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Comparison of Ta—MCM-41 and Ti—MCM-41 as catalysts for the enantioselective epoxidation of styrene with TBHP

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A B S T R A C T

Chiral Ti—MCM-41 and Ta—MCM-41 catalysts have been prepared by grafting of $Ti(O^iPr)_4$ and $Ta(OEt)_5$ and the modification with R-(+)-diethyl L-tartrate or R-(+)-diisopropyl L-tartrate. In general, the solid catalysts are more active and selective than their homogeneous counterparts in the epoxidation of styrene with tert-butyl hydroperoxide. The enantioselectivities depend on both the nature of the chiral ligand and the calcination temperature of the support, as it is supposed this controls the type of surface species that are formed. The best result of 71% ee is obtained with $DIPT—Ta—MCM_{550}$ and is the first example of the use of a Ta catalyst for the enantioselective epoxidation of unfunctionalized alkenes. Nonetheless, the recovered Ta catalysts are less active and selective.

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1. Introduction

Enantiomerically pure epoxides are very useful synthetic intermediates in the synthesis of different biologically active compounds [1]. Classically, the two most important methods for the enantioselective epoxidation of alkenes include the use of homogeneous chiral catalysts such as Ti—tartrates, which are used for the epoxidation of allylic alcohols with alkyl hydroperoxides [2], and Mn—salen catalysts, which are used for the epoxidation of unfunctionalized alkenes with different oxidants [3]. More recently, the use of hydrogen peroxide as an oxidant has been extensively studied using different Mn, Fe, and Ti complexes [4—6].

The immobilization of homogeneous catalysts on solid supports could feasibly yield the advantages of high activity and selectivity with the practical advantages that are associated with heterogeneous catalysts [7,8]. Chiral metal—salen complexes have been successfully immobilized on different solid supports using a variety of immobilization methods [9], but epoxidation is usually more effective with cis-disubstituted alkenes and with oxidants that are considered to be environmentally unfriendly (mCPBA, PhIO). The immobilization of Ti—tartrate complexes has been investigated to a lesser degree with a lower number of successful examples [10]. Polytartrates [11,12] and tartramides supported on inorganic siliceous materials [13] and Ti—tartrate grafted on silicas [14] are relevant examples. The later were prepared by grafting of $Ti(O^iPr)_4$ on a silica support [15] and then modified with a tartaric acid derivative [16]. In the same way that unmodified Ti—silica is able to catalyze the epoxidation of unfunctionalized alkenes with alkyl hydroperoxides [17], it has been shown that the modified solids lead to moderate enantioselectivity in the epoxidation of styrene [18,19].

Tantalum can be grafted on silica in the same way as Ti, and it has been shown that those solids are able to activate

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H_2O_2 in the epoxidation of alkenes [20–25]. These kinds of supported catalysts are also able to decompose alkyl hydroperoxides [26], and after being modified with chiral tartrates, they showed an excellent performance in the enantioselective epoxidation of allylic alcohols [27–29]. We recently described how tartrate modified Ta–MCM-41 catalyzed the enantioselective oxidation of methyl phenyl sulfide with both H_2O_2 and alkyl hydroperoxides, with moderate to low enantiomeric excesses [30].

In view of the parallel behavior of supported Ti and Ta in other reactions, we decided to compare the performance of these metals grafted on MCM-41 in the epoxidation of styrene with *tert*-butyl hydroperoxides (TBHPs) and the effect of the modification with *R*-(+)-diethyl L-tartrate (DET) and *R*-(+)-diisopropyl L-tartrate (DIPT) in an enantioselective variant of this reaction.

2. Experimental section

Ta catalysts were prepared by grafting Ta(OEt)$_5$ on MCM-41, which had been pretreated at different temperatures (550, 650, and 750 °C), and then modified with DET or DIPT as described in a previous article [30]. Ti catalysts were prepared in a similar way using Ti(O^{i}Pr)$_4$ as described in a previous article [19].

All the catalysts were characterized by powder small angle X-ray diffraction, N_2 adsorption–desorption isotherms at 77 K, metal analysis by inductively coupled plasma emission spectroscopy, organic analysis, and solid-state NMR, as described elsewhere [19,30]. The epoxidation of styrene (10 mmol) with TBHP (6 mmol, 5.5 solution in decane) was carried out in acetonitrile (10 mL) at 70 °C under an inert atmosphere with 0.015 mmol catalyst, as described elsewhere [19]. The catalysts were filtered, thoroughly washed with dichloromethane, dried under vacuum, and reused under the same conditions.

3. Results and discussion

3.1. Characterization of the catalysts

The grafting of the Ti and Ta precursors on the surface of MCM-41 may give rise to three types of species, monopodal, bipodal, and tripodal (Scheme 1). Monopodal species allow the chelation with the tartrate and leave at least one remaining alkoxy group, which is able to be substituted by the hydroperoxide oxidant. The same is true for the Ta-bipodal species, except that there is no remaining alkoxy group in the Ti-bipodal and Ta-tripodal species, and the activation of the hydroperoxide might be carried out by the cleavage of one Si–O–M bond (Scheme 1), keeping the chelate necessary for a higher enantioselectivity.

Table 1 gathers the results obtained from the elemental and textural analyses of the catalysts. The amount of grafted titanium and tantalum is always around 0.4 mmol g^{-1}, indicating that a complete grafting of the precursor has occurred. The increase in the calcination temperature produces a decrease in surface area, pore volume, and mean pore diameter values, but the hexagonal structure of MCM-41 is preserved, as shown by the XRD diffraction

patterns. After the grafting of the metal centers, these values are even lower, with a more significant effect in the case of Ta species. Nonetheless, the variations in site density are not significant, with values from 0.24 to 0.31 of Ti/nm^2 and from 0.27 to 0.32 of Ta/nm^2.

Carbon analyses (Table 1) of the unmodified catalysts are all of a similar value considering the isopropoxide/Ti ratios are found in the range of 1.7–2.4 and the ethoxide/Ta ratios in the range of 2.7–3.5. Although a mixture of surface species would be expected, the bipodal one appears to be the most significant contributor for both Ti and Ta catalysts. The treatment with chiral tartrates always increases the carbon content of the solids, although it is difficult to estimate the true content of tartrate. Assuming the correct formation of the species shown in Scheme 1, the C/Ti ratios would be in the range of 8–11 for DET and 10–13 for DIPT, and the experimental values (Table 1) are in the ranges of 9.5–12.9 and 11.1–13.6, respectively. For Ta, the C/Ta ratios would be 8–12 for DET and 10–14 for DIPT, and the experimental values are 8.5–10.6 and 9.0–13.7, respectively. The values less than the expected range may be attributed to the presence of sites without tartrate, because of intrapore diffusional problems, and the values beyond the expected one may be because of the complexation of tartrates without forming a chelate.

This possibility was explored by solid state ^{13}C NMR (Fig. 1). All the samples show two broad signals corresponding to the carboxylate group, at 184 and 175 ppm (as a shoulder for the Ti catalysts), in agreement with the presence of both coordinated and uncoordinated carboxylate groups, respectively [31]. In the same way, two signals appear in the methine (OOC–CHOH) zone, at around 75 ppm for free hydroxyls and at 85–90 ppm corresponding to the Ti-alkoxide or Ta-alkoxide [32,33]. These spectra seem to indicate the presence of chelated and unchelated tartrates on the active sites [19,30].

3.2. Epoxidation of styrene

All the catalysts were tested in the epoxidation of styrene with TBHP (Scheme 2), using an amount of oxidant below the stoichiometric one (0.6 equivalents) with respect to styrene, in an attempt to minimize the overoxidation of the products [34]. In fact, phenyl acetaldehyde and benzaldehyde were detected and identified in all the reactions, together with minor amounts of other products such as *tert*-butyl benzoate or 1-phenylethane-1,2-diol. The styrene conversion and the styrene oxide yield (Table 2) were calculated with respect to the added amount of oxidant. Acetonitrile was chosen as solvent, given its good general performance in epoxidation reactions with TBHP [35].

First of all, the catalytic performance of Ta(OEt)$_5$ and the two tartrate complexes was tested in solution. As can be seen in Table 2, the three homogeneous catalysts are not very active, as shown by the low conversion after 24 h, and activity is lower than the analogous Ti catalyst, with the only exception being DIPT–Ta(OEt)$_5$. The selectivity to styrene oxide is always very low, comparable with that obtained with the Ti catalysts. Interestingly, the Ta–tartrate complexes led to a moderate enantioselectivity of 61% ee
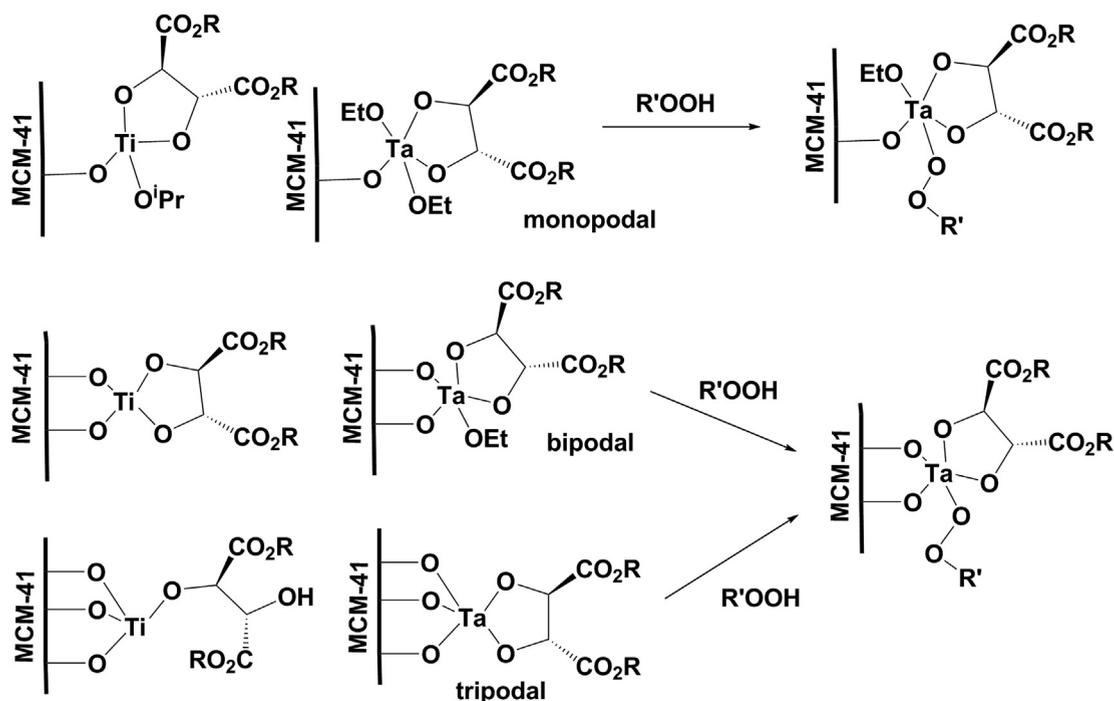
Scheme 1. Possible tartrate-modified surface Ti and Ta species on MCM-41 and activation of an alkyl hydroperoxide.

Table 1
Textural and structural properties and elemental analysis of the catalysts.

Sample	S_{BET} (m²/g)		V_p (cm³/g)		D_p (nm)		M (mmol/g)		C/M	
	Ti	Ta	Ti	Ta	Ti	Ta	Ti	Ta	Ti	Ta
MCM₅₅₀	1001		0.76		3.03		—		—	
MCM₆₅₀	945		0.75		2.87		—		—	
MCM₇₅₀	925		0.64		2.75		—		—	
M-MCM₅₅₀	966	876	0.75	0.65	2.99	3.01	0.38	0.39	5.2	7.0
M-MCM₆₅₀	921	784	0.61	0.63	2.66	2.52	0.38	0.41	7.3	5.5
M-MCM₇₅₀	814	822	0.57	0.49	2.35	2.54	0.38	0.39	6.9	7.1
DET−M-MCM₅₅₀	804	842	0.65	0.60	2.56	2.45	0.38	0.38	9.5	9.6
DET−M-MCM₆₅₀	820	743	0.55	0.54	2.62	2.60	0.38	0.40	11.2	10.6
DET−M-MCM₇₅₀	730	782	0.52	0.46	2.34	2.03	0.38	0.38	12.9	8.5
DIPT−M-MCM₅₅₀	928	732	0.65	0.51	2.80	2.32	0.38	0.38	11.1	13.7
DIPT−M-MCM₆₅₀	802	804	0.53	0.53	2.64	2.20	0.38	0.40	13.6	9.8
DIPT−M-MCM₇₅₀	788	797	0.49	0.44	2.04	1.99	0.38	0.38	11.3	9.0

S_{BET} = surface area; V_p = pore volume; D_p = mean pore diameter (determined by the BJH [Barrett–Joyner–Halenda] method).

with DET, lower than the 81% ee obtained with Ti, and a 75% ee with DIPT, thus improving on the 50% ee reached with Ti.

The grafting of Ta on MCM-41 significantly improves the catalytic activity, as seen in the conversions after 24 h, although not in the productivity at longer reaction times. The best result in catalytic activity was obtained with Ta−MCM₅₅₀ and it decreases when increasing the calcination temperature. Conversely, the selectivity to styrene epoxide was not improved in a similar way as it happened in the case of Ti, illustrating that the Ta sites remain highly active in the epoxide rearrangement and in the overoxidation reactions, in the same way as the soluble catalysts.

The most significant changes happen when the solids are treated with the chiral tartrates, DET and DIPT. In most cases, the epoxidation of styrene is faster. This behavior is

in agreement with a ligand accelerated catalytic reaction, as described for other closely related epoxidation reactions [36]. In the case of DET, the most active solids with both Ti and Ta are those prepared with MCM₅₅₀ and MCM₆₅₀. These solids are also the most selective to styrene oxide by Ti, with values of around 45% after 24 h, but the selectivity is lower with Ta, as it happened with the unmodified solids. The best result is 34% with DET−Ta−MCM₆₅₀. In the case of DIPT, the activity of the three solids is similar, thus improving the results obtained with Ti in the solids calcined at 650 and 750 °C. Conversely, the selectivity to styrene oxide is very different in the three solids, ranging from 53% after 24 h with DIPT−Ta−MCM₆₅₀ to only 11% with DIPT−Ta−MCM₇₅₀. The behavior with respect to calcination temperature is then completely different to that
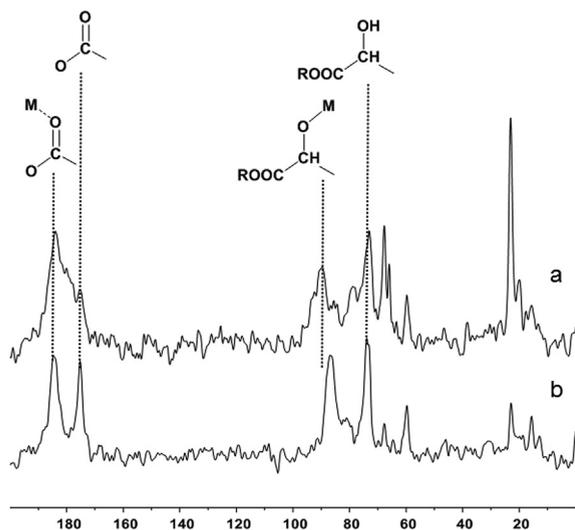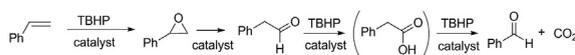
Fig. 1. CP-MAS ^{13}C NMR spectra: (a) DIPT–Ta–MCM$_{750}$ and (b) DIPT–Ti–MCM$_{750}$.

Scheme 2. Epoxidation of styrene with TBHP and side reactions.

observed for the Ti solids. Although the DIPT–Ti materials lead to similar enantioselectivities with very different catalytic activities, the DIPT–Ta catalysts show similar activities with very different enantioselectivities.

Regarding enantioselectivity, there is no clear trend and this must arise to an uncontrolled factor in the process of complex formation. The typical results with DET are similar with both Ti and Ta, leading to values in the range of 54–58% ee, although in each case one of the solids, DET–Ti–MCM$_{750}$ and DET–Ta–MCM$_{650}$, do not reach those results. Moreover, there is no apparent relationship between

the enantioselectivity and the rest of the catalytic results (activity and selectivity to epoxide). The effect of calcination temperature is more evident in Ta solids treated with DIPT, as enantioselectivity decreases in the order MCM$_{550}$ > MCM$_{650}$ > MCM$_{750}$. It is remarkable that the best result, 71% ee obtained with DIPT–Ta–MCM$_{550}$, is the best one described for this reaction with this kind of solids. In trying to rationalize this performance, the larger pore size of the support must be able to accommodate the Ta–tartrate chelate complex and may be one of the key parameters for this success.

Most of the heterogeneous catalysts described for styrene epoxidation are based on Mn–salen complexes, immobilized on different supports, and through different strategies. Many parameters including the oxidant used for epoxidation affect the final results of the reaction. Enantioselectivities with NaClO typically range between 25% and 52% ee with the Mn–salen catalyst covalently bonded to mesoporous materials [37], whereas it is lower (40% ee) with graphene oxide grafted catalysts [38], and a 78% ee can be reached with anionic Mn–salen complexes exchanged on Zn–La double hydroxides, albeit with only 25% conversion [39]. Results reported with m-chloroperbenzoic acid are also moderate, with values of 13–56% ee for catalysts immobilized on poly(styrene-phenylvinylphosphonate)-phosphate through anchored phenoxide groups as axial ligands [40], similar to 16–41% ee found with covalent-bonded complexes [37]. Only the use of iodosylbenzene allows reaching very high enantioselectivities (99% ee) with anionic exchanged complexes [39]. Thus, our results are comparable to those reported in the literature, using easily prepared Ti and Ta catalysts with commercially available chiral ligands and a more environmentally friendly oxidant.

Given the similar enantioselective results obtained with both Ti and Ta, it can be assumed that both types of catalysts follow the same mechanism. Although the Sharpless epoxidation with Ti–tartrate complexes takes place through a dimeric species [32], the site isolation obtained on the solid supports precludes these kinds of centers on

Table 2
Epoxidation of styrene with TBHP catalyzed by Ti and Ta catalysts.[a]

Entry	Catalyst	Conversion (%)[b]		Styrene oxide selectivity (%)[b]		% ee[c]	
		Ti	Ta	Ti	Ta	Ti	Ta
1	M(OR)$_n$[d]	56 (79)	40 (52)	5 (9)	16 (15)	–	–
2	DET–M(OR)$_n$[d]	52 (75)	26 (42)	6 (9)	4 (6)	80	61
3	DIPT–M(OR)$_n$[d]	16 (40)	23 (59)	11 (9)	4 (9)	50	75
4	M-MCM$_{550}$	36 (64)	58 (57)	28 (22)	14 (23)	–	–
5	M-MCM$_{650}$	38 (58)	37 (38)	32 (26)	18 (19)	–	–
6	M-MCM$_{750}$	23 (44)	29 (37)	29 (25)	4 (8)	–	–
7	DET–M-MCM$_{550}$	68 (79)	59 (69)	44 (36)	24 (23)	55	54
8	DET–M-MCM$_{650}$	62 (74)	73 (86)	45 (36)	34 (33)	56	26
9	DET–M-MCM$_{750}$	27 (54)	17 (28)	23 (32)	23 (21)	38	58
10	DIPT–M-MCM$_{550}$	59 (64)	43 (51)	46 (26)	24 (23)	62	71
11	DIPT–M-MCM$_{650}$	19 (73)	45 (60)	48 (34)	53 (42)	38	49
12	DIPT–M-MCM$_{750}$	26 (52)	41 (51)	42 (47)	11 (11)	45	37

[a] Reaction conditions: styrene (10 mmol), TBHP (6 mmol, 5.5 M in decane), acetonitrile (10 mL), catalyst (0.015 mmol of Ta), 70 °C, inert atmosphere.
[b] Determined by GC. Values after 24 h and in parenthesis values after 7 days.
[c] Determined by HPLC with a Chiralpack OD-H column.
[d] Ti(O^{i}Pr)$_4$ or Ta(Oet)$_5$.

the solids and monomeric species are more likely to be involved (Scheme 3). The monopodal Ti center (a) should activate TBHP by the substitution of the remaining iso-propoxide group (see Scheme 1) and additional coordination of the distal oxygen atom. The proximal oxygen is the most electrophilic one and hence is transferred to the alkene in a spiro-like transition state [41] (front view in Scheme 3b). In contrast to the epoxidation of allylic alcohols, the alkene is not coordinated to the metal center, and the oxygen transfer can be compared to the carbene transfer as in a cyclopropanation reaction [42]. The resulting Ti species would be similar to the starting one but with a *tert*-butoxy group instead of an isopropoxy one. In the case of Ta, the mechanism would be the same, but Ta would start in a five-coordinated state, expanded to six with the coordination of the distal oxygen of TBHP. In fact, this allows the successful reaction with bipodal Ta species (Scheme 3c), whereas in the case of Ti at least one of the C−O−Ti bonds (to tartrate) or Si−O−Ti (to silica support) would be broken. In all cases, as there is no other apparent interaction, the enantioselectivity must be controlled by steric effects, first of all in the orientation of the *tert*-butyl group, probably in the less hindered quadrant of the complex (see Scheme 3b) [41], and then in the approach of the styrene. The variations in enantioselectivity may be attributed to the partial formation of nonchelated complexes with tartrate in an uncontrolled manner, as indicated by the NMR spectra, making it difficult to draw in-depth conclusions about the steric effects.

Catalyst reusability is of major importance for heterogeneous catalysts and is often cited as an advantage over homogeneous catalysts. Some of the catalysts were recovered by filtration at the end of the reactions, then thoroughly washed with dichloromethane, and dried in vacuum at 60 °C for 12 h before reuse under the same conditions. The lack of activity in the liquid phase obtained by filtration experiments demonstrated that the solid catalysts were heterogeneous in nature. Nonetheless, the results in the reuse experiments showed a significant deactivation, more important in the case of Ta catalysts. The most important result to compare the relative stability of
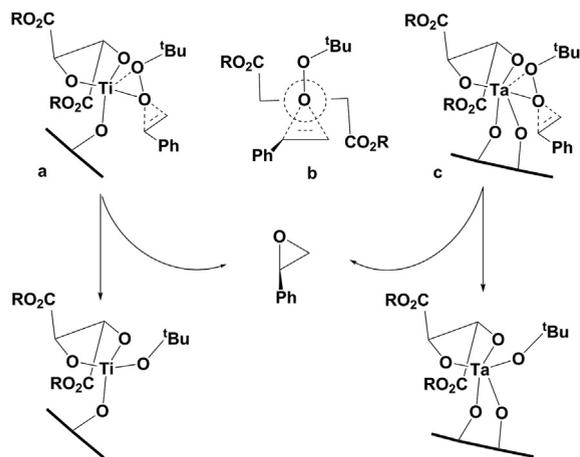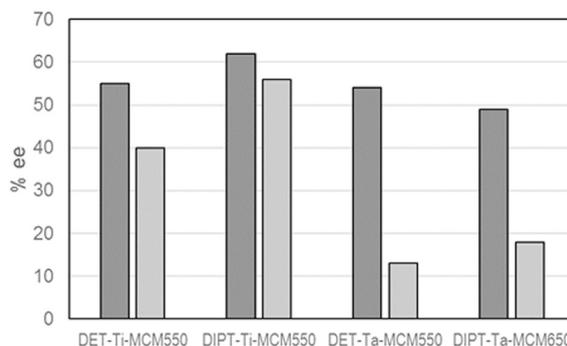

Fig. 2. Variation of enantioselectivity with reuse in some of the catalysts.

the complexes is the enantioselectivity, which is directly related to the presence of metal−tartrate species on the solid. As can be seen in Fig. 2, the drop in enantioselectivity is much more important in the case of Ta catalysts, indicating that the Ta−tartrate complexes are less stable than the Ti−tartrate. This drop in enantioselectivity is also accompanied with a decrease in the catalytic activity and the selectivity to epoxide, which can be attributed to the loss of the ligand acceleration effect. The tartrate was not detected in the solution by ^{1}H NMR, either because of the low concentration or because it remains retained on the silica surface of the solid support. The lack of Ta leaching even with more coordinating reagents and products, as in the sulfide oxidation with hydrogen peroxide [29], seems to confirm the hypothesis of the loss of ligand by decomplexation as the main deactivation mechanism.

4. Conclusions

Ti-MCM-41 and Ta−MCM-41, prepared by grafting of $Ti(O^iPr)_4$ and $Ta(OEt)_5$ on MCM-41, can be modified with chiral tartrates, leading to similar surface species with both metals. All the solids are active in the epoxidation of styrene with TBHP and produce improved activity and selectivity to styrene oxide, by comparison to the precursors and the analogous complexes in a solution. Moderate enantioselectivities are obtained, with values ranging between 26% and 71% ee depending on the metal, the nature of the chiral ligand, and the calcination temperature of the support. Interestingly, the best result is obtained with DIPT−Ta−MCM$_{550}$, and this is thus the first example of use of a Ta catalyst for the enantioselective epoxidation of a nonfunctionalized alkene. Nonetheless, the Ta catalysts seem to be less recoverable than Ti ones, probably because of a reduced stability of the tartrate complex. The way forward from this point will be the control of the species (monopodal, bipodal, or tripodal) formed on the surface, and the proper complexation with tartrate together with the search for ligands that can form more stable Ta complexes.

Scheme 3. Proposed mechanism for styrene epoxidation with Ti and Ta catalysts.

References

[1] A. Riera, M. Moreno, Molecules 15 (2010) 1041−1073.
[2] T. Katsuki, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Vol. II, Springer, Heidelberg, Germany, 2000, pp. 621−648.
[3] E.N. Jacobsen, M.H. Wu, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Vol. II, Springer, Heidelberg, Germany, 2000, pp. 649−678.
[4] G. De Faveri, G. Ilyashenko, M. Watkinson, Chem. Soc. Rev. 40 (2011) 1722−1760.
[5] E.P. Talsi, K.P. Bryliakov, Coord. Chem. Rev. 256 (2012) 1418−1434.
[6] H. Srour, P. Le Maux, S. Chevance, G. Simonneaux, Coord. Chem. Rev. 257 (2013) 3030−3050.
[7] D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs (Eds.), Chiral Catalysts Immobilization and Recycling, Wiley-VCH, Weinheim, Germany, 2000.
[8] H.U. Blaser, B. Pugin, in: G. Jannes, V. Dubois (Eds.), Chiral Reactions in Heterogeneous Catalysis, Plenum Press, New York, 1995, p. 33.
[9] C. Baleizão, H. García, Chem. Rev. 106 (2006) 3987−4043.
[10] Q.H. Xia, H.Q. Ge, C.-P. Ye, Z.-M. Liu, K.-X. Su, Chem. Rev. 105 (2005) 1603−1662.
[11] L. Canali, J.K. Karjalainen, D.C. Sherrington, O. Hormi, Chem. Commun. (1997) 123−124.
[12] J.K. Karjalainen, O.E.O. Hormi, D.C. Sherrington, Tetrahedron: Asymmetry 9 (1998) 1563−1575.
[13] S. Xiang, Y. Zhang, Q. Xin, C. Li, Angew. Chem., Int. Ed. 41 (2002) 821−824.
[14] W. Zhao, Z. Hao, C. Hu, J. Li, X. Xu, Microporous Mesoporous Mater. 112 (2008) 133−137.
[15] J.M. Fraile, J.I. García, J.A. Mayoral, L.C. de Mènorval, F. Rachdi, J. Chem. Soc., Chem. Commun. (1995) 539−540.
[16] J.M. Fraile, J.I. García, J.A. Mayoral, L. Salvatella, E. Vispe, D.R. Brown, G. Fuller, J. Phys. Chem. B 107 (2003) 519−526.
[17] C. Cativiela, J.M. Fraile, J.I. García, J.A. Mayoral, J. Mol. Catal. A 112 (1996) 259−267.
[18] Z. Fu, D. Yin, Q. Xie, W. Zhao, A. Lv, D. Yin, Y. Xu, L. Zhang, J. Mol. Catal. A 208 (2004) 159−166.
[19] M. Fadhli, I. Khedher, J.M. Fraile, J. Mol. Catal. A 420 (2016) 282−289.
[20] D.A. Ruddy, T.D. Tilley, Chem. Commun. (2007) 3350−3352.
[21] D.A. Ruddy, T.D. Tilley, J. Am. Chem. Soc. 130 (2008) 11088−11096.
[22] P.J. Cordeiro, T.D. Tilley, Langmuir 27 (2011) 6295−6304.
[23] N. Morlanes, J.M. Notestein, Appl. Catal., A 387 (2010) 45−54.
[24] N. Morlanes, J.M. Notestein, J. Catal. 275 (2010) 191−201.
[25] N.E. Thornburg, A.B. Thompson, J.M. Notestein, ACS Catal. 5 (2015) 5077−5088.
[26] R. Petroff Saint-Arromain, B. Didillon, A. de Mallmann, J.-M. Basset, F. Lefebvre, Appl. Catal., A 337 (2008) 78−85.
[27] D. Meunier, A. Piechaczyk, A. de Mallmann, J.-M. Basset, Angew. Chem., Int. Ed. 38 (1999) 3540−3542.
[28] D. Meunier, A. de Mallmann, J.-M. Basset, Top. Catal. 23 (2003) 183−189.
[29] D. Meunier, A. Piechaczyk, A. de Mallmann, J.-M. Basset, US Patent 6,642,170 (2003).
[30] M. Fadhli, I. Khedher, J.M. Fraile, J. Mol. Catal. A 410 (2015) 140−148.
[31] S.F. Pedersen, J.C. Dewan, R.R. Eckman, K.B. Sharpless, J. Am. Chem. Soc. 109 (1987) 1279−1282 (NMR spectra are included in the supporting information).
[32] M.G. Finn, K.B. Sharpless, J. Am. Chem. Soc. 113 (1991) 113−126.
[33] P.G. Potvin, B.G. Fieldhouse, Tetrahedron: Asymmetry 10 (1999) 1661−1672.
[34] J.M. Fraile, N. García, J.A. Mayoral, F.G. Santomauro, M. Guidotti, ACS Catal. 5 (2015) 3552−3561.
[35] M. Guidotti, N. Ravasio, R. Psaro, G. Ferraris, G. Moretti, J. Catal. 214 (2003) 242−250.
[36] D.J. Berrisford, C. Bolm, K.B. Sharpless, Angew. Chem., Int. Ed. Engl. 34 (1995) 1059−1070.
[37] R. Ji, K. Yu, L.L. Lou, S. Liu, J. Mol. Catal. A 378 (2013) 7−16.
[38] W. Zheng, R. Tan, S. Yin, Y. Zhang, G. Zhao, Y. Chen, D. Yin, Catal. Sci. Technol. 5 (2015) 2092−2102.
[39] X. Li, Q. Shen, G. Zhang, D. Zhang, A. Zheng, F. Guan, Y. Sun, Catal. Commun. 41 (2013) 126−131.
[40] X. Zou, K. Shi, C. Wang, Chin. J. Catal. 35 (2014) 1446−1455.
[41] Y.D. Wu, D.K.W. Lai, J. Am. Chem. Soc. 117 (1995) 11327−11336.
[42] Y. Minko, I. Marek, Org. Biomol. Chem. 12 (2014) 1535−1546.