

# Ti<sup>IV</sup> exchanged K10-montmorillonite: characterisation and catalytic properties in liquid-phase sulfide oxidation

I. Khedher<sup>a\*</sup>, A. Ghorbel<sup>a</sup>, J.M. Fraile<sup>b</sup> and J.A. Mayoral<sup>b</sup>

<sup>a</sup>Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis, 1060 Tunis, Tunisie

<sup>b</sup>Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

Titanium-containing K10 has been synthesised and characterised by X-ray diffraction, UV-visible reflectance, solid state NMR spectroscopy, N<sub>2</sub> nitrogen adsorption at 77K and chemical analysis. Two different titanium species have identified with a high dispersion in K10. The first is in an isolated penta- and hexa-coordinated state and the second is in the form of polymerised hexacoordinated species, which contains Ti–O–Ti bonds. These titanium species were found to be the catalytic sites that readily interact with oxidant to offer an active and selective catalytic system for the oxidation of sulfides. This catalytic system was studied in the asymmetric oxidation of methyl phenyl sulfide, using different types of chiral modifier, and gives excellent conversion and sulfoxide selectivity, together with a significant enantioselectivity in the range of 16–18% *ee* with (*R*)-binol.

**Keywords:** titanium exchange, K 10-montmorillonite, catalysis, sulfide oxidation, (*R*)-binol

Clays have been widely used as catalysts and supports in a large variety of organic reactions.<sup>1,2</sup> Clay-based catalysts are often obtained by modification with transition metals through either cationic exchange or pillaring.<sup>3–5</sup>

Titanium is the key component of many solids which have been found to exhibit excellent catalytic properties in redox reactions that encompass the oxidation of a variety of organic substrates.<sup>6,7</sup> In spite of this, the use of titanium-modified clays as oxidation catalysts has been rather limited<sup>8,9</sup> and has mainly focused on the synthesis of titanium-pillared clay in order to increase the surface area of the clay.<sup>3–5</sup>

Acid treatment is another way to activate clays for use as catalysts or supports.<sup>10</sup> One commercial example is K10 montmorillonite, which is obtained from the natural montmorillonite by treatment with mineral acids at high temperature. The natural montmorillonite structure is progressively destroyed, which results in a loss of crystallinity, but a significant increase in surface area and acidity in comparison to the natural clay.<sup>11</sup> These features of K10 montmorillonite have been proved to be positive in the preparation of vanadium-K10 catalysts.<sup>12</sup>

In the present work, we describe how the use of K10 allows the preparation of a titanium supported K10 catalyst (Ti-K10) containing an accessible and high dispersion of titanium sites, as shown by different spectroscopic techniques. These sites are able to catalyse the selective oxidation of sulfides to sulfoxide, with high yield and selectivity, using *tert*-butylhydroperoxide (TBHP) or H<sub>2</sub>O<sub>2</sub> as the oxidant (Fig.1). This catalytic system, modified by different chiral ligands, was studied in the asymmetric oxidation of thioanisole giving excellent conversion and sulfoxide selectivity, together with a significant enantiomeric excess (*ee*).

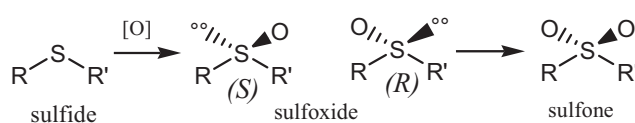
## Experimental

### Preparation of Ti-K10

A solution of Ti<sup>IV</sup> was prepared by first adding TiCl<sub>4</sub> (1.897 g, 10 mmol) to HCl (0.4 ml, 6 M) under an Ar atmosphere. This mixture was then diluted by slow addition of deionised water (12.2 ml). Cation exchange was performed by gradually adding this solution to a stirred suspension of K10-montmorillonite (1 g) in 250 ml of deionised water and stirring the suspension for 16 h. The solid was filtered off, washed with ionised water, dried and calcined in dry air at 573K.

### Physicochemical characterisation

The samples were characterised by X-ray diffraction and BET surface area and porosity measurements. To get further insight about the



**Fig.1** Oxidation of sulfide.

location and the nature of the titania species present in these catalysts, UV-visible and NMR investigations were performed on all samples.

Chemical analysis was carried out by atomic absorption spectrometry on a Perkin-Elmer 3100 apparatus, after sample dissolution through acid attack. X-ray diffractograms were recorded on a Philips PW 1130/00/60 diffractometer using Ni-filtred CuK $\alpha$  radiation and a Siemens goniometer. BET surface areas and pore volumes of the samples were measured on a Micrometrics ASAP 2000 apparatus. A Bruker MSL 400 spectrometer was used to obtain <sup>29</sup>Si and <sup>27</sup>Al-MAS-NMR spectra. UV-visible reflectance spectra were measured at room temperature with a Perkin-Elmer lamda 8 instrument with the use of BaSO<sub>4</sub> as reference. FT-IR spectra were obtained on a Bruker Vector22 spectrometer with KBr as reference.

### Oxidation reactions

All the reactions were carried in CH<sub>2</sub>Cl<sub>2</sub>. Ti-K10 (50 mg; 0.15 mmol as Ti) and the dry solvent (10 ml) were introduced into the reactor. The mixture was stirred at 0°C for 10 min, and 2.0 equivalent of chiral ligand per Ti was introduced. After an impregnation duration of 24 h at 0°C under stirring, 3 mmol of sulfide was introduced. The mixture was stirred for 20 min and 6 mmol of oxidant was added drop by drop for 10 min. The reaction was monitored by gas chromatography (SPB<sup>TM</sup>-5 Capillary, 30 m  $\times$  0.25 mm  $\times$  0.25 mm). The *ee* was determined by <sup>1</sup>H NMR.

## Results and discussion

### BET measurement

The textural properties, the nitrogen adsorption-desorption isotherms and BJH pore size distribution of K10 and Ti-K10 are summarised in Table 1 and Fig. 2. The K10 sample showed a BET surface area of 260 m<sup>2</sup>/g, which is much larger than that of natural montmorillonite (41 m<sup>2</sup>/g).<sup>12</sup> This increase of surface area is related probably to the delamination of natural montmorillonite *via* acid treatment, which leads to an acid-activated clay such as K10 having a proportion of broken clay layers and amorphous silica, as was shown in previous studies.<sup>11,13</sup>

After cation exchanging of the K10 sample with titanium precursor solution, the surface area increased slightly to 274 m<sup>2</sup>/g in Ti-K10 (Table 1) but the pore volume decreased from 0.39 to 0.22 cm<sup>3</sup>/g.

Based on the results summarised in Table 1, the increase of specific surface area could be explained by a significant addition of microporosity structure with 25 m<sup>2</sup>/g as microporous surface area.

For the decrease of pore volume, as shown in Fig 2, the K10 sample showed a bimodal pore size distribution, centred at 36 and 54Å. After the introduction of titania species, Ti-K10 shows a pore size distribution with uniform pore centred at 37 Å. This result is likely

\* Correspondent. E-mail: ilyeskhader@yahoo.com

**Table 1** Results of textural properties of the samples

Sample	Ti loading (mmoles/g)	S <sub>BET</sub> (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Microporous volume (cm <sup>3</sup> /g)	Microporous surface (m <sup>2</sup> /g)	Bimodal pore diameter (Å)
K10	–	260	0.39	–	–	36.54 <sup>a</sup>
Ti-K10	2.73	274	0.22	0.013	25	37 <sup>b</sup>

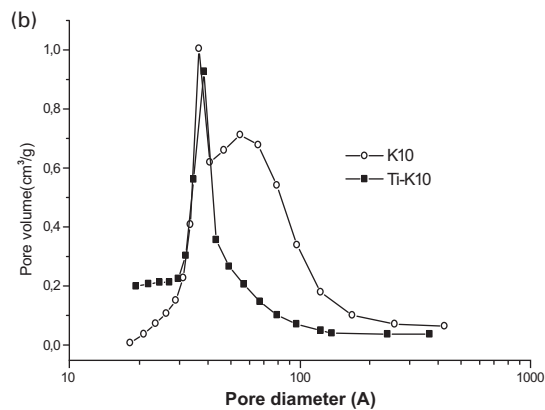
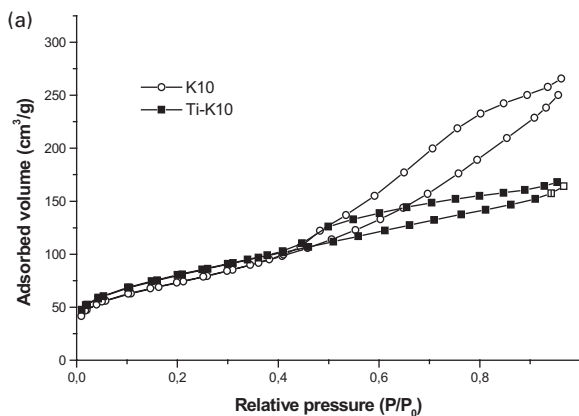
<sup>a</sup>Bimodal pore size distribution.<sup>b</sup>Monomodal pore size distribution.

due to a blockage of large pores centred at 54 Å by titanium species of large size as polymerised Ti species. This interpretation is supported by a UV-vis study, showed below (Fig. 4), where we note the presence of Ti atoms in the form of polymerised hexacoordinated Ti species.

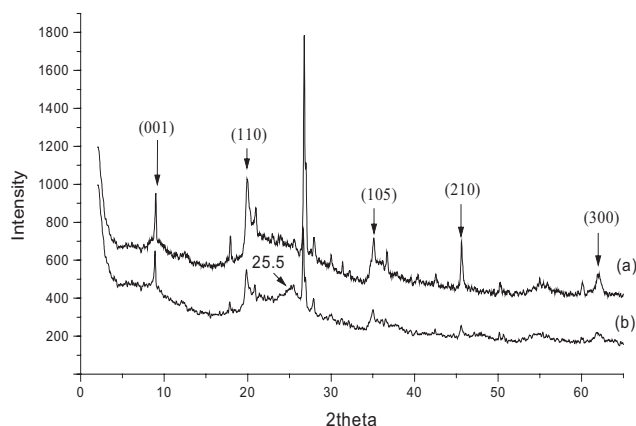
Taking account of these results of the textural study of Ti-K10 and K10, it may be assumed that the additional micropore structure in Ti-K10 suggests that the texture of K10 was not destroyed by the introduction of Ti species but was physically rearranged to expose a larger amount of adsorptive sites, increasing the specific area.

#### X-Ray diffraction (XRD)

Figure 3 shows that for both samples, some of the sharp diffraction peaks are attributed to the silica impurities of the precursor K10. Even with the interface by the sharp peaks due to the impurities, it is not difficult to distinguish several broad 2θ peaks located at about 20, 35, 54 and 62°, which are assigned to the diffraction of (110), (105), (210) and (300) reflections, respectively; these assignments are based on the XRD patterns of the non-acid-treated montmorillonite.<sup>13</sup> We also observed a (001) reflection (12.7Å), attributed to the proportion of the broken clay layers. This peak decreases slightly in the XRD patterns of Ti-K10 compared to K10. This observation suggests that the broken layers of K10 were not destroyed. The chemical structures of the broken clay layers of K10 were basically retained with a physical rearrangement in Ti-K10, as has been indicated previously in the textural study.



**Fig. 2** The nitrogen adsorption-desorption isotherms of K10 and Ti-K10 (a) and BJH pore size distribution curve of K10 and Ti-K10 calculated from the desorption branch (b).



**Fig. 3** XRD patterns of K10 (a) and Ti-K10 (b).

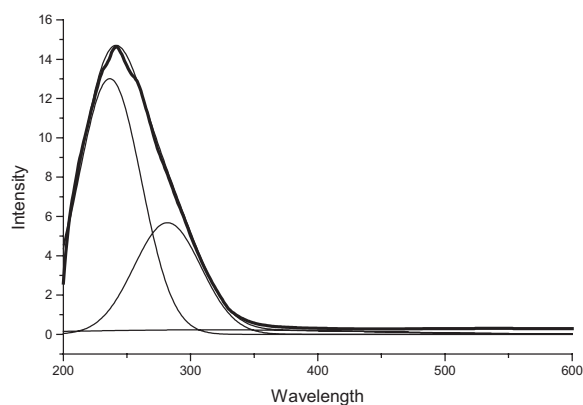
Bearing in mind the XRD patterns of Ti-K10 compared to TiO<sub>2</sub> anatase,<sup>14</sup> a slight reflection at 2θ = 25° (d = 3.55Å) was observed, which corresponds probably to anatase formation in Ti-K10, but in a very small amount. In fact, no band adsorption corresponding to anatase was clearly detected by UV-visible spectroscopy. This result can be taken as a parameter which shows the high dispersion of Ti species on Ti-K10.

#### UV-visible study

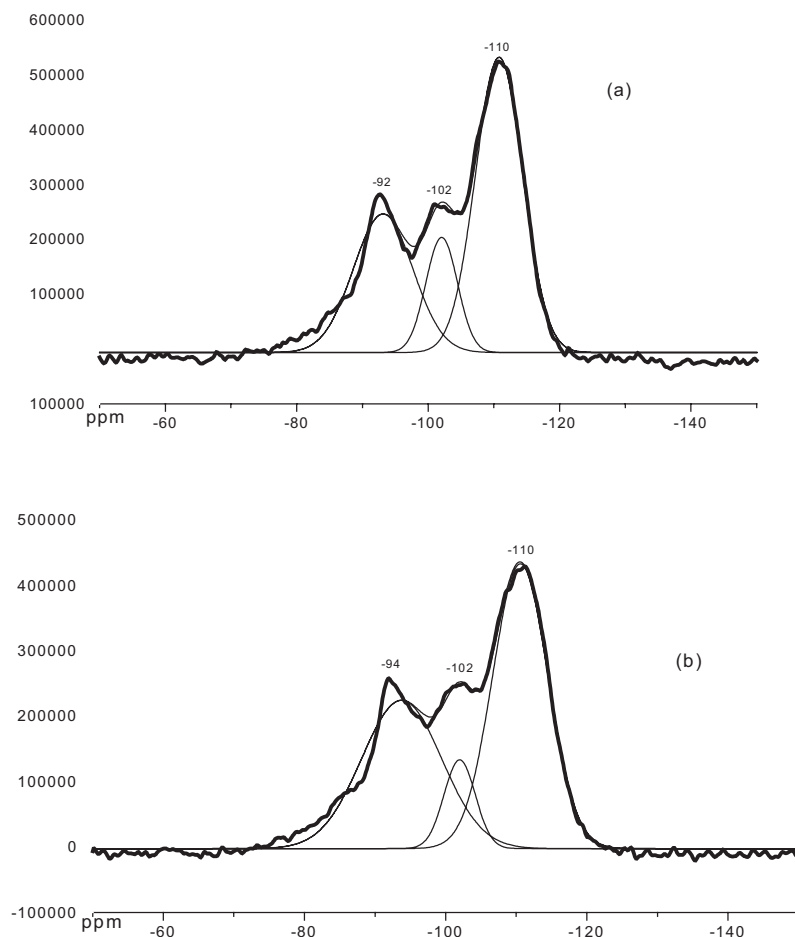
Figure 4 illustrates the UV-visible diffuse reflectance spectrum of the titanium K10 sample. A strong UV-visible absorption band at 230nm was observed. This band was due to the electronic transition from O<sup>2-</sup> to Ti<sup>4+</sup>. Similar high-energy absorption edges due to isolated penta- and hexa-coordinated Ti(IV) atoms of Ti have been observed for other titanium-containing mesoporous molecular sieves.<sup>15</sup> Moreover, a band at ~270nm is also present, and this would indicate that some Ti atoms are in the form of polymerised hexacoordinated Ti species, which contain Ti–O–Ti bonds.<sup>16</sup> No peak at 330 nm was clearly detected for the Ti-K10. This shows that the formation of a bulk titania, even if it exists, it will be in very small amount.

#### <sup>27</sup>Al and <sup>29</sup>Si NMR studies

The <sup>29</sup>Si and <sup>27</sup>Al MAS NMR spectra of K10 have been reported previously.<sup>17</sup> These spectra relative to K10 are reported also in Figs 5 and 6.



**Fig. 4** UV-visible diffuse reflectance spectra of the titanium K10 sample.



**Fig. 5**  $^{29}\text{Si}$  MAS NMR spectra of K10 (a) and titanium K10 (b).

Natural montmorillonite shows only one type of silicon resonance at  $-92$  ppm close to the value reported for Si in clays<sup>18,19</sup> and an intense peak in the range 2–5 ppm characteristic of octahedral Al, with small peaks at 67–70 ppm showing traces of tetrahedral Al. Compared to natural montmorillonite, K10 show the appearance of two other resonances at  $-110$  and  $-102$  ppm in the  $^{29}\text{Si}$  MAS NMR spectrum (Fig. 5a) and an increase of the intensity of the peak at 73 ppm in the Al spectra (Fig. 6a).

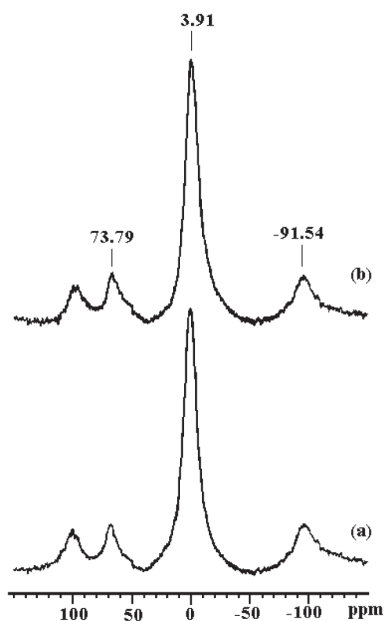
In their study of aluminosilicates, Magi *et al.*<sup>19</sup> assigned the signal at  $-110$  ppm to silicious impurities associated with the clay, and the peak at  $-92$  ppm to Si atoms in the tetrahedral layer of the clay, linked to three other Si atoms and an Al atom in the tetrahedral layer. The peak at  $-102$  ppm has been observed and may be explained by the presence of a  $\text{Q}^4$  (1Al) structure formed by Si–O–Al<sup>tet</sup> linkages. This interpretation is supported by the observation of the  $^{27}\text{Al}$  NMR signal at 73 ppm, which is typical of tetrahedral Al in aluminosilicates.

A  $^{27}\text{Al}$  MAS NMR study (Fig. 5) shows that the chemical shifts corresponding to the different Al species are not affected by the presence of titanium species in the lattice. In fact, the spectra of K10 are similar to those of Ti-K10. Thus the interaction of the titanium species with the Al species seems to be completely discarded.

On the other hand, the  $^{29}\text{Si}$  NMR data obtained for both titanium containing systems Ti-K10 suggest that the lattice silicon environment is in interaction with the titanium species (Fig. 5). It is worth noticing that the signal area at  $-110$  ppm does not change significantly, while signals area at  $-92$  and at  $-102$  ppm increases and decreases, respectively. The K10 structure modification is probably due to the distribution of the titanium species in the lattice which shows the interaction between the titanium and the Si species. It can be assumed that the titanium species were in interaction mainly with Si presented in the proportion of broken clay layers.

#### Catalytic oxidation of sulfide on Ti-K10

The above results prompted us to study Ti-K10 as an oxidation catalyst and the selective oxidation of sulfide to sulfoxide was selected as the benchmark reaction. The results obtained using different sulfides are given in Table 2. As it can be seen, in the absence of catalyst (entry 1)



**Fig. 6**  $^{27}\text{Al}$  MAS NMR spectra of K10 (a) and titanium K10 (b).

or in the presence of K10 as catalyst (entry 2) the reaction is very slow, but in the presence of Ti-K10 most of the substrates are oxidised to give high yields and excellent sulfoxide selectivities.

The possibility that the homogenous catalysis was by titanium ions leaching from the Ti-K10 catalysts has been strictly investigated. First the filtrate after the first reaction did not show any catalytic activity for the second oxidation reaction. The secondly, the titanium content in the filtrate was analysed by atomic adsorption spectroscopy and

**Table 2** Oxidation of sulfides

Entry	Catalyst	Oxidant	Substrate	Conversion/%	Sulfoxides/%	Sulfone/%
1	None	TBHP	Thioanisole	6	>99	0
2	K10	TBHP	Thioanisole	4	>99	0
3	Ti-K10	TBHP	Thioanisole	67	97	3
4	Recovered	TBHP	Thioanisole	58	92	8
5	Ti-K10	TBHP	Ethylmethylsulfide	64	97	3
6	Ti-K10	TBHP	Phenylvinylsulfide	64	96	4
7	Ti-K10	TBHP	2-methylthiophene	0	-	-
8	Ti-K10	H <sub>2</sub> O <sub>2</sub>	Thioanisole	48	65	35

Reaction conditions: sulfide, 3 mmol; Ti-K10, 0.15 mmol as Ti (50 mg); Oxidant, 3 mmol; CH<sub>2</sub>Cl<sub>2</sub> 10 ml; 293K; 4 h.

was below the limitation of detection. Thirdly, Ti-K10 recovered (entry 4) showed a slight decrease in the sulfide conversion and sulfoxide selectivity. It follows that there are not dissolved titanium ions in the solution and the oxidation of sulfide apparently proceeds on the surface of Ti-K10.

The high selectivity and the lack of reaction with 2-methylthiophene (entry 7) are consistent with the mechanistic hypothesis propose by previous studies<sup>20-22</sup> where the reagent acts as a nucleophile attacking the TBHP, which is activated by coordination to the titanium catalytic sites. Entry 8 shows that H<sub>2</sub>O<sub>2</sub> gave a less important sulfide conversion and sulfoxide selectivity than TBHP. This is not surprising in view of the fact that TBHP is an active oxidant in the homogenous and heterogenous oxidation reactions.<sup>9,20</sup> The results conclude that the combination of Ti-K10 and TBHP is essential to give high yields and excellent sulfoxide selectivities.

#### Catalytic oxidation of methyl phenyl sulfide on Ti-K10 with chiral modifier

Chiral titanium complexes have proved to be useful catalysts in several asymmetric oxidations.<sup>20,23</sup> This effect, together with the usefulness of the optically active sulfoxides in asymmetric synthesis of organic compounds, prompted us to study the present catalyst in asymmetric sulfoxidation using several chiral modifiers.

In Table 3 the chemical and optical yields of sulfoxide were compared under several reaction conditions. The asymmetric oxidation of methyl phenyl sulfide has been studied at the oxidant/sulfide molar ratio of 2.0 because the increase in the amount of oxidant has improved the degree of enantiomeric excess.<sup>20</sup>

As is shown in entry 3 of Table 3, there was no asymmetric oxidation without chiral modifier. In entry 1, it can be seen that the addition of (+)DET, which has been described as a chiral ligand for the same reaction in homogenous phase,<sup>20</sup> maintains a high sulfoxide selectivity but no enantioselectivity was observed. This is surprising in view of the fact that TBHP is an active oxidant in the homogenous asymmetric oxidation.<sup>20,23</sup> It is attributed to the difference between the properties of active sites on the surface and in the solution; the bulky *t*-butyl group would interfere with the appropriate coordination of chiral ligands with titanium ions in the pores. In the aqueous solution of H<sub>2</sub>O<sub>2</sub> case (entry 2), with the addition of (+)-DET, the catalyst is more active, giving high sulfoxide selectivity of 86% and notably an enantioselectivity of 10% *ee*. This result indicates that H<sub>2</sub>O<sub>2</sub> as oxidant seems to be more active in the heterogenous asymmetric oxidation than TBHP. Thus, the combination of Ti-K10 and H<sub>2</sub>O<sub>2</sub> was employed in the following study using other chiral modifiers. (+)-DIPT, which was also frequently used as a modifier of titanium ion in homogenous asymmetric reaction,<sup>24</sup> does not noticeably improve enantioselectivity, giving almost the same result with as for (+)-DET.

**Table 3** Results obtained in the asymmetric oxidation of methylphenyl sulfide

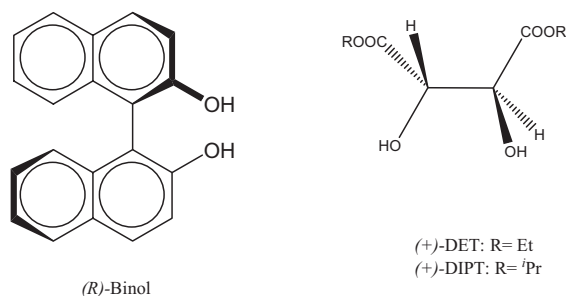
Entry	Chiral ligand <sup>a</sup>	Oxidant	Conversion (%)	Sulfoxides (%)	Sulfone (%)	<i>ee</i> (%) <sup>c</sup>
1	(+)-DET	TBHP	85	98	2	0
2	(+)-DET	H <sub>2</sub> O <sub>2</sub>	66	86	14	10
3	None	H <sub>2</sub> O <sub>2</sub>	70	75	25	0
4	(+)-DIPT	H <sub>2</sub> O <sub>2</sub>	63	85	15	9
5	( <i>R</i> )-BINOL	H <sub>2</sub> O <sub>2</sub>	62	83	17	16
6	( <i>R</i> )-BINOL <sup>b</sup>	H <sub>2</sub> O <sub>2</sub>	58	92	8	18

Reaction conditions: sulfide, 3 mmol; Ti-K10, 0.15 mmol as Ti (50 mg); chiral ligand, 0.30 mmol; oxidant, 6 mmol; CH<sub>2</sub>Cl<sub>2</sub> 10 ml; 273K; 72 h.

<sup>a</sup>The chiral ligands are shown in Fig. 7.

<sup>b</sup>The reaction was carried at 263K.

<sup>c</sup>The *ee*'s were determined from the <sup>1</sup>H NMR spectrum in the presence of (*S*)-N-(3,5-dinitrobenzoyl)- $\alpha$ -phenylamine as a chiral shift base.

**Fig. 7** Chiral modifiers used in the present study.

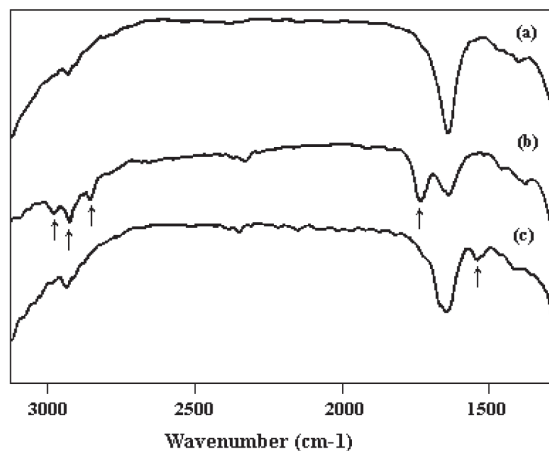
Another type of chiral modifier used is (*R*)-Binol, which in its complexation with Ti(O<sup>*i*</sup>Pr)<sub>4</sub> represents one of the most powerful classes of enantioselective catalysts employed in modern organic synthesis.<sup>24,25</sup> The use of this ligand (entry 6) improves slightly the enantioselectivity to 16%*ee*. This result shows that COOR groups in (+)-DET and (+)-DIPT do not play an important role in the enantioselective reaction. The decrease of the reaction temperature from 0 to -10°C does not show a significant improvement in enantiomeric excess 18%. These results open the way to further developments in this area.

In an attempt to verify the interaction of Ti-K10 with chiral modifiers, the adsorption of the chiral ligands onto Ti-K10 was followed by IR spectroscopy. Ti-K10 was impregnated at room temperature with a solution of chiral ligand in dichloromethane. After the solvent was eliminated by filtration and the solid was repeatedly washed with dichloromethane and acetone to eliminate the unbound chiral ligand. The obtained solid was dried under vacuum at room temperature.

The IR spectra of the Ti-K10 grafted with various chiral ligands are shown in Fig. 8. New peaks appear at 2979, 2952, and 2850 due to the C-H stretching vibrations, also a band at 1743 cm<sup>-1</sup> (curve b), in comparison with the inorganic supports before grafting (curve a). In the case of sample d (using binol as chiral ligand), a band appears at 1497 cm<sup>-1</sup> attributed to the stretching vibrations of C=C bonds. The IR spectra provided additional evidence for the exchange of chiral ligands with the Ti-K10 sample.

## Conclusion

The spectroscopic techniques adopted in this study indicate the presence of titanium in two different states in interaction with the lattice silicon environment, as an isolated penta- and hexacoordinated Ti and in the form of polymerised



**Fig. 8** FT-IR spectrum of untreated Ti-K10 (a), Ti-K10 impregnated with (+)-DET (b) and Ti-K10 impregnated with (R)-BINOL (c).

hexacoordinated Ti species. Ti-K10 is efficient for the selective sulfide oxidation reaction and this is probably due to the well-dispersed state of the active species via the oxidant-titanium intermediate. Ti-K10, when modified by chiral ligands, shows a good catalytic activity, leading to a low but significant (16-18%) enantiomeric excess (*ee*) with the use of (*R*)-binol as a chiral ligand.

Received 3 July 2008; accepted 14 August 2008

Paper 08/0035 doi:10.3184/030823408X360166

Published online: 17 October 2008

## References

- 1 R.S. Varma, *Tetrahedron*, 2002, **58**, 1235.
- 2 J.M. Adams, *Appl. Clay Sci.*, 1987, **2**, 309.
- 3 J. Sterte, *Clay and Clay Minerals*, 1986, **34**, 658.
- 4 S. Yamanaka, T. Nishimara and M. Hattori, *Mater. Chem. Phys.*, 1987, **17**, 1186.
- 5 A. Bernier, L.F. Admaiai and P. Grange, *Appl. Catal.*, 1991, **77**, 269.
- 6 B. Notari, *Catal. Today*, 1993, **18**, 163.
- 7 R.S. Reddy, J. Sudhakar Reddy, R. Kumar and P. Kumar, *J. Chem. Soc. Chem. Commun.*, 1992, 84.
- 8 B.M. Choudary, V.L.K. Valli and A. Duga Parasad, *J. Chem. Soc. Chem. Commu.*, 1990, 1186.
- 9 B.M. Choudary, S. Shobha Rania and N. Narender, *Catal. Lett.*, 1993, **19**, 299.
- 10 C.L. Thomas, J. Hickey and G. Stecker, *Ind. Eng. Chem.*, 1950, **42**, 866.
- 11 T. Cseri, S. Békassy, F. Figueras, E. Cseke, L.C. de Menorval and R. Dutartre, *Appl. Catal. A*, 1995, **132**, 141.
- 12 I. Khedher, A. Ghorbel and A. Tuel, *J. Chem. Res. (S)*, 2003, 309.
- 13 S. Kawi and Y.Z. Yao, *Micropor. Mesopor. Mater.*, 1999, **28**, 25.
- 14 M.C. Sanchez, J. Garcia, J.A. Mayoral, J. Blasco and M.G. Proietti, *J. Mol. Catal.*, 1994, **92**, 311.
- 15 A. Corma, M. Iglesias and F. Sánchez, *Catal. Lett.*, 1996, **39**, 153.
- 16 T. Balsco, A. Corma, M.T. Navarro and J. Pérez-Pariente, *J. Catal.*, 1995, **156**, 65.
- 17 C. Cativiela, F. Figueras, J.M. Freiele, J.I. Garcia, L.C. deMenorval and E. Pires, *Appl. Catal. A*, 1993, **101**, 253.
- 18 D.T.B. Tennakoon, W. Jones, J.M. Thomas, J.H. Ballatines and J.H. Purnell, *Solid State Ionics*, 1987, **24**, 205.
- 19 M. Magi, E. Lippmaa, A. Samoson, G. Engelhardt and T. Grimmer, *J. Phys. Chem.*, 1984, **88**, 1518.
- 20 P. Piychen and H.B. Kagan, *Tetrahedron Lett.*, 1984, **43**, 3135.
- 21 J.M. Brunel and H.B. Kagan, *Bull. Soc. Chim. Fr.*, 1996, **133**, 1109.
- 22 A. Lattanzi and A. Scettri, *J. Organometallic Chem.*, 2006, **691**, 2072.
- 23 T. Katsuki and K.B. Sharpless, *J. Am. Chem. Soc.*, 1980, **102**, 5974.
- 24 N. Komatsu, M. Hashizume, T. Sugita and S. Uemura, *J. Org. Chem.*, 1993, **58**, 4529.
- 25 A. Massa, A. Lattanzi, F.R. Siniscalchi and A. Scettri, *Tetrahedron Assym.*, 2001, **12**, 2775.