Chiral dioxomolybdenum(VI) and oxovanadium(V) complexes anchored on modified USY-zeolite and mesoporous MCM-41 as solid selective catalysts for oxidation of sulfides to sulfoxides or sulfones

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Abstract

Heterogenisation of new dioxomolybdenum and oxovanadium complexes bearing a trietoxysilyl group on modified ultra stable Y zeolite and mesoporous all-silica MCM-41 through covalent bonding to support is reported. All catalysts, homogeneous and heterogenised, are active and highly selective in the oxidation of alkyl phenyl sulfides to sulfoxides using TBHP or H_2O_2 as final oxidants. The corresponding sulfones were obtained in quantitative yield when 2.5 equivalents of oxidant were used. The heterogenised catalysts have shown a comparable activity respect to the corresponding homogeneous ones. Lifetime of heterogenised catalysts has been examined by repeated use of the complexes leading similar rates and yields of sulfoxide, without appreciable loss of metal over several runs, when molybdenum complexes were used as catalysts.
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1. Introduction

Sulfoxides are known to have interesting and useful biological and pharmacodynamic properties [1] as well as being one of the most widely used chiral auxiliaries [2,3]. They are obtained by oxidation of thioethers by peracids, peroxides and alkylperoxides using transition metal catalysts [4]. Depending on the catalysts selectivity and the method used, different proportions of sulfoxide and sulfone are produced. Among the metal catalysts for asymmetric sulfide oxidation titanium based systems are the most prominent ones [5,6]. The oxidation chemistry of titanium(IV) derivatives shares some common features with that of other d^0 transition metals species, e.g. V(V), Mo(VI) and W(VI). Thus, derivatives of all these metals readily react with hydrogen peroxide and alkyl hydroperoxides forming peroxocomplexes, which are effective and selective oxidants of organic and inorganic substrates, usually much stronger than the parent peroxides. Recently, the use of vanadium catalysts for sulfide oxidation

has been reviewed [7], high yields and enantioselectivities have been reached with a limited number of substrates, however, good enantiomeric excesses have never been achieved with simple sulfides like methyl phenyl sulfide.

One of the main targets of advanced organic synthesis is represented by the achievement of highly efficient, cheap and environmentally acceptable process. This result allows the formation of unwanted waste to be minimised and tedious and expensive purification procedures to be avoided. In the last decade, much effort has been paid to attach homogeneous transition-metal complexes to insoluble supports, such as organic polymers or metal oxides. Reaction of metallic complexes with solid surfaces may lead to stable solid catalysts, in which a transition-metal complex remains hooked or anchored to the surface atoms. These heterogenised catalysts may combine the ease of product separation with reactivity and selectivity founded with homogeneous catalysts [8].

Zeolites are crystalline aluminosilicates whose internal voids are formed by cavities and channels of strictly regular dimensions and of different sizes and shapes. In particular, the structure of Y zeolite consists of almost spherical 13 Å cavities interconnected tetrahedrally through smaller

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apertures of 7.4 Å diameter. The metal complex can be easily accommodated inside the supercages of Y zeolite. Also, there is now considerable interest in the application of new generation of structured mesoporous siliceous materials as catalyst support; MCM-41 is one member of this family [9]. The chemical reactivity of these mesoporous materials facilitates the covalent anchoring of various functional groups to its walls. The preparation of such inorganic–organic hybrid materials is of growing interest [10,11], especially for the attachment of various metal complexes. In recent years, selective oxidation of sulfides to sulfoxides has been carried out with a large number of heterogeneous and supported reagents based on zeolites [12–15], clays [16] or Al_2O_3 [17].

The coordination chemistry of molybdenum(VI) has assumed special importance due to its recently discovered biochemical significance [18–20] as well as for the involvement of Mo(VI) compounds as catalysts in several industrial processes, such as epoxidation of olefins [21], olefin metathesis [22] and isomerization of allylic alcohols [23]. We reported earlier the catalytic activity of molybdenum complexes covalently anchored onto the walls of functionalised USY zeolite in the selective epoxidation of allylic alcohols [24].

The objective of the present study was synthesise and examine the properties of a series of heterogenised molybdenum(VI) or vanadium(V)-catalysts and tests its activity toward the oxidation of organic sulfides, such as methyl phenyl sulfide and (2-ethylbutyl) phenyl sulfide, comparing to their homogeneous analogues and using H_2O_2 and *t*-butylhydroperoxide (TBHP) as oxygen source.

2. Experimental

2.1. General

All solvents were carefully degassed prior to use. The silylating agent $OCN(CH_2)_3Si(OEt)_3$ obtained from Fluka (96%) was distilled before use. An anhydrous solution of TBHP in CH_2Cl_2 (2.35 M) recently prepared from aqueous TBHP-70 according to a literature method was employed [25]. Molybdenyl acetylacetonate $[MoO_2(acac)_2)]$ and vanadium acetylacetonate $[VO(acac)_2]$ were used as supplied.

Preparations of complexes were carried out under dinitrogen by standard Schlenk techniques. C, H and N analysis were carried out by the analytical department of the Institute of Organic Chemistry (CSIC) with a Heraeus apparatus. Metal content was analysed by using inductively coupled plasma (ICP) with a Perkin-Elmer Plasma 40-ICP spectrometer. Infrared spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) as KBr pellets. ^{1}H- and ^{13}C NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers; chemical shifts are given in ppm with tetramethylsilane as internal standard. Optical rotation values were measured with a Perkin-Elmer 241 MC polarimeter. Gas chromatography (GC) analysis was performed using a Hewlett-Packard 5890 II with a

flame ionisation detector in a cross-linked methylsilicone column.

The inorganic supports are an ultrastable Y zeolite (USY) and a mesoporous MCM-41. USY zeolite was prepared by steam calcination at 1023 K from a partly (80%) ammonium exchanged NaY (SK40 Union Carbide), followed by treatment with a 1 N citric acid solution at 333 K for 30 min for removing of extraframework species. After this, the zeolite was thoroughly washed and dried at 403 K for 6 h. The final zeolite contained, besides the typical ∼12 Å micropores, a well-developed supermicropore–mesopore system (pore diameter 12–30 Å). The controlled dealumination promotes destruction of some sodalite units, which allowed direct communication between α-cages generating cavities wider than 12 Å. The formation of supermicropores and large mesopores has been detected by N_2 adsorption–desorption. The main characteristics of the resultant zeolite are: unit cell size: 24.40 Å, bulk SiO_2/Al_2O_3: 4.2, crystallinity: >95%. A detailed synthesis procedure for purely siliceous MCM-41 has been described [9,26]. The inorganic supports were dried at 415 K under 0.01 torr before the heterogenisation process. This treatment is sufficient to achieve complete thermosorption of physically absorbed water molecules from the surface.

The organic compounds used were analysis grade. The thioethers, methyl phenyl sulfide and (2-ethylbutyl) phenyl sulfide, were prepared by standard methods in the literature [27].

2.2. Preparation of ligands

The diastereomeric ligands (2*S*,4*S*)- and (2*S*,4*R*)-*N*-benzyl-4-hydroxy-4-phenyl-2-(1,1 - diphenylmethyl)pyrrolidinylmethanol (**1a** and **2a** respectively), (2*S*,4*R*)-*N*-*t*-butyl-aminocarbonyl-4-hydroxy-4-phenyl-2 - (1,1 - diphenylmethyl)pyrrolidinylmethanol (**2b**) and (2*S*,4*S*)- and (2*S*,4*R*)-*N*-(3-triethoxysilyl)propylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenyl methyl)pyrrolidinylmethanol (**1c** and **2c** respectively) were synthesised previously in our laboratory [24], see Scheme 1.
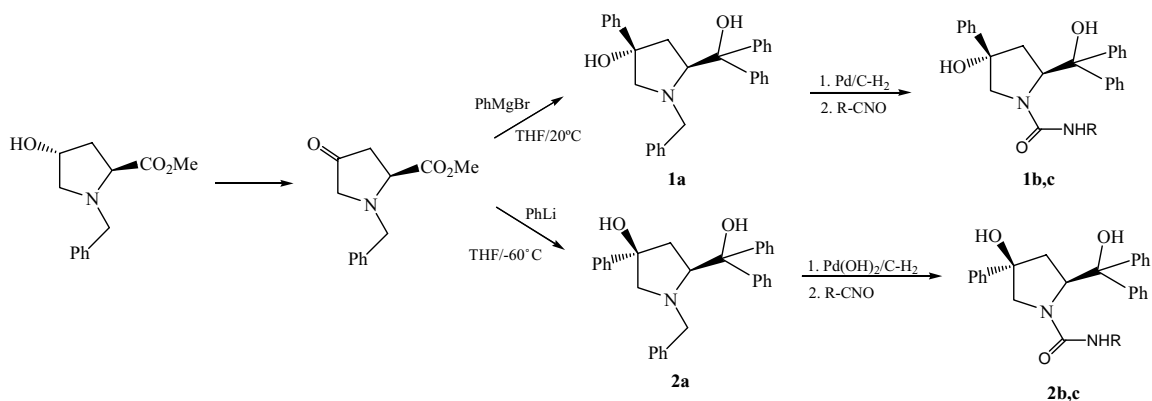
2.3. Synthesis of complexes

2.3.1. Dioxomolybdenum complexes

The dioxomolybdenum complexes used in this work [MoO$_2$L, L = **1**, **2a–c**] were prepared by the procedure reported in [24], see Scheme 2.

2.3.2. Oxovanadium complexes

Oxovanadium complexes **V-1**, **2a–c** were synthesised using the following general procedure: the corresponding ligand (**1**, **2a–c**) (0.7 mmol, 1 eq.) was added to a solution of [VO(acac)$_2$] (0.7 mmol, 1 eq.) in dichloromethane or dichloroethane (50 ml), in a Schlenk type flask under argon atmosphere. The reaction mixture was stirred for 24 h at reflux of solvent. The solution was filtered, the solvent

Scheme 1. Synthesis of ligands.

evaporated under reduced pressure and the solid crude complex washed with pentane and then dried in vacuum. Characterisation of the different complexes was carried out by a multitechnique approach (see above).
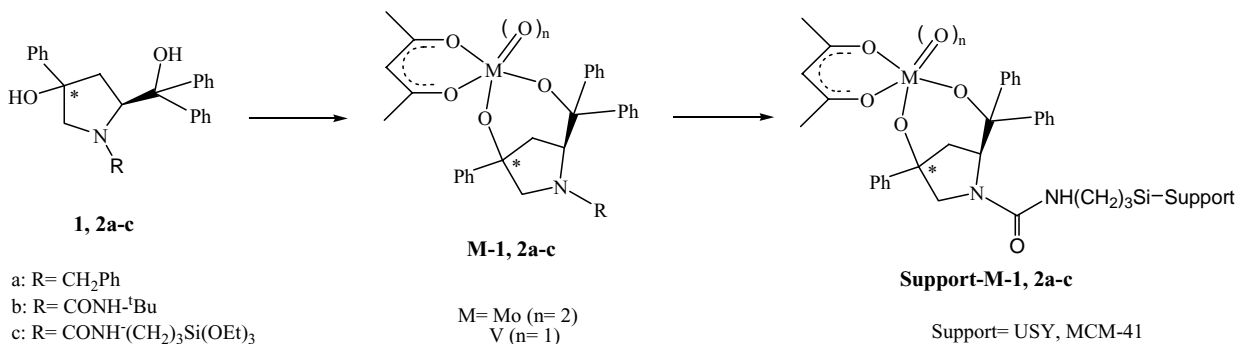
2.3.2.1. {V(O)(acac)[(2S,4S)-N-(3-triethoxysilyl) propylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol]} (V1c).
Yield: 99%. mp: 187–189. $[\alpha]_D^{20} = +7.6°$ ($c = 0.2$, ethanol). $C_{38}H_{49}N_2O_9SiV$ (756.8): calc.: C 62.6, H 6.8, N 3.8, V 7.0; found: C 62.2, H 6.8, N 4.1, V 6.8%. IR (KBr, cm^{-1}): 3700–3100 (NH); 3100–2800 (C–H); 1700, 1610 (N–CO–N); 1560, 1530 (C=O acac); 1550 (SiO–C); 1450 (C–C cycl.); 1380 (C–N cycl.); 1370, 1360 (C=C acac); 1100, 1070 (Si–O); 995 (V=O); 760, 700.

2.3.2.2. {V(O)(acac)[(2S,4R)-N-benzyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol]} (V2a).
Yield: 99%. mp: 108–109. $[\alpha]_D^{20} = +19.7°$ ($c = 0.5$, CH$_2$Cl$_2$). $C_{35}H_{34}NO_5V$ (599.6): calc.: C 62.2, H 6.8, N 4.1, V 6.8; found: C 62.6, H 6.8, N 3.8, V 7.0%. ^{1}H-NMR: δ = 7.60–7.10 (m, 20H, arom); 5.40 (s, 1H, CH, acac); 4.82–4.75 (m, 1H, CHN); 3.45, 2.98 (AB, 2H, $J = 10.1$ Hz, CH$_2$N); 3.25, 3.01 (AB, 2H, $J = 13.1$ Hz, CH$_2$–Ph); 2.48–2.15, (m, 2H, CH$_2$–CH); 2.10 (s, 6H, CH$_3$, acac). IR (KBr, cm^{-1}): 3400 (NH); 1645 (N–CO–N); 1560,

1530 (C=O acac); 1450 (C–C cycl.); 1380 (C–N cycl.); 1370, 1360 (C=C acac); 995 (V=O); 730, 700 cm^{-1}.

2.3.2.3. {V(O)(acac)[(2S,4R)-N-t-butylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl) pyrrolidinylmethanol} (V2b).
Yield: 99%. mp: 153–155. $[\alpha]_D^{20} = +26.8°$ ($c = 0.5$, CH$_2$Cl$_2$). $C_{33}H_{37}N_2O_6V$ (608.6): calc.: C 65.1, H 6.1, N 4.6, V 8.4; found: C 64.1, H 5.9, N 4.2, V 8.0%. ^{1}H-NMR: δ = 7.60–7.10 (m, 15H, arom); 5.47 (s, 1H, CH, acac); 5.15–5.06 (m, 1H, CHN); 4.22 (d, 1H, $J = 11.2$ Hz, CH$_2$N); 3.70–3.58 (m, 1H, CH$_2$N); 2.94–2.74, 2.56–2.42 (2m, 2H, CH$_2$–CH); 2.02 (s, 6H, CH$_3$, acac); 1.15 (s, 9H, C–CH$_3$). IR (KBr, cm^{-1}): 3400 (NH); 1645 (N–CO–N); 1560, 1530 (C=O acac); 1450 (C–C cycl.); 1380 (C–N cycl.); 1370, 1360 (C=C acac); 995 (V=O); 730, 700.

2.3.2.4. {V(O)(acac)[(2S,4R)-N-(3-triethoxysilyl) propylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol]} (V2c).
Yield: 99%. mp: 193–194. $[\alpha]_D^{20} = +19.7°$ ($c = 0.4$, ethanol). $C_{38}H_{49}N_2O_9SiV$ (756.8): calc.: C 62.6, H 6.8, N 3.8, V 7.0; found: C 61.3, H 6.2, N 3.5, V 7.1%. IR (KBr, cm^{-1}): 3700–3100 (NH); 3100–2800 (C-H); 1700, 1610 (N–CO–N); 1560, 1530 (C=O acac); 1550 (SiO–C); 1450 (C–C cycl.); 1380 (C–N cycl.); 1370, 1360 (C=C acac); 1100, 1070 (Si–O); 995 (V=O); 760, 700.

a: R= CH$_2$Ph
b: R= CONH-^{t}Bu
c: R= CONH-(CH$_2$)$_3$Si(OEt)$_3$

M= Mo (n= 2)
V (n=1)

Support= USY, MCM-41

Scheme 2. Synthesis of complexes and heterogenisation.

Table 1
Analytical data for the heterogenised dioxomolybdenum complexes

Catalyst	Elemental analysis (found (calculated)(%))				Anchored (%)	Mo=O ν (cm^{-1})
	C	H	N	Mo[a]		
USY-Mo1c	7.64 (7.61)	2.06 (0.82)	0.53 (0.46)	1.60	80	940, 910
USY-Mo2c	6.34 (6.04)	2.23 (0.65)	0.45 (0.37)	1.27	64	940, 910
MCM-Mo1c	3.52 (3.99)	1.19 (0.43)	0.31 (0.24)	0.84	42	940, 910
MCM-Mo2c	5.82 (3.85)	1.22 (0.42)	0.35 (0.23)	0.81	41	940, 910

[a] Measured by ICP.

Table 2
Analytical data for the heterogenised oxovanadium complexes

Catalyst	Elemental analysis [found (calculated) (%)]				Anchored (%)	V=O ν (cm^{-1})
	C	H	N	V[a]		
USY-V1c	11.47 (10.66)	2.13 (1.15)	0.61 (0.65)	1.19	59	995
USY-V2c	15.17 (14.69)	2.23 (1.59)	0.78 (0.90)	1.64	82	995
MCM-V1c	7.69 (7.08)	1.25 (0.77)	0.53 (0.43)	0.79	40	995
MCM-V2c	13.06 (13.89)	1.20 (1.50)	0.78 (0.85)	1.55	78	995

[a] Measured by ICP.

2.4. Heterogenisation of dioxomolybdenum and oxovanadium complexes on USY and MCM-41-zeolite

A dioxomolybdenum or oxovanadium complex bearing a triethoxysilyl group (0.3 mmol) in dry methylene chloride (2 ml) was added to a suspension of the inorganic support (modified USY-zeolite or MCM-41 dried at 413 K for 3–4 h "in vacuo") (1 g) in dry toluene (40 ml). The mixture was stirred, under argon, for 24 h at room temperature. Then, the solid was filtered and Soxhlet-extracted with CH$_2$Cl$_2$/ethyl ether (1:1) for 7 h to remove the remaining non-supported complex from heterogenised catalyst. The pale solid was dried in vacuo and characterised by elemental analysis of C, H, N, Mo and V and IR spectroscopy. The analytical data are shown in Table 1 (heterogenised dioxomolybdenum complexes) and Table 2 (heterogenised oxovanadium complexes).

2.5. General procedure for oxidation of sulfides

Oxidation reactions were carried out in a 25 ml flask equipped with a magnetic stirrer. The flask was charged with: (i) 5 ml of a solution or suspension of the catalyst (0.005 mmol) in acetonitrile; (ii) a solution of the corresponding thioether [methyl phenyl sulfide or (2-ethylbutyl) phenyl sulfide, 1 mmol]. The oxidant, either TBHP (1.1 mmol) or H$_2$O$_2$ (30%, 1.5 mmol or 1.1 mmol) were added dropwise while the overall suspension was heated at 313 K for dioxomolybdenum complexes or cooled at 273 K for oxovanadium complexes. Samples were taken

Table 3
Oxidation of alkyl phenyl sulfides catalysed by molybdenum-complexes ("neat" and heterogenised)[a]

Substrate	Catalyst	H$_2$O$_2$[b]		t-BuOOH[c]	
		Conversion (%, 1 h)	TOF[b]	Conversion (%, 1 h)	TOF[d]
Methyl phenyl sulfide	Mo1a	99.1	839	31.2	245
	USY-Mo1c	48.0	410	83.1	476
	MCM-Mo1c	100	591	100	698
	USY-Mo2c	73.4	266	81.2	286
	Mo2a	98.9	447	97.5	258
	MCM-Mo2c	100	618	100	794
(2-Ethylbutyl) phenyl sulfide	Mo1a	38.7	96	48.7	175
	USY-Mo1c	48.9	102	78.7	164
	MCM-Mo1c	88.5	335	100	443
	Mo2a	39.9	81	40.3	111
	USY-Mo1c	98.0	226	79.9	207
	MCM-Mo2c	98.7	357	100	498

[a] Blank tests achieved conversions lower than 3% with H$_2$O$_2$ and no reaction was observed with t-BuOOH.
[b] Reactions were performed with 1.5 eq. of H$_2$O$_2$.
[c] 1.1 eq. of t-BuOOH.
[d] Turnover: mmol product/mmol catalyst h.

Table 4
Oxidation of alkyl phenyl sulfides catalysed by vanadium complexes ("neat" and heterogenised)[a]

Substrate	Catalyst	H$_2$O$_2$[b]		t-BuOOH[c]	
		Conversion (%, 1 h)	TOF[b]	Conversion (%, 1 h)	TOF[d]
Methyl phenyl sulfide	V1a	90.1	483	92.6	556
	USY-V1c	95.7	559	100	367
	MCM-V1c	99.9	458	97.4	209
	USY-V2c	90.9	508	90.1	564
	V2a	95.4	530	100	832
	MCM-V2c	98.6	535	99.5	366
(2-ethylbutyl) phenyl sulfide	V1a	95.1	313	100	327
	USY-V1c	91.9	398	100	487
	MCM-V1c	98.3	270	98.7	323
	V2a	98.0	311	100	225
	USY-V1c	88.6	404	50.7	208
	MCM-V2c	97.7	433	68.9	285

[a] Blank tests achieved conversions lower than 3% with H$_2$O$_2$ and no reaction was observed with t-BuOOH.

[b] Reactions were performed with 1.1 eq. of H$_2$O$_2$.

[c] 1.1 eq. of t-BuOOH.

[d] Turnover: mmol product/mmol catalyst h.

at regular times and, after filtration, they were analysed. Chemical yields and enantiomeric excess of methyl phenyl sulfide were measured by GC with a chiral glass capillary column {15/85 mixture of methylsilicone (OV-1701) and methylsilicone-heptakis-[2,3-dipentyl-6-(t- butyldimethylsilyl)]-β-cyclodextrin as stationary phase} [28]. The enantiomeric excess for (2-ethylbutyl) phenyl sulfoxide was determined by ^{1}H-NMR using (R)-(−)-α-metoxyphenylacetic acid, (−)-MPPA, as chiral agent [29]. The catalytic results are summarised in Tables 3–4.

3. Results and discussion

3.1. Synthesis of complexes

The ligands (2S,4S)- and (2S,4R)-N-benzyl-4-hydroxy-4-phenyl-2 - (1,1 - diphenylmethyl)pyrrolidinylmethanol (**1a**, **2a**) were used as ligands. It is found to act as bidentate O,O-donors. Reaction of these ligands with bis(acetylacetonato)dioxomolybdenum(VI) or bis(acetylacetonato)oxovanadium(V) in dichloromethane or dichloroethane under refluxing conditions produced the complex [M(O$_n$)L(acac)] (**2a–c**) in excellent yields (Scheme 2). Difficulties were found to prepare complexes **V1a**, **V1b**, whose substituents in position 2 and 4 of the proline ring show *trans*-disposition and bulky groups (Bn, CONH^{t}Bu) are bonded to pyrrolidinic nitrogen, and ligand was recovered completely unreacted after prolonged treatment (24 h) under standard conditions. It was only possible synthesised those where bulky group (triethoxysilyl) is in a position remote to coordination centre, **V1c**. On account of the very poor solubility of the oxovanadium complexes **V1c**, **V2c** in deuterated solvents and the broadening of the signals because of the presence of vanadium, their ^{1}H NMR spectra were not of sufficient

quality, only in the case of **V2a** and **V2b** was able to obtain the spectra. The differences in the chemical shift between oxovanadium complex and free ligand in both catalysts are comparatively small, ≈0.4 ppm to low-field region. Similar behaviour was observed in the case of the dioxomolydenyl complexes with the same ligands [9].

IR spectra of these complexes do not exhibit the ligand bands at ∼3450 cm^{-1} (ν(OH)). All complexes exhibit two bands at 940 and 910 cm^{-1}, assigned to symmetric and antisymmetric vibrations of the *cis*-MoO$_2$ core [30] (**Mo1**, **2a–c**), or a single band at 995 cm^{-1} corresponding to V=O stretching mode (**V1**, **2a–c**), as well as bands of acetylacetonate group (1600, 1370 and 1360 cm^{-1}), and the corresponding chiral ligand. As compared to the free ligand spectra, they are shifted within several cm^{-1} and redistributed in intensity, thus evidencing the bonding of the fragments into the complexes. At the same time, no bands in the region of 860–790 cm^{-1} were observed, so the formation of polymeric species with Mo = O → Mo [31] or V = O → V [32] bridges can be discarded.

3.2. Anchoring of dioxomolybdenum and oxovanadium complexes

The homogeneous complexes that bearing a Si(OEt)$_3$ group, at position remote to the metal centre, were anchored to different inorganic support according to Scheme 2. Preparation of these materials was carried out by controlled hydrolysis of Si–OEt bond at room temperature and reaction with the free silanols (Si–OH) on the surface of USY and MCM-41 zeolites. The successful synthesis of the supported catalysts was confirmed by the analytical data of C, H, N and metal (Tables 1 and 2). M/ligand (1:1) stoichiometry was found and the loading of metal is always ≈ 1–2%, independently of support. These values have been used for calculating the ratio catalyst/substrate in the reaction tests.
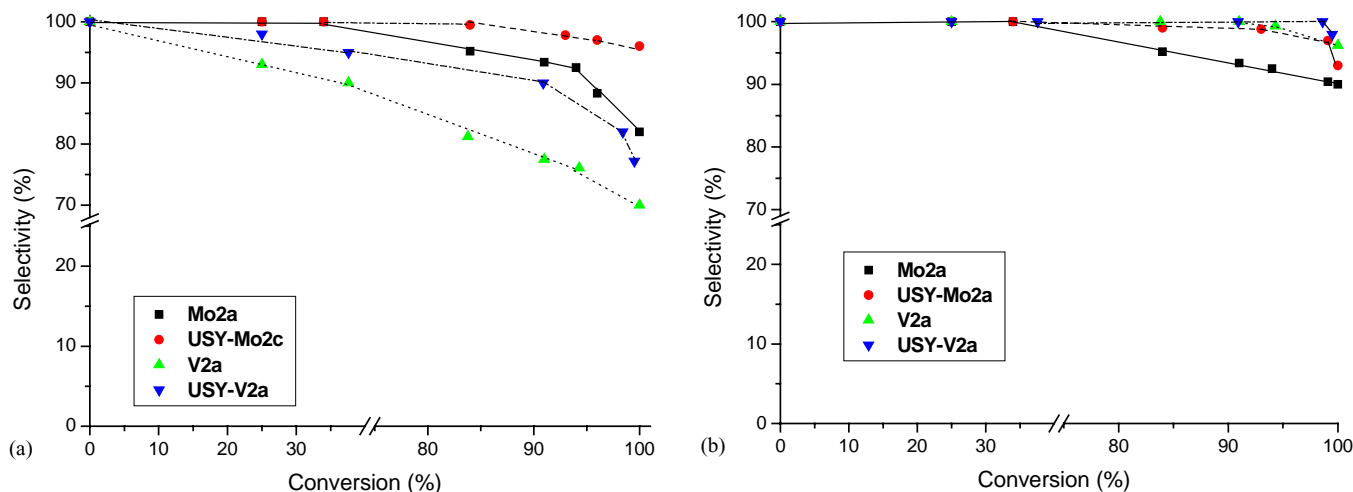
Fig. 1. Selectivity to methyl phenyl sulfoxide for the oxidation reaction carried out with homogeneous and heterogenised Mo- and V-catalysts using TBHP (1.5 eq.) as oxygen source (selectivity of 100% was achieved when 1 eq. of oxidant was added).

The presence of a *cis*-MoO$_2$ unit on the surface of support is confirmed by the IR spectra which show two bands in the expected range for the symmetric ($\sim$940 cm^{-1}) and antisymmetric (911 cm^{-1}) Mo=O stretching vibration; V=O appears at 990 cm^{-1}. The catalysts also showed evidence in the IR spectra for the retention of an acetylacetonate ligand. Based on these results it can be concluded that the species are covalently bonded to the surface and the co-ordination sphere around the metal is the same for the unsupported complexes under these reaction conditions. The ^{13}C CP-MAS NMR spectra of the solids verify the presence of covalently tethered Mo- and V-complexes (data not shown).

3.3. Catalytic oxidation of sulfides

The soluble and heterogenised molybdenum and vanadium catalysts were tested as catalysts for the oxidation of organic sulfides, using methyl phenyl sulfide and (2-ethylbutyl) phenyl sulfide as model substrates. TBHP or H$_2$O$_2$ were employed as oxygen source, always in excess with respect to the substrate (10%). Reactions were carried out at 313 K in the case of dioxomolybdenum catalysts, and at 273 K for oxovanadium catalysts. Higher reaction temperatures lead to a dramatic decrease in the selectivity to sulfoxide as well as significant loss of asymmetric induction. The outcome of the reaction was followed by GC and results are summarised in Tables 3 and 4 and Figs. 1–3. Blank experiments were carried out, with both sulphides and both oxidant agents, under identical test conditions. No reaction was observed when TBHP was used as oxidant and conversions lower than 3% after 2 h were obtained, even at room temperature, in the presence of H$_2$O$_2$.

The new materials are extremely efficient and catalyse the selective sulfoxide formation in concentration of 0.005 mmol of the Mo- or V-complexes under mild conditions. Total conversion was reached with most of the catalysts after 1 h of reaction. However, to high conversion of sulfide

(>90%), the oxidation does not stop at the sulfoxide level and proceeds yielding overoxidized products, such as sulfone (Fig. 1). The selectivity analysis shows that the sulfoxide is a primary and unstable product, while the corresponding sulfone appears as a secondary and stable product to high conversion. Similar results are obtained independently of the oxidant agent employed, *t*-butylhydroperoxide or hydrogen peroxide. Total conversion to the corresponding sulfone was obtained using 2.5 eq. of oxidant agent, after 1 h at 313 K, in the presence of a vanadium catalyst (**USY-V2c**).

Vanadium complexes are more active than the molybdenum analogues. It is noteworthy that the employment of 1.1 eq. of H$_2$O$_2$, in place of 1.5 eq. used with Mo-catalysts, and its controlled addition has allowed a significant improvement of the chemoselectivity of the process, and sulfoxide was obtained as unique product.
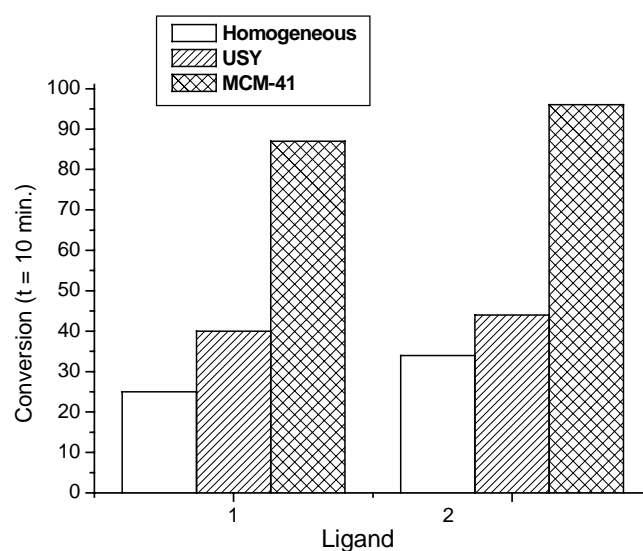

Fig. 2. Oxidation of methyl phenyl sulfide with diastereomeric Mo-catalysts ($T = 313$ K), using TBHP as oxidant.
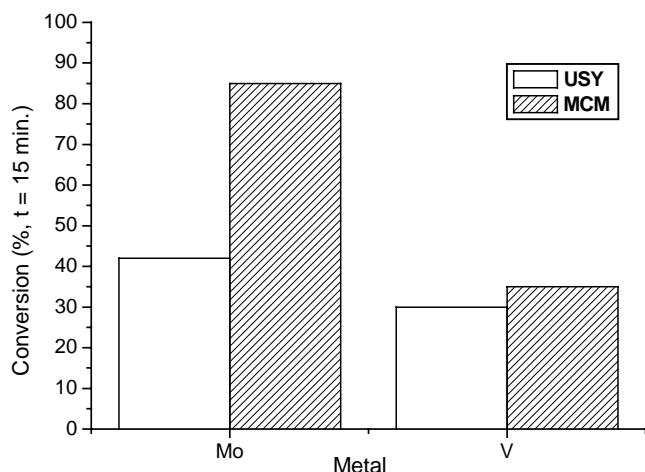
Fig. 3. Oxidation of methyl phenyl sulfide with heterogenised Mo- and V-catalysts, using TBHP as oxidant [$T = 313$ K (Mo); 273 K (V)].

To study the influence of the ligand stereochemistry on the sulfide oxidation, the activity of diastereomeric catalysts has been thoroughly compared (Fig. 2). The highest rates in the oxidation of methyl phenyl sulfide were observed with ligands having their coordinating donor groups in *cis*-disposition (2S,4R, derivatives of **2a–c**). Based on a mechanism in which simultaneous coordination of the substrate and oxidant agent to the metal ion at neighbouring position is involved, it can be concluded that the formation of the ternary diastereomeric key intermediate (metal-complex + substrate + hydroperoxide) must be favoured in these diastereomeric *cis*-ligands (**2a–c**). Similar behaviour has been observed by using their analogues V-catalysts, independently of support, oxidant agent or substrate used.

On the other hand, the results obtained for heterogenised catalysts are generally comparable with the corresponding soluble Mo- or V-complexes, which show similar pattern indicating that both reactions take place through the same mechanism, without any significant change in the reaction pathway. a logical slight decreasing rate is observed when a bulky substrate is oxidised [(2-ethylbutyl) phenyl sulfide].

The results given en Fig. 3 show that, for the case of methyl phenyl sulfide, MCM-heterogenised molybdenum catalysts are more active than USY-heterogenised analogues; it may be a consequence of the easier diffusion of the sulfide through the pores of MCM-41 (35 Å) than in the cavities and channels (12–30 Å) of USY zeolite. However, in the case of heterogenised vanadium catalysts the activity of USY-heterogenised ones is similar to that of MCM-heterogenised analogues. This fact may be explained taking into account the high affinity of vanadium to coordinate to free silanols from the surface of the supports. Thus, in the case of MCM-41, where the silanols content is higher, some of the catalytic active centres are not able for the reaction. This behaviour is corroborated by just about

every other catalysts, substrate and oxidant agent used in this research.

Although high yields and chemoselectivity have been reached with these homogeneous and heterogenised catalysts, poor enantioselectivities has been achieved (<10%). Due to these low values no significant differences were observed based on the catalyst structure; only the influence of the bulkiness in the case of (2-ethylbutyl) phenyl sulfide seems can be distinguished. In every case, the enantiomeric excess does not change during the reaction. The oxidation of (2-ethylbutyl) phenyl sulfide with hydrogen peroxide was carried out at different temperatures showing a significant enhancing enantioselectivity at lower temperatures (298 K, ee = 0.8%; 253 K, ee = 6.2%). This fact indicates that the sulfoxidation process is asymmetrically induced.

The major advantage of heterogeneous catalysis over its homogeneous counterpart are the ease of the recovering and recycling of the catalyst and the easier work up procedure that permits removing catalysts (metal and chiral inductor) from reaction media through a simple filtration. The lifetime of heterogenised catalysts was examined by using it in several reaction cycles. Before reuse the solid was separated from the reaction medium by filtration and washed with dichloromethane.

The heterogenised molybdenum catalysts (**USY-Mo1,2-c**, **MCM-Mo1,2-c**) could be reused at least four times without neither loss of activity (Fig. 4) nor selectivity with catalyst loading as low as 1.5 mol.%. The slight decreasing on the rate observed for the consecutive runs is due to the small amount of catalytic material losing by filtration. While the oxidation of sulfide continued in presence of the catalyst, there was no further significant conversion when the catalyst was removed from the reaction media. This conclusion was independently confirmed by the absence of molybdenum in the filtrate (measured by atomic absorption
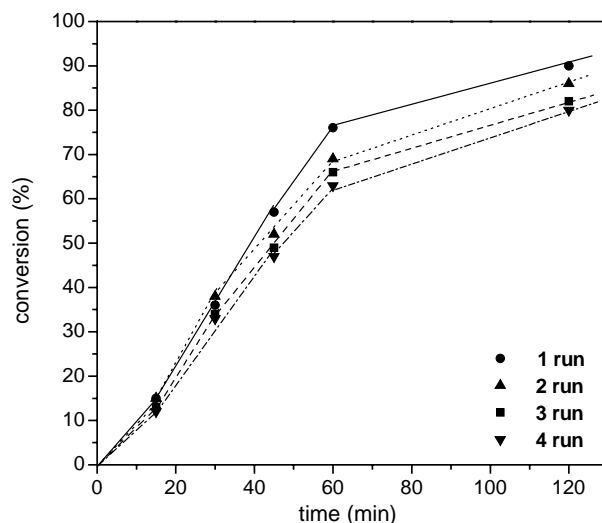

Fig. 4. Recycling experiments of catalyst **USY-Mo1c**: oxidation of (2-ethylbutyl) phenyl sulfide using TBHP as oxidant ($T = 313$ K).

Table 5
Vanadium content of filtrated solutions from recycling experiments with catalyst **USY-V1c**

	Solution (1 run)	Solution (2 run)	Solution (3 run)
Mg of vanadium[a]	0.104	0.045	0.022
Leaching percentage (%)[b]	21	9	4.5

[a] Measured by atomic absorption spectroscopy.
[b] Respect to initial content of V.

spectroscopy). The enhanced stability of the molybdenum complexes may be attributed to the stronger coordination of the dihydroxyligand to Mo than that of the acetylacetonate or hydroxyl group present on the *t*-butyl alcohol or hydroperoxide, and by dispersion the molecules of catalysts on the mesopores that avoids the dimerisation and polymerisation of Mo species. The filtered solid was characterised again by elemental and analysis and FTIR spectroscopy. The IR spectrum in the range 400–1500 cm^{-1}, comprising bands due to the silica host and also the Mo=O stretching vibrations, was very similar to that of the precursor catalyst, this suggest that the material was largely unchanged by the catalytic reaction. Elemental analysis confirmed only a small decrease in the molybdenum content (<3%).

However, in the case of heterogenised vanadium catalysts (**USY-V1,2-c**, **MCM-V1,2-c**) significant leaching was detected. While the loss of the catalytic activity was observed in the three consecutive runs, the values obtained by atomic absorption spectroscopy from the filtrated solutions confirmed the presence of different amounts of vanadium (Table 5).

The oxidation of sulfide was studied in these filtrated solutions, without additional catalyst, and moderate conversion was obtained. This fact is an evidence for formation of new homogeneous vanadium catalysts in the reaction media, due to the high affinity of vanadium to coordinate with donors group, such as hydroxyl groups. Vanadium passes to the solution forming a stable soluble complex with *t*-butyl alcohol or hydroxyl groups from the hydroperoxide. Certainly, these specimens may contribute to the observed activity but, due to their lower activity, it is possible to assume that it mainly derives from heterogenised-catalysed processes.

4. Conclusions

Molybdenum and vanadium complexes have been immobilised on USY zeolite and MCM-41. Immobilisation of metal complexes on supports has marked effects on the activity of molybdenum and vanadium complexes in the oxidation of organic sulfides to the corresponding sulfoxides. In general, the complexes immobilised are more active than the "neat" complexes and these could be reused in repeated cycles. For molybdenum derivatives, there was no leaching of the metal complex into the reaction medium and these immobilised catalysts can be recycled in the oxidation reactions. However, in the case of new heterogenised vanadium

catalysts leaching has been detected. The conditions applied easily cause dissociation of the ligand from the vanadium centre, and, therefore, metal passes to the solution forming a new soluble catalyst, which displays moderate activity in sulfoxidation reactions. For all heterogenised catalysts, a high selectivity is observed for bulky substrates, which is correlated to molecular sieving effects (reactants size, selectivity effect).

To summarise, zeolite-heterogenised complexes show interesting catalytic properties for the oxidation of sulfides and these properties are obviously related to the changes in the microenvironment of the ligand metal complex. The followed strategy is mainly based on the incorporation of the metal complex into the rigid inorganic support; its structural framework is what determines the reaction cavity surrounding the active site. The balance between the heterogeneous and homogeneous character can explain the success of our catalysts.

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