liquids and molecular solvents. Superior rates and selectivities with respect to the sulfoxide were found in the ionic liquids compared with the molecular solvents. The activity of the catalyst was strongly dependent on the anion–cation combination chosen; the best solvent under these conditions was [emim][BF_4]. Almost no leaching of titanium was found with Ti-SBA-15 in the ionic liquids, whereas significant leaching was observed in molecular solvents. In all solvents used, a surface rearrangement of titanium was observed after reaction, which may account for some loss in activity of the catalyst on recycle.

Keywords: Ti-SBA-15; UL-TS-1; 4,6-Dimethyl-2-thiomethylpyrimidine; Ionic liquid; Sulfoxidation; Heterogeneous

1. Introduction

The oxidation products of thioethers, namely sulfoxides and sulfones, are widely used as drug, agrochemical, and synthetic intermediates [1–3]. However, because of the value of the final products it is important to reduce the number of purification stages, and, therefore, a simple and highly selective method for controlling the oxidation is required. Oxidation of thioethers has been extensively studied [4,5] for a broad range of both organic and inorganic oxidants. However, it is only relatively recently that heterogeneous catalysts in sulfoxidation have been employed [6,7]. The use of various catalysts containing titanium [6–8], molybdenum and molybdenum-antimony oxides [9], or polyoxometalates [10] has been reported to show both high conversions and selectivities.

Porous titanium catalysts are largely used for these oxidations, and those reported include Ti-beta, Ti-MCMs, and TS-1; the last was found to be particularly active. These catalysts have been used in phenol hydroxylation [11], epoxidation, and hydroxylation of alkenes [12]. Although it is generally assumed that Ti does not leach from these catalysts, characterization of the catalysts after reaction has indicated that at least some leaching does occur in many cases [6, 13]. In addition to the high reactivity shown by the heterogeneous catalysts, these systems are able to use cheap oxidants such as hydrogen peroxide [6] and air [7]. Recently, ionic liquids have been shown to significantly improve the activity of mesoporous Ti or Ti and Ge catalysts for the sulfoxidation of pyrimidine and alkylthioethers [14]. High selectivities and significantly greater conversions compared with molecular solvents have been achieved; however, these catalysts suffer from poor recyclability.

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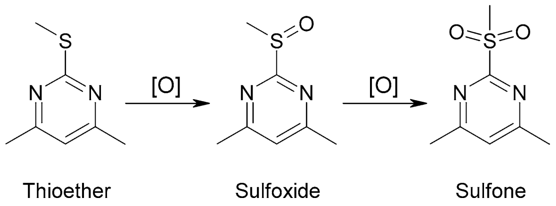

Scheme 1. Pathways in oxidation of 4,6-dimethyl-2-methylthiopyrimidine to the corresponding sulfoxide and sulfone.

Due to their ionic environment, the choice of catalyst and ionic liquid combination is important if the activity of the catalyst is to be maintained and the catalyst is retained as a heterogeneous catalyst or, in the case of homogeneous catalysts, is not removed during the workup. Ionic liquids have already shown their potential in a wide range of homogeneous and biocatalytic reactions, and these have recently been extensively reviewed [15]. There is also a growing interest in heterogeneously catalyzed and nanoparticle-catalyzed processes in ionic liquids [16–21]; however, in many cases the heterogeneity of the reaction is assumed and has not been fully investigated [22]. The aim of this study was to investigate the behavior of Ti-SBA and UL-TS-1 catalysts in the sulfoxidation of 4,6-dimethyl-2-methylthiopyrimidine in ionic liquids in comparison with molecular organic solvents (Scheme 1). In particular, the role of homogeneously catalyzed processes versus a surface process was investigated, as were the changes in the catalyst as a result of reaction.

2. Experimental

2.1. Catalyst preparation

2.1.1. Ti-SBA-15

An amorphous mesoporous titanium-containing silica, SBA-15, was synthesized with the use of tetraethyl orthosilicate (TEOS) and tetrapropyl orthotitanate (TPOT) as silicon and titanium sources, respectively, in a strongly acidic medium. A poly(alkylene oxide) triblock copolymer, $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$ (designated $EO_{20}PO_{70}EO_{20}$, Pluronic P-123, BASF), was used as a structure-directing agent, as described by Yang et al. [23]. Typically, 10 g of triblock $EO_{20}PO_{70}EO_{20}$ was dispersed in 75 g of double-distilled water at 40 °C. The resultant solution was stirred with 300 g of 2 M HCl solution containing the requisite amount of TPOT to obtain a homogeneous solution. Finally, 21.25 g of TEOS was added to the above mixture at 40 °C with vigorous stirring for 2 h. This solution was aged without stirring at 40 °C for 12 h (Ti/Si = 1.0 at%, Ti1) and 80 °C for 24 h (Ti/Si = 1.5 and 1.0 at%, Ti2 and Ti3, respectively). The solid products were recovered, washed, and air-dried at room temperature. The solid was calcined by slowly increasing the temperature from room temperature to 500 °C over 8 h and the temperature maintained at 500 °C for a further 6 h.

2.1.2. UL-TS-1

UL-TS-1 materials were obtained by a secondary templated crystallization of zeolites, starting from the amorphous mesoporous titanium-containing silica of corresponding elemental composition. It is of special concern that the walls of the amorphous mesoporous precursor materials should be as thick as possible. UL-TS-1 materials (Ti/Si = 1.0 and 1.5 at%, Ti4 and Ti5, respectively) were prepared with the use of the poly(alkylene oxide) triblock copolymer $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$ (designated $EO_{20}PO_{70}EO_{20}$, Pluronic P-123, BASF) and tetrapropylammonium hydroxide (TPAOH) as surfactant and template, respectively, as described by Kaliaguine and coworkers [24]. The synthesis of UL-TS-1 consists of two steps:

(i) Preparation of the amorphous mesoporous precursor:
The synthesis of the mesoporous silica followed the procedures reported by Stucky and co-workers [23,25]. Ti4 was prepared by dissolving 10 g of $EO_{20}PO_{70}EO_{20}$ in 100 g of ethanol. To this solution, 0.10 mol of $SiCl_4$ was added, followed by an appropriate amount of TPOT, with vigorous stirring for 12 h at room temperature. The solution was then heated to 40 °C to accelerate hydrolysis and evaporate the ethanol, during which the inorganic precursors hydrolyzed and polymerized into a network. The surfactant-containing mesoporous solid products were recovered and air-dried at room temperature and finally at 60 °C for 24 h. For Ti5 an amorphous mesoporous titanium-containing silica, Ti-SBA-15 (Ti/Si = 1.5 at%), was synthesized with the use of (TEOS) as a silicon source in a strongly acidic medium (2 M HCl solution), as presented above.

(ii) Transformation of the amorphous mesopore walls into crystalline walls:
The surfactant-containing mesoporous precursor was dried under vacuum at 60 °C for 24 h. Then 20 g of the dried mesoporous precursor was impregnated with 40 g of a 10 wt% solution of TPAOH (free from inorganic alkali). After aging at room temperature for 12 h, the solid was heated at 60 °C for 24 h to eliminate water and was left overnight at room temperature before being dried under vacuum for 24 h at room temperature. Finally, the solid was transferred into a Teflon-lined autoclave and heated at 120 °C for several days. It is assumed that the quantity of water adsorbed to the solid plays an important role in the crystallization. Therefore, the partly crystalline solid was further crystallized at 120 °C for a given time after the introduction of a small amount of water. Since the solid-state crystallization continues in the presence of this small amount of water, the above process makes it possible to control the crystallinity and the mesopore size of the solid materials. After 8 days (Ti4) and 10 days (Ti5), the catalysts were washed with distilled water, dried in air at 80 °C, and finally heated

from room temperature to 500 °C at 1 °C min^{-1} and calcined at 500 °C for 6 h to remove the organics.

The catalysts were characterized by N_2 adsorption–desorption isotherm measurements, XRD, TEM, and diffuse reflectance UV–vis (DR-UV–vis), as both fresh and used catalysts. Elemental analysis of samples dried overnight at 100 °C was performed by atomic emission spectroscopy with inductively coupled plasma atomization (ICP-AES). XPS spectra were obtained with a SSI X probe FISONS spectrometer (SSX-100/206) with monochrome Al-K_α radiation. The spectrometer energy scale was calibrated against the Au $4f_{7/2}$ peak (binding energy of 84.0 eV). The samples were moderately heated with a quartz lamp in the preparation chamber of the spectrometer to promote degassing, thus improving the vacuum in the analysis chamber. For the calculation of the binding energies, the C 1s peak at 284.8 eV was used as an internal standard. The peaks assigned to Si 2p, Ti 2p, and O 1s were recorded. DR-UV–vis measurements were carried out with a UV-4 Unicam spectrophotometer equipped with an integrating sphere. DR-UV–vis spectra of the fresh catalysts and of catalysts exposed to the reaction conditions in $[emim][BF_4]$ were measured. In the latter, the catalysts were washed with acetone and water to remove the ionic liquid reaction mixture and then dried at 120 °C under vacuum for 12 h. X-Ray powder diffraction (XRD) data were recorded on a Philips X-ray diffractometer (PW 1010 generator and PW 1050 computer-assisted goniometer) with nickel-filtered Cu-K_α ($\lambda = 1.5406$ Å) radiation, with a 0.025° step size and a 1-s step time. Nitrogen adsorption and desorption isotherms at −196 °C were established with an Omnisorb-100 instrument. Before the measurements, the samples were treated in vacuum at 200 °C for 5 h. The specific surface area, S_{BET}, was determined from the linear part of the BET plot ($P/P_0 = 0.05$–0.3). The mesopore size distribution was calculated with the use of the desorption branch of the nitrogen adsorption/desorption isotherms and the Barrett–Joyner–Halenda (BJH) formula. High-resolution TEM were obtained with a JEOL 200 CX transmission electron microscope operated at 120 kV. Samples were embedded in a polymeric resin and cut into sections approximately 20 nm thick with an ultramicrotome. They were then deposited on a holey carbon copper grid before TEM observation.

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

4,6-Dimethyl-2-methylthiopyrimidine was synthesized as described by Hunt et al. [26], and its purity was assessed by HPLC analysis and ^1H- and ^{13}C-NMR spectroscopy. 1-Ethyl-3-methylimidazolium tetrafluoroborate ($[emim][BF_4]$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[bmim][BF_4]$), 1-ethyl-3-methylimidazolium triflate ([emim][OTf]), and 1-ethyl-3-methylinidazolium bis(trifluoromethanesulfonyl)amide ($[emim][NTf_2]$) were synthesized from the appropriate organic chloride or bromide salt by standard literature preparative procedures [27–30] and dried under high vacuum at 80 °C for 12 h. The purity of the ionic liquids was confirmed by ^1H- and ^{13}C-NMR spectroscopy.

Table 1
Textural characteristics of the investigated catalysts

Catalyst	Catalyst structure	Ti/Si (mol%)	S_{BET} ($m^2\,g^{-1}$)	Pore diameter (nm)	Crystallinity (%)
Ti1	Ti-SBA 15	1.5	610	3.6	–
Ti2	Ti-SBA 15	1.5	920	5.6	–
Ti3	Ti-SBA 15	1.0	960	5.8	–
Ti4	UL-TS-1	1.0	520	12.8	80
Ti5	UL-TS-1	1.5	580	26.4	65

Typically, the sulfoxidations were performed with 5 mg catalyst suspended in 0.8 cm^3 of solvent, thereafter 0.66 mmols H_2O_2 (as a 2 M anhydrous solution in dioxane) was added followed by 0.2 mmols of thioether. The mixture was stirred at 40 °C for the specified time. The reaction products were analyzed by HPLC, ^1H- and ^{13}C-NMR spectroscopy.

NMR spectra were recorded with a Bruker Avance DRX spectrometer, operating at 300 MHz for ^1H and 75 MHz for ^{13}C. ^1H-NMR analysis was performed on the reaction mixture, which showed very good agreement with the HPLC results. HPLC analysis was performed on an Agilent 1200 liquid chromatograph, with the use of a C8 (Eclipse-XDC8) column with an eluent containing acetonitrile/water (1:1), at a flow rate of 1 $cm^3\,min^{-1}$.

The hydrogen peroxide content in the reaction mixture before and after the reaction was measured by the standard iodometric titration method [31]. The H_2O_2 efficiency represents the ratio between the moles of oxygen incorporated into the organic molecules to the moles of reacted peroxide.

Leaching tests were carried out with a double amount of catalyst (10 mg). After the reaction was complete, the suspension was centrifuged for 5 min at 3500 rpm, the liquid phase was decanted, and the titanium content of the solvent was determined by ICP-AES. To assess the activity of the solution following reaction, sulphoxidations were performed on the solvent after separation of the catalyst by the procedure described above.

For catalyst recycling experiments, the ionic liquid-catalyst system was separated by centrifugation. After removal of the liquid phase, the catalyst was washed three times with 5 cm^3 HPLC-grade acetone and dried for 2 h at 120 °C. Fresh reagents and solvent were stirred with the dried catalyst and the reaction was repeated. The washing step was used to ensure that the mass of catalyst used for each recycle was measured accurately, without a contribution from the ionic liquid, therefore ensuring a constant catalyst-to-substrate ratio for each reaction.

3. Results

3.1. Catalyst characterization

TEM analysis of all samples yielded typical pictures of the hexagonal structure of SBA-15-type materials [32].

XPS analysis of these samples showed a Ti 2p doublet containing symmetric curves. The binding energies determined for these levels in Ti-SBA-15 catalysts agreed with those reported previously for a titanium-containing SBA-15 material, prepared by impregnation of SBA-15 with titanium isopropoxide in ethanol followed by calcination (Table 2) [33]. In contrast, for UL-TS-1 catalysts, the Ti $2p_{3/2}$ was shifted to slightly lower binding energies and was found to be closer to that reported for titanium dioxide [34]. For all catalysts, the Ti/Si ratio determined from XPS is smaller than from chemical analysis, indicating that the titanium is contained within the pores of the catalyst and that there is a good dispersion of titanium. Ti1 showed the highest surface concentration of titanium.

3.2. Catalytic data

The activity of the catalysts was compared in a range of ionic liquids and molecular organic solvents (Table 3). From the results it is clear that the activity is a strong function of the anion of the ionic liquid; the order of reactivity has been found to be $[BF_4]^- > [NTf_2]^- > [OTf]^-$, with each ionic liquid showing much higher activities than either dioxane or ethanol. In all of the ionic liquids, the selectivity for sulfoxide remained higher than 90%, even at $>70\%$ conversion for all of the catalysts studied. Conversions close to 100% were possible, but only at extended reaction times and with reduced sulfoxide selectivity. For example, with Ti4 in [emim][BF_4] at 40 °C, 95% conversion with 93% sulfoxide selectivity was achieved, but only after 45 h (Fig. 1). Rates comparable to those of [emim][OTf] and [emim][NTf_2] were achieved with hexane and dichloromethane. For example, with Ti2, conversions of 22 and 14%, with 100% selectivity, were found after 10 h at 40 °C in hexane and dichloromethane, respectively. It should be noted that the latter results are not directly comparable to the other solvents studied, as these reactions were biphasic.

Changing the cation also had an effect on the rate of reaction. Table 4 compares the catalytic performances of the catalysts, Ti1–Ti5, in [emim][BF_4] and [bmim][BF_4]. With increasing chain length, it is clear that regardless of the catalyst, the activity was found to decrease. In all cases, at these conversions, the selectivity was found to be 100% with respect to the sulfoxide.

These changes in rate with the solvent are not associated with secondary reactions affecting the concentration of available oxidant. Regardless of the solvents used, the hydrogen peroxide efficiency was very high, with at most 14% of the oxidant being unselectively decomposed after 10 h, as shown in Table 5. However, it is clear that the type of catalyst used does influence the extent of peroxide decom-

Table 2
XPS binding energy of Ti $2p_{3/2}$ and Si 2p levels and comparative XPS and chemical Ti/Si ratios determined by ICP-AES

Catalyst	XPS binding energy (eV)		Ti/Si atomic ratio × 10^2	
	Ti $2p_{3/2}$	Si 2p	XPS	Chemical analysis
Ti1	459.5	104.3	0.67	1.50
Ti2	459.5	104.2	0.54	1.50
Ti3	459.4	104.2	0.34	1.00
Ti4	459.1	104.2	0.33	1.00
Ti5	459.2	104.2	0.31	1.50

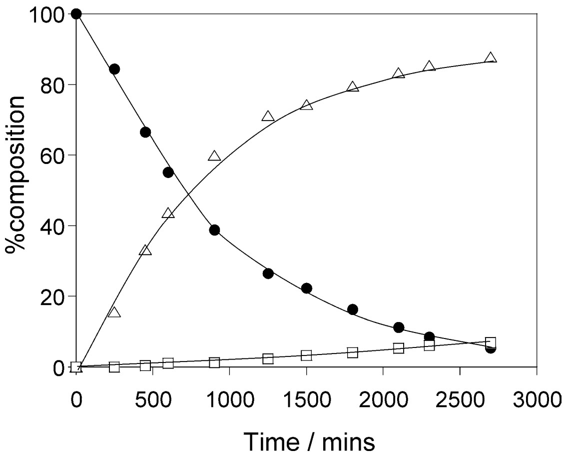

Fig. 1. Variation of percentage composition with respect to 2-thiomethyl-4,6-dimethylpyrimidine (●), sulfoxide (△), and sulfone (□) as a function of time using Ti4 and hydrogen peroxide in [emim][BF_4] at 40 °C.

Table 3
Conversion and selectivity to sulfoxide as a function of solvent and catalyst used after 10 h reaction time at 40 °C

Solvent	Catalyst									
	Ti1		Ti2		Ti3		Ti4		Ti5	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
[emim][NTf_2]	31.3	95.2	25.6	94.1	20.5	100	21.4	93.3	22.9	92.6
[emim][OTf]	29.6	98.1	14.8	100	12.3	100	14.7	98.5	10.3	100
[emim][BF_4]	72.1	90.1	60.5	92.3	41.5	94.2	52.3	94.5	43.9	97.8
Dioxane	18.9	100	6.7	100	5.1	100	6.5	100	2.9	100
Ethanol	4.8	100	2.9	100	6.1	100	2.0	100	4.0	100

Table 4
Turnover frequency (TOF) and conversion after 5 h for Ti1–Ti5 catalysts, in [emim][BF_4] and [bmim][BF_4] at 40 °C, in all case the sulfoxide selectivity was 100%

Ionic liquid	Catalyst	TOF[a] (min^{-1})	Conversion (%)
[emim][BF_4]	Ti1	1.70	25.3
	Ti2	1.45	21.7
	Ti3	1.04	10.6
	Ti4	0.63	9.4
	Ti5	0.76	11.3
[bmim][BF_4]	Ti1	1.10	16.2
	Ti2	0.92	13.8
	Ti3	0.75	9.7
	Ti4	0.68	9.3
	Ti5	0.49	7.1

[a] TOF expressed as g of oxidized thioether per g of Ti per min, after 60 min.

Table 5
Hydrogen peroxide efficiency as a function of solvent and catalyst after 10 h reaction

Solvent	Hydrogen peroxide efficiency (%)		
	Ti1	Ti4	Ti5
[emim][BF_4]	95	90	87
[emim][NTf_2]	92	92	88
Ethanol	93	90	86
Dioxane	91	93	90

position. For both molecular and ionic media the SBA-15 catalysts showed higher hydrogen peroxide efficiencies than the UL-TS-1 catalyst, for a given solvent.

The high selectivities for the sulfoxide observed here are not associated with an uncatalyzed reaction; less than 0.5% conversion was found over 30 min in the absence of a catalyst, regardless of the solvent used [14]. Robinson et al. showed that oxidation to the sulfoxide in the absence of a catalyst was possible, whereas oxidation to the sulfone required the use of TS-1; with the addition of a base, the uncatalyzed reaction rate was reduced [13]. The low uncatalyzed rate to the sulfoxide in the present case may therefore be due to the basicity of the pyrimidine substrate.

3.3. Catalyst leaching and recycling

After reaction for 10 h, the amount of titanium leached from the catalyst was determined by ICP-AES. In comparison with ethanol, significantly less leaching is found in [emim][BF_4] for all of the catalysts examined (Fig. 2). It is also noticeable that the nature of the mesoporous material strongly influences the amount of leaching, for ionic liquids in particular. In [emim][BF_4], all of the Ti-SBA-15-type catalysts were more stable than the UL-TS-1 materials, with less than 0.3% Ti leaching found for Ti-SBA-15, whereas up to 2.5% Ti is lost from UL-TS-1. Although a strong correlation is found for the ionic liquid, similar trends are not observed in ethanol.

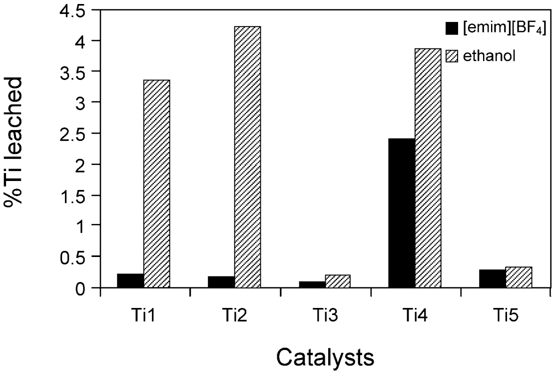

Fig. 2. % Titanium leached as a function of the catalysts in [emim][BF_4] and ethanol.

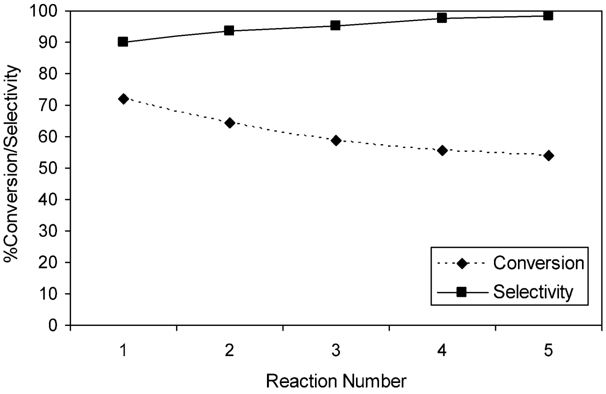

Fig. 3. Variation of conversion of the substrate and sulfoxide selectivity for the oxidation of 4,6-dimethyl-2-methylthiopyrimidine over Ti1 during successive runs in [emim][BF_4] after 10 h reaction time at 40 °C.

The low level of leaching found in the ionic liquids is in agreement with the small activity of the ionic liquid after reaction in the absence of the catalyst. For example, after a reaction time of 4 h in [emim][BF_4], Ti1 was separated from the reaction mixture, and the reaction conditions were maintained for a further 4 h. Although there was still some reaction, indicating that the leached ions had activity, the conversion was less than 20% of that found in the reaction performed in the presence of the catalyst over the same time period.

Although the amount of titanium leaching was small in the ionic liquids, some loss in activity was found with recycling of the ionic liquid-catalyst system. After five reactions in [emim][BF_4], the rate was found to decrease to 75% of the fresh Ti1 (Fig. 3). The reduction in rate with recycling is thought to be associated with changes in the catalyst and not with the ionic liquid. Little change was observed in the ionic liquid by ^{1}H-NMR, ^{13}C-NMR, and HPLC analysis. In comparison, the DR-UV–vis spectra of the catalyst before and after reaction showed significant changes.

Fig. 4 shows DR-UV–vis spectra for the fresh catalysts and for catalysts after reaction in [emim][BF_4]. All of the spectra exhibit bands at ca. 240 nm, which can be assigned to titanium in isolated octahedral positions, in pentacoordination or possibly as isolated tetrahedral titanium

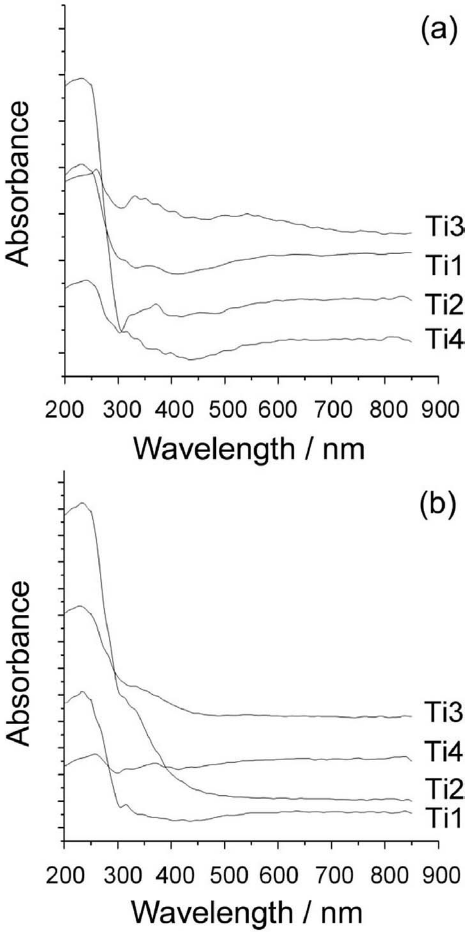

Fig. 4. DR-UV–vis spectra of (a) fresh catalysts and (b) catalysts after sulfoxidation reaction in [emim][BF_4].

species [35–37]. The DR-UV–vis spectra for Ti-SBA-15 catalysts (Ti1, Ti2, Ti3) also contained bands in the range of 310–380 nm, which can be ascribed to either Ti–O–Ti cluster frameworks or to segregated nanosized anatase particles [38,39]. For UL-TS-1 samples (Ti4) these bands are absent. After reaction, all Ti-SBA-15 catalysts showed a decrease in the band assigned to segregated titanium species and a shift in the absorption to lower wavelength. This change is likely to correspond to solubilization and subsequent redispersion of titanium on the catalyst. In contrast, following reaction, a decrease in the isolated titanium octahedral species was observed in the UL-TS-1 catalyst. This was accompanied by the appearance of a band centered at 370 nm, which indicated some segregation of titanium. Similar changes in the catalyst were observed for all of the ionic liquids and molecular solvents studied.

4. Discussion

It is clear that for both the ionic liquids and molecular solvents, the rates observed are dependent on the ability of the solvent to complex to the catalyst or oxidant. With increasing chelation strength, the activity decreases, and, in the ionic liquid, this is determined by the coordinating ability of the anion, that is, $[BF_4]^- < [NTf_2]^- < [OTf]$. The cation effect observed between $[emim]^+$ and $[bmim]^+$ may be associated with the solvent becoming more viscous as the chain length increases, that is, 29.4 cP for [emim][BF_4] and 59.1 cP for [bmim][BF_4] at 40 °C [40]. However, little change in rate was found with increased stirrer speed, and therefore mass transfer within the liquid phase may not be important [14]. It is more likely that the drop in activity is associated with a reduction in the accessibility of the catalyst pores as the size of the cation increases. The effect of cation size on the transport of the reagents and ionic liquid within catalyst pores has been observed previously in both sulfoxidation reactions and Friedel–Crafts acylations with meso- and microporous catalysts, respectively [14,20].

Selectivities similar to those reported here were also observed for MCM-41 and UVM-type mesoporous catalysts containing Ti, or Ti and Ge, reported for the oxidation of pyrimidine thioethers in ionic liquids [14]. However, in comparison with the sulfoxidation of 4,6-dimethyl-2-methylthiopyrimidine, the catalysts studied earlier showed much higher activities. For example, after 120 min, conversions of $> 70\%$ were reported for many ionic liquids, for a solution of hydrogen peroxide in dioxane as the oxidant, at 40 °C. These catalysts also showed significant leaching of the titanium, $> 8\%$, even in the presence of the ionic liquid, and a significant part of the activity of these systems was therefore attributable to homogeneous catalyzed reactions taking place. This led to a rapid decrease in the activity of the catalyst on recycling; after five reactions the conversions after 2 h dropped from 58 to 21%. In contrast, both types of catalyst studied here showed very low levels of leaching of the titanium and more robust recyclability.

The reactions carried out with the Ti-SBA-15 and UL-TS-1 catalysts in sulfoxidation of 4,6-dimethyl-2-methylthiopyrimidine indicate that the characteristics of the catalysts are very important; the conversion is influenced by the titanium content, surface area, and pore size. The characterization of Ti-SBA-15 and UL-TS-1 catalysts indicated typical features for these materials. Ti-SBA-15 samples exhibit high surface areas and pores in the range of 3.6–5.8 nm, whereas UL-TS-1 had surface areas in the range of 500–600 $m^2\,g^{-1}$ and very large pores, between 12.8 and 27.0 nm. The XPS binding energy corresponded to the Ti $2p_{3/2}$ level, indicating the presence of a higher degree of octahedrally coordinated titanium in SBA-15 samples. DR-UV–vis characterization of these samples also showed that in fresh catalysts, Ti-SBA-15 contained both isolated octahedral and segregated titanium species, whereas in UL-TS-1 only isolated titanium species have been detected. For all of the reaction conditions the Ti-SBA-15 catalyst Ti1 was found to be the most active catalyst. This corresponds to the catalyst for which XPS analysis indicated the highest fraction of surface titanium. DR-UV–vis spectra for the catalysts after reaction also showed that,

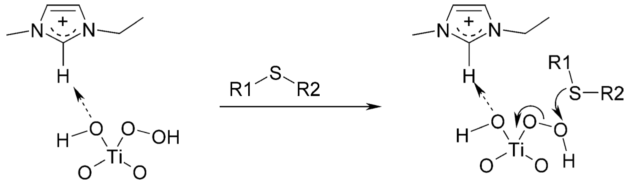

Fig. 5. Schematic for the activation of Ti–O bonds by 1,3-dialkylimidazolium based ionic liquids.

although titanium leached into the solution, significant surface rearrangement also takes place. In the case of the Ti-SBA-15 catalysts, much of the aggregated titanium species redispersed, leading to an increased population of isolated octahedral species. The loss in activity observed with recycling is probably due to these surface morphology changes and not due to the solubilization of the titanium. UL-TS-1 catalysts also showed surface rearrangement, with superficial segregation of the titanium species. However, in this case the surface changes were accompanied by substantial leaching in solution.

The higher activity of the ionic liquid compared with the organic solvents may suggest that it can activate the active site on the catalyst, as shown in Fig. 5. The activation can be understood from consideration of the acidity of 2-H of the imidazolium cation [41]. This interaction induces a polarization of the Ti–O bond, increasing the overall Lewis acidity of the catalytic site, and, as a consequence, the activity of the peroxo species toward the thioether increases. A similar activation was observed previously in a comparison of 1,3-dialkylimidazolium-based ionic liquids with those based on the 1,2,3-trialkylimidazolium cation. In this case, the C(2) methyl-protected ionic liquid showed a much reduced activity compared with the ionic liquid with a hydrogen at the C(2) position [14].

Analogous increases in activity are not observed with protic molecular solvents, such as ethanol, despite the fact that they are also capable of forming strong hydrogen bonds. As well as with the catalyst, the molecular solvents can hydrogen bond strongly with the oxidant and hence reduce its activity. Although the ionic liquid can also hydrogen bond with the oxidant, it has been shown that, in general, hydrogen bonding solute interactions occur with the anion and not with the cation [42]. With the reduction of the ability of the anion to hydrogen bond the oxidant activity is enhanced, as shown by the higher reaction rates for tetrafluoroborate based ionic liquids compared with those containing triflate. In addition, these catalysts have been shown to deactivate because of the presence of water molecules, which can block the active sites from reagents [43,44]. It is known that the ionic liquids bind strongly to water and the water is deactivated at low concentrations [45]. Water is formed during the sulfoxidation reaction, and, therefore, it is possible that the ionic liquid is able to dehydrate, and thus reactivate, the catalyst surface, resulting in a higher activity in the ionic liquid than in molecular solvents.

5. Conclusions

Sulfoxidation of 2-thiomethyl-4,6-dimethylpyrimidine over a range of Ti-SBA-15 and UL-TS-1 catalysts in ionic liquids occurred with high rates and selectivities at high conversion. A comparison with typical molecular solvents indicated that much higher activities were possible in the ionic liquid, which may be due to activation of the catalyst via a hydrogen bonding interaction. Differences were also found among the investigated ionic liquids, with both the anion and cation contributing to an effective ionic liquid. The best solvent was found to be [emim][BF_4]. Leaching of titanium into the solvent was insignificant in the ionic liquids studied, for Ti-SBA-15 catalysts, whereas leaching was found for UL-TS-1 catalysts in both ionic liquids and molecular solvents. The small degree of leaching observed and good recyclability for the Ti-SBA-15 catalysts indicated that, in the ionic liquids, the activity observed was due to a surface catalyzed process. DR-UV–vis showed that the leaching was accompanied by changes in the superficial dispersion of titanium. For SBA-15 catalysts, this surface rearrangement corresponds to an increase in the isolated titanium species, whereas for UL-TS-1 catalysts an increase in segregated titanium is observed. A decrease in activity with recycling is observed in the ionic liquid, and, for the SBA-15 catalysts, it is likely that this is due to the change in surface titanium species, as opposed to the dissolution of titanium.

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