Non-hydrolytic synthesis of mesoporous silica–titania catalysts for the mild oxidation of sulfur compounds with hydrogen peroxide

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A SiO$_2$–TiO$_2$ mesoporous xerogel prepared in one-step by a non-hydrolytic route shows excellent performance in the mild oxidation of sulfides, sulfoxides and thiophenes with aqueous solutions of H$_2$O$_2$.

Catalytic sulfoxidation reactions are important reactions notably in the synthesis of molecules of pharmaceutical interest.[1,2] Over the past ten years, they have also been attracting increasing attention for the removal of sulfur-containing pollutants. Thus, catalytic oxidative desulfurization is a promising alternative technology for ultra-deep desulfurization of fuel[3–5] by conversion of sulfides and thiophene derivatives into the corresponding sulfoxides and sulfones, which are easily extracted due to their increased polarity. Selective catalytic sulfoxidation was also proposed as an effective method for treating wastewater contaminated with dimethyl sulfoxide,[6] by converting it into biodegradable dimethyl sulfone.

Typically, sulfoxidation reactions are carried out in the liquid phase in the presence of oxidizing agents such as organic peroxyacids, peroxides, and hydroperoxides, or hydrogen peroxide. Hydrogen peroxide is particularly attractive owing to its high effective-oxygen content, cleanliness (water being the only by-product), and acceptable safety in storage and operation. Therefore, over the past few years the importance of hydrogen peroxide as a "green" oxidizing agent for liquid-phase organic reactions has grown considerably[7,8] and the catalytic oxidation of sulfur-containing compounds by H$_2$O$_2$ has been extensively studied.

Microporous Ti-containing crystalline silicates (TS-1, Ti-β, etc.), with strong oxidation capacity and high stability, are particularly effective heterogeneous catalysts for the sulfoxidation with H$_2$O$_2$.[9–11] However, their application is limited to reactants with molecular sizes smaller than 0.7 nm due to their small micropore openings. The synthesis of Ti-containing mesoporous templated silicates (Ti-MCM-41, Ti-MCM-48) having uniform mesopores ranging from 2 to 10 nm in diameter opened new possibilities for the oxidation of bulky molecules.[12,13] Unfortunately, these materials exhibited a lower catalytic activity and lower H$_2$O$_2$ selectivity in the oxidation of organic molecules with hydrogen peroxide than crystalline Ti-containing silicates. This behavior has been ascribed to the large number of surface silanol groups, leading to extensive water adsorption hindering the access to the active Ti sites. Amorphous SiO$_2$–TiO$_2$ mixed oxides with well-dispersed Ti sites have been synthesized by both hydrolytic[14–16] and non-hydrolytic[17,18] sol–gel procedures. The latter method offers a very simple and efficient way to synthesize mesoporous titania–silica xerogels with controlled texture,[18] avoiding the use of templates or supercritical drying. These non-hydrolytic SiO$_2$–TiO$_2$ mixed oxides, with good homogeneity and textural properties, proved to be efficient catalysts for olefin epoxidations with alkylhydroperoxides as the oxidizing agent.[19]

In this communication we report the one-step non-hydrolytic synthesis from cheap chloride precursors of a SiO$_2$–TiO$_2$ mesoporous xerogel (hereafter designated as NH SiO$_2$–TiO$_2$) with a high dispersion of Ti and unprecedented textural properties. This xerogel was used for the first time as a heterogeneous catalyst in the oxidation of sulfur-containing compounds with hydrogen peroxide. Under mild conditions (20–60 °C), very high conversions of the sulfur-containing compounds to sulfones and excellent hydrogen peroxide selectivities were obtained.
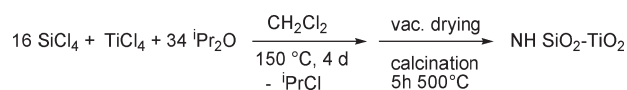
NH SiO$_2$–TiO$_2$ was prepared by reaction of SiCl$_4$ and TiCl$_4$ (molar ratio Si/Ti = 16) with ^{i}Pr$_2$O (diisopropyl ether) as shown in Scheme 1. The reaction temperature was fixed at 150 °C and CH$_2$Cl$_2$ was added in order to increase the pore volume.[17]†

Powder X-ray diffraction data indicated that the solid was amorphous. The Ti and Si content, measured by energy dispersive X-ray analysis (EDX), were 3.8 wt% and 46.9 wt%, respectively.

The textural properties of NH SiO$_2$–TiO$_2$, derived from the nitrogen physisorption isotherm (Fig. 1), were remarkable. The specific surface area and pore volume (1215 m^2 g^{-1} and 2.4 cm^3 g^{-1}) were much higher than those reported for SiO$_2$–TiO$_2$ xerogels (525 m^2 g^{-1} and 0.17 cm^3 g^{-1}),[15] Ti-MCM41 (936 m^2 g^{-1} and 0.49 cm^3 g^{-1}),[12] and even aerogels (518 m^2 g^{-1} and 0.99 cm^3 g^{-1})[14] with similar or lower Ti contents. A t-plot analysis showed that the surface area located in the micropores was negligible (about 50 m^2 g^{-1}).

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$$16\ SiCl_4 + TiCl_4 + 34\ {}^iPr_2O \xrightarrow[\substack{150\ °C,\ 4\ d \\ -\ {}^iPrCl}]{CH_2Cl_2} \xrightarrow[\substack{calcination \\ 5h\ 500\ °C}]{vac.\ drying} NH\ SiO_2\text{-}TiO_2$$
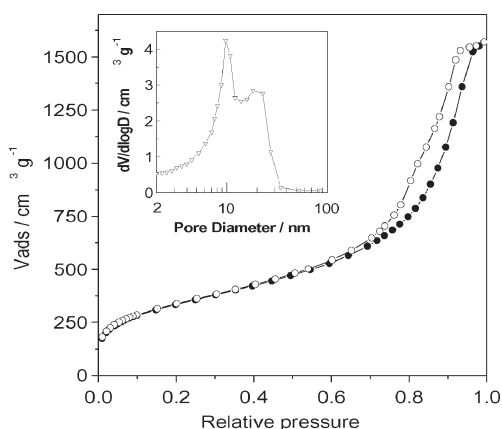
Scheme 1 Synthetic route to NH SiO$_2$–TiO$_2$.

Fig. 1 N₂ adsorption–desorption isotherm at 77 K and pore size distribution (inset) of NH SiO₂–TiO₂ (open and filled symbols correspond to the adsorption and desorption branches, respectively).

Barrett–Joyner–Halenda (BJH) analysis of the desorption isotherm indicated the presence of a broad distribution of pores in the 3–40 nm range, with two maxima centered at about 10 and 20 nm, and an average pore diameter of 8.2 nm.‡

The coordination environment of Ti atoms in NH SiO₂–TiO₂ was investigated using diffuse reflectance UV-Vis spectroscopy (Fig. 2).‡ The major absorption band in the range of 210–240 nm, may be ascribed to the isolated four-coordinate Ti atoms[20] that are considered responsible for the peroxo species activation. The shoulder in the 250–320 nm region would indicate the presence of higher-coordinated Ti atoms resulting from the oligomerization of Ti species, or the presence of very small TiO₂ nano-domains (quantum size effect).[20,21] The absence of a band at 330 nm shows that anatase is not present in significant quantities.

Three representative molecules were chosen in order to evaluate the potential of NH SiO₂–TiO₂ as a catalyst for the sulfoxidation reaction with H₂O₂: methyl-phenyl sulfide (MPS), dibenzothiophene (DBT) (a model compound for organic sulfur in fossil fuels) and dimethyl sulfoxide (DMSO) (Scheme 2).§

Thus, using a stoichiometric amount of H₂O₂, complete oxidation required only 60 min for MPS and 45 min for DMSO. In the case of DBT, the less reactive molecule, 92%
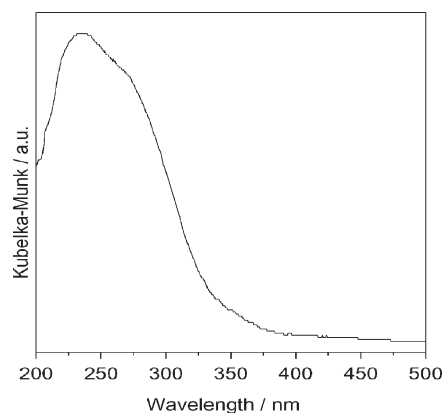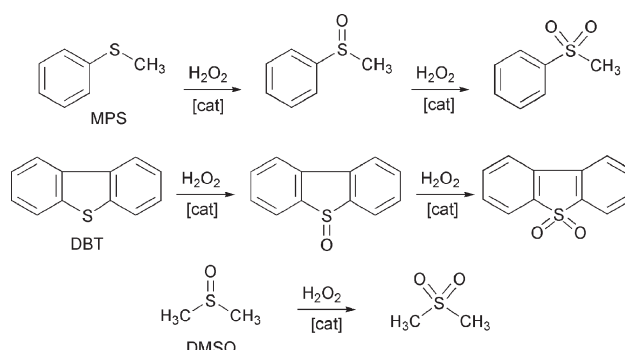

Fig. 2 Diffuse reflectance UV-Vis spectrum of NH SiO₂–TiO₂.

Scheme 2 Sulfoxidation reactions investigated.

could be oxidized after 360 min at 60 °C (Fig. 3). The conversions measured under the same conditions but in the absence of catalyst were 8%, 0.5% and 12% for MPS, DBT and DMSO, respectively. The intermediate formation of sulfoxide was not observed with DBT (Fig. 3).

The selectivity to H₂O₂ (corresponding to the ratio between the H₂O₂ consumed in the sulfoxidation and the H₂O₂ converted) was 100% for MPS and DMSO, and 95% for DBT, indicating that H₂O₂ was mainly consumed in the sulfoxidation reaction and that direct decomposition of the oxidizing agent into water and oxygen was negligible.

In order 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 (30% conversion) then the solution was further reacted for 60 min at 60 °C. Only a very small increase in conversion of DBT (from 30% to 32%) was observed (Fig. 3).

The recycling of the catalyst in the oxidation of DBT was also investigated. After each run (60 min, 60 °C), the catalyst was separated by filtration, washed with acetonitrile, and then placed into a fresh reagent mixture. The conversion of DBT for the four runs was 61, 59, 58, and 57%, respectively, indicating that our catalyst was stable under operating conditions.

For the sake of comparison, the oxidation of MPS was carried out with a Ti-MCM41 catalyst (795 m² g⁻¹, 0.7 wt% Ti) prepared as described in the literature.[12] After 15 min, the conversion of MPS with Ti-MCM41 was 9% instead of 82% with NH SiO₂–TiO₂. After 60 min, the conversion of MPS was 36% with Ti-MCM41 and the H₂O₂ selectivity was 60%. Accordingly, our catalyst exhibited significantly higher activity (even taking into account the higher Ti content) and H₂O₂ selectivity than Ti-MCM 41. This behavior might be related to the high degree of condensation typical of non-hydrolytic SiO₂–TiO₂ xerogels,[18] that would lead to a lower amount of surface silanols and a lower hydrophilicity than in Ti-MCM 41 samples. Indeed, the low activity and H₂O₂ selectivity of Ti-MCM 41 in the oxidation of alkenes (in comparison to titanosilicalites) has been ascribed to the high density of silanols in Ti-MCM 41.[12] In order to test this hypothesis, the hydrophilicities of the surface of NH SiO₂–TiO₂ and of our Ti-MCM 41 sample were characterized by water adsorption. After dehydration for 8 h at 350 °C under dry nitrogen and equilibration over a saturated NH₄Cl solution (79% relative humidity) for 24 h, NH SiO₂–TiO₂ adsorbed 0.26 mg H₂O

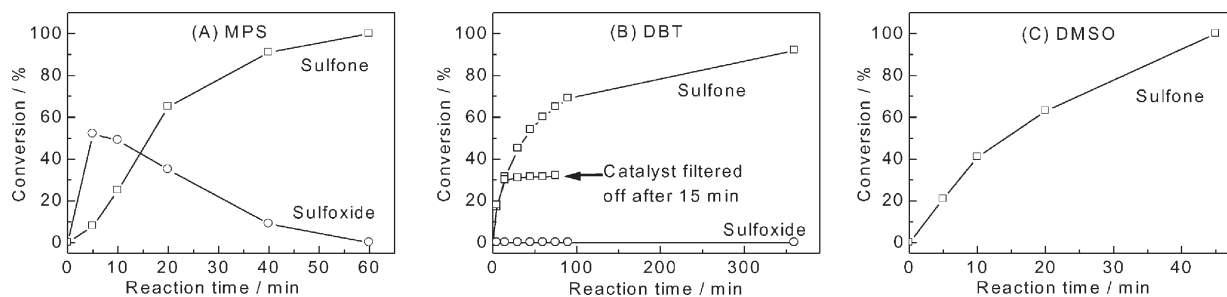**Fig. 3** Sulfoxidation with 30 wt% H_2O_2 aqueous solution catalyzed by NH TiO_2–SiO_2 of: (A) methyl-phenyl sulfide in acetonitrile at 40 °C, (B) dibenzothiophene in acetonitrile at 60 °C, and (C) dimethyl sulfoxide in water at 20 °C. Conditions: 50 ml batch reactor, 50 mg catalyst, 1.5 mmol substrate, 15 ml solvent, $H_2O_2/MPS = H_2O_2/DBT = 2$, $H_2O_2/DMSO = 1$.

per m^2, whereas under the same conditions the Ti-MCM 41 sample adsorbed 0.42 mg H_2O per m^2.

The unique catalytic performances of NH SiO_2–TiO_2 thus likely resulted from its relatively high amount of well-dispersed Ti species, its outstanding texture, and its high degree of condensation.

In conclusion, the non-hydrolytic sol–gel route described here provided a simple one-pot method for the synthesis of a mesoporous SiO_2–TiO_2 xerogel with outstanding textural properties. After calcination, this xerogel proved to be an excellent sulfoxidation catalyst with H_2O_2 under mild conditions, exhibiting high activity and selectivity to H_2O_2, even in the case of dibenzothiophene, which is considered a refractory substrate. Such materials open new possibilities for the oxidation with high H_2O_2 efficiency of bulky substrates for fine chemicals synthesis and environmental applications.

Notes and references

† NH SiO_2–TiO_2 was prepared by adding, in a glovebox, $SiCl_4$ (38.8 mmol), $TiCl_4$ (2.4 mmol), $^iPr_2O$ (80 mmol) and CH_2Cl_2 (10 ml) into a 150 ml, Teflon-lined, stainless steel autoclave. After heating under autogenous pressure for 4 days at 150 °C, the gel was filtered off, washed with dry CH_2Cl_2, dried under vacuum at 110 °C for 6 h and calcined in dry air at 500 °C for 5 h.
‡ N_2 physisorption experiments were done at −196 °C on a Micromeritics ASAP 2010 sorptometer. The samples were desorbed under vacuum at 200 °C for 15 h. Diffuse reflectance UV-Vis spectra were recorded under ambient conditions on a Perkin-Elmer Lambda 14 spectrometer equipped with a $BaSO_4$ integration sphere; the samples were diluted in $BaSO_4$; the spectra were plotted using the Kubelka–Munk function.
§ Catalytic sulfoxidation reactions were carried out at atmospheric pressure in a 50 ml glass batch reactor, equipped with magnetic stirrer, thermometer, and condenser, and placed in a thermostated bath. 50 mg of catalyst (NH SiO_2–TiO_2 or Ti-MCM 41) was suspended under stirring (800 rpm) in a mixture containing 1.5 mmol of organic substrate and 15 ml solvent. The adequate volume of hydrogen peroxide (30 wt% aqueous solution) was added at the beginning of experiment. Blank runs were carried out mixing the reactants in the absence of catalyst. Samples of the reaction mixture were withdrawn periodically and analyzed on a Varian 3900 chromatograph equipped with a capillary column (DB-1, 60 m, 0.20 mm id, 0.25 μm film thickness). The hydrogen peroxide concentration was measured by standard iodometric titration.

1 K. Kaczorowska, Z. Kolarska, K. Mitka and P. Kowalski, *Tetrahedron*, 2005, **61**, 8315.
2 *Sulfones in Organic Synthesis*, ed. N. S. Simpkins, Pergamon Press, Oxford, 1993.
3 F. M. Collins, A. R. Lucy and C. Sharp, *J. Mol. Catal. A: Chem.*, 1997, **117**, 397.
4 V. Hulea, F. Fajula and J. Bousquet, *J. Catal.*, 2001, **198**, 179.
5 H. Lü, J. Gao, Z. Jiang, Y. Yang, B. Song and C. Li, *Chem. Commun.*, 2007, 150.
6 A. L. Maciuca, E. Dumitriu, F. Fajula and V. Hulea, *Chemosphere*, 2007, **68**, 22.
7 *Application of Hydrogen Peroxide and Derivatives*, ed. C. W. Jones, Royal Society of Chemistry, Cambridge, 1999.
8 *Selective Oxidation by Heterogeneous Catalysis*, ed. G. Centi, F. Cavani and F. Trifirro, Kluwer Academic-Plenum Publishers, New York, 2001.
9 R. S. Reddy, J. Sudhakar Reddy, R. Kumar and P. Kumar, *J. Chem. Soc., Chem. Commun.*, 1992, 84.
10 T. Balsco, A. Corma, M. T. Navarro and J. P. Pariente, *J. Catal.*, 1995, **156**, 65.
11 V. Hulea, P. Moreau and F. Di Renzo, *J. Mol. Catal.*, 1996, **111**, 325.
12 A. Corma, M. T. Navarro and J. Pérez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 147; T. Blasco, A. Corma, M. T. Navarro and J. Pérez-Pariente, *J. Catal.*, 1995, **156**, 65.
13 W. Zhang and T. J. Pinnavaia, *Catal. Lett.*, 1996, **38**, 261.
14 R. Hutter, T. Mallat and A. Baiker, *J. Catal.*, 1995, **153**, 177.
15 S. Klein, S. Thorimbert and W. F. Maier, *J. Catal.*, 1996, **163**, 476.
16 R. J. Davis and Z. F. Liu, *Chem. Mater.*, 1997, **9**, 2311.
17 M. Andrianainarivelo, R. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1996, **6**, 1665.
18 V. Lafond, P. H. Mutin and A. Vioux, *Chem. Mater.*, 2004, **16**, 5380.
19 V. Lafond, P. H. Mutin and A. Vioux, *J. Mol. Catal. A: Chem.*, 2002, **182–183**, 81.
20 L. Marchese, T. Maschmeyer, E. Gianotti, S. Coluccia and J. M. Thomas, *J. Phys. Chem. B*, 1997, **101**, 8836.
21 X. Gao, S. R. Bare, J. L. G. Fierro, M. A. Banares and I. E. Wachs, *J. Phys. Chem. B*, 1998, **102**, 5653.