Large pore Ti-zeolites and mesoporous Ti-silicalites as catalysts for selective oxidation of organic sulfides

A. Corma [1]

Instituto de Tecnología Química, UPV-CSIC,
Universidad Politécnica de Valencia, Avda. de los Naranjos s/n, 46022 Valencia, Spain

M. Iglesias

Instituto de Ciencia de Materiales, Sede D, CSIC, Serrano 113, 28006 Madrid, Spain

and

F. Sánchez

Instituto de Química Orgánica, CSIC, C/ Juan de la Cierva, 3, 28006 Madrid, Spain

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The oxidation of bulky thioethers has been carried out on Ti-Beta and Ti-MCM-41 catalysts, using H_2O_2 and *t*-butyl hydroperoxide (TBHP) as oxidants. The intrinsic activity of Ti-Beta was higher than that of Ti-MCM-41 for the oxidation of methyl phenyl sulfide which can penetrate in the pores of Beta, while in the case of the larger isopentyl phenyl sulfide, which diffuses more slowly in Ti-Beta zeolite, Ti-MCM-41 gives a larger activity. Ti-Beta is able to perform better for the more demanding oxidation of sulfoxides to sulfones giving, therefore, higher selectivities to sulfones than Ti-MCM-41. Similar results were obtained when using either H_2O_2 or TBHP as oxidants. However, the sterical effects were enhanced when TBHP was used as oxidant.

Keywords: oxidation of thioethers; Ti-zeolites; Ti-silicalites; size effects

1. Introduction

Sulfoxide derivatives are known to have interesting and useful biological and pharmacodynamic properties [1]. The sulfoxides are obtained by oxidation of thioethers by peracids, peroxides and alkyl peroxides using transition metal catalysts. Depending on the catalyst selectivity and the method used, different proportions of sulfoxide and sulfone are produced. The introduction of Ti-containing zeolites has opened new industrial perspectives for carrying out selective oxidations of hydrocarbons and hydrocarbons containing heteroatoms [2]. Titanium silicalite with either MFI (TS-1) or MEL structure (TS-2) has been used to oxidize thioethers to sulfoxides and sulfones [3]. It has been claimed that these medium pore zeolites are active and selective for carrying out the oxidation of relative small size sulfide molecules, but their activity strongly decreases when bulkier thioethers are to be oxidized.

In this work we have carried out the selective oxidation of thioethers of different sizes (methyl phenyl sulfide and isopentyl phenyl sulfide) on the large pore Ti-Beta and the ultralarge pore Ti-MCM-41 material, using H_2O_2 and *t*-butyl hydroperoxide (TBHP) as oxidants, with the aim of exploring the possibilities of these recently synthesized materials for oxidation of thioethers.

2. Experimental

2.1. Materials

The Ti-Beta catalyst was prepared starting with a gel of the following characteristics: $T^{IV}O_2/Al_2O_3 = 2000$; $TEAOH/T^{IV}O_2 = 0.54$; $H_2O/T^{IV}O_2 = 10$. Aerosil (Degussa 200) and Ti tetraethoxide (Alpha) were used as Si and Ti sources. The synthesis procedure has been described in ref. [4]. The final zeolite contained, after calcination, 3.2% TiO_2. The Ti-MCM-41 sample was prepared from a gel of the following characteristics: $CTMABr/T^{IV}O_2 = 0.3948$; $TMAOH/T^{IV}O_2 = 0.2547$; $H_2O/T^{IV}O_2 = 20.68$. Aerosil (Degussa 200) and Ti tetraethoxide (Alpha) were used as Si and Ti sources. The synthesis procedure has been described in ref. [5]. The final TiO_2 content, after calcination, was 2.0 wt% TiO_2.

The catalysts were characterized by X-ray powder diffraction using Cu Kα radiation, with a Phillips PW 1830 diffractometer equipped with a graphite monochromator (fig. 1). Pure phases of Ti-Beta and Ti-MCM-

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[1] To whom correspondence should be addressed.

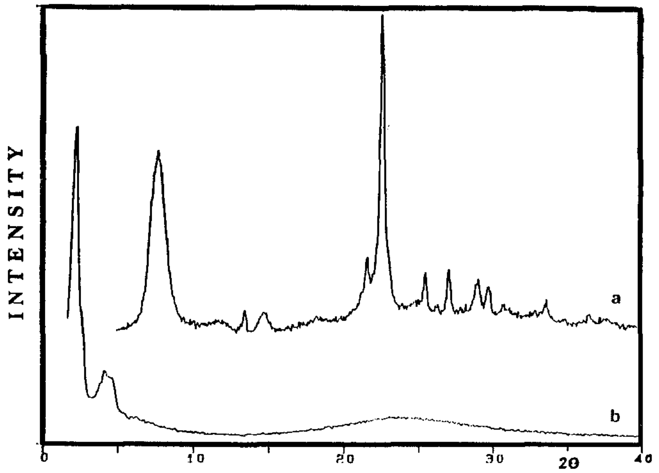


Fig. 1. X-ray powder diffraction of Ti-Beta (a) and Ti-MCM-41 (b).

41 were obtained and the crystallinity of Ti-Beta zeolite was determined measuring the peak area at 20–22.4°. The position of this peak was accurately measured after dehydration of the samples for 1 h at 383 K and further rehydration over a $CaCl_2$ saturated solution (35% relative humidity) for 16 h using Si as internal standard. X-ray fluorescence (Outokumpu-X-MET 840) was used to determine the amount of Ti in the samples. Concentrations of Al and alkali metal cations were determined by atomic absorption (Perkin-Elmer 403) and flame emission spectroscopy (Ependorf ELEX 6361) respectively. Diffuse reflectance spectra were recorded in the 190–800 nm range with a Shimadzu UV-2101 PC spectrophotometer equipped with a diffuse reflectance attachment using $BaSO_4$ as a reference. IR spectra were recorded with a Nicolet FTIR spectrometer using the KBr pellet technique. The surface area was obtained from N_2 adsorption (ASAP-2000) using the BET procedure. Pore diameter distribution was obtained using Ar as adsorbate and following the Horvath–Kawazoe method [6]. Following this, the pore size of the Ti-MCM-41 is 35 Å.

The organic compounds used were analytical grade. The thioethers were synthesized in this work following standard methods reported in the literature [7].

2.2. Procedure

The catalytic experiments were carried out in a batch reactor at atmospheric pressure, 313 K, and using acetonitrile as solvent (10 ml). 50 mg of catalyst were stirred in a suspension containing the solvent and 1.0 mmol of the corresponding thioether. The oxidant, either TBHP (1.1 mmol) or H_2O_2 (3 eq., 30%) were added dropwise, while the overall suspension was heated at 313 K. Samples were taken at regular times, and after filtration, they were separated using a 18 m column of 0.32 mm, 0.32 μ and SE 54 phase, and analyzed by GCMS.

Since thioethers can be oxidized by 30 wt% H_2O_2 to sulfoxides, blank experiments were carried out under the reaction conditions in order to determine the extension of the uncatalyzed reaction. At 315 K, using acetonitrile as solvent (10 ml), 1 mmol of the methyl phenyl sulfide and 3 eq. of 30% H_2O_2, the homogeneous reaction accounted for a conversion of 5 and 15% after 0.40 and 1 h of reaction time respectively. Under the same conditions but using 1.1 mmol of TBHP instead of H_2O_2, the conversion after 5 h was 10%.

3. Results and discussion

Both catalysts showed a band at about 960 cm^{-1} in the IR spectra (fig. 2). After impregnation with H_2O_2 this band dissappears and the titanium aluminosilicates become yellow, the initial conditions being restored by heating the sample at 353 K overnight.

The presence of this band could be consistent with the presence of Ti in framework position [8]. In previous work [9] we have shown that the diffuse reflectance spectra in the UV–Visible region (DR-UV) of the calcined Ti-Beta samples has a strong peak at 205 ± 3 nm and a band at $\leqslant$225 nm. No band at ~ 330 nm corresponding to anatase was detected. In that work [9] the peak at 205 nm was assigned to the presence of isolated Ti(IV), probably as tetracoordinated species. The larger band at ~ 225 nm would indicate the presence of isolated penta- and hexacoordinated Ti(IV) atoms. In conclusion, it appears that the Ti-Beta sample has a

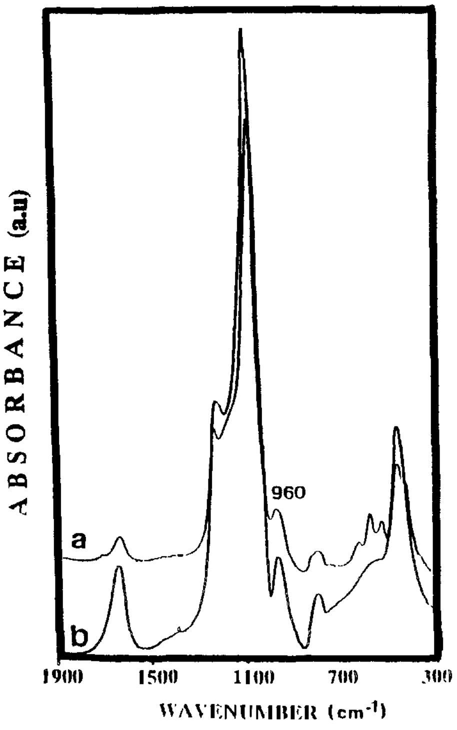


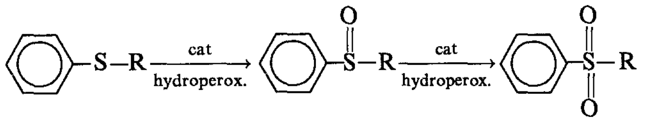
Fig. 2. IR spectra of Ti-Beta (a) and Ti-MCM-41 (b).

majority of Ti tetrahedrally and pentacoordinated; therefore most of the Ti atoms in this sample are coordinatively unsaturated and, consequently, they could act as active sites for oxidation reactions. Nevertheless, the presence of tetra-, penta- and hexacoordinated Ti initially present on the zeolite would indicate that sites with different efficiencies for carrying out the oxidation reaction exist on Ti-Beta, and the order of this efficiency should increase from the hexa- to the tetracoordinated Ti sites.

On the other hand, in the case of the Ti-MCM-41 sample the diffuse reflectance spectrum [10] clearly showed that a larger proportion of Ti atoms are penta- and hexacoordinated. Moreover, a band at ~ 280 nm is also present, and this would indicate that some Ti atoms are in the form of polymerized hexacoordinated Ti species, which contain Ti–O–Ti bonds, and which are not expected to be active for the desired selective oxidation.

Thus, from the above discussion one could expect the intrinsic activity of the Ti-Beta to be higher than that of the Ti-MCM-41 for oxidation in general, and more specifically for the oxidation of thioethers. Previous results [10] on the oxidation of linear olefins are in good agreement with this assumption.

In the case of the oxidation of thioethers:



where R = CH_3 or iso-C_5H_{11}.

The results given in fig. 3 show that for the case of methyl phenyl sulfide, which can penetrate in Ti-Beta, the activity of Ti-Beta is higher than the activity of Ti-MCM-41, in agreement with the higher intrinsic activity expected for Ti-Beta, and also in line with the larger Ti content of the zeolite. Moreover, the selectivity curves given in fig. 4 show that the sulfoxide is a primary and unstable product, while the corresponding sulfone appears as a secondary and stable product. Ti-MCM-41 is more selective towards the formation of sulfoxide than Ti-Beta. This would also be consistent with the presence of stronger oxidation sites on Ti-Beta, if one takes into account that the oxidation of sulfoxide to sulfone is a more demanding reaction than the oxidation of thioether to sulfoxide. Moreover, if one considers that the diffusion of the sulfoxide should be slower in the narrower pores of Ti-Beta than in the 35 Å pores of Ti-MCM-41, it is not surprising that the selectivity to the intermediate sulfoxide product is lower on the Ti-Beta catalyst.

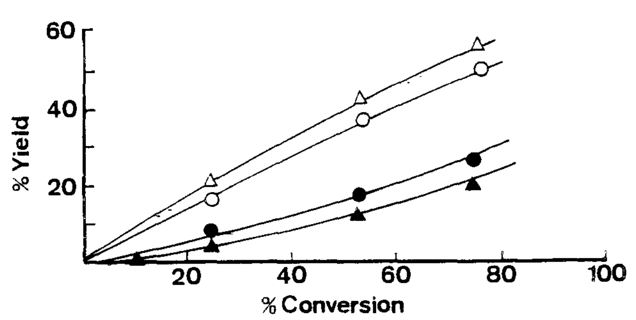


Fig. 4. Selectivity curves for sulfoxide (empty points) and sulfone (full points) in the oxidation of methyl phenyl sulfide in the presence of H_2O_2 on Ti-Beta (○, ●) and Ti-MCM-41 (△, ▲).

When a larger molecule (isopentyl phenyl sulfide) was oxidized, the results in fig. 5 show that the intrinsically more active Ti-Beta catalyst is now less active, as a consequence of the large size of the reactant whose diffusion is strongly limited in the 12 membered ring pores of the zeolite. Furthermore the oxidation of the isopentyl phenyl sulfide is much slower than that of methyl phenyl sulfide. As a consequence, the competitive reaction involving H_2O_2 decomposition occurs proportionally in a larger extent during the oxidation of isopentyl phenyl sulfide, and practically no H_2O_2 is left after 5 h of reaction. Consequently, the sulfide conversion is limited to 59% and 20% conversion on Ti-MCM-41 and Ti-Beta, respectively. The selectivity results (fig. 6) show again a lower selectivity for sulfoxide on Ti-Beta zeolite.

When the reactions were carried out using TBHP as oxidating agent, analogous results were obtained (fig. 7), i.e. Ti-Beta is more active than Ti-MCM-41 for methyl phenyl sulfide and less active for isopentyl phenyl sulfide oxidation. The oxidation activity with TBHP is lower than with H_2O_2. This is to be expected taking into

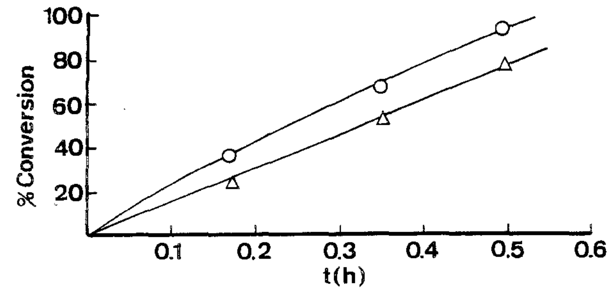


Fig. 3. Catalytic oxidation of methyl phenyl sulfide in the presence of H_2O_2, on Ti-Beta (○) and Ti-MCM-41 (△) catalysts.

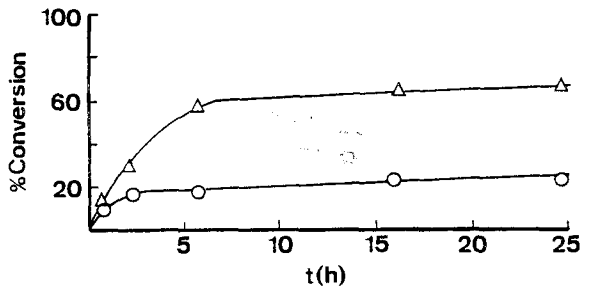


Fig. 5. Catalytic oxidation of isopentyl phenyl sulfide in presence of H_2O_2 on Ti-Beta (○) and Ti-MCM-41 (△).

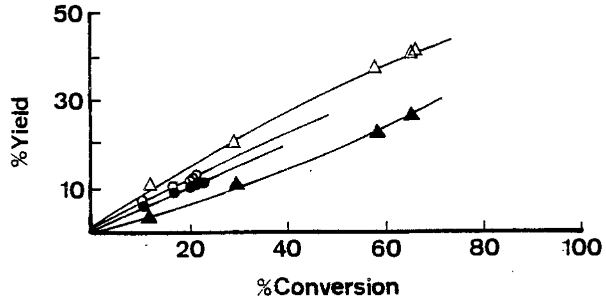


Fig. 6. Selectivity curves for sulfoxide (open symbols), and sulfone (filled symbols) in the oxidation of isopentyl phenyl sulfide in presence of H_2O_2 on Ti-Beta (○, ●) and Ti-MCM-41 (△, ▲).

account the oxidation ability of the two peroxides. A similar observation has been reported for oxidation of hydrocarbons on Ti-Beta using H_2O_2 and TBHP [11] as oxidation agent.

4. Conclusions

It has been shown that both Ti-Beta and Ti-MCM-41 are active and selective catalysts for the oxidation of thioethers to the corresponding sulfoxides. In a consecutive reaction the sulfoxides are oxidized to sulfones; this reaction requiring stronger oxidation sites than the oxidation of the thioether to sulfoxide.

The presence of intrinsically more active oxidation sites in Ti-Beta, together with a higher Ti content in our sample, gives rise to higher conversion for oxidation of thioethers which can penetrate into the pores of the zeolite. When the size of the molecule increases and diffusion limitations start to be important, then the large channel of the Ti-MCM-41 sample becomes the most important factor and this material gives a higher conversion and selectivity than Ti-Beta zeolites. Analogous results are obtained when TBHP is used as an oxidation molecule, but in this case the rate of reaction is lower than with H_2O_2.

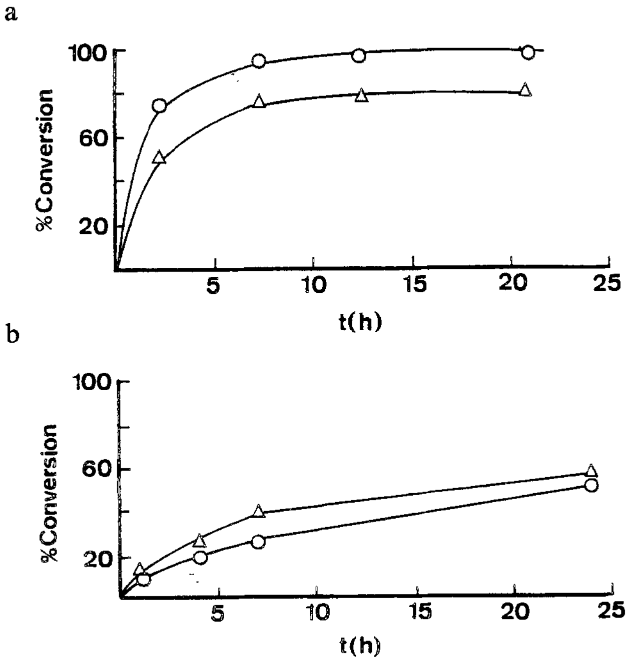


Fig. 7. Catalytic oxidation of methyl phenyl sulfide (a) and isopentyl phenyl sulfide (b) in the presence of TBHP on Ti-Beta (○) and Ti-MCM-41 (△).

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