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Thioethers oxidation on dispersed Ta-silica mesoporous catalysts in ionic liquids

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Abstract

The oxidation of the various aliphatic, aromatic and heteroaromatic thioethers was carried out in a range of ionic liquids, 1-butyl-3-methylimidazolium triflate, 1-butyl-1-methyl-pyrolidinium bis(trifluoromethanesulfonyl)amide, 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)amide, 1-butyl-3-methyl-imidazolium tetrafluoborate and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethane-sulfonyl)amide, using sol–gel prepared mixed oxide silica tantalum and tantalum grafted MCM-41 catalysts. For comparison catalytic tests in molecular solvents (acetone, acetonitrile, dioxane and ethanol) were also performed. Excellent hydrogen peroxide efficiencies were obtained on these catalysts. The conversion data has been correlated with the Kamlet–Taft π^*, α and β solvent parameters. Characterization of the catalysts was made by ICP-AES, adsorption–desorption isotherms of N_2 at 77 K, XRD, SEM and TEM.

Keywords: Oxidation of thioethers; Ionic liquids; Dispersed Ta-silica mesoporous catalysts

1. Introduction

Liquid-phase selective oxidation using hydrogen peroxide and heterogeneous catalysts is of significant interest to both the fine chemical and pharmaceutical industries. Specifically, the oxidation of thioethers to the corresponding sulfoxides is important in the production of biological-active compounds and synthons in synthesis of natural products [1]. A number of heterogeneous catalysts which are active and selective for sulfoxidation reactions have been reported, to date, including those based on titanium [2,3], molybdenum and molybdenum–antimony mixed oxides [4] or polyoxometalates [5]. In many of these studies, leaching of the active metal species has been detected which limits their application as heterogeneous catalysts. Furthermore, although the titanium-based catalysts have been reported to have very high stability, significant leaching is still found in molecular solvents [6]. Recently, we have reported that by replacing the molecular solvents with ionic liquids the stability of mesoporous materials based on MCM and SBA-type [7,8] materials can be increased. Remarkably, the increase in the stability was accompanied by an increase in the activity and selectivity of the catalysts. In these systems the catalyst is truly heterogeneous and the role of the leached species is insignificant. In another attempt to enhance the performances of liquid-phase oxidations, Yamaguchi et al. [9] indicated that peroxotungstate species immobilized on ionic liquid modified silica act as effective catalysts.

This paper describes a continuing study of ionic liquid mediated sulfoxidation reactions investigating highly dispersed Ta catalysts in a mesoporous-like matrix for oxidation of thioethers (Scheme 1). Recently, the efficient and selective sulfoxidation of 4,6-dimethyl-2-thiomethylpyrimidine over Ta sol–gel and grafted materials, using hydrogen peroxide as an oxidizing agent in a range of ionic liquids and organic solvents was reported [10]. Tantalum has been used in several cases as a redox element in heterogeneous catalysis. Grafting Ta on silica led to catalysts capable to perform asymmetric oxidation of allylic alcohols in presence of tartric esters [11]. Other studies

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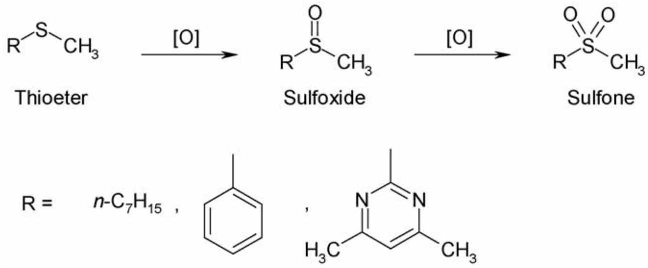


Scheme 1. Oxidation of the thioethers.

have shown that tantalum-containing oxidic materials exhibit high activity in oxidation of *n*-butane [12] and *i*-butane [13]. In a dispersed form, tantalum oxide is also a powerful promoter in selective oxidation of propene, butanes and xylenes [14]. Very recently, Ta–Si xerogels and grafted Ta-SBA-15 were prepared and used for liquid-phase oxidation of cyclohexene with hydrogen and organic peroxides [15].

The present report extends the premlinary results [10] by examining the same dispersed tantalum oxide clusters in a non-ordered monomodal mesoporous silica matrix in the oxidation of thioethers with different reactivity, namely heptyl-methyl-sulfide (**S1**), methyl-phenylsulfide (thioanisole) (**S2**), and 4,6-dimethyl-2(methylthio)-pyrimidine (**S3**).

In addition, the role of the solvent in these reactions has been examined by correlating the Kamlet–Taft π^*, α and β solvent parameters with the activity of the catalysts. The use of the Kamlet–Taft equation allows the separation of various solvent properties, *e.g.* specific and non-specific solvent interactions over a chemical process [16]. π^* represents the solvent's dipolarity/polarizability, and α and β are measures of the solvent's HBD (hydrogen bond donor) acidity and HBA (hydrogen bond acceptor) basicity [17]. For ILs these parameters have contributions from both anion and cation, and these aspects were recently discussed by Welton and co-workers [18].

This approach has been chosen as it has been shown that the polarity of solvents is very important in such reactions influencing both the catalytic properties and leaching. For example, Hulea et al. reported that the solvent polarity, expressed as the E_T^N parameter, could be correlated with the reaction rate for sulfoxidation on Ti-containing zeolites as catalysts [3]. The Kamlet–Taft parameterisation allows a more detailed examination of the solvent–reactivity relationship and has recently been applied to ionic liquid reactions to understand the effect of the anion and cations on the kinetics observed [17,18].

2. Experimental

Ta_2O_5 (15 wt%)-SiO_2 catalysts were prepared using a procedure reported elsewhere [10]. They were obtained using two families of quaternary ammonium salts, $C_nH_{2n+1}(CH_3)_3NBr$ (n = 14, 16, 18) and $(C_nH_{2n+1})_4NBr$ (n = 10, 12, 16, 18) as surfactants. In accordance, the catalysts were denoted as Ta-*n* or Ta-4-*n* (Table 1). A Ta-MCM-41 catalyst was also prepared by grafting from an alcoholic solution of tantalum ethoxide, the preparation is described in detail elsewhere [10].

The characterization of the catalysts was carried by ICP-AES, adsorption–desorption isotherms of N_2 at 77 K, XRD, SEM and TEM. Sorption isotherms of N_2 were obtained at 77 K with a Micromeritics ASAP 2000 apparatus after outgassing the samples at 423 K for 12 h under vacuum. The analysis of the isotherms was made using the BET and BJH formalisms. The XRD patterns were obtained with a SIEMENS D-5000 diffractometer operating at 40 kV and 50 mA, equipped with a variable-slit diffracted-beam monochromator and scintillation counter. The diffraction patterns were recorded in the range 0–80° (2θ) using Cu Kα radiation (λ = 1.54183 Å). The electron microscopic analysis was performed using a FEI Tecnai F20 ST operated at 200 kV. The samples were prepared for TEM analysis by grinding the bulk material resulting in a fine powder, which was distributed on 200 mesh carbon coated copper grids. SEM analysis was made using an ISI 60 apparatus combined with automatic PRODAS storage system.

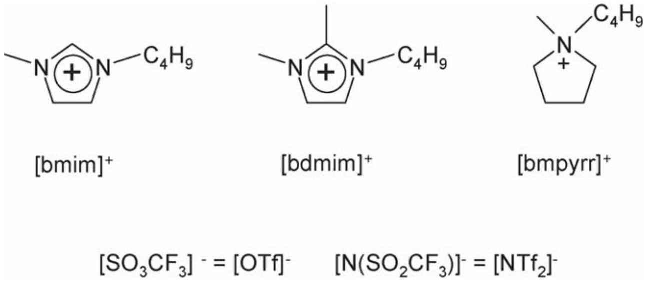
Heptyl-methylsulfide and thioanisole were obtained from Aldrich and used as received. 4,6-dimethyl-2(methylthio)-pyrimidine was prepared using literature data [19], and purified by column chromatography. The purity was checked by ^1H NMR and HPLC.

1-Butyl-3-methylimidazolium triflate ([bmim][OTf]), 1-butyl-1-methyl-pyrolidinium bis(trifluoromethanesulfonyl)amide ([bmpyrr][NTf_2]), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([bmim][NTf_2]), 1-butyl-3-methylimidazolium tetrafluoborate ([bmim][BF_4]) and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethane-sulfonyl)amide ([bdmim][NTf_2]), were prepared in house from the

Table 1
Structural properties of the investigated catalysts

Catalyst	BET surface area ($m^2 g^{-1}$)	Micropore area from *t*-plot surface analysis ($m^2 g^{-1}$)	Pore size (nm)	
			N_2 adsorption	SAXS
Ta-14	724	181	3.4[a]	3.7
Ta-16	692	171	3.4[a]	3.7
Ta-18	698	178	3.6[a]	3.7
Ta-4-10	984	179	4.2[a]	3.5
Ta-4-12	832	297	4.2[a]	3.6
Ta-4-16[b]	187	25	2.3, 24[a]	–
Ta-4-18[b]	145	11	2.3, 24[a]	–
Ta-TCM	845	45	2.8	3.1

[a] Monomodal mesopore size distribution; [b] Bimodal mesopore size distribution.



Scheme 2. Ionic liquids used in this study.

corresponding halide salts by anion exchange using standard literature methods [20–22]. The ionic liquids used are shown schematically in Scheme 2. Each ionic liquid was dried under high vacuum at 80 °C for 12 h. The purity of the ionic liquids was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Acetone and acetonitrile were Fluka HPLC grade products, dioxane and ethanol were Aldrich p.a. quality and were used as received.

The oxidation reactions were carried out at 40 °C in 10 cm^3 glass microreactors. The reaction mixture consisting of 0.1 mmol substrate, 5 mg catalyst, 0.2 mmol oxidant (30% H_2O_2 in water (HPW)), and 0.5 ml solvent was mixed under vigorously stirring at 1000 rpm for the time required. The experiments related to the solvent effects were performed in similar conditions, but at 25 °C in order to correlate with previously reported Kamlet–Taft coefficients [18].

The analysis of the reactant and products was performed by HPLC and/or by ^{1}H NMR. The HPLC analyses were run on an Agillent 1200 system, (C8 column, acetonitrile: water 1:1 ratio) using a UV–vis detector at 254 nm. The ^{1}H NMR spectra were acquired on a Bruker Avance 300, operating at 300 MHz.

3. Results and discussion

3.1. Catalysts characteristics

Table 1 compiles the textural characteristics of the investigated tantalum catalysts.

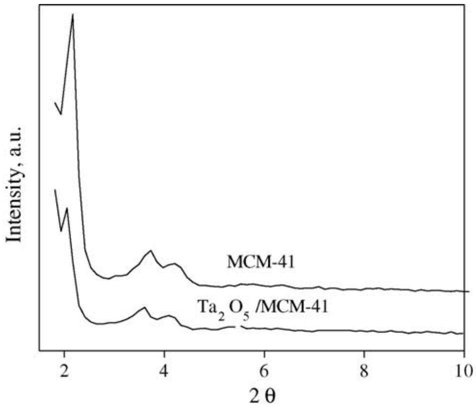


Fig. 2. Comparative XRD patterns of parent MCM-41 and Ta-MCM-41 catalysts.

It is evident the textural differences arose for Ta-4-16 and Ta-4-18. The lower specific area and bimodal pore size distribution could be explained by structural changes during the calcination. Since the surfactants used, tetra-hexadecyl- and tetra-octadecyl ammonium bromides are characterized by a high molecular volume, it is very likely the large micellar structure formed during the sol–gel process collapses at 500 °C. All the other materials exhibit high specific areas, and mesopores that allow easy access of the investigated substrates to the active centres. The porosity of these materials was also been confirmed by SEM measurements (Fig. 1). The sol–gel prepared samples were shown to amorphous by XRD with. No diffraction peaks associated with the tantalum species observed. In contrast the diffraction is clearly observed for the MCM-41 based catalysts where the MCM-41 structure is well preserved. Again, no reflections assignable to tantalum species were detected. However, grafting of tantalum onto the MCM-41 did result in a decrease in crystallinity of the support as shown by the decrease in diffraction line intensities. The grafting also resulted in a shift of the (1 0 0), (1 1 0) and (2 0 0) reflections to lower 2θ values corresponding to a partial degradation of the hexagonal structural order (Fig. 2).

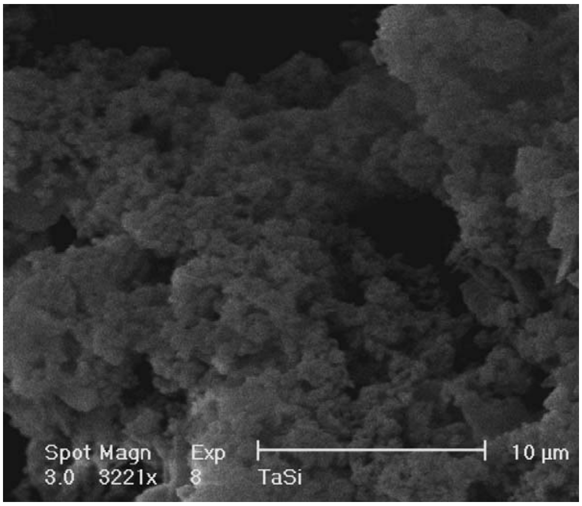


Fig. 1. SEM picture of Ta-14.

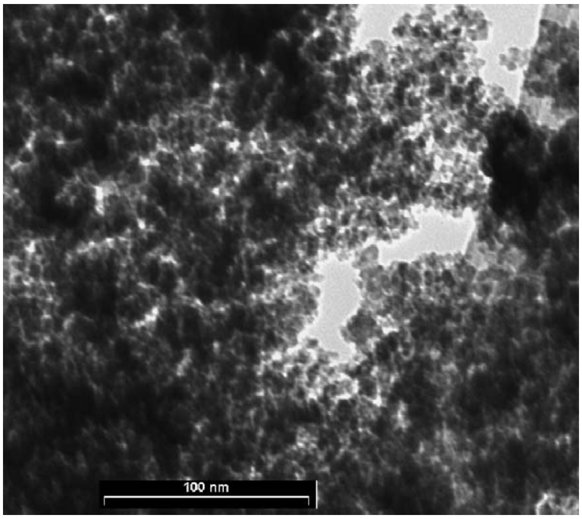


Fig. 3. TEM picture of Ta-16.

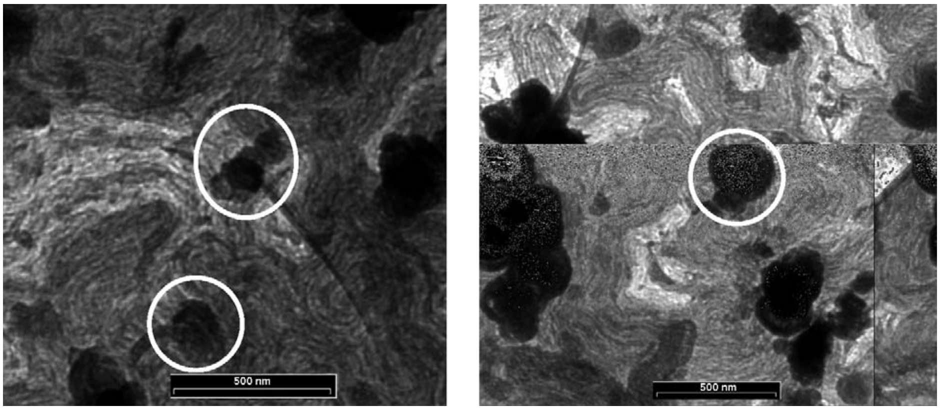


Fig. 4. TEM pictures of grafted Ta-MCM-41.

Fig. 3 shows a typical TEM image of mixed oxide sol–gel silica-tantalum catalysts. No particular textural features were observed and no evidence of tantalum agglomeration was detected indicating that in these oxides tantalum is well dispersed, consistent with the XRD patterns. Fig. 4 shows equivalent TEM images for the Ta-MCM-41 catalyst. Following deposition of tantalum on MCM-41 by grafting and calcinations of the catalyst, two forms of tantalum oxide were observed. Large amorphous agglomerates as 200 nm were found on the external surface of the support, while small oxide clusters (<10 nm) were deposited both inside and at the entrance of the pores.

3.2. Catalytic behaviour

Fig. 5 shows the variation of the conversion for the sulfoxidation of thioethers **S1**–**S3** in [bmim][NTf$_2$] as a function of the catalyst preparation using an aqueous solution of 30% hydrogen peroxide, as the oxidant. The corresponding variation in the sulfoxide selectivity at 20% conversion is shown in Fig. 6.

With the exception of the catalysts Ta-4-16 and Ta-4-18, there was little variation between the catalysts studied. For Ta-4-16 and Ta-4-18, the conversion after 15 min was <3% which is comparable with the reaction in the absence of catalyst. The lack of activity of these catalysts is probably associated with the very small surface areas in comparison with other catalysts. Previous studies suggested that for Ta-*n* catalysts, the tantalum is more highly dispersed than in the Ta-4-*n* materials with little variation in the Ta/Si ratio with the length of the hydrocarbon chain used in the preparation [10]. On the contrary, samples prepared using $(C_nH_{2n+1})_4NBr$ exhibited a more inhomogeneous incorporation of tantalum and the non-homogeneity was increased in the case of catalysts Ta-4-16 and Ta-4-18.

The results show higher conversions for the aliphatic thioether, the lowest values being determined for the heteroaromatic thioether. Based on these results it is possible to speculate that two factors control the reaction rate, the redox potential of the substrate, which exhibits similar values (~1.4 V *versus* SCE) for heptyl-methylsulfide **S1** and thioanisole **S2** [23] and the substrates shape and molecular volume, which determines the accessibility of the sulfur atom for the superficial peroxidic active centre. However, the latter must only be a minor factor, as the order of the substrate reactivity was the same for the surface catalysed processes as for the reaction in the absence of the solid catalyst. The oxidation mechanism may be similar to the reaction catalysed by titanium as, like titanium, isolated tantalum species on solid supports have been shown to catalyse Sharpless oxidations of allylic alcohols [13] and peroxidic compounds of Ta are well established [24,25] with tantalum being able to coordinate up to four peroxo groups in salts such as K_3TaO_4. Titanium is thought to catalyze these oxidations via oxygen transfer from peroxides or hydroperoxides. In this case, the presence of oxygen, light or radical scavenger (hydroquinone) does not

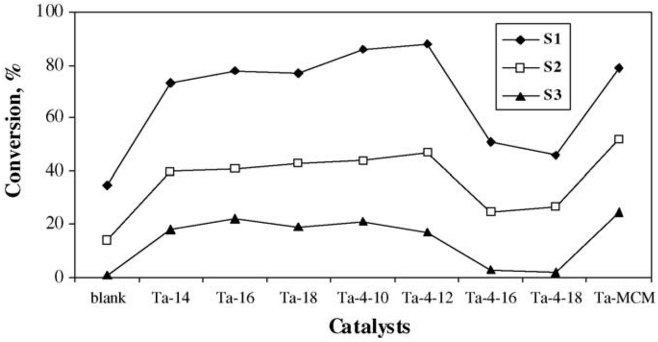


Fig. 5. Conversion of thioethers on Ta catalysts using [bmim][NTf$_2$] as solvent and hydrogen peroxide 30% as oxidant at 40 °C, 15 min, 5 mg catalyst.

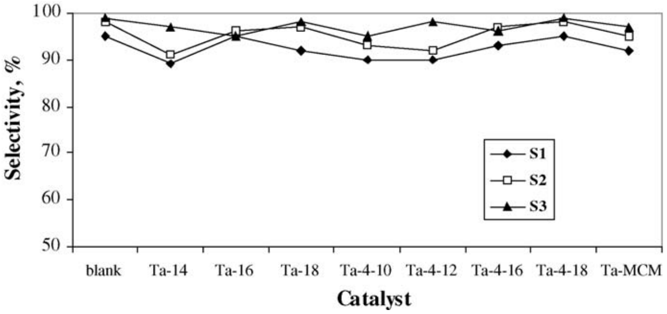


Fig. 6. Selectivity in sulfoxide at 20% conversion on Ta catalyst, 5 mg catalyst, [bmim][NTf$_2$] as solvent and hydrogen peroxide 30% as oxidant at 40 °C.

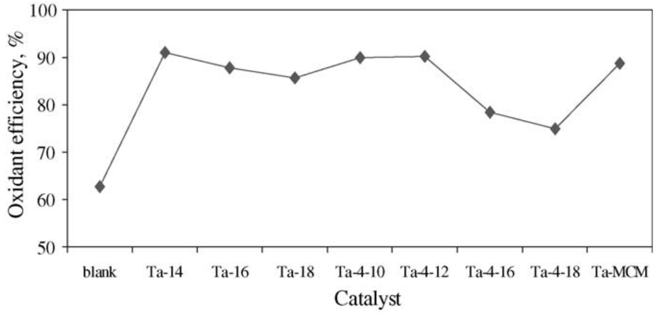


Fig. 7. Hydrogen peroxide efficiency at 20% conversion, 40 °C, 5 mg catalyst, [bmim][NTf_2] as solvent and hydrogen peroxide 30% as oxidant.

have any significant effect over sulfoxidation rate using H_2O_2 and Ti-polyoxometalates as catalysts. For the titanium catalysed process the electron-transfer mechanism is not an important contribution [25]. Therefore, if the reaction mechanisms are similar, the redox potentials, which govern the electron transfer rate are also not likely to a major contributing factor in the reactivity order of the thioethers, particularly where the substrates have similar redox potentials. It is, therefore, likely that the difference between the molecules **S1** and **S2** is due to steric hindrance. The oxygen transfer requires a short distance between the reacting species, in the case of thioanisole, and the bulkiness of Ph moiety may partially obstruct the sulphur leading to a lower oxygen transfer rate and a lower conversion, although the oxidation potentials are similar. Steric effects cannot be used to explain the lower reactivity of **S3** compared with **S2** and although a small effect, the fact the **S3** has a higher oxidation potential of 2.06 V (*versus* SCE) may be the important factor [26].

Little variation of the sulfoxide selectivity with catalyst preparation was also found (Fig. 6). A slight dependence was found with the substrate structure, with the exception of the reaction over Ta-14, the oxidation of **S3** showed the highest selectivity towards the sulfoxide and **S1** the lowest. This may be explained by the increased electron density on the sulfur atom, due to the electron-withdrawing character of the 2-pyrimydil moiety [27], in the **S3** compared with **S2** and the smallest electron density in the case of **S1**. More importantly only at low conversion was high selectivity achieved. Whilst the selectivity was >95% for conversions 20%, 70% selectivity was found at conversions of 40% and this decreased further to 40% for conversions of 80%. For all substrates and conversions, the sulfoxide selectivity in the absence of catalyst was at least 20% lower smaller than in the presence of the catalyst.

Fig. 7 shows the variation of the hydrogen peroxide efficiency in [bmim][NTf_2] as a function of the catalyst for the sulfoxidation of **S1**. With the exception of the Ta-4-16 and Ta-4-18 catalysts, all other Ta-*n* and Ta-4-*n* catalysts showed high efficiencies, around 90% in [bmim][NTf_2]. Similar values were obtained for the other ILs tested. In comparison, the efficiency of the hydrogen peroxide catalysed oxidation is only ~62% in the absence of the catalyst.

The ICP-AES analysis of the reaction products indicated that Ta leached by Ta-*n* and Ta-4-*n* catalysts was smaller than 2%. In contrast, for Ta-MCM-41 the amount of leached Ta was almost 7% in the first cycle, and almost 4% after the second run. TEM picture of Ta-MCM-41 after the second run is given in Fig. 8. A comparison of the TEM images in Figs. 4 and 8 clearly show that the leaching is due to dissolution of the large aggregates whilst the smaller particles remained unaffected. This is in good agreement with previously reported results on these catalysts [12]. Whilst the leaching is low, it is possible that the leached tantalum is highly active as a homogeneous catalyst. However, after removal of the solid catalyst, little reaction in the mother liquor was observed over a 2 h period indicating that the dissolved tantalum species are not active in this reaction. This may be contrasted with the high activity for dissolved titanium species in analogous reactions [12].

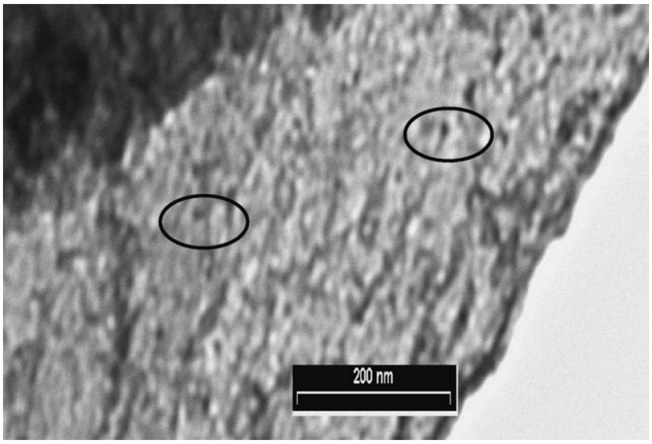


Fig. 8. TEM picture of grafted Ta-MCM-41 after the second run. Tests carried out in [bmim][OTf].

Table 2 compares the conversions of **S3** in a range of ionic and molecular solvents using Ta-14 as catalyst and an aqueous solution of hydrogen peroxide 30 wt%, as oxidant at 25 °C over 2 h. In order to explain the reactivity found as a function of the solvent the Kamlet–Taft equation coefficients associated with these solvents are also summarised [18]. Based on these data a correlation function was obtained between the measured

Table 2
Substrate conversion on Ta-14, and Kamlet–Taft coefficients for several ionic and molecular solvents [18]

Solvent	Kamlet–Taft coefficients			Fractional conversion	Fractional selectivity to sulfoxide
	π^*	α	β		
[bmim][BF_4]	1.047	0.627	0.376	0.312	92.2
[bmim][NTf_2]	0.984	0.617	0.243	0.375	86.0
[bdmim][NTf_2]	1.010	0.381	0.239	0.227	91.5
[bmim][OTf]	1.000	0.625	0.464	0.085	100
[bmpyrr][NTf_2]	0.954	0.427	0.252	0.195	97.8
Acetone	0.710	0.080	0.480	0.091	97.5
Acetonitrile	0.750	0.190	0.310	0.291	79.4
Dioxane	0.553	0.000	0.370	0.382	80.7
Ethanol	0.540	0.830	0.770	0.415	75.4

Reaction conditions: 5 mg catalyst, 0.2 mmol substrate, 0.4 mmol HPW, 1 cm^3 solvent, 25 °C, 120 min.

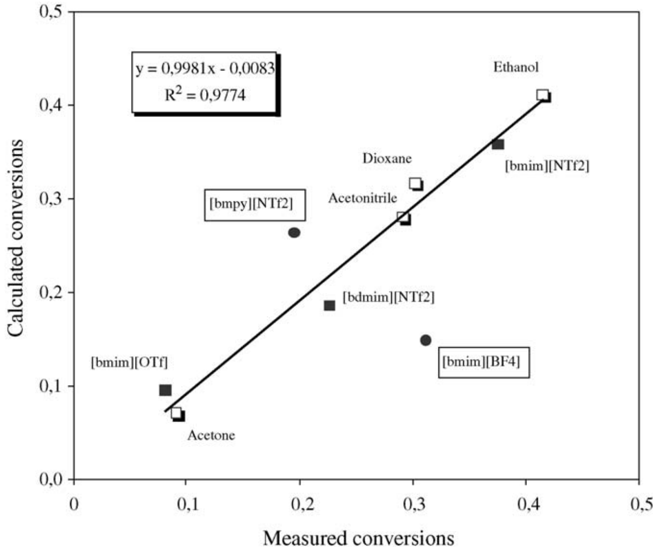
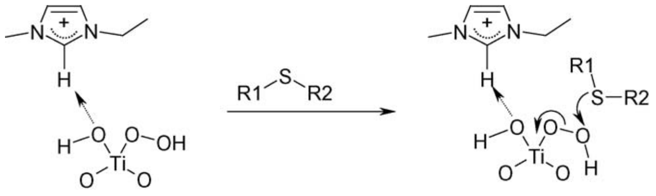


Fig. 9. Measured *vs*. calculated conversions for Ta-14 catalyst in sulfoxidation of **S3**.

conversions and Kamlet–Taft coefficients, using a linear regression method shown as Eq. (1):

$$\text{Conversion} = 1.343 - 1.121\pi^* + 0.625\alpha - 1.098\beta \qquad (1)$$

Fig. 9 shows a parity plot between the calculated conversions and the experimentally determined values for all the solvents studied. Whilst good agreement was found for all the molecular solvents and three of the ionic liquids poor agreement was found for [bmim][BF_4] and [bmpyrr][NTf_2]. For [bmpyrr][NTf_2] the measured conversion was considerable smaller than that expected, while for [bmim][BF_4] was much higher. Data presented in Table 2 allows a comparison between the different ILs. The values of π^* were very close for these solvents. This parameter, accounts for the solvent's dipolarity/polarizability and is in line to the fact these ILs belongs to the same family. Therefore the observed differences are likely to be associated with the α and β parameters. On first examination, the increase of β parameter leads to a decrease of the conversion. However, the values determined for [bdmim][NTf_2] and mostly for [bmpyrr][NTf_2] were out of the line. It is thus logical to consider that these two parameters correlate. In the case of both [bmpyrr][NTf_2] and [bdmim][NTf_2] the α parameter is smaller compared with [bmim][NTf_2] or [bmim][OTf] (0.427 *versus* 0.617 and 0.625, respectively) indicating a weaker ability for hydrogen bond donation. This property seems to have a key role in heterogeneous catalytic sulfoxidation in ILs, *via* activation of superficial peroxide [7] with strong hydrogen bonding activating the oxidant as illustrated in Scheme 3. Clearly the α parameter is not the only influence on the rate as for [bdmim][NTf_2] the α parameter is even smaller (0.381) than for [bmpyrr][NTf_2] yet the reaction rate is higher. Whilst the α parameter gives an indication of the hydrogen bond donation using a probe molecule, in a practical system other factors may also be important. For example, the cation geometry of IL can perturb an efficient activation of the superficial tantalum peroxide, and therefore result in lower reaction rates. In the case of [bdmim][NTf_2] the hydrogens at the C(4,5) positions are the most acidic and can hydrogen bond easily with the peroxide species. In constrast, in [bmpyrr][NTf_2] the acidic protons are at the C(2,5) positions each of which is sterically hindered by the quaternarised nitrogen centre. In addition, it is possible that a high number of protons which can form hydrogen bonds, may lead to a higher value of α than expected. Welton et al. inidicated that this may be true for the $[\text{bmpyrr}]^+$ cation where nine protons are available, albeit some only forming weak hydrogen bonds, which may be responsible for the higher value of α [18].



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

The behavior of [bmim][BF_4] should be associated to its intrinsic properties. Based on the α and β parameters of this IL a smaller conversion was expected. Therefore in this case, the measured conversion should be related to the traces of protic acids generated by anion hydrolysis, a phenomenon that was recently evidenced for $[BF_4]^-$ based ionic liquids [28]. The protic acids have a proven effect of acceleration over sulfoxidation reactions in ILs [7] thus overlapping the effect of the smaller β value.

The correlation line presented in Fig. 6 also includes molecular solvents, which show increasing conversions when π^* parameter decreased, correlated with variations in α and β parameters too. It should be noted that this comparison between the molecular and ionic solvents is just qualitative, since the nature of the interactions and constituents is very different.

For ILs, a high value of α and a small one of β, seem to describe an appropriate solvent for the investigated catalytic process. As it was pointed out above, for ILs π^* parameter is very similar due to their ionic nature. In the case of molecular solvents, since π^* are different, it is likely that all three parameters had a specific contribution. Hulea et al. [3] have found also a correlation between reaction rate and E_T^N parameter of the employed solvent.

As well as these parameters several other effects should be also considered. Viscosity may play an important role as well as the solvent solid interactions as well as the water miscibility. In addition, mass transport across the water IL boundary is strongly effected by the miscibility and therefore the [oxidant] will be different as well.

The reactions carried out in molecular solvents corresponded to moderate selectivities in oxidation of the pyrimidinic substrates (Table 2).

4. Conclusions

High surface area tantalum-based catalysts prepared either via sol–gel or grafting methods are effective catalysts in oxidation of different types of thioethers, using molecular or ionic solvents. The reaction rate of various thioethers is highly dependent of the substrate structure, and as expected, aliphatic thioethers react faster than aromatic and hetaromatic substrates. Excellent hydrogen peroxide efficiencies were obtained on these catalysts. In addition they presented a high stability the leaching being very small. In the case of grafted Ta-MCM-41, some agglomerates on the external surface occurred. After two catalytic runs, these leached and the catalyst behaved as the mixed oxides.

The use of the Kamlet–Taft coefficients allowed the calculation of a conversion function which fitted very well with the experimental data. The correlation between the Kamlet–Taft parameters and conversion was found for both types of solvents.

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