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# Non-hydrolytic $SiO_2$–$TiO_2$ mesoporous xerogels—Efficient catalysts for the mild oxidation of sulfur organic compounds with hydrogen peroxide

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## ABSTRACT

$SiO_2$–$TiO_2$ mixed oxides with molar ratios Ti/(Si + Ti) ranging from 0.03 to 0.09 were prepared by a non-hydrolytic sol–gel process using $SiCl_4$ and $TiCl_4$ precursors. The texture and the distribution of Ti atoms in the resulting xerogels strongly depended on the Ti concentration as precursor and the reaction temperature. Mesoporous xerogels with very high surface area (up to 1200 $m^2\,g^{-1}$) and pore diameters (up to 7.9 nm) can be obtained at 150 °C with a Ti loading of 6 mol%. These mesoporous materials showed excellent catalytic performances in the sulfoxidation reaction of different bulky sulfides (methyl phenyl sulfide, diphenyl sulfide), and thiophenes (benzothiophene, dibenzothiophene, tetrahydrothiophene, 4,6-dimethyl dibenzothiophene) with $H_2O_2$. In all the cases a very high selectivity toward $H_2O_2$ consumption as oxidizing agent was observed (>98%).

## 1. Introduction

Ti-containing microporous and mesoporous materials are attractive heterogeneous catalysts for the oxidation of organic compounds with $H_2O_2$ [1–3]. The best catalysts are the crystalline Ti-silicates with zeolite framework (TS-1, TS-2, Ti-beta, etc.), but their applications are limited to reactants with molecule size smaller than 0.7 nm. The synthesis of amorphous Ti-containing mesoporous templated silica (Ti-MCM-41, Ti-MCM-48) having uniform mesopores ranging from 2 to 10 nm in diameter opened new opportunities for the oxidation of bulky molecules [4–6]. Homogeneous, and amorphous $SiO_2$–$TiO_2$ mixed oxides have been prepared by conventional sol–gel processes based on the hydrolysis and condensation of silicon and titanium alkoxides. However, the xerogels obtained by vacuum-drying are usually microporous [7,8] and elaborated drying procedures are required to obtain mesoporous materials [9], such as extraction with supercritical $CO_2$ or washing with hexane and silylation before drying. Generally, the amorphous $SiO_2$–$TiO_2$ mixed oxides exhibit much lower performance than the crystalline titanosilicates in the oxidation of organic substrates with aqueous solutions of $H_2O_2$ and thus their use is limited to oxidation reactions with dry organic hydroperoxides.

On the other hand, mesoporous $SiO_2$–$TiO_2$ xerogels can be obtained using non-hydrolytic sol–gel routes [10,11]. Thus, the reaction of $SiCl_4$ and $TiCl_4$ with diisopropyl ether offers a very simple and efficient route to obtain homogeneous $SiO_2$–$TiO_2$ xerogels starting from cheap precursors, without any organic templating agent. We recently reported that these materials are effective catalysts for the mild oxidation of sulfur-containing compounds with $H_2O_2$ [12]. This behavior has been related to the high degree of condensation typical for $SiO_2$–$TiO_2$ xerogels obtained by non-hydrolytic methods, which results in low amount of surface silanols and low hydrophilicity.

In this work we study the influence of Ti content and synthesis temperature on the texture and structure of the non-hydrolytic $SiO_2$–$TiO_2$ xerogels, as well as their catalytic performance in the sulfoxidation of bulky sulfides and thiophenes with $H_2O_2$. As previously reported [2,13,14], these reactions can be considered as model processes for two important industrial applications: sulfoxides/sulfones synthesis and fuels catalytic oxidative desulfurization. It is important to note that there are only few papers dealing with oxidation of bulky sulfide using Ti catalysts [15].

## 2. Experimental

### 2.1. Catalysts preparation

The $SiO_2$–$TiO_2$ mixed oxides were prepared by reaction of $SiCl_4$ and $TiCl_4$ with $^iPr_2O$. In a glove box under argon atmosphere, $SiCl_4$

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**Table 1**
Composition and textural data of the different catalysts.

| Sample | mol% Ti[a] nominal | mol% Ti[a] experimental[b] | $S_{BET}$ ($m^2 g^{-1}$) | $V_p$ ($cm^3 g^{-1}$) | $D_p$[c] (nm) |
|---|---|---|---|---|---|
| Ti3-110 | 3.0 | 1.8 | 600 | 0.3 | 2.0 |
| Ti5-110 | 5.0 | 4.2 | 880 | 0.7 | 3.2 |
| Ti6-110 | 5.9 | 6.4 | 950 | 0.9 | 3.8 |
| Ti7-110 | 7.3 | 6.5 | 900 | 0.9 | 4.0 |
| Ti9-110 | 8.9 | 8.0 | 965 | 1.0 | 4.1 |
| Ti3-150 | 3.0 | 3.1 | 800 | 0.5 | 2.5 |
| Ti5-150 | 5.0 | 4.6 | 970 | 1.2 | 4.9 |
| Ti6-150 | 5.9 | 6.3 | 1215 | 2.4 | 7.9 |
| Ti9-150 | 9.0 | 9.1 | 920 | 2.6 | 11.3 |

[a] molar ratio 100 × Ti/(Si + Ti).
[b] Estimated error ± 1%.
[c] Average pore diameter ($4000V_p/S_{BET}$).

and $TiCl_4$ (total amount 40 mmol), $^iPr_2O$ (8.17 g, 80 mmol) and $CH_2Cl_2$ (10 mL) were added successively with syringes into a 150-mL, Teflon-lined stainless steel autoclave. The autoclave was heated under autogenous pressure for 6 days at 110 or 150 °C. After cooling, the autoclave was opened in a glove box. The gel was filtered off, washed three times with dry $CH_2Cl_2$, dried under vacuum first at room temperature for 2 h, then at 110 °C for 6 h, and calcined in dry air at 500 °C for 5 h. The samples were labeled Ti*x*–*y* where *x* is the nominal molar percentage of Ti (100 × Ti/(Si + Ti)) and *y* is the reaction temperature.

### 2.2. Catalysts characterization

The Ti content of xerogels was determined by ICP-MS at the "Service Central d'Analyse" USR-59/CNRS. $N_2$ physisorption experiments were done at −196 °C on a Micromeritics ASAP 2010 sorptometer with samples previously degassed under vacuum at 200 °C for 15 h. The pore size distribution was obtained from the desorption branch using the BJH method and the Harkins and Jura standard isotherm. Diffuse reflectance UV–vis (DRUV–vis) spectra were recorded under ambient conditions on a PerkinElmer Lambda 14 spectrometer equipped with a $BaSO_4$ coated integration sphere; the samples were diluted in $BaSO_4$; the spectra were plotted using the Kubelka–Munk function.

### 2.3. Catalytic studies

The catalytic oxidation reactions were performed at atmospheric pressure in a thermostated glass batch reactor. In a typical experiment, 50 mg of catalyst were suspended under stirring (650 rpm) in a mixture containing 1.5 mmol of organic substrate, 3 mmol $H_2O_2$ (aqueous solution, 50 wt%) and 15 mL of acetonitrile as solvent. Samples of the reaction mixture were withdrawn periodically and analyzed by GC (DB-1, 60 m, 0.20 mm id, 0.25 μm film thickness). The hydrogen peroxide concentration was measured by standard iodometric titration.

## 3. Results and discussion

### 3.1. Synthesis and characterization of $SiO_2$–$TiO_2$ mixed oxides

The non-hydrolytic sol–gel process used here provides a simple, one-step route to amorphous $SiO_2$–$TiO_2$ materials, starting from cheap chloride precursors. This process is based on the following etherolysis and condensation reactions (M = Si or Ti):

$$\text{M–Cl} + {}^i\text{Pr}_2\text{O} \rightarrow \text{M–O}^i\text{Pr} + {}^i\text{PrCl} \quad (1)$$

$$\text{M–Cl} + \text{M–O}^i\text{Pr} \rightarrow \text{M–O–M} + {}^i\text{PrCl} \quad (2)$$

In the case of $SiO_2$–$TiO_2$ gels, the condensation reactions around Si atoms are catalyzed by Ti species. The molar ratio Ti/(Si + Ti) investigated ranged between 0.03 and 0.09. Two reaction temperatures were used, 110 and 150 °C. Elemental analysis indicated that, within experimental error, the Ti content in the materials was close to the nominal Ti content, indicating that all the Ti atoms were incorporated into the silica matrix (Table 1). Both Ti content and synthesis temperature strongly influenced the textural properties of solids, as shown in Fig. 1. The pore volume and pore diameter increased with the Ti content and synthesis temperature (Table 1). Thus, the xerogel Ti3-110 contained a significant amount of micropores, whereas the xerogels synthesized at higher temperature or with a higher Ti loading were mesoporous (Fig. 1), with average pore diameters ranging from 3.2 to 11.3 nm. The calcined xerogels Ti6-150 and Ti9-150 exhibited truly outstanding textures, with pore volumes around 2.5 $cm^3 g^{-1}$ usually associated with aerogels. The increase of the pore volume and pore diameter with Ti content

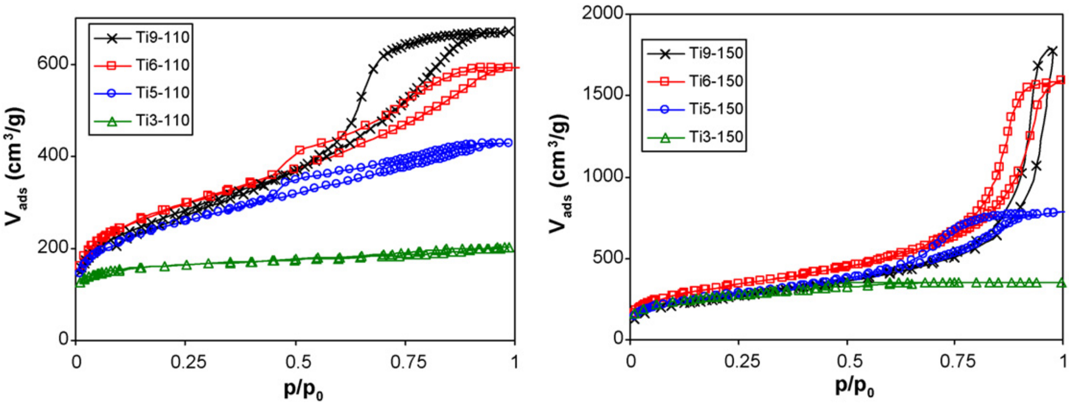


**Fig. 1.** $N_2$ adsorption–desorption isotherms at −196 °C of the catalysts prepared at 110 (left) and 150 °C (right).

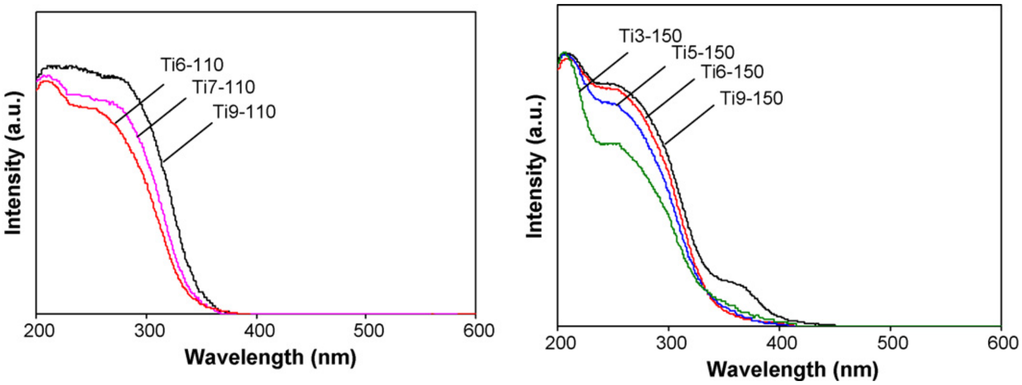


**Fig. 2.** Normalized DRUV–vis spectra of the catalysts prepared at 110 (left) and 150 °C (right).

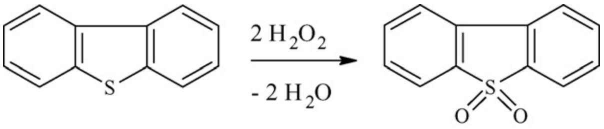
and reaction temperature can be ascribed to the increase of the condensation rate leading to gels with higher degree of crosslinking, able to withstand the high capillary pressures imposed on the gel network during the drying process that are responsible for the collapse of unsufficiently crosslinked gels [10].

The distribution of the Ti atoms in the silica framework was investigated using DRUV–vis spectroscopy. DRUV–vis is commonly used to establish the environment of Ti-sites in Ti-containing silicates. Thus, bands at 210–230 nm have been attributed to oxygen-to-metal charge transfer (CT) at isolated tetrahedral Ti(IV) centers [16,17]. The CT band at 260–280 nm has been ascribed to partially polymerized penta- and hexacoordinated Ti atoms [18,19]. Conversely, the presence of a segregated anatase phase leads to a characteristic absorption at 320–340 nm [20,21].

The spectra of all the calcined xerogels showed two large absorption bands in the range of 210–230 nm (ascribed to the isolated four-coordinated Ti atoms) and 260–280 nm (attributed to Ti oligomers (Fig. 2)). The relative intensity of the band at 260–280 nm increased with the Ti loading, as the probability of Ti–O–Ti bond formation increases. The formation of anatase domains occurred only in the case of Ti9-150, as shown by the weak band at 350 nm. It is known that anatase is responsible for the direct decomposition of $H_2O_2$ into oxygen and water.

### 3.2. *Catalytic studies*

The catalytic potential of $SiO_2$–$TiO_2$ mixed oxides was evaluated in the sulfoxidation reaction of dibenzothiophene (DBT), a bulky and weakly reactive molecule, using $H_2O_2$ as oxidizing agent. The reactions were carried out at 60 °C in acetonitrile, a solvent fully miscible with both organic substrate and the aqueous hydrogen peroxide solution. Typically, the experiments were carried out with a $H_2O_2$/DBT ratio of 2. Under the present experimental conditions the DBT oxidation was highly selective to the sulfur atom, leading directly to the corresponding sulfone (Eq. (3)).



(3)

In the absence of catalyst, using the same experimental conditions, DBT conversion was negligible. For the sake of comparison, the oxidation of DBT was carried out with a TS-1 catalyst (400 $m^2 g^{-1}$, 1.2 wt% Ti) prepared and characterized as described previously [22]. Under the above-mentioned conditions only 5% of DBT was converted after 360 min, indicating that this molecule hardly penetrates within the TS-1 micropores with 0.53–0.56-nm aperture.

The kinetics profiles of DBT oxidation over the $SiO_2$–$TiO_2$ mixed oxides prepared by non-hydrolytic sol–gel are plotted in Fig. 3. For all the catalytic materials the oxidation reaction occurred with significant conversions. These data indicate, on the one hand, the high intrinsic activity of the Ti-sites, and on the other hand, the highly beneficial effect of the catalyst mesoporosity for the accessibility and mobility of DBT molecule inside the pores. The reaction rate strongly depends on the Ti loading and the preparation temperature. Thus, for a given preparation temperature, the DBT conversion increased with the Ti loading in the catalysts; for a given Ti loading, the DBT conversion increased with the preparation temperature. A notable exception is Ti9-150, which showed only moderate activity. This could be related to the presence of anatase domains in this sample (Fig. 2), favoring the direct decomposition of the $H_2O_2$ into oxygen and water ($H_2O_2 \rightarrow H_2O + (1/2)O_2$). Indeed, the measured $H_2O_2$ efficiency (defined as the ratio between the number of $H_2O_2$ moles required for the DBT oxidation and the number of $H_2O_2$ moles converted) was only 80% for Ti9-150, whereas it was higher

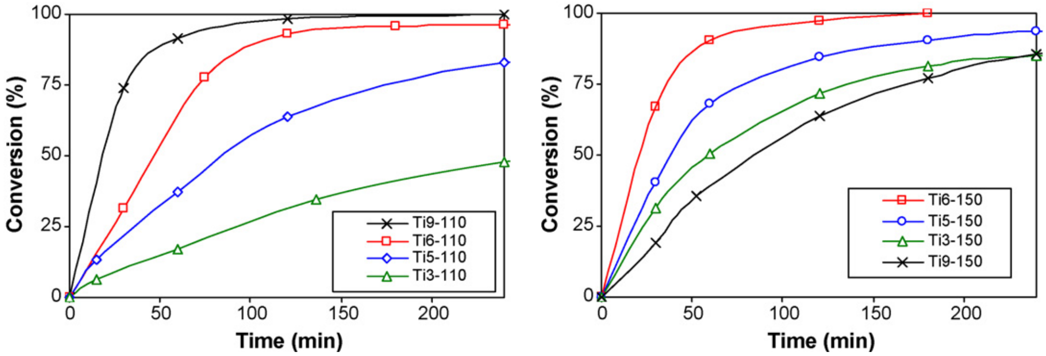


**Fig. 3.** Kinetics profiles of DBT oxidation on catalysts prepared at 110 (left) and 150 °C (right). Conditions: $T = 60$ °C, $H_2O_2$/DBT = 2/1 (mol/mol).

**Table 2**
DBT oxidation over Ti6-150 under different conditions.

| Parameter | Value | Initial rate (mol $L^{-1}$ $h^{-1}$ $g_{catal}^{-1}$) | DBT conversion after 120 min (%) |
|---|---|---|---|
| Temperature (°C)[a] | 50 | 2.6 | 96 |
| | 60 | 3.0 | 97 |
| | 70 | 3.5 | 100 |
| $H_2O_2$/DBT (mol/mol)[b] | 2/1 | 3.0 | 97 |
| | 3/1 | 3.8 | 99.5 |
| | 4/1 | 4.4 | 100 |
| Oxidizing agent[c] | $H_2O_2$ 50% in $H_2O$ | 3.0 | 97 |
| | TBHP 70% in $H_2O$ | 3.2 | 94 |
| | TBHP 5.5 M in decane | 3.1 | 96 |

[a] Conditions: $H_2O_2$/DBT = 2/1 (mol/mol).
[b] $T$ = 60 °C.
[c] $T$ = 60 °C, oxidizing agent/DBT = 2/1 (mol/mol); solvent = acetonitrile.

**Table 3**
Catalytic behavior of Ti6-150 for the oxidation of various substrates (S) with $H_2O_2$.

| Substrate (solvent) | $H_2O_2$/S (mol/mol) | $C_i$ (mol $L^{-1}$) | Temperature (°C) | Reaction time (min) | S conversion (%) into: | | $H_2O_2$ efficiency (%) |
|---|---|---|---|---|---|---|---|
| | | | | | Sulfoxide | Sulfone | |
| THT (MeCN) | 2/1 | 0.1 | 40 | 5 | 55 | 45 | 100 |
| | | | | 20 | 2 | 98 | |
| | | | | 30 | 0 | 100 | |
| MPS (MeCN) | 2/1 | 0.1 | 40 | 20 | 15 | 85 | 100 |
| | | | | 30 | 5 | 95 | |
| | | | | 45 | 0 | 100 | |
| DPS (MeCN) | 2/1 | 0.1 | 40 | 30 | 46 | 54 | 100 |
| | | | | 120 | 15 | 85 | |
| | | | | 180 | 0 | 100 | |
| BT (MeCN) | 2/1 | 0.1 | 60 | 60 | 0 | 45 | 98 |
| | | | | 360 | 0 | 93 | |
| 4,6-DMDBT (MeOH) | 10/1 | 0.01 | 80 | 60 | 0 | 30 | 98 |
| | | | | 360 | 0 | 97 | |

than 98% for all other catalysts. The influence of the preparation temperature on the DBT conversion can be related to the significantly higher surface area and pore size of the catalysts prepared at 150 °C (Table 1).

In order to investigate the effect of the oxidation temperature and $H_2O_2$/substrate ratio in the sulfoxidation, several tests were performed with DBT as a model substrate and Ti6-150 as catalyst. The initial rate and the conversion of the organic substrate are summarized in Table 2. As expected, both the initial rate and the conversion of DBT increase when the reaction temperature increases. As shown in Table 2, an excess of $H_2O_2$ has a favorable effect on the catalytic performances. However, it is important to note that the DBT conversion reached 100% after 180 min even without any excess of $H_2O_2$, indicating a high catalytic activity for 6Ti-150 and a very selective consumption of hydrogen peroxide for the sulfoxidation reaction.

The catalytic oxidation of DBT was also carried out in the presence of anhydrous TBHP (5.5 M in decane) and 70% TBHP in aqueous solution as oxidants. The results included in Table 2 indicate that the catalytic behaviour of $H_2O_2$ and TBHP were very close.

Some sulfides and thiophenes with different molecule sizes and reactivities, such as tetrahydrothiophene (THT), methyl phenyl sulfide (MPS), diphenyl sulfide (DPS), benzothiophene (BT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) were also oxidized with $H_2O_2$ in the presence of Ti6-150. The oxidation of sulfides led to the corresponding sulfoxides and sulfones, while the oxidation of the thiophene derivatives led directly to the corresponding sulfone. The catalytic results and the oxidation conditions are summarized in Table 3. Very high conversion and $H_2O_2$ efficiency were obtained for all the substrates. These data indicate that even the larger molecules easily penetrate the mesopores of Ti6-150 to reach the active Ti catalytic sites. As expected, the sulfides are oxidized much faster than the thiophene derivatives. It is known that the reactivity of sulfur compounds can be correlated to the nucleophilicity of the sulfur atom, which is higher in sulfides than in thiophenes [2,14]. Finally, it is important to point out that 4,6-DMDBT, a less reactive molecule which is present in the fuels processed by the hydrodesulfurization plants, can be effectively oxidized with $H_2O_2$ in diluted methanol solution. Methanol was used as solvent in this test because 4,6-DMDBT is not soluble in acetonitrile.

In order to obtain information on the stability of active Ti species in the $SiO_2$–$TiO_2$ matrix, Ti6-150 was reused several times in the DBT oxidation reaction performed at 60 °C for 60 min in acetonitrile with a ratio $H_2O_2$/DBT of 2. The catalyst was separated by filtration after reaction, washed with acetonitrile, and then placed into a fresh reagent mixture. The conversion of DBT for the four runs was 90%, 91%, 89%, and 87%, indicating that our catalyst was stable under operating conditions.

On the other hand, to demonstrate that the activity of our catalyst was not due to the leaching of Ti species, an additional catalytic test was performed with DBT: the catalyst was filtered off at 60 °C after 15 min reaction (35% conversion) then the solution was further reacted for 60 min at 60 °C. Only a small increase in conversion of DBT (from 35% to 37%) was observed.

## 4. Conclusion

The non-hydrolytic sol–gel process based on the etherolysis and condensation of chloride precursors offers a simple one-step route to prepare mesoporous $SiO_2$–$TiO_2$ xerogels with a good dispersion of Ti species and outstanding textural properties.

We have investigated the sulfoxidation reaction of sulfur compounds with aqueous solution of hydrogen peroxide over $SiO_2$–$TiO_2$ xerogels. It has been shown that these large-pore catalytic materials are active for the selective oxidation of bulky sulfides and thiophenes to the corresponding sulfoxides/sulfones. An excellent selectivity based on hydrogen peroxide consumption was observed for these reactions, which makes these materials very promising for fine chemicals synthesis and environmental applications.

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