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Epoxidation of cyclohexene over crystalline and amorphous titanosilicate catalysts

Amber Welch[a], N. Ravindran. Shiju[a], Ian D. Watts[a], G. Sankar[a,]*, Sergey Nikitenko[b], and Wim Bras[c]

[a]*Davy Faraday Research Laboratory, The Royal Institution of GB, 21 Albemarle Street, London W1S 4BS, UK*
[b]*DUBBLE@ESRF, University of Leuven, BP 220, Grenoble 38143, France*
[c]*DUBBLE@ESRF, Netherlands Organisation for Scientific Research (NWO), BP 220, Grenoble 38143, France*

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A microporous titanosilicate (TS-1) catalyst was synthesised from an amorphous titanosilicate precursor, and both the amorphous precursor and TS-1 were characterised by Ti K-edge X-ray absorption spectroscopy which revealed that Ti (IV) ions are in tetrahedral coordination in the calcined state. Each of these solids is catalytically active for the conversion of cyclohexene to cyclohexene oxide in the presence of H_2O_2. Use of urea–H_2O_2 adduct as oxidant increased the activity and selectivity for the formation of the epoxide with TS-1 as catalyst. However, a significant loss in catalytic activity is seen for the amorphous precursor.

1. Introduction

It has long been recognised that titanosilicate catalysts are highly effective for a host of organic transformations including epoxidation and ammoxidation. Since the discovery of crystalline, microporous TS-1, several studies have been published; hence perhaps making TS-1 one of the most widely studied titanosilicate materials [1–3]. Preparation of TS-1 is usually carried out under hydrothermal conditions using a range of titanium and silicate sources; Taramasso *et al.* have established a specific method for producing TS-1 catalysts [4]. More recently Serrano and co-workers developed a method of converting a dried gel into TS-1 or zeolite β [5–7]. This precursor gel can be prepared using a variety of methods [5,6,8–10]. Here we report a simple procedure to prepare a co-precipitated gel (cogel) containing a specific Si/Ti ratio and subsequent transformation of this cogel into crystalline TS-1 catalysts. Both the starting cogel and the TS-1 materials were characterised in detail by Ti K-edge X-ray absorption spectroscopy (XAS), which is known to be an ideal technique [11–16] for the study of catalytically active sites when present in small concentrations [17]. In addition, we carried out detailed catalytic reaction studies using both the amorphous cogel and TS-1, which allowed us to compare directly the nature of the titanium centres in both these systems and their relation to the catalytic conversion of cyclohexene in the presence of both H_2O_2 (30 wt% in H_2O) and urea–H_2O_2 adduct [18,19]. Both catalysts were found to be active when aqueous H_2O_2 was used as the oxidant. However, whilst a significant improvement in the activity and selectivity towards epoxide was seen for TS-1 in the presence of urea-H_2O_2 adduct, a decrease in catalytic activity was seen for the cogel.

2. Experimental

In a typical cogel (of specific Si/Ti ratio) preparation, tetraethylammonium hydroxide was slowly added to a solution containing tetraethyl orthosilicate and titanium tetrabutoxide; the solution was continuously agitated using an ultrasonic bath. The gel formed by this procedure was carefully dried, then calcined in air (530°C for 4 h), before use as a precursor for the preparation of TS-1. In a typical TS-1 synthesis, cogel (2.0 g) was added to tetrapropylammonium hydroxide (TPAOH) (3.6 g, 20%), which is traditionally used as structure directing agent in the preparation of TS-1. The resultant gel was subjected to hydrothermal treatment at *ca* 170°C for 24 h. The extracted solid was washed and dried before further characterisation and catalytic use.

X-ray diffraction patterns were recorded using a Bruker D4 X-ray diffractometer equipped with copper target. TS-1 and cogel materials were calcined in air at *ca* 530°C, for about 4 h prior to *in situ* XAS measurements and catalytic studies. Ti K-edge XAS data were recorded at BM26A (DUBBLE) at ESRF, Grenoble (which operates at 6 GeV with a typical current in the range of *ca* 100 mA). The station was equipped with a double crystal Si(111) monochromator, ion chambers for measuring the incident and transmitted beam intensities (Io and It, respectively) and a nine element monolithic fluorescence detector (Ortec) using XPRESS

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* To whom correspondence should be addressed.

electronics for measuring the XAS data in fluorescence mode. All the Ti K-edge XAS data were collected in the fluorescence mode. Ti–$(OSiPh_3)_4$ and titanosilicate ETS-10 were used as model compounds. The data were processed employing the suite of programs available at Daresbury laboratory: EXCALIB (for converting the collected data into energy versus absorption coefficient), EXBROOK for extracting the normalised X-ray Absorption Near Edge Structure (XANES) data.

Cyclohexene epoxidation reactions were carried out in a 50 mL glass reactor equipped with a reflux condenser and a magnetic stirrer. In a typical reaction, the oxidant and cyclohexene were introduced in to the reactor and the mixture was heated to the reaction temperature (333 K, maintained using an oil bath) under constant stirring prior to the introduction of 100 mg of calcined titanosilicate catalyst. Acetonitrile was used as the solvent and mesitylene used as the internal standard. Aliquots were removed from the reactor, periodically over six hours to follow the kinetics of the catalytic reaction. In separate experiments, silicates (without titanium) prepared using identical procedures to titanosilicate cogel and TS-1 synthesis were tested for cyclohexene conversion; in addition to a blank experiment without any catalyst. The liquid samples were analysed using a Gas Chromotograph (Clarus 500, PerkinElmer) equipped with flame ionisation detector and 30 m capillary column (Ellite-1, crossbond 100% dimethyl polysiloxane).

3. Results and Discussion

The X-ray diffraction patterns (figure 1) show the as-prepared cogel to be amorphous and the TS-1 to be a highly crystalline phase pure material. Evidence for the incorporation of titanium ions within the framework sites of TS-1 was seen in the Ti K-edge XANES data (figure 2); the pre-edge (marked A in figure 2c) is known to be sensitive to coordination geometry. Comparison of the Ti K-edge XANES data, (recorded in the hydrated and dehydrated state of all the titanosilicates), with the model compounds ($Ti(OSiPh_3)_4$ and ETS-10) [17,20,21] reveals several interesting points. Firstly, the pre-edge intensity (highest when Ti(IV) is present in tetrahedral coordination and lowest for octahedrally coordinated titanium centres [11,17]), shows a higher value for TS-1 compared to the corresponding cogel, although both materials were calcined and hydrated prior to the XAS measurement. This clearly suggests that the majority of the titanium centres in TS-1 are protected from the coordination of water molecules due to the hydrophobic nature of the silicalite system. Upon *in situ* dehydration, the pre-edge intensity of all the samples increased to a higher value (close to that of the model compound), indicating that the removal of loosely bound water resulted in tetrahedrally coordinated Ti(IV) centres. The pre-edge intensity and its energy position for both the cogel and TS-1 are listed in table 1. Thus, irrespective of the nature of the titanosilicate, whether it is TS-1 or cogel, both should be active for catalytic epoxidation of cyclohexene in the presence of hydrogen peroxide.

The catalytic activity after 6 h of reaction (table 1), clearly shows that all the calcined titanosilicates are active for the conversion of cyclohexene in the presence of H_2O_2 and the activities for all the materials were found to be closely similar to one another. The amorphous cogels were found to be marginally better than the corresponding TS-1. However, the selectivity (figure 3) (figure 4) towards the formation of epoxide is higher for TS-1 compared to the cogel. Significant amounts of diol (the product formed from epoxide due to the presence of acid sites) were formed with the cogel catalyst compared to TS-1. This may be due to the highly disordered structure of the cogel which contains more hydroxyl groups in contrast to the crystalline

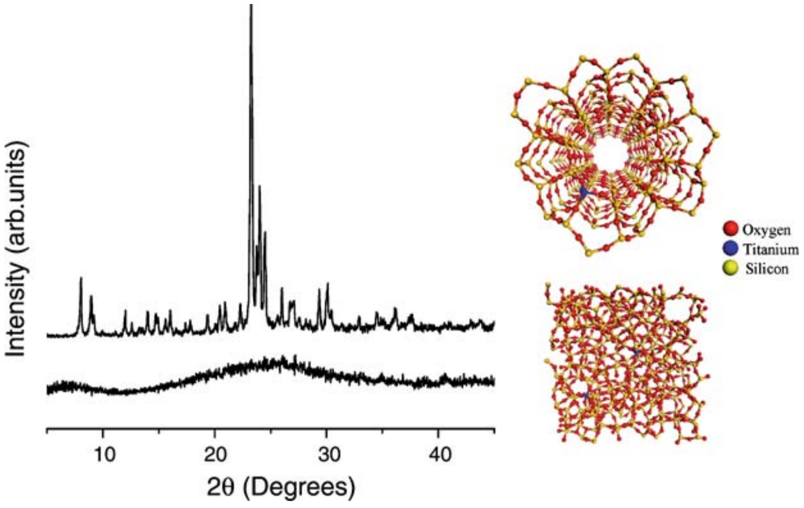

Figure 1. X-ray diffraction patterns of the as-synthesised cogel and the TS-1 crystallised from the cogel. On the right we show structural model representing amorphous titanosilicate (bottom) and crystalline TS-1 (top).

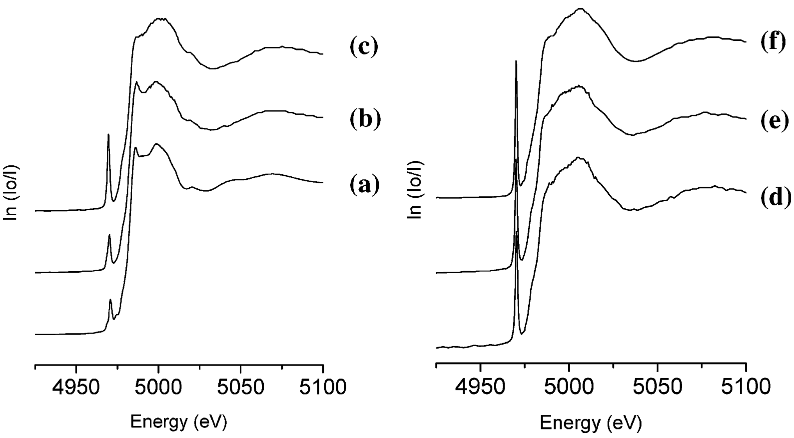

Figure 2. On the left, Ti K-edge XANES data recorded at room temperature of (a) ETS-10 material, (b) amorphous cogel prepared by conventional stirring method and (c) as-prepared TS-1 from cogel. On the right, Ti K-edge XANES, recorded *in situ*, of the calcined (d) cogel and (e) TS-1. For comparison the model compounds $Ti(OSiPh_3)_4$ is also given in (f). It has been shown previously that the $Ti(OSiPh_3)_4$ and ETS-10 contains Ti(IV) ions in tetrahedral and octahedral coordination geometries, respectively.

Table 1

Comparison of the characteristics and catalytic performance of amorphous titanium silicate cogel and microporous TS-1 catalyst prepared from the amorphous titanium silicate cogel

	XRD	Pre-edge Intensity (Arb. Units)	Pre-edge Position (eV)	Cyclohexene conversion (percent)	
				Aqueous H_2O_2[1]	Urea–H_2O_2 Adduct[1]
As-synthesised Ti–silicate co-gel	Amorphous	0.25	4969.28	–	–
As-synthesised TS-1	Crystalline	0.49	4968.53	–	–
Calcined Ti–silicate co-gel	Amorphous	0.76	4968.51	13.3	1.2
Calcined TS-1	Crystalline	0.77	4968.50	13.9	22.3

[1] Cyclohexene conversion evaluated after 6 h of reaction.

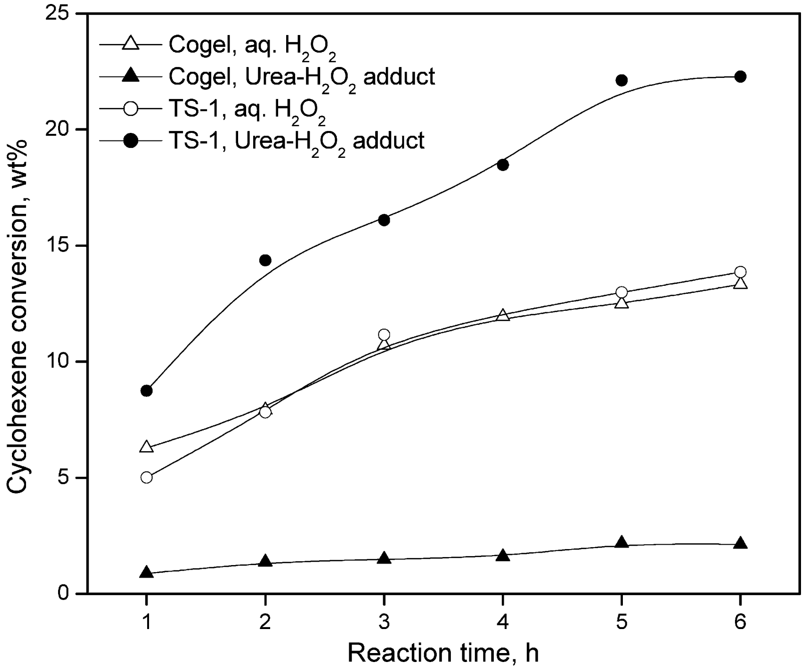

Figure 3. Kinetics of cyclohexene oxidation in presence of aqueous H_2O_2 and urea–H_2O_2 adduct over TS-1 and amorphous titanosilicate catalysts. In a typical reaction, 100 mg of pre-dried catalyst, 6 millimoles of cyclohexene and oxidant (30% aqueous solution of H_2O_2 or urea–H_2O_2 adduct), 5 g acetonitrile (solvent) and mesitylene (internal standard) were used.

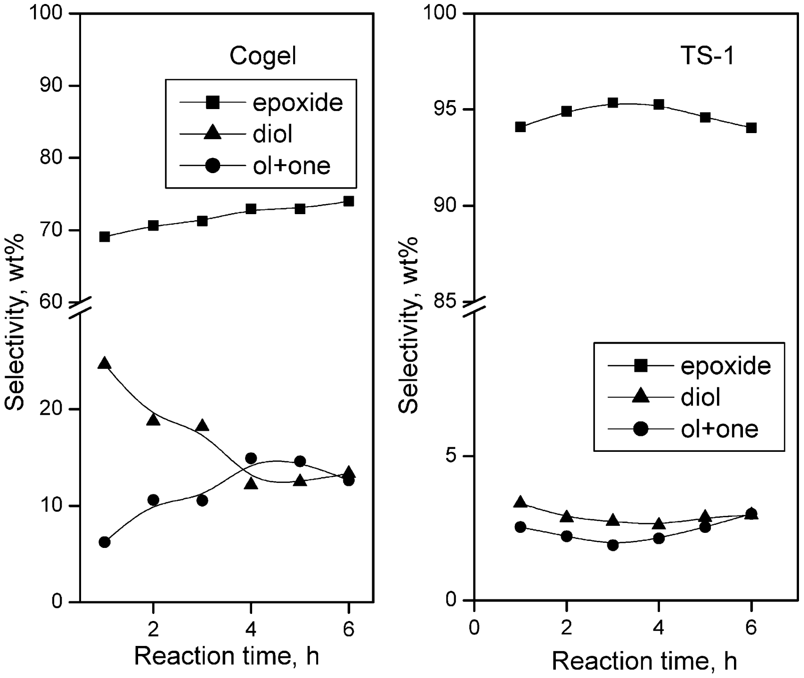

Figure 4. Comparison of selectivities of epoxide and diol over crystalline and amorphous titanosilicate catalysts in presence of aqueous H_2O_2 and urea–H_2O_2 adduct.

TS-1. In a separate experiment, an anhydrous urea–H_2O_2 adduct was used as the oxidant instead of aqueous H_2O_2. The catalytic activity of the TS-1 increased from ca 16% to about 25%. However, it is surprising that the catalytic activity of the amorphous titanosilicate cogel decreased significantly; from *ca* 16% to *ca* 2%. The epoxide selectivity increased dramatically (to in excess of 90% compared to about 60% with aqueous H_2O_2) for the TS-1 catalysts. While it appears that the presence of urea blocks the acid sites thus favouring the stability of the epoxide, this has the opposite effect on the catalytic performance of the cogel. In order to confirm that the effect was due to the presence of urea, urea was added to a reaction mixture after 2 h of reaction. Analysis of the product extracted after adding urea showed that there was no further conversion of cyclohexene. Further investigations on the effect of urea on the catalytic activity of amorphous titanosilicate are in progress.

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