Synthesis and catalytic activity of aluminium-free zeolite Ti-β oxidation catalysts

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Al-free Ti-β zeolite is synthesized and it shows an enhanced activity and selectivity to the epoxide in the oxidation of alkenes with H_2O_2 in protic solvents with respect to the previously reported (Al)-Ti-β samples.

Zeolite Ti-β[1] is the only Ti-containing zeolite synthesized up to now possessing a three-dimensional pore system of 12-membered ring channels. Owing to its unique large-pore channel system, Ti-β is more active than the medium-pore TS-1 catalyst for the oxidation of cyclic and branched alkanes and alkenes with aqueous hydrogen peroxide.[2] Moreover, in contrast to TS-1, Ti-β shows a high activity and selectivity when using organic hydroperoxides as the oxidizing agent.[3] This has been shown to be of importance when the desired selectivity during the oxidation process requires the absence of water.[4] However, in the usual synthesis conditions, Ti-β crystallizes with some Al as a framework constituent (Si/Al molar ratios $\leqslant 150$).[5] This leads after calcination to the presence of acid centres which, while being useful for bifunctional acid/redox catalytic processes,[4] have a detrimental effect on the activity[6] and selectivity[2] of zeolite Ti-β catalysts. More specifically, the acid sites lower the selectivity to the epoxide during the oxidation of alkenes with H_2O_2. There is therefore a strong incentive for the production of Al-free Ti-β catalysts by clean and reproducible direct synthesis methods. Here we report for the first time, a new and reproducible procedure based on a seeding technique affording very high yields of an Al-free Ti-β oxidation catalyst. The organic additive used to direct the crystallization of zeolite-β was tetraethylammonium hydroxide, for which previous reports suggested there was an upper limit for the Si/Al molar ratio of the zeolite-β synthesized.[5,7] Under the conditions of the present work, Si/Al from 150 to infinity can be obtained. It is shown that the Al-free Ti-β produced an enhanced activity and a much higher selectivity to the epoxide during the oxidation of alkenes in the presence of H_2O_2.

The design of this synthetic procedure was developed from the observation that during the syntheses in the presence of Al and tetraethylammonium ion, titanosilicate zeolite-β continues to grow after all the Al is incorporated into the zeolite.[5] However, under those reaction conditions it was not possible to synthesize the material in the absence of Al, and this suggested that Al-free Ti-β could not nucleate. We have found that, if highly efficient zeolite-β seeds are used, Al-free Ti-β can grow over the seeds and the Al content of the seeds determines the total Al content in the reaction mixture. This can be reduced to a trace level (total Si/Al molar ratio > 10 000) if dealuminated zeolite-β crystals are used as seeds. In this way, Al-free Ti-β was prepared according to the following procedure: tetraethylorthosilicate was hydrolysed under stirring in an aqueous solution of tetraethylammonium hydroxide and hydrogen peroxide, tetraethylorthotitanate was added, and the mixture was left under stirring to allow for evaporation of the ethanol produced. A clear homogeneous solution of approximate composition $TiO_2:60\ SiO_2:33\ TEAOH:400\ H_2O:20\ H_2O_2$ was obtained. Finally, dealuminated zeolite-β seeds were added under stirring (4 g of solid per 100 g of total SiO_2 in the reaction mixture). The crystallization was carried out in rotated (60 rpm) PTFE-lined stainless steel 60 ml autoclaves at 413 K. After 14 days at the crystallization temperature a highly crystalline zeolite Ti-β was obtained in high yield (26.1 g of zeolite per 100 g of initial reaction mixture). Chemical analysis of this material reveals only traces of Al (Si/Al > 5000). The Al concentration is similar to that found in a reference Al-free zeolite TS-1 (EUROTS-1,[8] Si/Al > 4000) and in samples reported to be all-silica zeolite-β (Si/Al > 5000, Si/B > 1000).[9]

A synthesis using non-dealuminated zeolite-β seeds (Si/Al ≈ 25) under the same experimental conditions reported above was also performed. A Ti-β with an Si/Al ratio of 820 was obtained. Interestingly, the rate of crystallization of zeolite-β is, within experimental error, independent of the degree of dealumination of the zeolite-β seeds. We believe this is due to the fact that the seeds do not dissolve in the media because of the high concentration of dissolved silica, so the important parameters for the rate of crystallization are the amount and crystallite size of the seeds rather than Al content. No MTW, MFI, cristobalite or any other impurities were found in these synthesis conditions.

Calcined Al-free Ti-β zeolite displays the typical spectroscopic features of zeolite Ti-β: the 960 cm^{-1} IR band [assigned to Si–O(H) defect groups promoted by framework Ti][10] and the narrow diffuse reflectance UV band at 205–225 nm assigned to isolated framework Ti.[11] Thus, Al-free Ti-β is indistinguishable from previously synthesised Al-containing Ti-β zeolite, except for its chemical composition. In order to examine possible differences in its activity and selectivity for catalytic oxidations, we studied hex-1-ene epoxidation with H_2O_2 as a test reaction† and a series of Ti-β samples with different Al content as catalysts. All the samples were synthesized by the method reported in this work except the samples with Si/Al = 142 and 300, which were synthesized using a new recently described co-gel method.[12]. As seen in Fig. 1, as the Al content decreases the selectivity to the epoxide increases, which is due to the decreasing concentration of strong-acid centres catalysing the opening of the epoxirane ring to yield the methyl glyco ether by addition of one molecule of methanol (solvent). Thus, the selectivity to the epoxide is at a maximum for the Al-free Ti-β catalyst. Furthermore, a very high efficiency for H_2O_2 utilization (selectivity >95%) is obtained on Al-free Ti-β. However, it is remarkable that opening of the epoxide, though slow, still occurs on the Al-free material. This means that in Ti-β zeolite there are sites other than bridging hydroxy groups which are able to catalyse the opening of the oxirane ring. These could be Si–OH groups, the concentration of which increases when the Al content decreases, and/or centres related to framework Ti. Indeed, it has been reported that TS-1 develops acid centres in the presence of H_2O_2 in alcoholic or aqueous solutions (with enhanced acidity in methanol).[13] These acid centres, which have been assigned to cyclic species **I**, are able to catalyse the opening of *cis* and *trans*-2,3-epoxybutane.[13]

In order to check the possible contribution of both types of acid centres to the opening of the epoxide on the Al-free Ti-β material, we synthesized a pure silica β-zeolite, using the method described in this paper for the Al-free Ti-β but without introducing Ti in the gel mixture. This sample only contains defect Si–OH groups according to IR spectroscopy (not shown) as the possible source of acidity. Then, 1,2-epoxyhexane was reacted on both the Al-free Ti-β and the pure silica-β samples under the same experimental conditions.‡ No epoxide conversion was observed on the all-silica zeolite, while the oxirane ring was substantially opened on the Al-free Ti-β sample (Table 1), suggesting that acid centres associated to framework Ti (species **I**) are mostly responsible for the opening of the epoxide during the epoxidation of alkenes with H_2O_2 on the Al-free Ti-β catalyst.

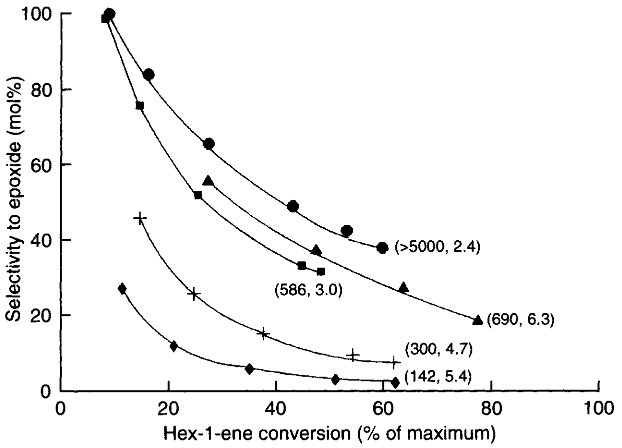

Fig. 1 Selectivity to the epoxide as a function of conversion in the oxidation of hex-1-ene with aqueous H_2O_2 using Ti-β catalysts. The numbers near each trace represent the Si/Al ratio and Ti content (as mass% TiO_2) in the different catalysts.

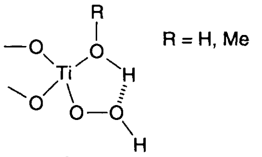

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Table 1 Aperture of the oxirane ring of 1,2-epoxyhexane on different zeolites

Zeolite	Epoxide conversion* (mol %)
Al-free Ti-β	13.4
All-silica β	0.0
TS-1	3.0

* To methyl glycol ether after 7 h reaction time.

As shown in Table 1, the epoxide ring was also opened on the medium-pore Ti-silicalite (TS-1), although at a significantly lower rate than on the Al-free Ti-β sample. Thus, the differences in epoxide selectivity between TS-1 and Al-free Ti-β during the epoxidation of alkenes with H_2O_2 could be explained by a different acidity of species **I** in both materials, although other parameters, such as differences in the adsorption properties for reactants and products and/or shape-selective factors, cannot be disregarded. Further work is in progress in our Institute to determine the reasons of a different intrinsic activity/acidity of the active Ti species in both Al-free Ti-β and TS-1 zeolites.

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Footnotes

† *Reaction conditions*: 323 K, 16.5 mmol hex-1-ene, 11.8 g methanol, 0.4 g H_2O_2 aqueous solution (35 mass%) and 0.1 g catalyst.

‡ *Reaction conditions*: 323 K, 16.5 mmol epoxide, 11.8 g methanol, 0.1 g catalyst and 0.4 g H_2O_2 (35 mass% in water).

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