



# Mesoporous SiO<sub>2</sub>-TiO<sub>2</sub> epoxidation catalysts: Tuning surface polarity to improve performance in the presence of water

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## ABSTRACT

Herein, we present the preparation by the non-hydrolytic sol-gel (NHSG) route of a mesoporous SiO<sub>2</sub>-TiO<sub>2</sub> epoxidation catalyst with high specific surface area and large pores, and we discuss its modification by methylation. The pristine NHSG catalyst is tested for the catalytic conversion of cyclohexene with H<sub>2</sub>O<sub>2</sub> in acetonitrile, showing performance comparable to a reference TS-1 catalyst. To expand the scope of the catalysts, we study their performance in the presence of water – present in aqueous solutions of H<sub>2</sub>O<sub>2</sub>, formed as a by-product of the epoxidation reaction, or used as a co-solvent. While TS-1 maintains high epoxidation activity, the pristine amorphous and mesoporous SiO<sub>2</sub>-TiO<sub>2</sub> catalysts strongly deactivate when water is used as co-solvent. In order to circumvent this deactivation in the presence of water, we investigate the effect of surface hydrophobization with methyl groups on the catalytic activity and selectivity. Two functionalization methods are investigated: one-pot synthesis with methyltrichlorosilane and post-synthesis silanization with methyltrimethoxysilane. On the one hand, the one-pot methylation does not increase water resistance, in spite of an increased surface hydrophobicity. We interpret this result in the light of a poorer Ti dispersion and lower Ti<sup>4+</sup> surface content in these catalysts. On the other hand, post-synthesis grafting was successful, allowing to maintain good epoxidation activity even in the presence of water. This result is explained by a combination of a hydrophobic surface with a high active site content in this catalyst.

## 1. Introduction

Olefin epoxidation is widely represented in the chemical industry, from the production of pharmaceuticals to the polymer industry, due to the extensive use of these reactions for the synthesis of active intermediates (e.g. ethylene and propylene oxide, epichlorhydrin, cyclohexene oxide, etc.) [1]. With the recent advent of *green chemistry* and its associated principles [2], industrially relevant chemical processes, including olefin epoxidation, have to be re-designed. Sustainable routes are highly sought-for, not necessarily to maximize conversion or yield, but rather to minimize energy consumption and waste [3,4]. In the field of heterogeneous catalysis, this trend fosters the emergence of a new class of materials with relatively high activity and selectivity under mild conditions, i.e. in water-based media at moderately low temperatures [5,6].

Among the available catalysts and oxidants, the combination of titanium-containing zeolite TS-1 and hydrogen peroxide H<sub>2</sub>O<sub>2</sub> represents one of the success-story of industrial epoxidation reactions. First, the efficiency of TS-1 in terms of catalytic activity and selectivity to

epoxidation products, even at low temperatures and in the presence of water, stems from its success as an oxidation catalyst [7]. Second, H<sub>2</sub>O<sub>2</sub> is commonly considered as one of the greenest oxidants, since it produces water as the only by-product. However, the atomic percentage of active sites in the MFI crystal structure is limited to a maximum of 2.5% (n Ti / (n Ti + n Si)) [8]. Additionally, the intrinsic microporosity of TS-1 proscribes the use of this catalyst for the epoxidation of large olefins due to diffusional limitations. There is therefore a high demand for mixed oxides – either crystalline or amorphous – with larger pores and high surface area in order to extend the versatility of Ti-containing catalysts to a wider range of substrates [8–12]. Several challenges have to be addressed for the preparation of such materials, from the true incorporation of the active species (i.e. Ti<sup>4+</sup>) by the levelling of the precursors reactivity (e.g. pre-hydrolysis of alkoxide precursors [13]) to the control over the texture by the choice of the templating agent, as well as proper drying conditions (e.g. supercritical drying [14]).

Sol-gel methods represent a versatile toolbox for the bottom-up preparation of heterogeneous catalysts [15]. Controlling the transition metal dispersion as well as the texture and functionalization of the

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catalyst surface, it is possible to obtain mesoporous silica-based epoxidation catalysts with high activity and selectivity. In particular, we put our focus on non-hydrolytic sol-gel (NHSG), which is currently emerging as a powerful preparation technique for mesoporous mixed oxide catalysts [16–19]. This approach allows reaching remarkable specific surface area (ca.  $1000 \text{ m}^2 \text{ g}^{-1}$ ) and pore volume (ca.  $1.0\text{--}1.5 \text{ cm}^3 \text{ g}^{-1}$ ), associated with a tunable pore size and a high active phase dispersion without the need for organic templating agent, supercritical drying or pre-hydrolysis of the precursors [20,21]. In those conditions, catalysts with a high content of active sites can be obtained, with benefits for the catalytic performance compared to single TS-1 nanocrystals.

Despite the promising improvement brought by the fine control over the catalyst textural properties, amorphous  $\text{SiO}_2\text{-TiO}_2$  mixed oxides are easily deactivated in water [22]. This issue has to be addressed when running epoxidation reactions with aqueous solutions of  $\text{H}_2\text{O}_2$  (with concomitant production of  $\text{H}_2\text{O}$ ) and/or in the presence of large amounts of water in the solvent.

An exception to deactivation by  $\text{H}_2\text{O}$  is provided by TS-1: its crystallinity and intrinsic hydrophobicity accounts for its good performance in aqueous media [22,23]. Increasing surface hydrophobicity of epoxidation catalysts was previously shown to be a pertinent strategy to increase the catalytic performance, when using  $\text{H}_2\text{O}_2$  or organic peroxides as oxidant [24–30]. However, to the best of our knowledge, the improvement of the catalytic performance of amorphous titanosilicates in the presence of large amount of water by surface hydrophobization has not been addressed previously. Here, in order to circumvent the deactivation of the amorphous and mesoporous  $\text{SiO}_2\text{-TiO}_2$  catalyst prepared by NHSG, we investigated the effect of surface hydrophobization on the catalyst activity using water as co-solvent for the epoxidation of cyclohexene. The surface functionalization was achieved either in one-pot during the gel synthesis or by post-synthesis silanization with a methylated precursor.

Not only the activity but also the selectivity is expected to be influenced by the surface hydrophobization. Considering the reaction pathway for cyclohexene oxidation (Fig. 1), the epoxide can be produced by two competitive paths, either by *direct epoxidation* of cyclohexene with  $\text{H}_2\text{O}_2$  or by the formation of cyclohexenyl hydroperoxide responsible for the oxidation of the olefin through a radical mechanism called *allylic oxidation* [22,26,31]. The second path should be avoided since it leads to the concomitant formation of undesired side products (2-cyclohexen-1-ol and its oxidation product 2-cyclohexen-1-one [32]). The mechanism implies the formation of a radical species on the Ti active site (i.e.  $\text{TiO}\cdot$ ) due to the over-adsorption of  $\text{H}_2\text{O}_2$  onto the catalyst surface, which is favoured by a high  $\text{H}_2\text{O}_2/\text{Ti}$  ratio [26,33,34]. We put forward that increasing the surface hydrophobicity will locally reduce this ratio by repelling  $\text{H}_2\text{O}_2$  molecules from the surface and thus from Ti active sites.

Consecutive to the formation of the epoxide, the ring opening of the epoxide to form a diol (cyclohexane diol) is another unwanted process (Fig. 1). This hydrolysis reaction is promoted by the presence of  $\text{H}_2\text{O}$  [27,28] and therefore thought to be mitigated by surface

hydrophobization.

## 2. Experimental

The catalysts were prepared with a 6% at. Ti loading ( $\text{Ti}/(\text{Ti} + \text{Si})$ ) according to the non-hydrolytic sol-gel (NHSG) method, following a procedure described elsewhere [21]. Briefly,  $\text{SiCl}_4$  (4.267 g, Acros Organics, 99.8%),  ${}^1\text{Pr}_2\text{O}$  (5.449 g, Acros Organics, 99%) and  $\text{TiCl}_4$  (0.304 g, Acros Organics, 99.9%) were successively transferred into a  $100 \text{ cm}^3$  teflon-lined stainless steel autoclave along with  $\text{CH}_2\text{Cl}_2$  (8.867 g, VWR Chemicals, 99.8%) in a glovebox. Prior to use,  ${}^1\text{Pr}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$  were dried using metallic sodium and  $\text{P}_2\text{O}_5$ , respectively, down to a water concentration below 15 ppm. The other reactants were used as received. The clear solution, with a molar composition of 1  $\text{SiCl}_4$ : 0.064  $\text{TiCl}_4$ : 2.127  ${}^1\text{Pr}_2\text{O}$ : 4.165  $\text{CH}_2\text{Cl}_2$ , was manually stirred for 10 min. The autoclave was subsequently sealed and kept in an oven at  $150^\circ\text{C}$  for 6 days. Afterwards, it was opened in the glovebox and the as-synthesized gel was ground and dried overnight under vacuum. The solid catalyst, in powder form, was obtained after calcination at  $500^\circ\text{C}$  for 5 h ( $10^\circ\text{C min}^{-1}$ ). It is denoted “NHSG”. As a reference material, titanosilicate-1 (TS-1) was synthesized with a Ti atomic content of 1.8% [35].

**One-pot functionalization.** The gel was obtained by the same method as depicted above, but replacing part of the  $\text{SiCl}_4$  by  $\text{MeSiCl}_3$  (Sigma-Aldrich, 99%) [24]. The catalysts are denoted “NHSG\_XMe”, where “X” represents the nominal molar ratio  $\text{MeSiCl}_3/\text{Si}$ . The final composition was 1  $\text{SiCl}_4$ : 0.111  $\text{SiCl}_3$ : 0.071  $\text{TiCl}_4$ : 2.309  ${}^1\text{Pr}_2\text{O}$ : 4.628  $\text{CH}_2\text{Cl}_2$  (NHSG\_0.1Me) and 1  $\text{SiCl}_4$ : 0.429  $\text{SiCl}_3$ : 0.091  $\text{TiCl}_4$ : 2.825  ${}^1\text{Pr}_2\text{O}$ : 5.950  $\text{CH}_2\text{Cl}_2$  (NHSG\_0.3Me).

**Two-step functionalization.** The pristine NHSG catalyst (200 mg) was methylated by a dry impregnation method using methyltrimethoxysilane (MTMS) (0.206 g, TCI, > 98%) in water-saturated toluene (0.062 g, Sigma-Aldrich,  $\geq 99.7\%$ ). The impregnation solution was mixed with the solid sample and the mixture was further homogenised by vortexing for 10 min in a closed vial. Afterwards, the solid was put to rest in a toluene saturated atmosphere for 48 h. Then, the solid was heated at  $90^\circ\text{C}$  for 1 h, washed successively with 50 ml toluene and 50 ml pentane, and dried overnight at  $120^\circ\text{C}$  under vacuum. The nominal methylation ratio ( $\text{MeSi}(\text{OMe})_3/\text{Si}$ ) was 30%, and the catalyst is denoted “NHSG@0.3Me”.

Textural properties were determined from  $\text{N}_2$  adsorption/desorption isotherms at  $-196^\circ\text{C}$  using a Tristar 3000 instrument (Micromeritics, USA). Prior to measurement, the samples were first degassed overnight under vacuum at  $150^\circ\text{C}$ . The pore size distribution was obtained from the desorption branch using the BJH method. The surface area was evaluated by the BET method in the relative pressure range of 0.05–0.30. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature on a Siemens D5000 diffractometer equipped with a Ni filter using  $\text{CuK}\alpha$  radiation (Bragg-Brentano geometry) operated at 40 kV and 40 mA. Diffractograms were taken between  $5^\circ$  and  $80^\circ$  ( $2\theta$ ) with a step size of  $0.02^\circ$  ( $2\theta$ ). Diffuse reflectance

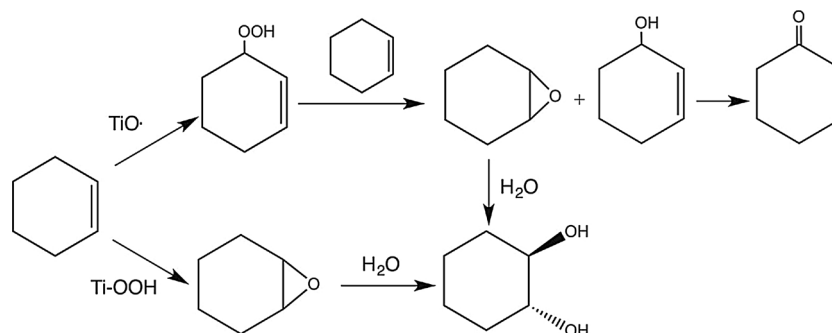


Fig. 1. Reaction scheme for the epoxidation of cyclohexene via the *allylic oxidation* (up) or the *direct epoxidation* routes (bottom) [26].

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