Modified Ta/MCM-41 catalysts for enantioselective oxidation of thioanisole

Marwa Fadhli,[a]* Ilyes Khedher[a] and José M. Fraile[b]*

[a] *Laboratoire de Chimie des Matériaux et Catalyse. Département de Chimie, Faculté des Sciences de Tunis, Université de Tunis El-Manar, Campus Universitaire Farhat Hached d'El-Manar, Tunis 2092, Tunisia.*

[b] *Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Facultad de Ciencias, CSIC-Universidad de Zaragoza, E-50009 Zaragoza, Spain.*

Abstract

Ta-MCM41 catalysts have been prepared by grafting of $Ta(OEt)_5$ on MCM41, pre-calcined at three different temperatures (550, 650 and 750°C). These solids have been modified with two chiral ligands: R-(+)-diethyl L-tartrate (DET) and R-(+)-diisopropyl L-tartrate (DIPT). The formation of the chiral tantalum species and their influence on the structure of MCM41 have been studied by several characterization techniques, such as XRD, FTIR, N_2 adsorption isotherms and MAS-NMR. The grafted tantalum species are always much less active than the homogeneous analogues in the oxidation of thioanisole (methyl phenyl sulfide) with either aqueous H_2O_2 or alkyl (*tert*-butyl, TBHP, or cumyl, CHP) hydroperoxides. The enantioselectivities obtained with the heterogeneous catalysts are also always lower than those obtained with the homogeneous ones under the same conditions, and the best results are obtained with the DIPT-modified solids, up to 25% ee. The calcination temperature of the support and the nature of the oxidant are also parameters that significantly affect the enantioselectivity. The recovered catalysts show an increase in the catalytic activity and a decrease in the enantioselectivity, in agreement with a loss of chiral tartrate, whereas the Si-O-Ta bond remains stable and recoverable.

Keywords: Tantalum; MCM-41; Enantioselective oxidation; Sulfoxide.

* Corresponding authors:

Marwa Fadhli, e-mail: marwafadhli@hotmail.fr

José M. Fraile, e-mail: jmfraile@unizar.es

1. Introduction

Since the first synthesis of MCM-41 was described in 1992 [1], many different types of mesoporous silica materials have been described [2]. Among a good number of different applications, they have been used as supports in heterogeneous catalysis [3,4], due to their unique features, such as the extraordinarily regular structure, with very high surface area, and very narrow pore size distribution, with an arrangement of regular parallel pores in the case of MCM-41, resembling in some way the honeycomb structure. The catalytic sites can be introduced into the framework of the mesoporous silica [5] or by anchoring the catalytic precursor on the surface silanol groups [6,7]. Tantalum is not among the most commonly used metals grafted on the surface of mesoporous materials, although the tantalum hydride species on MCM-41 have shown their usefulness as catalysts in the activation of methane [8] and the hydrogenolysis of alkanes [9].

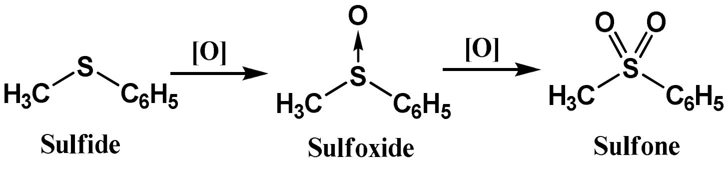
Chiral sulfoxides are very interesting compounds, useful as synthetic intermediates of various chemically, biologically, agrochemically active compounds [10]. They can be prepared in different ways, although the asymmetric sulfoxidation of sulfides is the most common methodology [10,11], using in many cases metal catalysts [12,13]. However, the number of examples of successful heterogeneous catalysts for enantioselective sulfoxidation is rather scarce. Polymer supported metalloporphyrins led to moderate to good enantioselectivities (up to 75% ee) but using PhIO as an oxidant [14]. However, due to sustainability issues, hydrogen peroxide and alkyl hydroperoxides (cumene, CHP, and *tert*-butyl, TBHP, hydroperoxides as the most common ones) are more interesting oxidants. Moderate to good enantioselectivities, in the range of 50-75% ee, have been obtained in the enantioselective sulfoxidation with H_2O_2 using different catalysts, such as WO_3 modified with cinchona alkaloids [15], polymer supported VO-Schiff base complexes [16], or Fe(salan) complexes encapsulated into the nanocages of mesoporous silicas [17]. In some cases the moderate enantioselectivities were improved by kinetic resolution in the over-oxidation to sulfone [15]. VO-salen complexes on silica have been much less efficient with regard to enantioselectivity [18,19].

Titanium complexes have been the most commonly immobilized catalysts for this purpose. Ti-binol has been supported on polystyrene [20], on an ionic liquid film deposited on a modified SBA-15 silica [21], or self-supported by using a polytopic binol ligand [22]. Very high enantioselectivities were obtained in the sulfoxidation with TBHP or CHP, combining the direct enantioselective sulfoxidation with a partial kinetic resolution by over-oxidation. The immobilized Ti-tartrate complexes, analogous to the classical homogeneous catalysts

[23], have been much less successful in the enantioselective sulfoxidation. Early attempts of immobilization on silica by titanium grafting [24], or modification of Ti-containing MCM-41 [25], showed that the best results were obtained with tartaric acid as chiral ligand and H_2O_2 as an oxidant, but in all cases low enantioselectivities were obtained. Better results (up to 58% ee) were obtained by intercalation of the Ti-tartrate complex in the interlayer space of double hydroxides [26].

Tantalum alkoxides supported on silica are able to decompose alkyl hydroperoxides [27] and even the modification with chiral tartrates promoted the enantioselective epoxidation of allylic alcohols [28]. More recently, tantalum alkoxides on mesoporous silica SBA-15 have shown high efficiency in the epoxidation of alkenes with aqueous H_2O_2 when the environment of the catalytic site is hydrophobic [29-31]. Recently, $TaCl_5$ and $Ta(OEt)_5$ have been described as excellent catalyst for sulfides oxidation with H_2O_2 in homogeneous phase, with selectivity for sulfoxide or sulfone depending on the catalyst and the reaction conditions (solvent, temperature, time) [32]. Tantalum containing heterogeneous catalysts have been also used in sulfoxidation reactions. Ta-Si mixed oxides prepared by sol-gel were tested in the sulfoxidation of 4,6-dimethyl-2-methylthiopyrimidine with different oxidants in a range of ionic liquids and organic solvents [33,34]. Hydrogen peroxide was much more efficient than TBHP, attributed to the steric hindrance of the bulky *tert*-butyl group in TBHP. A tantalum catalyst prepared by grafting of $Ta(OEt)_5$ on MCM-41 silica was also prepared and tested, with an analogous behavior to that of the mixed oxides [33,34].

In the present study, $Ta(OEt)_5$ has been grafted on MCM-41 silica, treated at different temperatures and it has been tested as catalyst in the oxidation of thioanisole (Scheme 1) using aqueous hydrogen peroxide and alkyl hydroperoxides (cumene and *tert*-butyl hydroperoxides, CHP and TBHP) in organic medium as oxidizing agents. These solids have been also modified with chiral tartrates, R-(+)-diethyl and R-(+)-diisopropyl L-tartrates (DET and DIPT), in an attempt to obtain methyl phenyl sulfoxide in an enantioselective manner.



Scheme 1. Oxidation of thioanisole.

2. Experimental

2.1 Preparation of catalysts

CTMAB (cetytrimethylammonium bromide, Aldrich) was dissolved in distilled water at 40°C until clear solution; TEOS (tetraethylorthosilicate) and NH_4OH (28 % wt) were added. The molar composition of the mixture was TEOS : CTMAB : NH_4OH : H_2O = 1 : 0.2 : 8 : 114. The mixture was stirred for 2 h at room temperature. The resulting solid was separated by simple filtration and washed several times with distilled water. The solid was dried at 110°C under vacuum for 72 h and then calcined in O_2 flow at a heating rate of 1°C/min to remove the surfactant from the pores of MCM-41. Three different temperatures (550, 650 and 750°C) were tested and the resulting supports are denoted as MCM_{550}, MCM_{650} and MCM_{750}.

A mixture of $Ta(OEt)_5$ (0.1625 g, 0.4 mmol) and calcined MCM-41 (1 g) in anhydrous toluene (20 mL) was refluxed for 24 h under Ar atmosphere. The resulting solid was vacuum-filtered, successively washed with dry dichloromethane and diethyl ether, and then dried at 110°C under vacuum. The resulting catalysts are referred to as Ta-MCM_{550}, Ta-MCM_{650} and Ta-MCM_{750}.

Diethyl L-tartrate (DET) or diisopropyl L-tartrate (DIPT) (0.5 mmol) was added to a suspension of Ta-MCM (1 g) in anhydrous toluene (20 mL), and the mixture was refluxed for 12 h under inert atmosphere. After cooling at room temperature, the solid was filtered, thoroughly washed with anhydrous dichloromethane, and dried at 50ºC under vacuum overnight prior to use. The chiral catalysts are denoted as DET-Ta-MCM_{temp} or DIPT-Ta-MCM_{temp}.

2.2 Characterization methods

Powder small angle X-ray diffraction patterns were recorded using Cu Kα radiation (40 kV and 30 mA) from $2\theta = 1°$ up to $2\theta = 10°$. BET surface area and pore size distribution were determined from the N_2 adsorption-desorption isotherms at 77 K using a micrometrics ASAP 2000 apparatus. Infrared spectra of samples were recorded in the range of 4000-400 cm^{-1} with discs of solids mixed with dry KBr on a Perkin-Elmer FT-IR paragon 1000PC spectrometer. The tantalum content was carried out by plasma atomic emission spectroscopy (ICP-OES) using a Thermo Elemental IRIS Intrepid spectrometer. Diffuse reflectance UV-Vis (DR-UV) spectra were recorded on a Unicam UV4 spectrometer equipped with a labsphere diffuse reflectance attachment. Elemental analysis (CHNS) was performed on a Perkin Elmer 2400 elemental analyzer. MAS NMR spectra were recorded in a Bruker Avance III WB400 spectrometer with 4 mm zirconia rotors spun at magic angle in N_2 at 10 kHz. ^1H-^{13}C CP spectra (12000-20000 scans) were measured using a ^1H $\pi/2$ pulse length of 3 μs, with a contact time of 3 ms, and spinal64 proton decoupling sequence of 5.3 μs pulse length, with 7 s recycle delay.

2.3 Catalytic tests

Homogeneous reactions with alkyl hydroperoxides:

To a solution of methyl phenyl sulfide (124 mg, 1 mmol), ethyl benzoate (internal standard, 15.2 mg), and $Ta(OEt)_5$ (4.9 mg, 0.012 mmol) in 10 mL of anhydrous dichloromethane under Ar atmosphere, TBHP (*tert*-butyl hydroperoxide, 90.1 mg of a 5.5 M solution in decane, 1 mmol) or CHP (cumene hydroperoxide 88%, 152.2 mg, 1 mmol) was added. The reaction mixture was stirred at room temperature and monitored by GC (sulfide conversion and sulfoxide and sulfone yields).

In the case of enantioselective reactions, a solution of $Ta(OEt)_5$ (4.9 mg, 0.012 mmol) and either diethyl L-tartrate (DET, 3.1 mg, 0.015 mmol) or diisopropyl L-tartrate (DIPT, 3.5 mg, 0.015 mmol) in 10 mL of anhydrous dichloromethane under Ar atmosphere was stirred at room temperature for 1h. Then methyl phenyl sulfide, the internal standard and the oxidant were added as described above. The enantiomeric excess was determined by HPLC with a Chiralpack OD-H column.

Homogeneous reactions with hydrogen peroxide:

To a solution of methyl phenyl sulfide (124 mg, 1 mmol), ethyl benzoate (internal standard, 15.2 mg), and $Ta(OEt)_5$ (4.9 mg, 0.012 mmol) in 10 mL of anhydrous methanol under Ar atmosphere, aqueous H_2O_2 (60% wt, 68.9 mg, 1 mmol). was added. The reaction mixture was stirred at room temperature and monitored by GC.

In the case of the enantioselective reactions, a solution of $Ta(OEt)_5$ (4.9 mg, 0.012 mmol) and either diethyl L-tartrate (DET, 3.1 mg, 0.015 mmol) or diisopropyl L-tartrate (DIPT, 3.5 mg, 0.015 mmol) in 10 mL of anhydrous methanol under Ar atmosphere was stirred at room temperature for 1h. Then methyl phenyl sulfide, the internal standard and aqueous H_2O_2 were added as described above. The enantiomeric excess was determined by HPLC with a Chiralpack OD-H column.

Heterogeneous reactions:

The solid catalyst (0.012 mmol Ta, around 30 mg) was added to a solution of methyl phenyl sulfide (124 mg, 1 mmol) and ethyl benzoate (internal standard, 15.2 mg) in 10 mL of anhydrous dichloromethane under Ar atmosphere. Then TBHP (*tert*-butyl hydroperoxide, 90.1 mg of a 5.5

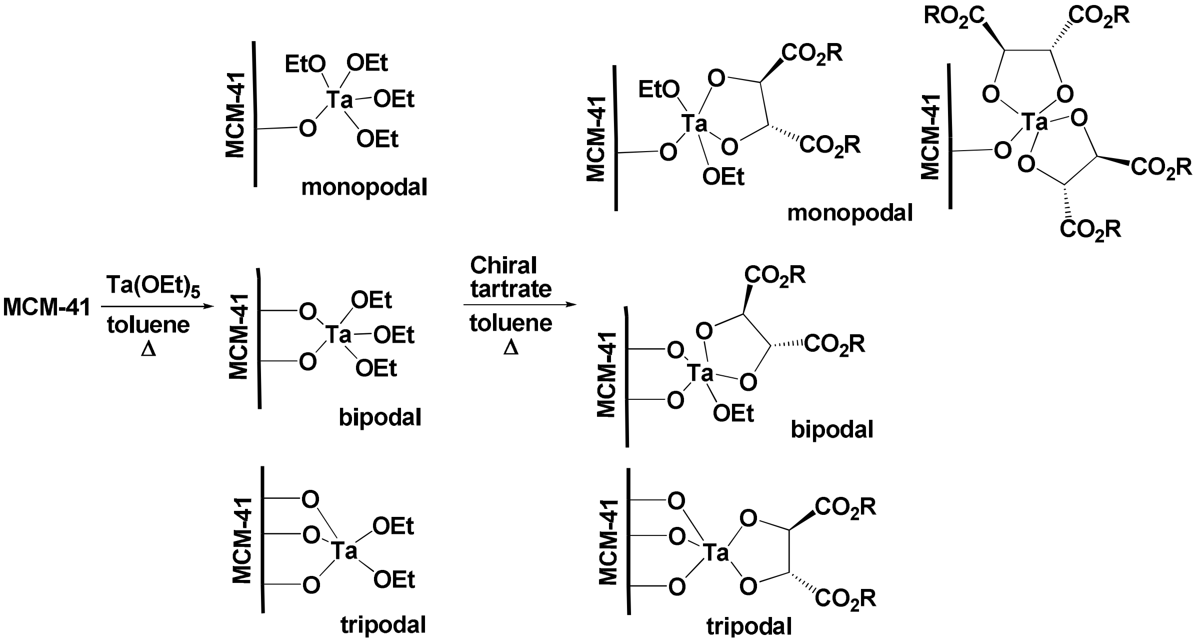
M solution in decane, 1 mmol) or CHP (cumene hydroperoxide 88%, 152.2 mg, 1 mmol) was added, the reaction mixture was stirred at room temperature and monitored by GC. At the end of the reaction, the solid was separated by filtration, washed several times with CH_2Cl_2 and then dried at 50°C under vacuum.

In the case of using H_2O_2 as an oxidant, the procedure was the same but using anhydrous methanol as solvent and aqueous H_2O_2 (60% wt, 68.9 mg, 1 mmol). was added to the reaction mixture.

3. Results and discussion

3.1 Preparation and characterization of the catalysts

The grafting of $Ta(OEt)_5$ on MCM-41 surface may give rise to three types of species, monopodal MCM-$Ta(OEt)_4$, bipodal MCM=$Ta(OEt)_3$ and tripodal MCM≡$Ta(OEt)_2$ (Scheme 2), as in the case of $Ti(OR)_4$ grafting [35]. In principle this situation should be less problematic than in the case of Ti [36], as in all the surface species exist the possibility of chelation with at least one molecule of tartrate [28] (Scheme 2).



Scheme 2. Preparation of catalysts by immobilization of $Ta(OEt)_5$ and subsequent modification with tartrates (R = Et, DET; R = ^{i}Pr, DIPT).

The X-ray diffraction patterns of the different mesoporous solids (with and without tantalum) are shown in Figure 1. The low angle XRD patterns of calcined MCM_{550}, MCM_{650} and MCM_{750} were compared with those of Ta- MCM_{550}, Ta-MCM_{650} and Ta-MCM_{750}. The three diffraction peaks, (100) (110) and (200), typical of the hexagonal structure of MCM-41 are well preserved at increasing calcination temperatures up to 750°C. However the incorporation of tantalum (V) ethoxide species on the silica materials did result in a decrease in long range order of MCM-41, detected by the decrease in the (100) diffraction line intensity, as well as the broadening of the (110) and (200) diffraction peaks, indicating a partial degradation of the hexagonal structural order, in agreement with the shift of the (100) diffraction line towards higher 2θ values.

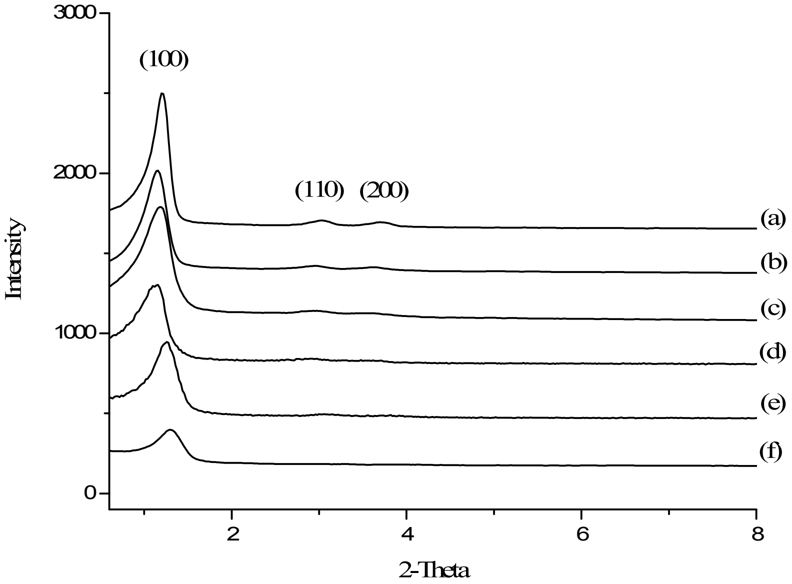


Figure 1.The low-angle XRD patterns of the different mesoporous solids: a) MCM_{550}, b) MCM_{650}, c) MCM_{750}, d) Ta-MCM_{550}, e) DET-Ta-MCM_{550}, f) DIPT-Ta-MCM_{550}.

The textural properties of the catalysts have been determined by the absorption-desorption isotherms of N_2 at 77 K (Figure 2). According to the IUPAC classification, MCM-41 and Ta-MCM-41 materials show type IV isotherms and H1 hysteresis. Surface area, pore volume and mean pore diameter values (Table 1) of the MCM-41 supports are in good agreement with those reported in the literature [1], with slightly decreasing values with the increasing calcination temperature from 550 to 750ºC. The amount of grafted tantalum is always around 0.4 mmol g^{-1} (Table 1), indicating that the grafting of the precursor is complete. As expected [37], the tantalum grafting significantly decreases the surface area (by more than 100 m^2 g^{-1}), pore volume (by more than 0.1 cm^3 g^{-1}), and mean pore diameter (by 0.2-0.3 nm, except in the case of MCM$_{550}$), in agreement with a grafting of the Ta(OEt)$_x$ species on the surface of the mesopores and the loss of long range order. The average surface density of tantalum sites is only 1 site per 4 nm^2, which can be due either to a very good dispersion of the sites or to a limitation in the diffusion inside the mesoporous network and a concentration of the sites in the pore mouths. The latter would explain better the significant changes in the textural properties with a so low functionalization. Moreover, the modification with chiral tartrates reduces even more the values of surface area, pore volume and mean pore size.

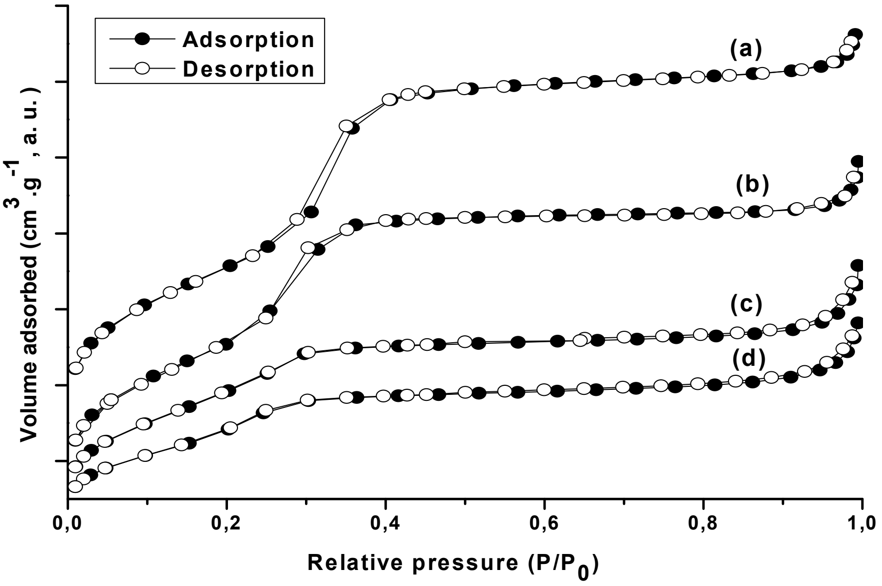


Figure 2. N$_2$ adsorption-desorption isotherms at 77 K of the different mesoporous solids: a) MCM$_{550}$ b) Ta-MCM$_{550}$, c) DET-Ta-MCM$_{550}$, d) DIPT-Ta-MCM$_{550}$.

Carbon analyses (Table 1) of the unmodified catalysts are compatible with an ethoxide/Ta ratio of 3.5, indicating the presence of monopodal (4 ethoxides) and dipodal (3 ethoxides) species. Unexpectedly, this ratio is slightly lower in Ta-MCM650 (2.7). The treatment with chiral tartrates increases the carbon content of the solids, although it is difficult to estimate the true content of tartrate. In case of the properly formation of a chelate, two ethoxide groups (4 carbon atoms) would be substituted by a tartrate (8 carbon atoms in DET, 10 carbon atoms in DIPT). The estimation in such case (Table 1) gives values of tartrate/Ta ratio in the order of 0.7-1.3 for Ta-MCM$_{550}$ and Ta-MCM$_{650}$, whereas this ratio is much lower (0.3) in the solid calcined at 750ºC. This result is surprising taking into account that the higher calcination temperature should favor the formation of larger amount of monopodal MCM-Ta(OEt)$_4$ species, able to accommodate two tartrate molecules. However, the EtO/Ta ratio is not higher in Ta-MCM_{750}, whereas at the same time it is the solid with lower pore volume and the one with the textural properties most deeply modified upon treatment with tartrates, in spite of the lower amount of chiral ligand immobilized, which seems to indicate some kind of restriction to diffusion of tartrates through the pore system.

Table 1. Textural properties[a] and elemental analysis of the tantalum catalysts.

Sample	S_{BET} (m^2/g)	Vp (cm^3/g)	Dp (nm)	Ta (mmol/g)	C (mmol/g)	C/Ta	tartrate/ Ta[b]
MCM_{550}	1001	0.76	3.03	–	–	–	–
MCM_{650}	945	0.75	2.87	–	–	–	–
MCM_{750}	925	0.64	2.74	–	–	–	–
Ta-MCM_{550}	876	0.65	3.01	0.39	2.71	7.0	–
Ta-MCM_{650}	784	0.63	2.52	0.41	2.24	5.5	–
Ta-MCM_{750}	822	0.49	2.54	0.39	2.77	7.1	–
DET-Ta- MCM_{550}	842	0.60	2.45	0.38	4.38	9.6	0.7
DET-Ta- MCM_{650}	743	0.54	2.60	0.40	5.09	10.6	1.3
DET-Ta- MCM_{750}	782	0.46	2.03	0.38	3.86	8.5	0.3
DIPT-Ta- MCM_{550}	732	0.51	2.32	0.38	6.25	13.7	1.1
DIPT-Ta- MCM_{650}	804	0.53	2.2	0.40	4.68	9.8	0.7
DIPT-Ta- MCM_{750}	797	0.44	1.99	0.38	4.08	9.0	0.3

[a] S_{BET} = surface area; V_p = pore volume; D_p = mean pore diameter determined by the BJH (Barrett–Joyner–Halenda) method. [b] Estimated from the carbon content of the unmodified Ta-MCM solid and considering the substitution of 2 EtO by one DET or DIPT molecule.

Tantalum containing materials were also characterized by FT-IR between 4000 and 400 cm^{-1} (Figure 3). The spectra of calcined MCM supports include a large broad band between 3700 and 3000 cm^{-1} which is associated to the O-H stretching of the hydrogen-bound silanol groups. In addition, they also show a very large and intense band centered at 1100 cm^{-1} due to the Si-O-Si linkage. The band at 960 cm^{-1} is attributed to Si-O stretching of the silanol groups. The band at 1630 cm^{-1} is due to deformation vibrations of absorbed water molecules. The peak near 800 cm^{-1} was attributed to the symmetric stretching of Si-O-Si [38].

After $Ta(OEt)_5$ grafting, the FT-IR spectrum shows a series of bands at 3000-2800 cm^{-1} corresponding to the aliphatic C-H bonds of the remaining ethoxy groups. The band corresponding to the Si-O-metal bond appears at 910-970 cm^{-1}, for example in the case of Si-

O-Ti [39] but also in that of Si-O-Ta [40,41]. However, it overlaps with the band corresponding to the remaining Si-OH groups of the support. After modification with the chiral tartrates, a new band appears at 1730 cm^{-1} corresponding to the C=O bond of carboxylic esters, in principle without coordination to Ta (1738 cm^{-1} in solution spectra of Ti(DIPT) complexes [42]), whereas the coordinated C=O bond (1638 cm^{-1} [42]) would be masked by the water band.

The formation of Ta-tartrate complexes on the solid surface can be studied by solid state NMR. From the results of Ti-tartrate complexes in solution [42,43], the most relevant change in the NMR spectrum is the shift of the methine signal (-OOC-*C*HOH-) from ≈70 ppm in the free ligand to ≈80-86 ppm in the form –*C*HO-Ti. In the case of the carboxylate groups, uncoordinated ones appear at around 170 ppm, whereas the coordinated ones are shifted 10-15 ppm downfield. These features are also observed in the solid state NMR of complexes with different nuclearity ($Ti_3(DIPT)_3$ and $Ti_4(DIPT)_4$) [44]. In the case of DET-Ta-MCM solids, all of them show similar NMR spectra (Figure 4), irrespective from the calcination temperature, and completely different from the spectrum of DET physisorbed on MCM_{750}. Two broad signals at 183 and 171 ppm fit well with the presence of both coordinated and uncoordinated carboxylate groups, respectively, and in both cases with restricted mobility in comparison with the adsorbed DET. A signal at 84 ppm clearly indicates the formation of CH-O-Ta bonds, whereas the presence of the signal at 72 ppm points to a possible non-chelating structure (see Figure 4), but again the difference in line broadening seems to preclude the presence of physisorbed DET on the silica surface. At least two different OEt groups are present (signals at 60 and 12 ppm), probably coming from coordinated and uncoordinated –COOEt, and the remaining Ta-OEt species. The spectrum of DIPT-Ta-MCM solids is very similar (Figure 4), showing a similar arrangement around the Ta centers. Taking into account this possible coordination of tartrates to Ta, the estimation of the number of tartrate moieties on the solid is even more uncertain than expected.

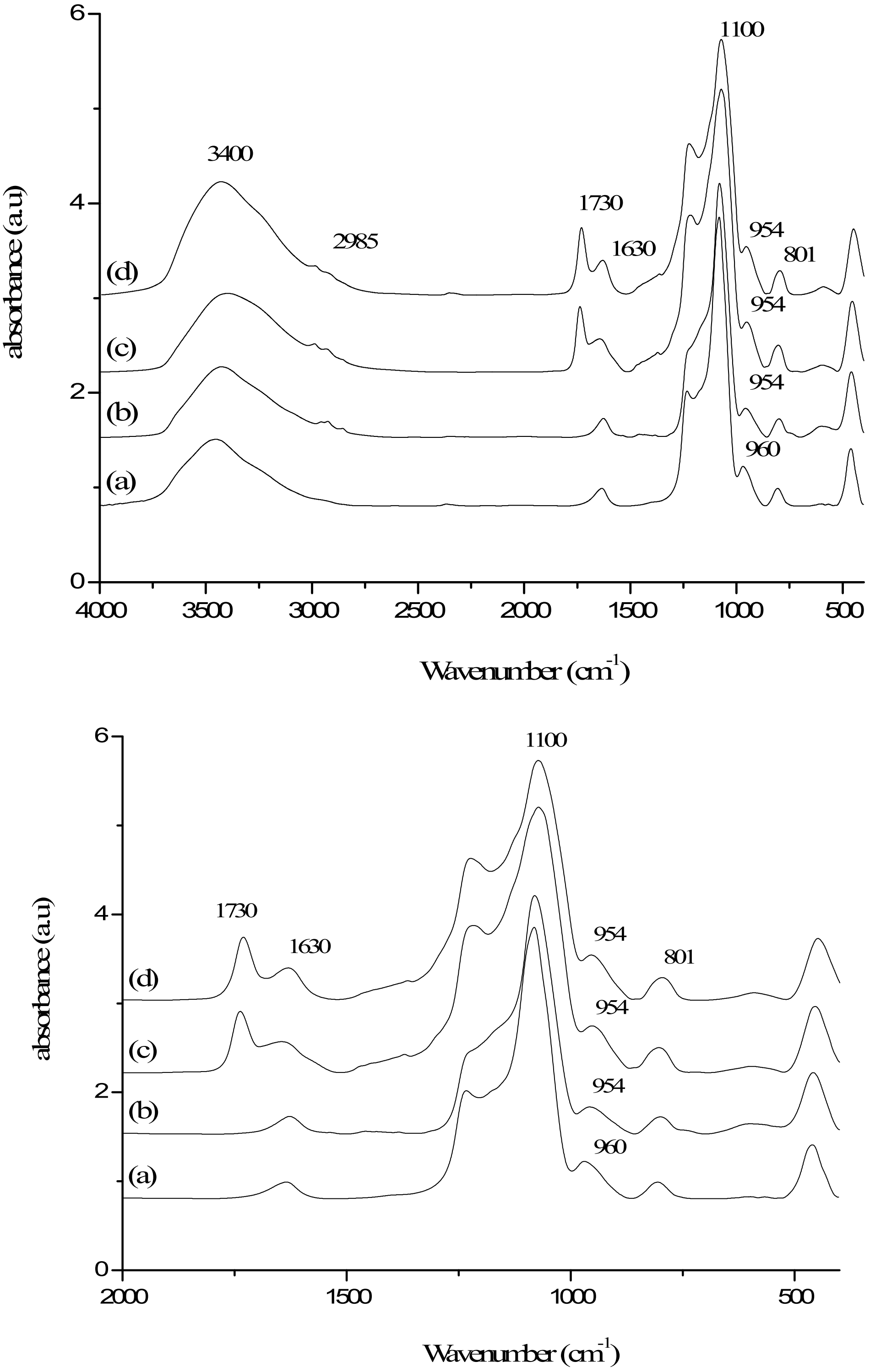


Figure 3. FT-IR spectra of: (a) MCM_{550}, (b) Ta-MCM_{550}, (c) DET-Ta-MCM_{550}, and (d) DIPT-Ta-MCM_{550}.

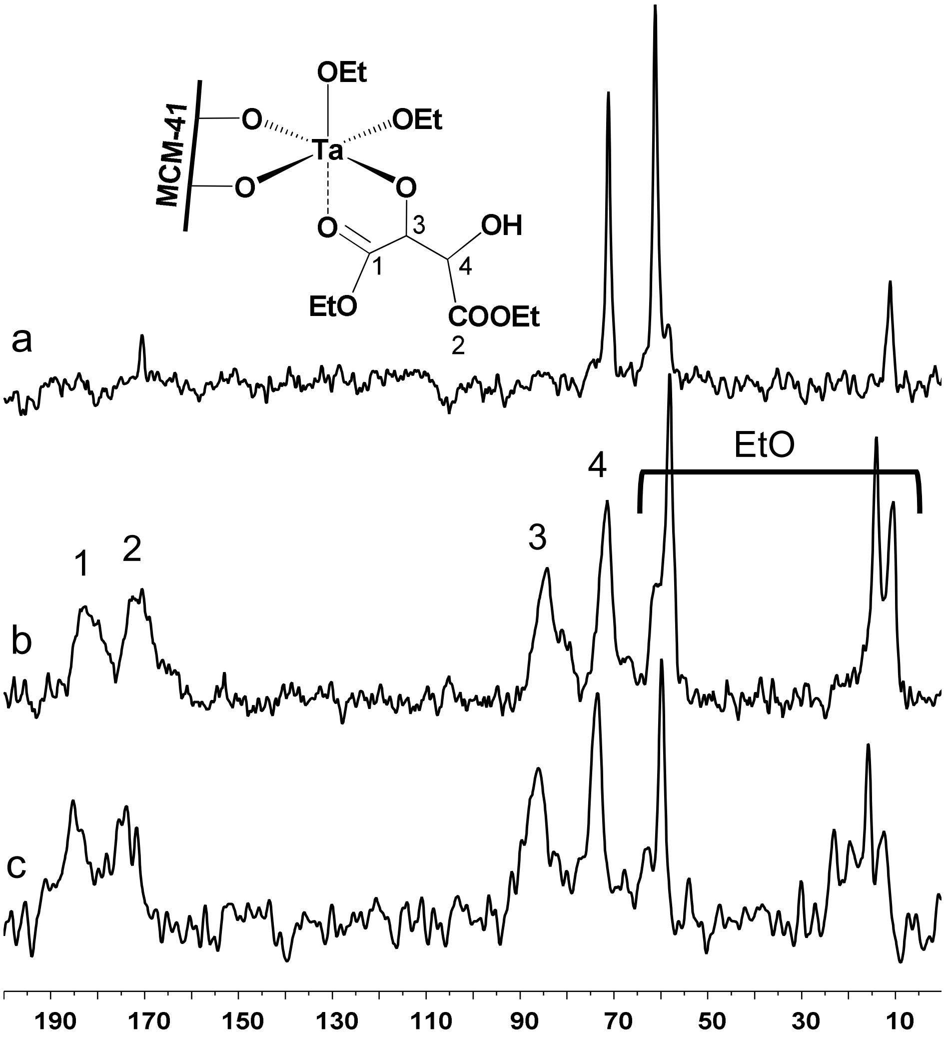


Figure 4. CP-MAS ^{13}C-NMR spectra: a) DET physisorbed on MCM$_{750}$, b) DET-Ta-MCM$_{550}$, c) DIPT-Ta-MCM$_{750}$, with the proposed structure for the coordination of DET.

3.2 Tantalum catalyzed oxidation of thioanisole

These catalysts were tested in the oxidation of thioanisole with three different oxidants, namely aqueous hydrogen peroxide and two alkyl hydroperoxides (*tert*-butyl hydroperoxide, TBHP, and cumyl hydroperoxide, CHP) in organic medium. The reaction solvent was changed, methanol for H_2O_2 and dichloromethane for alkyl hydroperoxides, in order to allow the solubility of the oxidant and the sulfide.

First of all the catalytic performance of the unmodified Ta-MCM solids was tested and compared with that of the precursor $Ta(OEt)_5$ in solution. Some relevant results are represented in Figure 5. As can be seen, the Ta catalysts are more efficient in the oxidation with H_2O_2 than with alkyl hydroperoxides, in agreement with the results reported in the literature [33]. A Ta(V)(η^2-O_2) species, stabilized by hydrogen bonding, has been proposed as the intermediate in oxidation reactions [30], and the alternative Ta-O-OR formed with alkyl hydroperoxides is probably less reactive. Moreover, in the case of CHP, the homogeneous reaction is less selective, from 82% sulfoxide selectivity at the beginning of the reaction up to only 56% selectivity at the end (after 6h most of the oxidant is consumed in the sulfoxide oxidation to sulfone), whereas the fast reaction with H_2O_2 leads to a 97% sulfoxide selectivity. The heterogeneous catalysts are less efficient than the homogeneous precursor, and also less selective with H_2O_2, around 80% sulfoxide selectivity, as expected for a slower reaction. However, the reaction with hydroperoxides almost completely stops after 5-6 h and oxidant consumption is only 40-50%, with sulfoxide selectivities ranging from 75 to 82%. The modification with the chiral tartrates should produce a variation in the kinetics of the oxidation, due to both steric and electronic effects. In fact this is observed (Figure 6) with all the oxidants tested. With alkyl hydroperoxides (TBHP has been chosen as example in Figure 6) the effect of both tartrates is similar, with a decrease in the initial fast rate of the unmodified solid and then a similar slow rate for longer reaction times. The sulfoxide selectivity is higher in the modified solids, as expected for the slower reactions, with values >98% for oxidations with TBHP and >90% in most of cases with CHP (see below). With H_2O_2 the effect of modification with tartrates is also similar, with slower reaction rates and higher sulfoxide selectivities. A rather surprising difference is that in general the modification with DET has a more pronounced effect than the modification with DIPT. Two possible explanations for this observation will be exposed below.

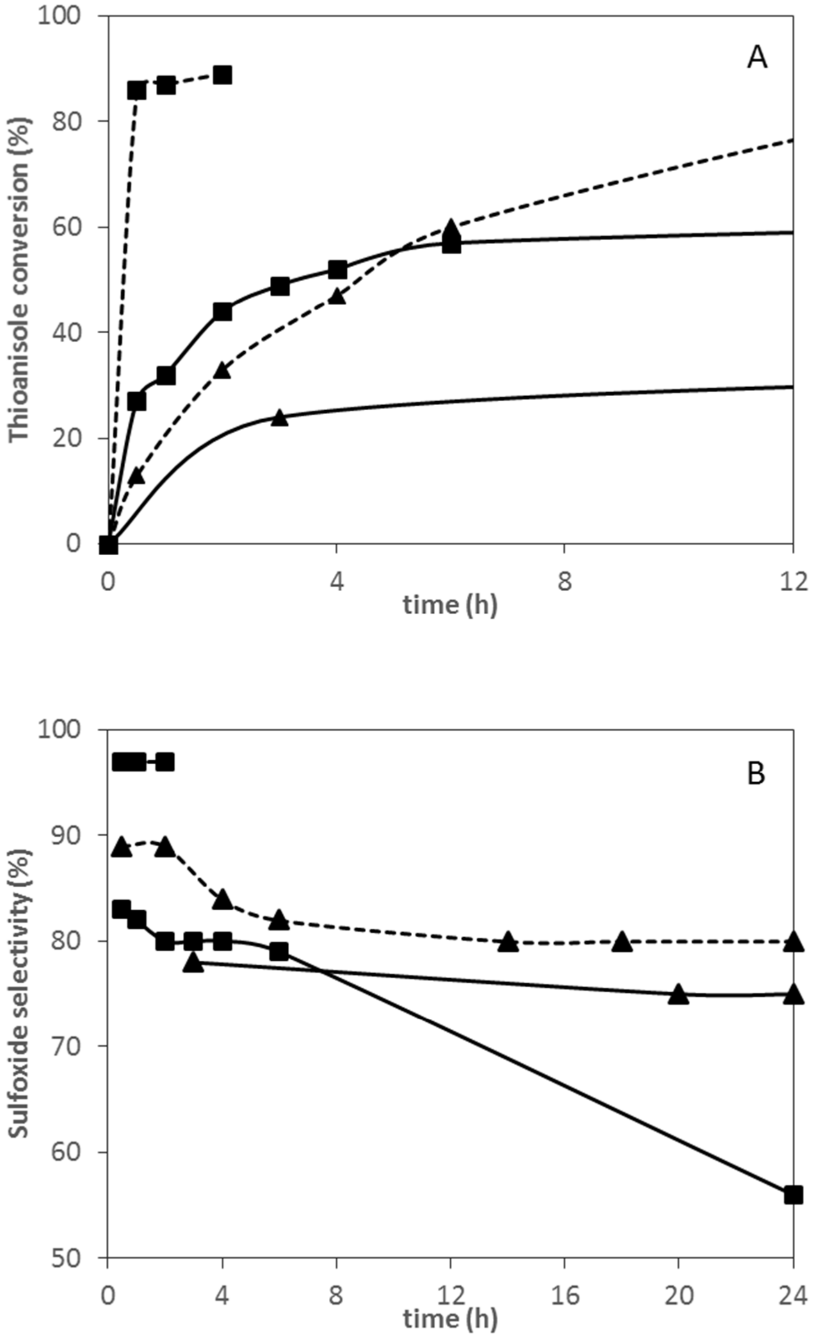


Figure 5. Thioanisole conversion (A) and sulfoxide selectivity (B) in the oxidation with H_2O_2 (dashed line) and CHP (continuos line), catalyzed by $Ta(OEt)_5$ (■) and Ta-MCM$_{550}$ (▲). Reaction conditions: 1 mmol thioanisole, 1 mmol oxidant, 0.012 mmol Ta, 10 mL solvent (methanol for H_2O_2, dichloromethane for CHP), at room temperature.

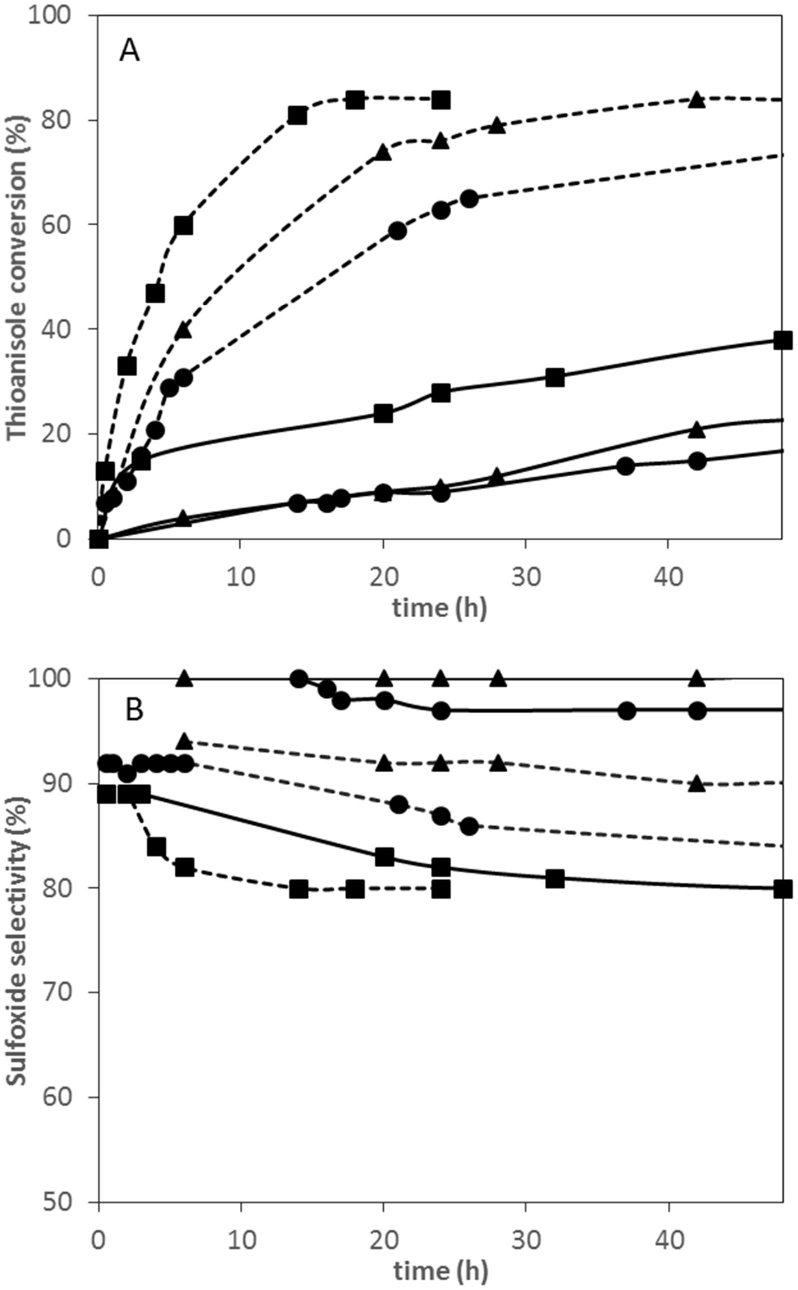


Figure 6. Effect of the modification with chiral tartrates on thioanisole conversion (A) and sulfoxide selectivity (B) in the oxidation with H_2O_2 (dashed line) and TBHP (continuos line), catalyzed by Ta-MCM$_{550}$: unmodified solid (■), modified with DET (●) and with DIPT (▲). Reaction conditions: 1 mmol thioanisole, 1 mmol oxidant, 0.012 mmol Ta, 10 mL solvent (methanol for H_2O_2, dichloromethane for TBHP), at room temperature.

The calcination temperature of the MCM41 support has also some effect, but it is different depending on the modification of the Ta sites and the oxidant used in the catalytic reaction (Figure 7). With no modification with tartrate, the Ta-MCM catalysts behave in the order 550 > 650 > 750. The Ta-MCM$_{550}$ keeps its better performance after modification with chiral tartrates in the oxidations with H_2O_2. In the case of oxidation with alkyl hydroperoxides there is not a clear relationship between the activity and the calcination temperature. With TBHP Ta-MCM_{550} is always clearly worse than the other two solids, whereas with CHP Ta-MCM_{750} and Ta-MCM_{550} behave in a similar way when modified with DET, and Ta-MCM_{550} is the best support when modified with DIPT.

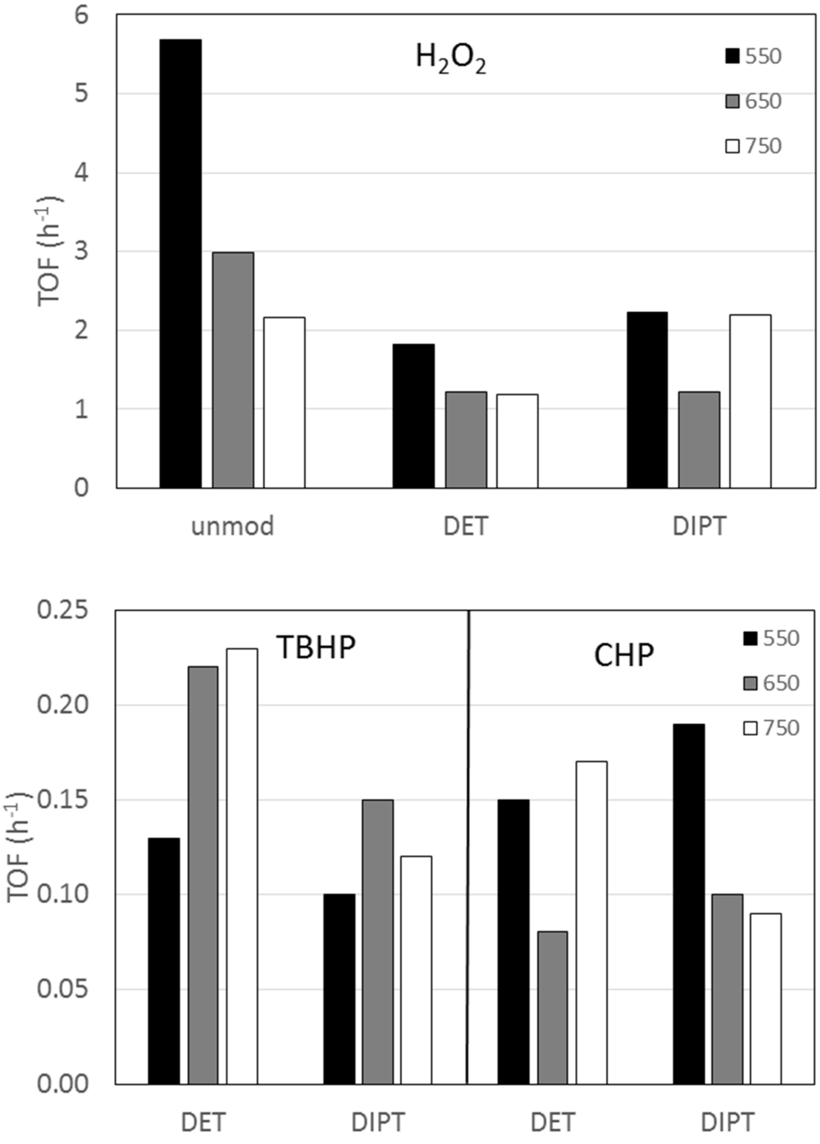


Figure 7. Effect of the calcination temperature on the catalytic activity (TOF calculated with the linear part of the conversion vs time plots) of the Ta-MCM solids with the three oxidants. Reaction conditions: 1 mmol thioanisole, 1 mmol oxidant, 0.012 mmol Ta, 10 mL solvent (methanol for H_2O_2, dichloromethane for TBHP and CHP), at room temperature.

Regarding enantioselectivity, the performance of the supported catalysts was compared with that of the corresponding Ta-tartrate in homogeneous phase, prepared by addition of the chiral tartrate to the solution of $Ta(OEt)_5$. The results are summarized in Figure 8. In homogenous phase the enantioselectivities obtained are in the range of 28-34% ee with DET and 29-38% ee with DIPT, showing a minor influence of both the type of tartrate and the nature of the oxidant, either H_2O_2 or alkyl hydroperoxides. Enantioselectivities obtained with the heterogeneous catalysts are always lower than in solution, and in general better and more consistent results are obtained with DIPT-modified solids. The oxidant has an important effect in that case, with enantioselectivities in the order H_2O_2 > TBHP > CHP, and the same is true with respect to the calcination temperature, as MCM_{650} is the best support that allows obtaining the highest enantioselectivities, namely 16% ee with CHP, 22% ee with TBHP, and 25% ee with H_2O_2.

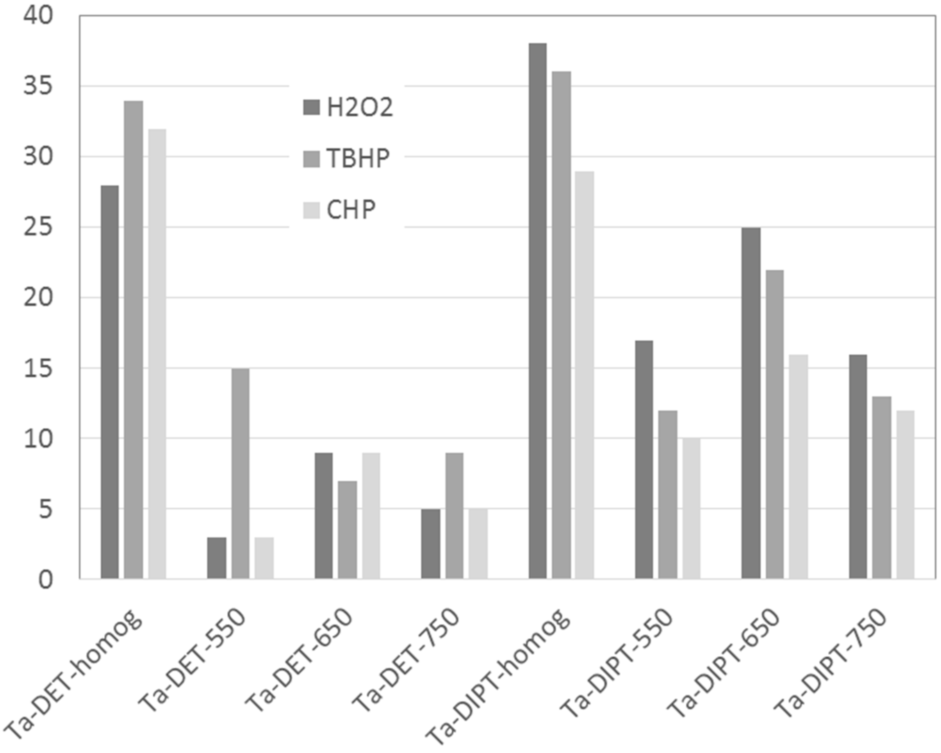


Figure 8. Enantiomeric excess (measured at maximum thioanisole conversion) of methyl phenyl sulfoxide obtained in the tantalum catalyzed oxidations of thioanisole. Reaction conditions: 1 mmol thioanisole, 1 mmol oxidant, 0.012 mmol Ta, 10 mL solvent (methanol for H_2O_2, dichloromethane for TBHP and CHP), at room temperature.

As the reaction is slower in the presence of the chiral tartrate, the reaction rate should give an indication about the degree in the modification of the Ta sites with tartrate ligand. In fact, when the enantioselectivity of the oxidation with TBHP is represented vs TOF (calculated from the initial data of conversion) a linear correlation is obtained (Figure 9). The extrapolation to TOF = 0 gives a maximum enantioselectivity of 27% ee, lower than the 36% ee obtained with the homogeneous catalyst. This type of correlation cannot be observed either with CHP, as the variations in both reaction rates and enantioselectivities are lower, or H_2O_2, whose results are more disperse. In this case it might be possible that sites in the most inner part of the pores, not modified with the chiral ligand due to accessibility problems, would be however accessible to the reagents, participating in the reaction in this way in the reaction.

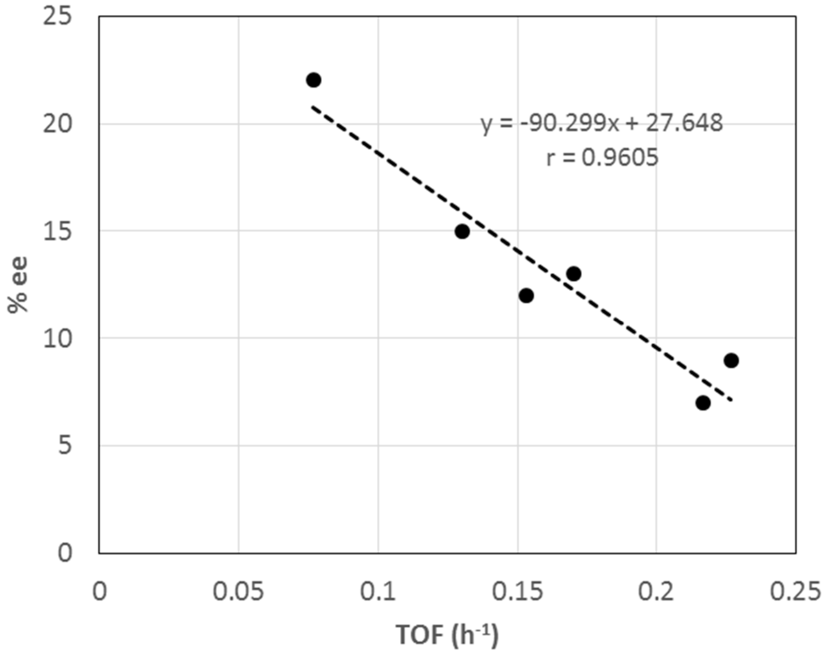


Figure 9. Correlation between % ee and the initial TOF in the oxidation of thioanisole with TBHP promoted by the heterogeneous catalysts.

The catalysts were recoverable in all the cases, with tantalum contents identical to those of the freshly prepared catalysts (within the experimental error of the analysis). However, the recovered catalysts were more active than the fresh ones, as can be seen in Figure 10, with activities very similar to that of the unmodified Ta-MCM solids, which seems to indicate that the tartrate is lost during the first run. Elemental analysis of the recovered catalysts show a significant sulfur content, from 0.5 to 1.3% S, with an increase in the carbon content. In fact, the CP-MAS ^{13}C-NMR spectrum of the recovered samples (Figure 11) shows the presence of oxidized sulfur compounds, as demonstrated by the signal at 47 ppm, although it is difficult to assign to either sulfoxide or sulfone. Although the signals corresponding to the tartrate also remain on the solid, the intensity seems to be reduced in comparison with the spectrum of the fresh catalyst. After thorough washing with dichloromethane, the sulfur content is eliminated and the carbon content is reduced to values below those of the starting material, confirming in this way the decomplexation of tartrate from the tantalum sites, either by the solvent methanol or by water produced in the reaction. In the case of oxidations with alkyl hydroperoxides (TBHP and CHP) the same effect is observed, although the increase in activity after recovery is less significant due to the low activity of the unmodified solids. As enantioselectivity is also reduced to almost zero (values up to 4% ee were obtained) the loss of chiral tartrate can be proposed, in this case promoted by the hydroperoxide and/or the concomitant produced alcohol, *tert*-butanol or cumyl alcohol.

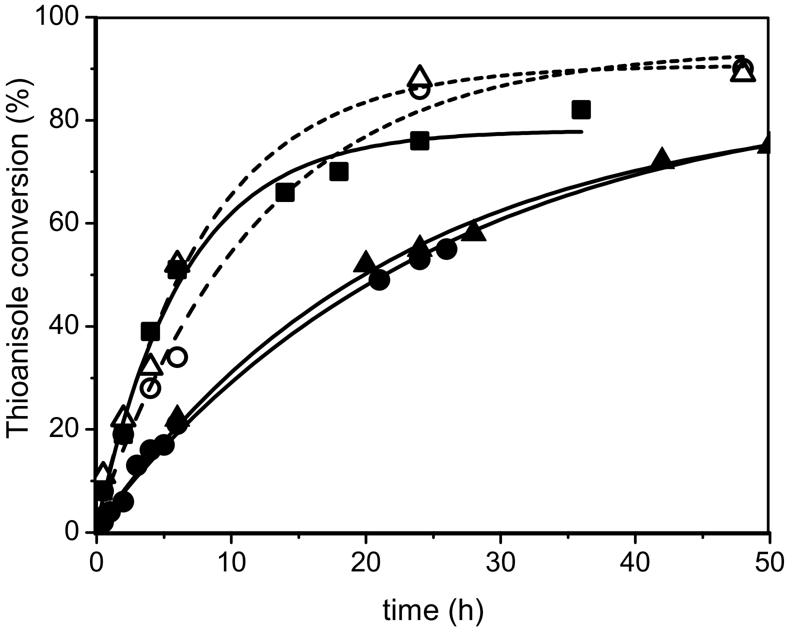


Figure 10. Thioanisole conversion in the oxidation with H_2O_2 catalyzed by DET-Ta-MCM$_{650}$ (●) and DIPT-Ta-MCM$_{650}$ (▲) in the first (continuous) and second (dashed) run, in comparison with unmodified Ta-MCM$_{650}$ (■). Reaction conditions: 1 mmol thioanisole, 1 mmol oxidant, 0.012 mmol Ta, 10 mL methanol, at room temperature.

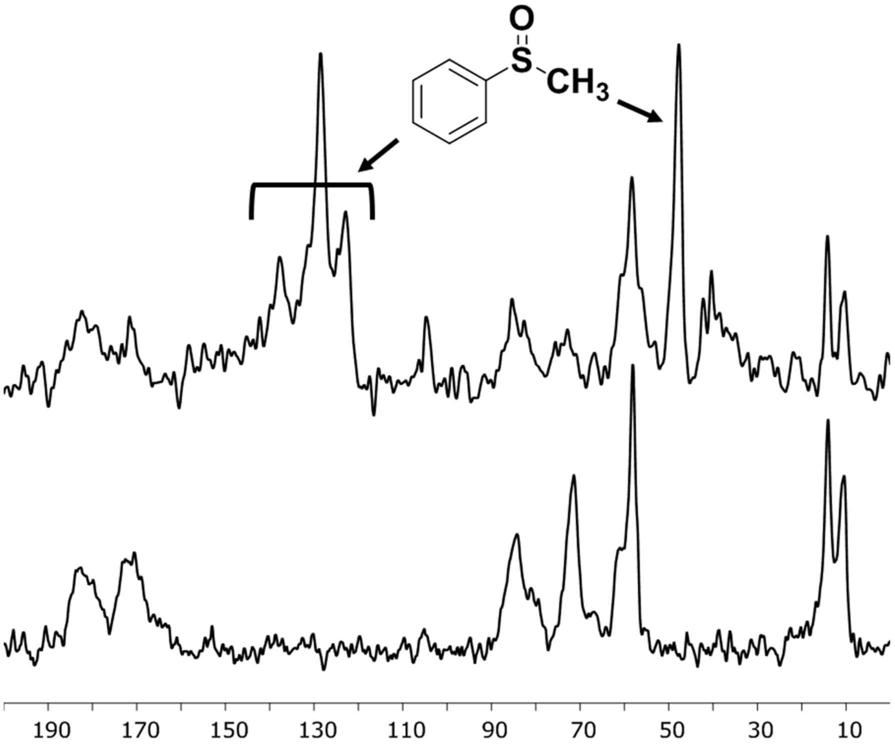


Figure 11. CP-MAS ^{13}C-NMR spectra of DET-Ta-MCM$_{550}$ (bottom) and the same solid used in the oxidation of thioanisole (top). The signals corresponding to the adsorbed sulfoxide are outlined.

Conclusion

Tantalum sites have been efficiently introduced in MCM41 by post-synthesis modification with Ta(OEt)$_5$, keeping the textural properties of the starting material. The addition of chiral tartrates (diethyl and diisopropyl tartrates) produce catalytic sites able to oxidize thioanisole in an enantioselective manner with different oxidants, namely aqueous H_2O_2 and alkyl hydroperoxides in organic medium. The oxidation is much more efficient with H_2O_2, leading to a faster oxidation with high selectivity to sulfoxide (up to 90% at 85% conversion in the case of solids modified with DIPT). The enantioselectivities obtained (up to 25% ee) were in all cases lower than those obtained with the analogous tartrate-Ta(OEt)$_5$ complex in solution. This result must be due to a combination of factors, including the only partial complexation of the Ta sites on the solid, as shown by the elemental analysis and the enantioselectivity vs activity correlation, and also the formation of non-chelated complexes, with only one σ-bonded oxygen atom (HC-O-Ta) y probably a π-coordinated carboxylate (C=O···Ta), as shown by the CP-MAS ^{13}C-NMR spectra. The best and most consistent results were obtained with diisopropyl tartrate as chiral modifier on the support pre-calcined at 650ºC (DIPT-Ta-MCM$_{650}$). The recovered solids are still active, without Ta leaching due to the stability of Ta-

O-Si bonds, but enantioselectivity is almost completely lost, due to the decomplexation of the chiral tartrate.

Acknowledgement

Financial support from the Spanish Ministerio de Economía y Competitividad (Project CTQ2011-28124) and the Diputación General de Aragón (E11 Group co-financed by the European Regional Development Funds) is gratefully acknowledged. M. F. thanks the Tunisien Ministère de l'Enseignement Supérieure et la Recherche Scientifique for a short-mobility grant (bourse d'alternance).

References

[1] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834–10843.
[2] V. Meynen, P. Cool, E. F. Vansant, Microporous Mesoporous Mater. 125 (2009) 170–223.
[3] D. Trong On, D. Desplantier-Giscard, C. Danumah, S. Kaliaguine, Appl. Catal. A 222 (2001) 299–357.
[4] A. Taguchi, F. Schüth, Microporous Mesoporous Mater. 77 (2005) 1–45.
[5] A. Tuel, Microporous Mesoporous Mater. 27 (1999) 151–169.
[6] C. Copéret, R. Chabanas, R. P. Saint-Arroman, J. M. Basset, Angew. Chem. Int. Ed. 42 (2003) 156–181.
[7] V. Dal Santo, M. Guidotti, R. Psaro, L. Marchese, F. Carniato, C. Bisio, Proc. R. Soc. A 468 (2012) 1904–1926.
[8] S. Soignier, M. Taoufik, E. Le Roux, G. Saggio, C. Dablemont, A. Baudouin, F. Lefebvre, A. De Mallmann, J. Thivolle-Cazat, J.-M. Basset, G. Sunley, B. M. Maunders, Organometallics 25 (2006) 1569–1577.
[9] V. Polshettiwar, F. A. Pasha, A. De Mallmann, S. Norsic, J. Thivolle-Cazat, J. M. Basset, ChemCatChem 4 (2012) 363–369.
[10] I. Fernandez, N. Khiar, Chem. Rev. 103 (2003) 3651-3706.
[11] E. Wojaczynska, J. Wojaczynski, Chem. Rev. 110 (2010) 4303-4356.
[12] K. P. Bryliakov, E. P. Talsi, Current Org. Chem. 12 (2008) 386-404.
[13] H. Srour, P. Le Maux, S. Chevance, G. Simonneaux, Coord. Chem. Rev. 257 (2013) 3030-3050.

[14] Y. Ferrand, R. Daviaud, P. Le Maux, G. Simonneaux, Tetrahedron: Asymmetry 17 (2006) 952–960.

[15] V. V. Thakur, A. Sudalai, Tetrahedron: Asymmetry 14 (2003) 407-410.

[16] A. Barbarini, R. Maggi, M. Muratori, G. Sartori, R. Sartorio, Tetrahedron: Asymmetry 15 (2004) 2467–2473.

[17] B. Li, S. Bai, P. Wang, H. Yang, Q. Yang, C. Li, Phys. Chem. Chem. Phys. 13 (2011) 2504–2511.

[18] T. B. Zid, I. Khedher, A. Ghorbel, React. Kinet. Mech. Catal. 100 (2010) 131-143

[19] T. B. Zid, I. Khedher, J. M. Fraile, J. Chem. Res. 37 (2013) 766–773.

[20] B. H. Lipshutz, Y.-J. Shin, Tetrahedron Lett. 41 (2000) 9515–9521.

[21] S. Sahoo, P. Kumar, F. Lefebvre, S. B. Halligudi, J. Catal. 262 (2009) 111–118

[22] X. Wang, X. Wang, H. Guo, Z. Wang, K. Ding, Chem. Eur. J. 11 (2005) 4078–4088.

[23] P. Pitchen, E. Duñach, M. N.Deshmukh, H. B. Kagan, J. Am. Chem. Soc 106 (1984) 8188–8193.

[24] J. M. Fraile, J. I. García, B. Lázaro, J. A. Mayoral, Chem. Commun. (1998) 1807–1808.

[25] M. Iwamoto, Y. Tanaka, J. Hirosumi, N. Kita, S. Triwahyono, Microporous Mesoporous Mater. 48 (2001) 271–277.

[26] H. Shi, J. He, J. Catal. 279 (2011) 155–162.

[27] R. Petroff Saint-Arromain, B. Didillon, A. de Mallmann, J. M. Basset, F. Lefebvre, Appl. Catal. A 337 (2008) 78-85.

[28] D. Meunier, A. Piechaczyk, A. de Mallmann, J. M. Basset, Angew. Chem. Int. Ed. 38 (1999) 3540-3542.

[29] D. A. Ruddy, T. D. Tilley, Chem. Commun. (2007) 3350–3352.

[30] D. A. Ruddy, T. D. Tilley, J. Am. Chem. Soc. 130 (2008) 11088–11096.

[31] P. J. Cordeiro, T. D. Tilley, Langmuir 27 (2011) 6295–6304.

[32] M. Kirihara, J. Yamamoto, T. Noguchi, Y. Hirai, Tetrahedron Lett. 50 (2009) 1180-1183.

[33] V. Cimpeanu, V. Pârvulescu, V. I. Pârvulescu, M. Capron, P. Granger, J. M. Thompson, C. Hardacre, J. Catal. 235 (2005) 184-194.

[34] V. Cimpeanu, V. Pârvulescu, V. I. Pârvulescu, J. M. Thompson, C. Hardacre, Catal. Today 117 (2006) 126-132.

[35] J. M. Fraile, J. I. García, J. A. Mayoral, E. Vispe, J. Catal. 233 (2005) 90-99.

[36] I. Khedher, A. Ghorbel, J. Chem. Res. 34 (2010) 589-595.

[37] J. M. Jehng, W. C. Tung, C. H. Huang, I. E. Wachs, Microporous Mesoporous Mater. 99 (2007) 299-307.

[38] H. A. Benesi, A. C. Jones, J. Phys. Chem. 63 (1959) 179-182.

[39] X. Gao, I. E. Wachs, Catal. Today 51 (1999) 233-254.

[40] Y. S. Ko, W. S. Ahn, Microporous Mesoporous Mater. 30 (1999) 283-291.

[41] D. M. Pickup, G. Mountjoy, M. A. Holland, G. W. Wallidge, R. J. Newport, M. E. Smith, J. Mater. Chem. 10 (2000) 1887-1894.

[42] M. G. Finn, K. B. Sharpless, J. Am. Chem. Soc. 113 (1991) 113-126.

[43] P. G. Potvin, B. G. Fieldhouse, Tetrahedron: Asymmetry 10 (1999) 1661-1672.

[44] See supporting information of: S. F. Pedersen, J. C. Dewan, R. R. Eckman, K. B. Sharpless, J. Am. Chem. Soc. 109 (1987) 1279-1282.