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By-product formation causes leaching of Ti from the redox molecular sieve TS-1

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Triols, formed as by-products from the titanium silicalite (TS-1) catalysed epoxidation of allylic alcohols, can cause leaching of Ti from the microporous framework.

The titanium(IV) silicalite known as TS-1 has been considered by many to be a unique redox molecular sieve since its discovery by Enichem researchers.[1,2] TS-1 has been shown to be an active heterogeneous catalyst for the epoxidation of alkenes[3] and allylic alcohols.[4] Two features are responsible for the uniqueness of TS-1. First, incorporation of Ti into the microporous silicate framework increases the hydrophobicity[5] and enables H_2O_2 to be used as an oxidant. Other redox molecular sieves are ineffective with H_2O_2 and require more active oxygen sources, *e.g. tert*-butyl hydroperoxide.[6] Secondly, TS-1 is considered very stable under the reaction conditions and to date, loss of Ti from the framework of TS-1 has not been studied in detail. These features have been emphasised recently by Sheldon *et al.*,[7] who also stress that most papers pay scant attention to the loss of framework transition metal ions from redox molecular sieves. Recently, it has been shown that other redox molecular sieves containing Cr and V leach these metal cations into solution during reaction, and therefore act as reservoirs for active homogeneous catalysts.[8,9] If leaching is common for transition metals incorporated into microporous frameworks, then it is surprising that this should not be the case for Ti in TS-1. We have now studied the stability of TS-1 with respect to loss of Ti during reaction and we demonstrate that by-product formation unfortunately can lead to the loss of Ti from titanium(IV) silicalite.

TS-1 (2.4 wt% Ti) was prepared according to the following method, which has been used in many previous studies. Titanium butoxide (3.4 g Aldrich) was added dropwise to tetraethyl orthosilicate (62.5 g Merck) and the resulting mixture stirred for 30 min. Tetrapropylammonium hydroxide (40 wt% in H_2O, 76.3 g Alfa) was added dropwise with stirring. The resulting mixture was then heated at 60 °C for 2 h to evaporate ethanol produced by the hydrolysis/condensation reactions between the silicon and titanium reagents. Water was then added to the synthesis gel to return the volume of the gel to that prior to the evaporation step. The gel was mixed thoroughly and autoclaved under autogeneous pressure at 175 °C for 48 h. The resulting solids were filtered off, washed and dried at 100 °C for 4 h. The materials were calcined at 550 °C in air for 16 h prior to use. The material was characterised by X-ray diffraction, scanning electron microscopy, FTIR and reflectance laser Raman spectroscopy. The data were found to be in agreement with literature data and the crystallites of TS-1 were found to be uniform, rhombohedral and 0.2 μm in diameter. The sample of TS-1 was used as a catalyst for the hydroxylation of phenol with H_2O_2 at 70 °C. After 75 min, the products formed were 49% catechol and 50% hydroquinone; this is in agreement with previous literature studies[10] confirming the quality of the TS-1.

The TS-1 was also shown to be an effective catalyst for the epoxidation of allylic alcohols [Fig. 1(a) and (b)]. In a typical reaction, crotyl alcohol (0.1 mol) was reacted with aqueous

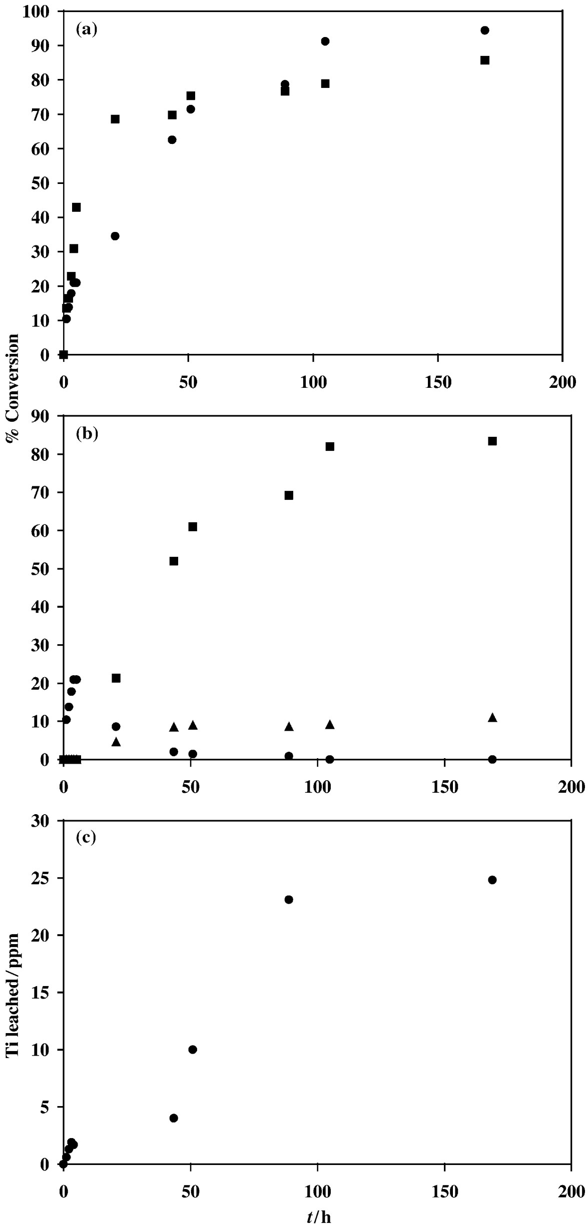

Fig. 1 Reaction of crotyl alcohol with H_2O_2 at 50 °C with TS-1 in methanol. (a) Conversion: (●) crotyl alcohol, (■) H_2O_2; (b) reaction products: (●) epoxide, (▲) ether diols, (■) triol; (c) Ti leaching.

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H_2O_2 (30% vol, 0.11 mol) at 50 °C with TS-1 (0.1 g) in methanol (10 ml) in a stirred flask fitted with a reflux condenser. Samples were withdrawn at various time intervals and the products analysed by GC using dimethyl sulfone as an internal standard. Samples were also filtered hot through a heated sinter funnel which contained a bed of Celite to remove small particles of zeolite. Blank experiments confirmed that this method was effective in removing any particulate Ti-containing material and, furthermore, that any titanium observed in solution did not originate from the Celite. The solutions were then analysed by ICPMS to determine the Ti content [Fig. 1(c)]. Initially, TS-1 is active and selective for the formation of the oxirane product and, at this stage, no Ti leaching is observed. However, in a sequential reaction the oxirane ring opens by nucleophilic attack by the solvent to form the triol (reaction with water) or ether diols (reaction with methanol). At this time, Ti is observed to leach from TS-1 and the pH of the reaction mixture decreases. These results clearly demonstrate that the structural integrity of TS-1 is not maintained in the presence of the secondary reaction products formed under typical reaction conditions.

In a further set of experiments, TS-1 (crystallisation period 2 d) was slurried with a range of reagents at 50 °C for 35 h. No Ti leaching was observed with hydrogen peroxide in methanol (30% by vol, <3 ppm Ti), crotyl alcohol (<0.3 ppm Ti), butane-2,3-diol (<2 ppm Ti) or hydrochloric acid (1 M, <0.7 ppm Ti). Several further experiments were conducted with glycerol as a model triol. No Ti leaching was observed with glycerol and hydrochloric acid (<2 ppm Ti), or glycerol together with hydrochloric acid and methanol (<1.3 ppm Ti). However, when TS-1 was slurried with glycerol and hydrogen peroxide using methanol as solvent, extensive leaching of Ti was observed (3571 ppm Ti) corresponding to removal of 16% of the Ti from TS-1. These model experiments confirm that the necessary condition for Ti-leaching from TS-1 is the combined presence of a triol together with hydrogen peroxide, and hence for the successful operation of TS-1 as a truly heterogeneous catalyst the formation of triols must be avoided.

It is interesting to comment on the mechanism by which Ti is removed from the framework of TS-1. Detailed UV–VIS spectroscopy[11] has shown that TS-1 contains four-coordinate Ti^{4+} in the absence of water. When TS-1 is suspended in water or water–H_2O_2 mixtures, the Ti^{4+} species becomes six co-ordinate, retaining three Ti–O–Si bonds, which are considered to anchor the Ti firmly within the microporous framework. The solvent molecules, in our case methanol, could be expected to displace one or more of the water molecules. We suggest that, when this site is exposed to triols, further Ti–O–Si bonds are broken and this leads to the irreversible loss of Ti from the structure (Fig. 2). Since triol by-product formation can be commonly observed in TS-1 catalysed reactions, we suggest that Ti leaching from TS-1 is probably more common than has previously been considered. It is also interesting to determine if the Ti that is leached during the catalytic reaction originates from the surface of the TS-1 crystallites. To determine if this is so, a further experiment was carried out in which the non-calcined TS-1 was silanised according to the method of Beck *et al.*[12] using trimethylsilyl chloride and hexamethyldisiloxane. As the non-calcined TS-1 retains the template within the intra-crystalline pores, this procedure effectively silanises just the exterior surface. On subsequent calcination (550 °C, 4 h), the template is removed and TS-1 crystallites covered on the external surface with silica are formed. Using this material as a catalyst for crotyl alcohol oxidation did not result in any significant leaching of Ti, yet the catalytic performance was essentially the same as that observed for the non-silanised sample [Fig. 1(a), (b)]. These data indicate that it is Ti located on the external surface of the TS-1 crystallites that is preferentially leached by the by-product triol.

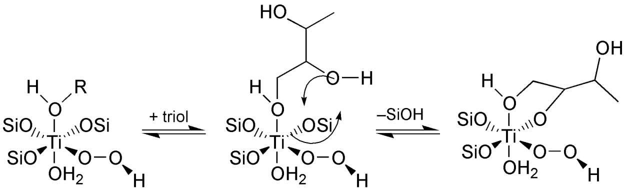

Fig. 2 Interaction of triols with the active site of TS-1.

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