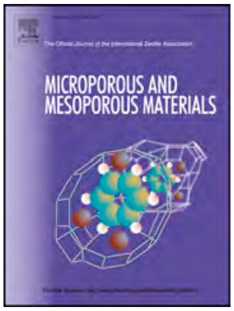

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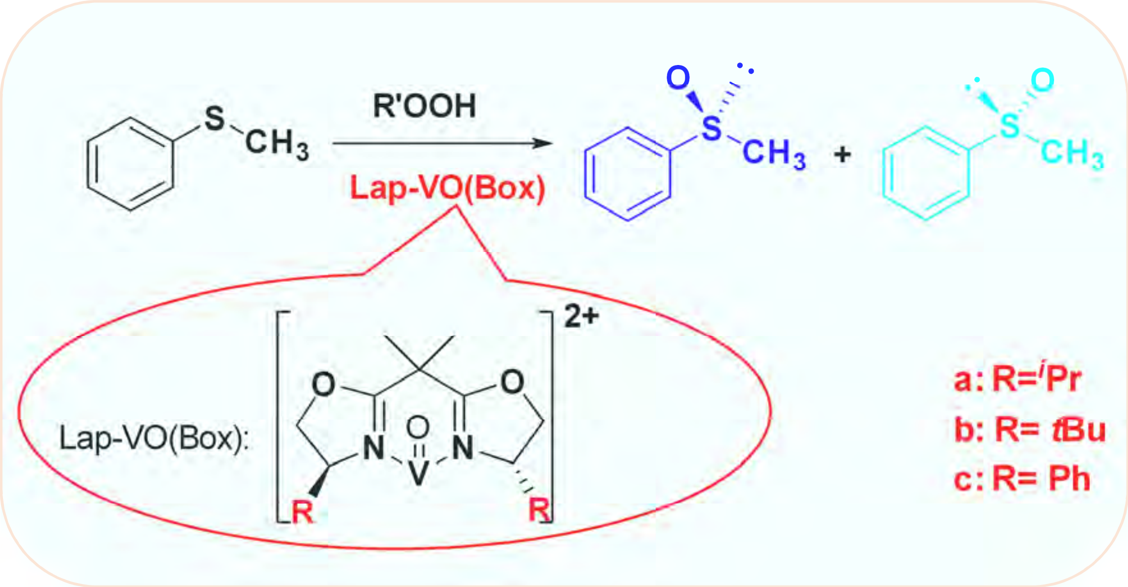
Graphical Abstract



New bis(oxazoline)–vanadyl complexes, supported by electrostatic interaction in Laponite clay, asheterogeneous catalysts forasymmetric oxidation of methyl phenyl sulfide

T. Ben Zid[a]*, M. Fadhli[a], I. Khedher[a] and J.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 de Tunis El-Manar, Tunis 2092, Tunisia*

(*email: benzidtakwa@gmail.com) tel : +216 52318282

[b]*Instituto de Síntesis Química y Catálisis Homogénea, Facultad de Ciencias, CSIC-Universidad de Zaragoza, C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain*

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Abstract

Chiral bis(oxazoline) ligands are used for the first time to promote the enantioselective vanadium-catalyzed oxidation of sulfides with alkyl hydroperoxides. Several bis(oxazoline)-VO complexes have been prepared and supported by cation exchange in Laponite clay. The substituent in the oxazoline ring, and the type of hydroperoxide are relevant parameters that control the activity and selectivity of the resulting catalysts. *Tert*-butyl hydroperoxide is more reactive but less enantioselective than cumenehydroperoxide, both with the neat and supported VO-bis(oxazoline) complexes. Activities and enantioselectivities obtained with the heterogeneous catalysts are always lower than in solution, and in general better and more consistent results are obtained with box(^{i}Pr) ligand which seems to be also the best chiral auxiliary in homogeneous phase, leading to a modest but significant enantioselectivity of 20% ee in heterogeneous phase and of 28% in homogeneous phase. The recovered of the best catalyst shows a decrease in the catalytic activity and in the enantioselectivity, in agreement with some decomplexation of the chiral ligand, whereas the supported vanadium species remain stable and recoverable.

Keywords: Laponite, bis(oxazoline), vanadium, catalyst, oxidation, asymmetry.

1 Introduction

Enantiopure sulfoxides have been shown to be efficient auxiliaries in asymmetric synthesis and relevant compounds in pharmaceutical research, given their biological activity [1]. Consequently, various approaches to obtain these compounds in enantiopure form have been developed [2], althoughthe catalytic asymmetric oxidation of prochiral sulfides remains as the most effective route for this purpose [2,3]. Since the discovery of the enantioselective oxidation of sulfides promoted by the Ti(^{i}OPr)$_4$-chiral tartrate systems in 1984 [4], the catalytic asymmetric oxidation catalyzed by chiral complexes of transition metals, such us titanium [5], vanadium [6], and manganese [7] have been extensively studied, using hydrogen peroxide or alkyl hydroperoxides as the oxygen source. The most successful chiral ligands for this application include diols, binols, tridentate Schiff bases and tetradentate salen type ligands [2, 3]. Bis(oxazoline) ligands have played a very important role in asymmetric catalysis over last 25 years[8]. In fact, bis(oxazoline) ligands are able to coordinate many different metals such as Cu, Pd, Fe, Zn, Mg, Ni or Sc and those bis(oxazoline)-metal complexes have been used as catalysts in a large variety useful enantioselective reactions, including cyclopropanation, aziridination, allylic substitution, Diels-Alder, aldol-like and Michael reactions. However, the number of applications of bis(oxazoline)-metal complexes in asymmetric oxidation reactions is rather scarce, with most of the examples corresponding to the Kharasch allylic oxidation of alkenes catalyzed by copper complexes [9]. Vanadium is a typical metal used as catalyst for oxidation reactions, including enantioselective epoxidations and sulfoxidations [10]. …..the use of chiral bis(oxazoline)-vanadium complexes has not been explored, to the best of our knowledge. Only vanadium complexes with hydroxyphenyloxazolines [11] and hydroxymethyloxazolines [12] have been prepared and tested in oxidation reactions [12, 13], and in one case a chiral hydroxyphenyloxazoline-vanadium complex was tested in epoxidation and sulfoxidation, but it led to the racemic mixture of products [14].

Due the practical advantages of heterogeneous catalysts, such as easy separation and recycling of catalysts, purification of products, and better handling properties, various strategies have been reported to immobilize chiral transition metal complexes onto solid supports and a good number of examples are related to the use of metal complexes immobilized by binding onto organic or inorganic supports. In most cases, the heterogenisation is achieved through a covalent bond between the ligand and the support. From a practical point of view, the immobilization without covalent linkage is simpler because very often it avoids the need for functionalizing the complex [15]. There are several strategies of non-covalent heterogenisation. As far as this latter strategy is concerned, the interaction of transition metal complexes into lamellar solids is a valuable method to easily support metal complexes with catalytic activity. Clays with cation exchange capacity can be used to support cationic complexes by electrostatic interactions with aluminosilicate sheets. In this field, it has been shown also that bis(oxazolines)-metal complexes are suitable candidates for heterogenisation by electrostatic interaction with anionic solids. In fact, in a previous communication, it have shown that bis(oxazoline)–copper complexes can be supported by cationic exchange into clays, and that the solids thus obtained are able to promote the benchmark cyclopropanation reaction between styrene and ethyl diazoacetate [16]. Natural clays show a large variability in chemical composition and particle size, which may produce undesirable and irreproducible effect on the catalytic performance. Laponite is a synthetic clay that precludes those problems, and that has shown in several cases positive effects on selectivities, including enantioselectivity of asymmetric reactions [17]

In this study, a series of vanadyl complexes of chiral C_2-symmetric bis(oxazoline) ligands were prepared *in situ* from $VO(OTf)_2$ (as V-source)and its immobilization on the Laponite clay by cations exchange, including an experimental description and details on the preparation and characterization of the catalysts. These solids were assessed as chiral catalysts in the asymmetric oxidation of methyl phenyl sulfide using tert-butyl hydroperoxide (TBHP) or cumylhydroperoxide (CHP) as a terminal oxidant (Scheme 1). The effects of the structure of the chiral auxiliary on the behaviors of the vanadyl-based catalyst systems were studied. The combination of the structure information and the catalytic properties can establish the molecular structure–reactivity relationship of the vanadyl centres in these catalytic materials.

2 Experimental

2.1 Preparation of Catalysts

The chiral box ligands (R = phenyl, isopropyl, tert-butyl)were prepared from the corresponding amino acids by reduction with $NaBH_4$ and I_2 in THF [18] and subsequent condensation of the resulting amino alcohol with dimethylmalonitrile in the presence of $Zn(OTf)_2$ in toluene as a solvent [19]. Laponite clay was a gift from Laporte Adsorbents and it was used as received.

A methanolic solution (20 ml) of the chiral box ligand (1 mmol) with 1 mmol of $VO(OTf)_2$was stirred for 2 h. To this solution 1 g of Laponite clay is slowly added, and the resulting suspension is stirred for 24 h. The solid is filtered, thoroughly washed with anhydrous dichloromethane, anddried at 50°C under vacuum overnight prior to use. The resulting catalystsare denoted as Lap-VO(box-^{i}Pr), Lap-VO(box- ^{t}Bu) and Lap-VO(box-Ph).

2.2. Characterization of the catalysts

XRD patterns were recorded on a Philips PW1130/00/60 diffractometer using Ni-filtered Cu Kαradiation and a Siemens goniometer. BET surface areasand pore volumes of the samples were measured ona Micrometrics ASAP 2000 apparatus.Infrared spectra of samples wererecorded in the range of 4000–400 $cm^{-1}$with discs of solids mixed with dry KBr on a PerkinElmer FT-IR paragon 1000PC spectrometer. Diffuse reflectance UV–vis (DR-UV) spectra were recorded on a Unicam UV4 spectrometer equipped with a lab-sphere diffuse reflectance attachment.ESR spectrum was recorded with a Bruker ER 200tt spectrometer at 77 K. Elemental analysis (C, H, N) of organic compounds were carried out on a perkin-Elmer analyser. Vanadium loading was measured by atomic absorption spectrometry on a Perkin-Elmer 3100 apparatus, after sample dissolution through acid attack.

2.3 Catalytic test

Homogeneous reactions: To a solution of methyl phenyl sulfide (1 mmol) and Vanadyl trifluoromethane sulfonate ($VO(OTf)_2$) (0.012 mmol) in 5 mL of anhydrous dichloromethane under Ar atmosphere, TBHP (tert-butyl hydroperoxide, 90.1 mg of a 5.5 M solution in decane, 1.1 mmol) or CHP (cumene hydroperoxide 88%,152.2 mg, 1.1 mmol) was added. The reaction mixture was stirred at room temperature and monitored by GC.

In the case of the enantioselective reactions, a solutionof Vanadyl trifluoromethane sulfonate ($VO(OTf)_2$) (0.018 mmol) and bis(oxazoline) ligand (0.02mmol) were dissolved in CH_2Cl_2 (5mL), and the mixture was stirred at room temperature for 15min under inert atmosphere. A solution of methyl phenyl sulfide (1mmol) in dichloromethane (1 mL) was added followed by the dropwise addition of the oxidant (TBHP or CHP) (1.1mmol). The reaction was monitored by GC-FID analysis, using a 5% phenyl silicone capillary column (30 m×0.25 mm× 0.25 μm).After 8 h, the resulting solution was extracted with CH_2Cl_2 and the organic layer was dried over $MgSO_4$. The solvent was evaporated under vacuum. The enantiomeric excess was determined by HPLC with a Chiralpack OD-H column and hexane/iPrOH (91:9) as an eluent.

Heterogeneous reactions: The solid catalyst (amount contains 0.012 mmol of V) was added to a solution of methyl phenyl sulfide (1 mmol) and ethyl benzoate (internal standard, 15.2 mg) in 5 mL of anhydrous dichloromethane under Ar atmosphere. Then TBHP (tert-butylhydroperoxide, 90.1 mg of a 5.5 M solution in decane, 1.1 mmol) or CHP (cumene hydroperoxide 88%, 152.2 mg, 1.1 mmol) was added, the reaction mixture was stirred at room temperature and monitored by GC. After 8 h, the solid was separated by filtration, washed several times with CH_2Cl_2 and then dried at 50◦Cunder vacuum. The reaction mixture was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$. The solvent was evaporated under vacuum. The enantiomeric excess was determined by HPLC with a Chiral pack OD-H column and hexane/^{i}PrOH (91:9) as an eluent.

3 Results and discussion

3.1 Characterization of catalysts

N_2 adsorption-desorption isotherms of all samples were measured and shown in Fig.1. The adsorption isotherms are type II in the classification of Brunauer, Deming, Deming and Teller [20], whereas the hysteresis loops are of type B in the classification of de Boer [21]. Among the materials showing this typeof hysteresis are those in which the pore structure is built-up of parallel plates. The physicochemical characterization values are tabulated in Table1.

The mean pore diameter determined by the BJH method, shows a decrease of 15–36Å in Lap-VO(box) samples on exchange of the metal complexes with clay. This decrease is due to the exchange of VO(box) complex into the interlamellar space. BET surface area calculated using adsorption data in the relative pressure range 0.05–0.35 shows a decrease of 59- 153 m^2/g on impregnation of catalysts in the interlayer of clay (Table 1). The same decrease was also seen in the total pore volume of the sample estimated on the basis of the amount of N_2 adsorbed at a relative pressure of about 0.95.On the other hand, we note that the steric hindrance of the substituent in the oxazoline ligand exhibits a considerable influence in the change of textural parameters. In fact, the decrease of the mean pore diameter, BET surface area and the total pore volume is more pronounced in the order Ph>^{t}Bu>^{i}Pr.

The XRD diffractogramms of clay and clay-supported complexes VO(box) (Fig. 2) indicate that clay structure is retained during loading of the metal complex. The most intensive XRD peak of these samples is (001). However, the d_{001} basal spacing measured in Lap-VO(box) samples shows an expansion of 1.15-2 Å in the interlayer space compared to pure Laponite case. In fact, a slight displacement of (001) peak to a lower θ values was observed after the treatment the clay with the metal complexes, indicating the exchange of VO(box) complexes in the interlayer space. Furthemore, the expansion of the interlayer space increases with the increase of bulk of the substituent in the oxazoline ligand.

The results obtained from elemental analyses show that, in Lap-VO(box- ^{i}Pr) and Lap-VO(box-^{t}Bu) cases, the 2N:V ratios are within the range of values expected for 1:1 complexes (Theory: 2N/V =1). However, the vanadium excess in the Lap-VO(box-Ph) may be attributed to the decomplexation of box(Ph) during the exchange process due the restriction to its diffusion through the pores, caused by the large size of phenyl group. This problem has been detected in the immobilization of copper-bis(oxazoline) complexes, but associated with box-^{t}Bu [22].The presence of VO(box) complexes exchanged in interlayer clay can be assessed spectroscopically. The solid reflectance UV–vis spectrum of the VO(box) complex supported on Laponite (fig.3, curve b shows the spectrum of Lap-VO(box-^{i}Pr) as an example), is similar to that of the homogeneous analogue complex (Fig.3 curve a). The spectrum of homogeneous VO(box) complex shows three bands which could be the superposition of the charge-transfer transitions between the ligand and the central vanadium atoms [23] and n–π* and π-π* transitions in bis(oxazoline) ligand. These bands are present in the immobilized complex spectrum but with a slight shift from 360, 390 and 412 nm to 368, 394 and 417 nm, respectively. Moreover, the absorption band of C=N group appears in the range 360–370 nm, as reported for similar metal complexes [24].In addition, a broad band at 630 nm attributed to V(IV) d–d transition [25] was also observed in the immobilized complex spectrum though with a lower resolution than that for the transmission spectrum of homogeneous VO(box) complex.

From the IR study (Fig. 4), the most significant band of the chiral VO(box) complexes is that corresponding to the C=N bond, which appears at 1543cm^{-1} (Fig. 4c, shows the spectrum of VO(box-^{i}Pr) as an example). This band is absent in IR spectrum of pure laponite (Fig. 4a), but can be clearly observed for the supported catalyst (Fig. 4b, shows the spectrum of Lap-VO(box-^{i}Pr)).

In order to gain insight into the location and the nature of the vanadium centres, ESR investigations have been undertaken. All Lap-VO(box) catalysts show the similar signal to that of the homogeneous analogues complexes (Fig. 5), which is typical of V(IV) 3d^1 centres, with eight-line hyperfine patterns derived from the interaction of the free unpaired electron of V^{4+} and the nuclear magnetic moment of ^{51}V (I= 7/2). The spectrum is very similar to those obtained by Rigutto and al. [26] at 77 K, showing a monomeric vanadyl-like species, with g and A anisotropic tensor values (as deduced from the signal) that are characteristic of square pyramidal coordination with approximate axial symmetry. This allows us to deduce that VO(box) keeps even coordination after exchange in interlayer clay. The spectra exhibit a well-resolved hyperfine structure, indicating a good dispersion of vanadium.

3.2 Catalytic activity

The neat and the supported VO(box) catalysts were tested and compared in the asymmetric sulfoxidation to explore the steric effect of the R group in position 4 of the oxazoline ring. The reactions were carried out using thioanisole (methyl phenyl sulfide) as the model substrate. As terminal oxidant, we used the alkyl hydroperoxides (ROOH), which includes, in contrast to H_2O_2, the presence of another large group in the intermediate V-oxidant and then in the oxidation state of transition. Thus, the size of this group can play a role in the asymmetric induction and TBHP was tested to compare its performance with that of CHP. In all the cases >97% methyl phenyl sulfoxide selectivity was obtained, with very low over oxidation to sulfone. The yield of the sulfoxide and enantioselectivity results are summarized in Table 2.

As it can be observed in Table 2, in the absence of catalyst (entry 1) no reaction was observed and in the presence of Laponite as catalyst (entry 2) the reaction is very slow. Laponite, in contrast with clays from natural sources, does not contain active metals for oxidation, such as iron, copper or titanium, to cite the most commonly found in natural clays. Moreover, its acidity and basicity are very low. Thus, the activity for sulfide oxidation is not significant. The neat VO(box) complex, under the same reaction conditions (solvent, reaction temperature, etc.,), is in general more efficient than the supported catalyst, both with TBHP and CHP, as shown by the lower yield. This is predictably due to the required diffusion of the reactant and the oxidant molecules into the pores of the clay from the solution. However, homogeneous catalysts are known to be generally less attractive from an economic viewpoint since they cannot be recovered and reused to the opposite of the heterogeneous catalysts.

Furthermore, *tert*-butyl hydroperoxide is more reactive, as the yield obtained is, in all the cases both with heterogeneous and homogeneous catalysts, higher than that reached with cumenehydroperoxide. This can be explained by the bulkiness of the phenyl group of CHP, which would interfere with the appropriate coordination of chiral ligands with vanadium. However, the enantioselectivity is always lower than that obtained with CHP, mainly in the case of box(^{t}Bu) (entry 5 vs 6 and entry 12 vs 13). The relationship between activity and enantioselectivity points to a ligand accelerated reaction, in competition with a non-catalyzed oxidation.

As expected, the steric hindrance of the substituent in the oxazoline ligand exhibits a considerable influence on the catalytic performance, both with regard to activity and enantioselectivity which decrease with the increase of bulk of the substituent in the oxazoline ligand, either with the homogeneous or the heterogeneous catalysts, then the efficiency order is ^{i}Pr>^{t}Bu>Ph. This result contrasts with many examples described in the literature of catalysis with box-metal complexes, as *tert*-butyl and phenyl are by far the most successful substituents in this field [8]. However, in some cases it has been described that less hindered groups, such as isopropyl, are better than the other bulkier groups, depending on the type of reaction and the nature of the substrate [27]. Moreover, in the case of heterogeneous catalysts, this effect can be also attributed to the presence of some kind of restriction to diffusion of substrate and oxidant through the pores which are more narrow in the following order Ph>^{t}Bu> ^{i}Pr as indicated previously by textural study or to a better accommodation of the chiral complex on the laponite layers, more similar to the structure in solution, due to its lower bulkiness.

About the enantioselectivity, the best results are then obtained with Lap-VO(box-^{i}Pr), reaching values in the range of 16-20% but always lower than in solution. This can be explained by the presence of some non-complexed VO^{2+}, leading to racemic products. However, the 2N:V ratios are within the range of values expected for these complexes, they are near of 1 (table 1), which indicate probably that the basic ligand interacts with some of the acidic sites of the clay during the exchange process leading some non-complexed VO^{2+}, as reported in the literature [28].

According to the results obtained with Lap-VO(box-^{i}Pr), we can affirm that the catalysts generated by the ion exchange process can reveal, despite the weak interaction of the active phase with the support, optical and catalytic activity comparable or even higher than those obtained in the case of the similar catalysts prepared by covalent immobilization method. Indeed, VO-salen complexes on silica as an example have been much less efficient with regard to enantioselectivity in the asymmetric sulfoxidation [29].

Catalyst reusability is of major importance for heterogeneous catalysts, which makes them preferable over homogeneous catalysts. The recyclability of the best catalyst was investigated, using CHP as the reaction leading to the best enantioselectivity. The catalyst was recovered by filtration after the end of the reaction, then thoroughly washed with dichloromethane solvent, and dried in vacuum at 60 °C for 12 h. A new reaction was then performed with reactants and solvent under identical reaction conditions. The results showed that there was a deactivation in the catalyst as shown by the decrease of the yield (entry 11 vs 10) indicating probably the increase of diffusional resistance due to the partial blockage of the pore system by some insoluble degraded product obtained by side reaction. In fact, a change in the pore structure of the support after the reaction in the case of the used catalyst (Lap-VO(box-^{i}Pr) as an example) due the decease of the BET surface area, pore volume and pore diameter compared to the fresh catalyst ones (Table 1). Moreover, not the leaching of the metals into the solution during the reaction. The filtrate after third run was measured for the V quantities using ICP/AES showing a trace amount of V ions, which suggested that the leaching of metals did not obviously take place during the oxidation of sulfide in liquid phase. About the nature of the vanadium centers after the reaction, the signal recorded in the catalyst used (Lap-VO(box-^{i}Pr) as an example, Figure 5) is similar to that observed in the fresh catalyst but with a lower resolution of the structure hyperfine. This observation can be explained by the presence of a slight change in the oxidation state from V^{4+} to V^{5+} (d^0).

As enantioselectivity is also reduced from 20 to12% due probably to a some decomplexations of the chiral ligand since the value of 2N:V ratio in the used catalyst case (Lap-VO(box-^{i}Pr) as an example), decreases compared to the new catalyst one (Table 1).

Conclusion

The chiral complexes of bis(oxazolines) with $VO(OTf)_2$ were prepared and supported on the Laponite clay by cation exchange, as it has been demonstrated by a variety of physico-chemical methods . Immobilized VO(box)are able to promote the enantioselective oxidation of methyl phenyl sulfide to the sulfoxide especially with cumenehydroperoxide as terminal oxidant, leading to results always lower those obtained in homogeneous phase. The isopropyl substituted bis(oxazoline) leads to the best results, both with homogeneous and heterogeneous, reaching a moderate 28% and 20%ee, respectively. The recovered solids are less active, without V leaching due to the stability of its interaction with the support. The enantioselectivity is also reduced indicating the decomplexation of the chiral ligand.

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References

[1]I. Fernandez, N.Khiar,Chem.Rev 103(2003) 3651-3706.

[2]E. Wojaczynska, J. Wojaczynski, Enantioselective synthesis of sulfoxides: 2000-2009,Chem.Rev. 110(2010) 4303-4356.

[3]H. Srour,P. Le Maux, S. Chevance,G. Simonneaux, Coord.Chem. Rev. 257(2013) 3030-3050.

[4]P. Pitchen,H. B Kagan, Tetrahedron Lett. 25(1984)1049-1052.

[5]C. Sasaki,K. Nakajima, M. Kojima, J. Fujita, Preparation and characterization of optically Active quadridentate Schiff Base-Titanium (IV),Bull. Chem. Soc. Jpn. 64 (1991)1318-1324.

[6]C. Bolm,G. Schlingloff, F. Bienewald,J. Mol. Catal. A: Chem. 117 (1997)347-350.

[7]S. Schoumacker, O. Hamelin, J. Pécault, M. Fontecave,Inorg. Chem.42 (2003)8110-8116.

[8]G. Desimoni, G.Faita,K. A. Jorgensen, Chem. Rev. 111(2011) PR284–PR437.

[9]M. B. Andrus, J. C. Lashley,58(2002) 845-866.

[10]C. Bolm C, Coord. Chem. Rev. 237 (2003) 245-256.

[11]P. G Cozzi,C. Floriani,Inorg. Chem 34:(1995)2921-2930.

[12]M. M. Javadi, M. Moghadam, I. Mohammadpoor-Baltork, S.Tangestaninejad, V.Mirkhani, J. Iran. Chem. Soc. 12 (2015) 477-485.

[13]H. J. Hwang, M.Abu-Omar,Tetrahedron Lett. 40 (1999)8313-8316.

[14]C. Bolm,T. K. K.Luong, Harms, Chem.Ber.-Recl. 130 (1997)887-890.

[15]H. U. Blaser,Tetrahedron: Asymmetry. 2 (1991) 843-866.

[16]J. M. Fraile, J. I. García, J. A. Mayoral,T. Tarnai, Tetrahedron: Asymmetry. 9 (1998) 3997-4008.

[17]J. M. Fraile, P. López-Ram-de-Viu, J. A. Mayoral, M. Roldán, J. Santafé-Valero, Org. Biomol. Chem. 9 (2011) 6075-6081.

[18]M. J.McKennon, A. I.Meyers,J. Org. Chem.58 (1993)3568-3571.

[19]A. Cornejo, J. M. Fraile,J. I. García, M. J. Gil, V. Martínez-Merino,J. A. Mayoral, E.Pires,I. Villalba, Syn.Lett.15(2005) 2321-2324.

[20]S. J. Gregg,K. S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1991, (Chapter I).

[21]J. H. de Boer, B. G. Linsen, T.Osinga,J. Catal. 4 (1965) 643-648.

[22]J. M. Fraile, J. I. García, C. I. Herrerías, J. A. Mayoral, M. A. Harmer, J. Catal. 221 (2004) 532-540.

[23]D. Chatterjee, A. Mitra,RE. Shephered,Inorg. Chim. Acta. 357 (2004) 980-990.

[24]M. Salavati-Niasari, Z. Salimi, M. Bazarganipour, F. Davar,Inorg.Chim. Acta. 362 (2009) 3715-3724.

[25]M. A. Camblor, A. Corma, J.Perez-Pariente,J.Chem. Soc.Chem.Commun.(1993) 557-559.

[26]M. S.Rigutto, H. V. Bekkum, J. Mol. Catal.81 (1993)77-98.

[27]M. P. Sibi, M. Liu, Org. Lett. 3(2001)4181-4184.

[28]L. Aldea, J. M. Fraile, H.García-Marín,J. I. García, C. I. Herrerías, J. A. Mayoral, I.Pérez, Green Chem. 12 (2010) 435-440.

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

Table 1. Physicochemical characterization of Laponite and Lap-VO(box) catalysts

Samples	**V loading (mmol/g)**[a]	**2N/V**	**d_{001} (Å)**	**V_p (cm^3/g)**	**D_p (nm)**	**S_{BET} (m^2/g)**
Laponite	---	---	13.58	0.22	37	307
Lap-VO(box-^{i}Pr)	0.45	1.2	14.73	0.21	35.5	248
Lap-VO(box-*t*Bu)	0.32	1.1	14.80	0.18	34.9	197
Lap-VO(box-*Ph*)	0.22	0.85	15.55	0.17	33.4	154
Lap-VO(box-^{i}Pr)[b]	0.39	0.7	--	0.16	37.6	149

[a] Vanadium content determined by ICP-OES analysis.

S_{BET} = surface area; V_p = pore volume; D_p = mean pore diameter (determined by the BJH (Barrett-Joyner–Halenda) method); d_{001} = basal spacing.

[b] Recycled catalyst.

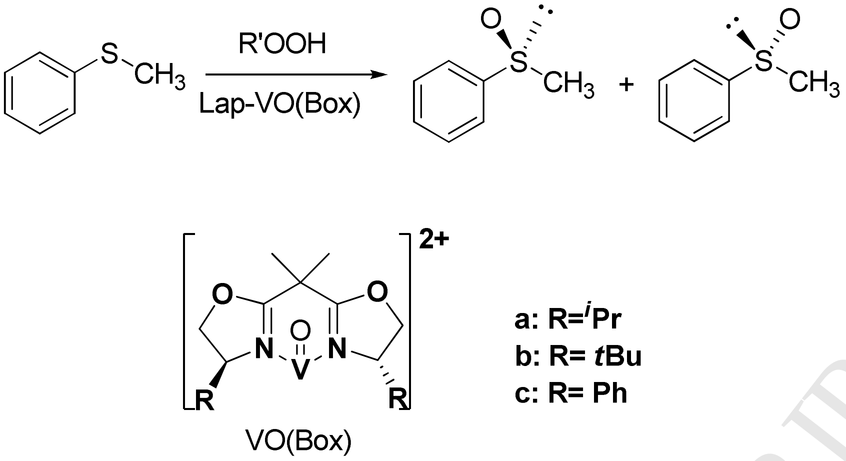
Table 2. The catalytic activity of the neat and the supported VO(box) complexes in the asymmetric oxidation of methyl phenyl sulfide

Entry	Catalyst	Oxidant	Yield (%)	Ee (%)[a]
1	None	TBHP	No reaction	--
2	Laponite	TBHP	4	--
3	VO(box-^{i}Pr)	TBHP	91	22
4		CHP	85	28
5	VO(box-^{t}Bu)	TBHP	90	9
6		CHP	68	23
7	VO(box-Ph)	TBHP	70	<5
8		CHP	48	<5
9	Lap-VO(box-^{i}Pr)	TBHP	82	16
10		CHP	63	20
11		CHP [b]	43	12
12	Lap-VO(box-^{t}Bu)	TBHP	76	<5
13		CHP	59	11
14	Lap-VO(box-Ph)	TBHP	68	<5
15		CHP	51	<5

Reaction conditions: 1 mmolthioanisole, 1.1 mmol oxidant, 0.012 mmol V, in 5mLof dichloromethane, at room temperature, 8h.

[a] The enantiomeric excess was determined by HPLC with a Chiralpack OD-H column and hexane/^{i}PrOH (91:9) as an eluent.

[b] The reaction was carried with a recycled catalyst.



Scheme.1

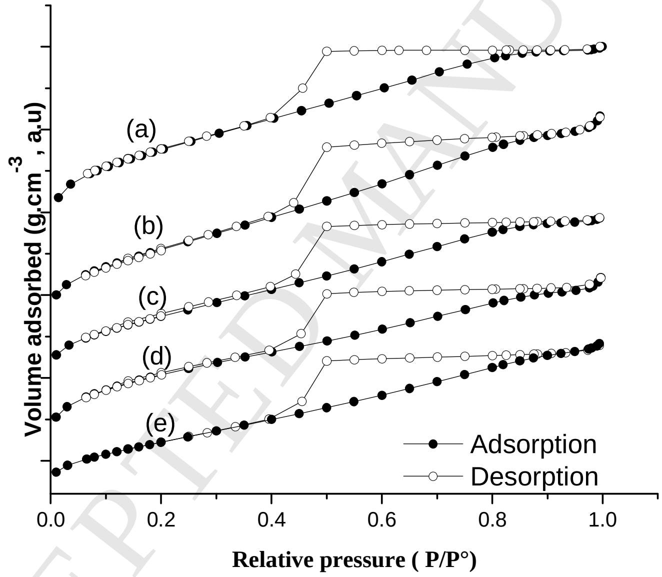


Fig. 1. N_2 adsorption–desorption isotherms at 77 K of : (a) Laponite, (b) Lap-VO(box-^{i}Pr), (c) Lap-VO(box-^{t}Bu), (d) Lap-VO(box-Ph) and (e) Lap-VO(box-^{i}Pr) recycled

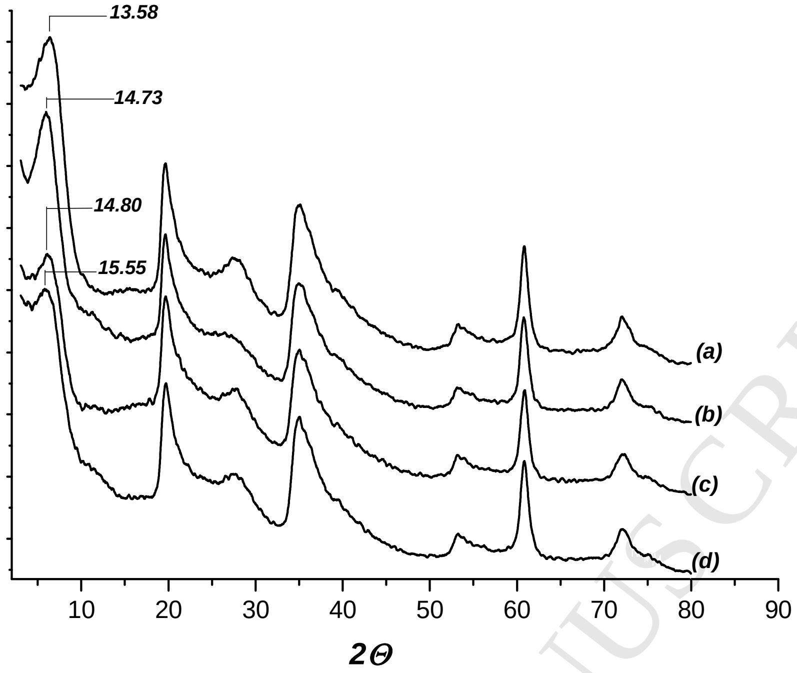


Fig. 2. DRX patterns of the different Laponite solids: (a) Laponite,(b) Lap-VO(box-^{i}Pr), (c) Lap-VO(box-^{t}Bu), and (d) Lap-VO(box-Ph).

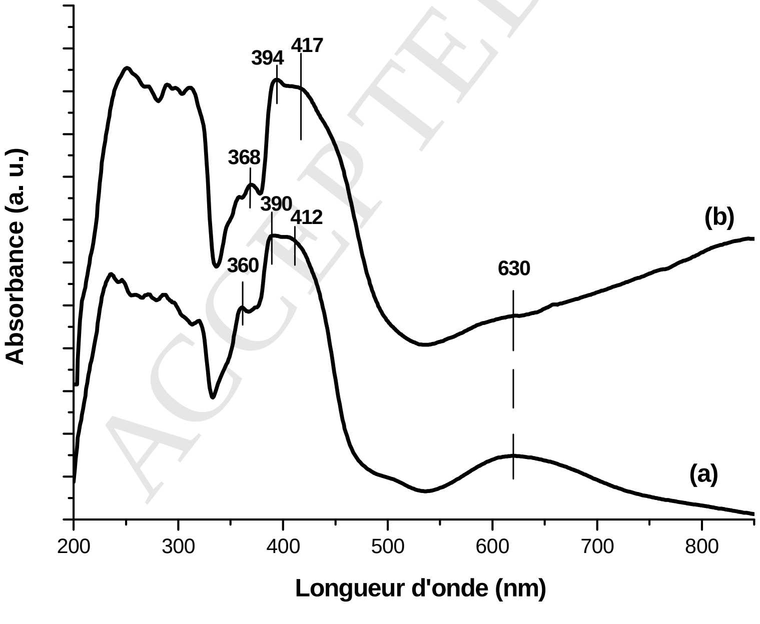


Fig. 3. Diffuse reflectance UV–Vis spectra of (a) VO(box-^{i}Pr) and (b) Lap-VO(box-^{i}Pr).

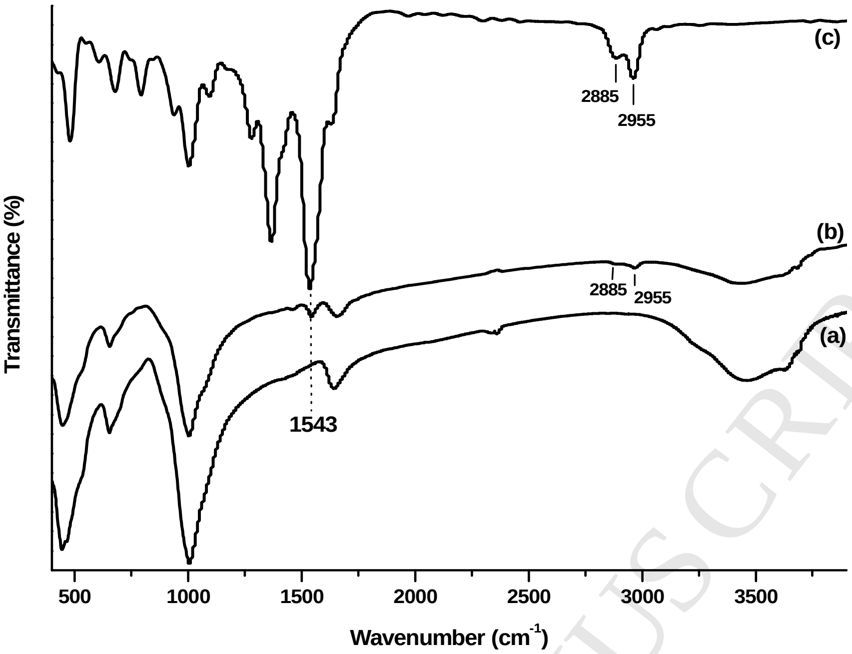


Fig.4. IR spectra of the different Laponite solids: (a) Laponite, (b) Lap-VO(box-^{i}Pr) and (c) VO(box-^{i}Pr).

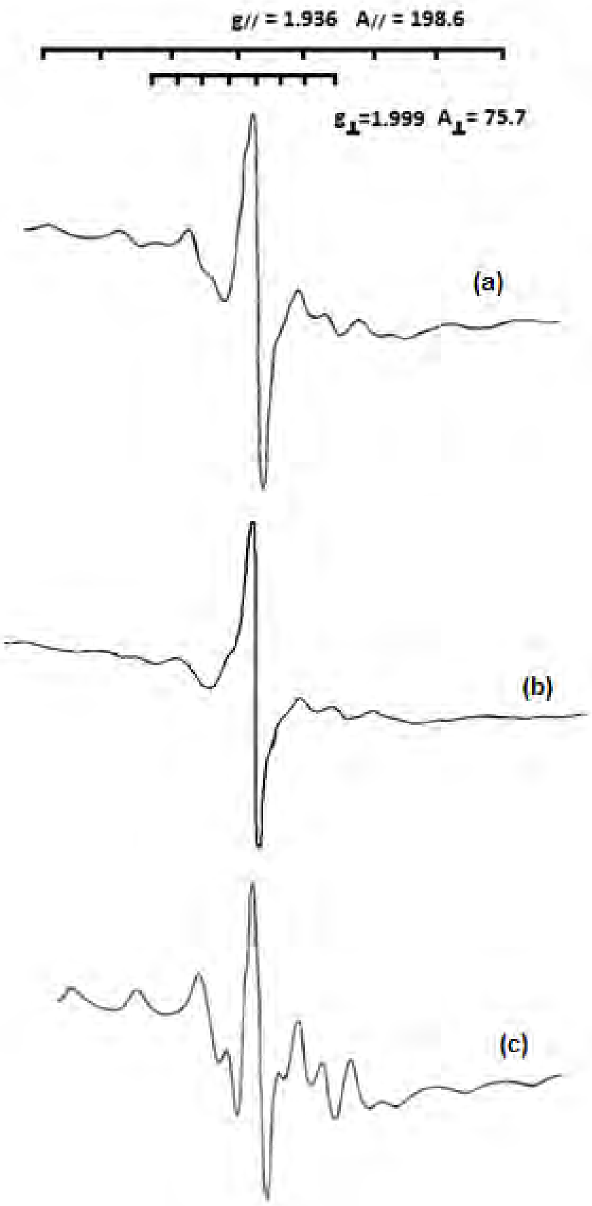


Fig. 5. ESR spectra of (a) Lap-VO(box-^{i}Pr), (b) recycled Lap-VO(box-^{i}Pr) and (c) VO(box-^{i}Pr) at 77 K.

Highlights

- Bis(oxazoline)-vanadium complexes were synthesized and exchanged on the Laponite.
- All complexes were tested as catalysts in the asymmetric oxidation of methyl phenyl sulfide.
- The isopropyl substituted bis(oxazoline) leads to the best results.