Ti/ITQ-2, a new material highly active and selective for the epoxidation of olefins with organic hydroperoxides

Avelino Corma,* Urbano Díaz, Vicente Fornés, José L. Jordá, Marcelo Domine and Fernando Rey

Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avda. de los Naranjos s/n, 46022 Valencia, Spain. E-mail: acorma@itq.upv.es

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Materials containing highly accessible and well ordered titanium sites prepared by grafting titanocene on ITQ-2 material are excellent catalysts for epoxidation of olefins, yielding high conversions and selectivities to the desired epoxides.

In recent years Ti containing molecular sieves, which are able to catalyze the selective oxidation of hydrocarbons using peroxides as oxidants, have been developed.[1] In this way, Ti-silicalite and Ti-beta are able to carry out successfully the epoxidation of olefins using H_2O_2,[2,3] while Ti-MCM-41 materials, incorporating the Ti, either by one-step synthesis or by post-synthesis, are active and selective catalysts to perform the epoxidation of olefins using organic hydroperoxides.[4–7] A successful Ti/MCM-41 catalyst was obtained when a titanocene was grafted on the surface of a MCM-41,[7] opening the possibility for preparing highly accessible and isolated Ti sites on a very high surface area silica. However, this material still presents some drawbacks related with the stability of the material and the formation of Ti–O–Ti linkages owing to the closeness of the silanol groups. Then, in order to design new Ti grafted solid catalysts, it would be highly desirable to start with a highly stable material with a high surface area accessible to reactants, and containing a well defined distribution of silanol groups on which Ti species can be grafted. Such characteristics coincide with those of the large or extralarge pore Ti-zeolites. Unfortunately, the Ti-zeolites prepared up to now are not successful epoxidation catalysts when reactants with large molecular diameters are involved.[5] Looking for new structures which combine the benefits of the mesoporous and zeolitic materials, we have recently obtained a new material denoted as ITQ-2,[8] which is prepared by delaminating the precursor of the pure siliceous MWW polymorph (ITQ-1).[9] ITQ-2, consists of very thin silica layers of 2.5 nm height with an extremely high and well defined (>700 m^2 g^{-1}) external surface. As shown in Fig. 1, an hexagonal array of 'cups' of 0.7×0.7 nm penetrate into these layers from each side of the sheet. The structure of this layer is completed by a double 6-ring window which connects the bottom of the cup to the bottom of another cup located at the other side of the layer. In between the cups, *i.e.* inside the sheet, runs a smooth 10-membered ring (10 MR) channel system. Moreover the external surface formed by the array of cups has an important population of silanol groups which are located in specific positions as corresponding to the lamellar precursor of the MWW structure.[10] Such highly accessible well defined silanols are clear candidates to anchor Ti precursors, which can lead to highly dispersed and stable Ti catalytic active sites. This approach has been pursued by first preparing the pure silica layered precursor as follows: 6.164 g of hexamethyleneimine (HMI) and 1.88 g of NaCl were dissolved in 131.40 g of a 0.38 M solution of trimethyladamantamonium hydroxide (TMAdaOH). 37.56 g of H_2O and 12.02 g of SiO_2 (Aerosil 200) were added to the above solution, and a gel was obtained with the following composition: $1SiO_2 : 0.25$ TMAdaOH : 0.31 HMI : 0.1 NaCl : 44 H_2O

The resultant gel was mechanically stirred for 90 min at room temperature. Crystallisation of the lamellar precursor was performed at 150 °C over 5 days at 60 rpm. The material which was filtered off and dried at 100 °C for 12 hours, shows an XRD pattern characteristic of the laminar precursor of the MWW structure.[9,10]

The purely siliceous ITQ-2 was prepared from the lamellar precursor following a previously described procedure[8] and the resultant material shows a BET surface area of 800 m^2 g^{-1}.

Ti was grafted on the surface of the pure silica ITQ-2, by the procedure illustrated in Fig. 1:[7] 10 g of ITQ-2 was dehydrated at 300 °C at 10^{-3} Torr over 2 h. Then, a solution containing an appropriate amount of titanocene dichloride in 90.0 g of $CHCl_3$ was added. The suspension was stirred for 1 h at room temperature under an inert atmosphere. Subsequently, triethylamine dissolved in 10 g of $CHCl_3$ giving a ratio $NEt_3/TiCp_2Cl_2 = 1$ was added and the suspension changed from orange–red to yellow–orange indicating a change of coordination around the Ti atoms. The solids were recovered by filtration and after prolonged washing with CH_2Cl_2, calcination at 540 °C for 1 h

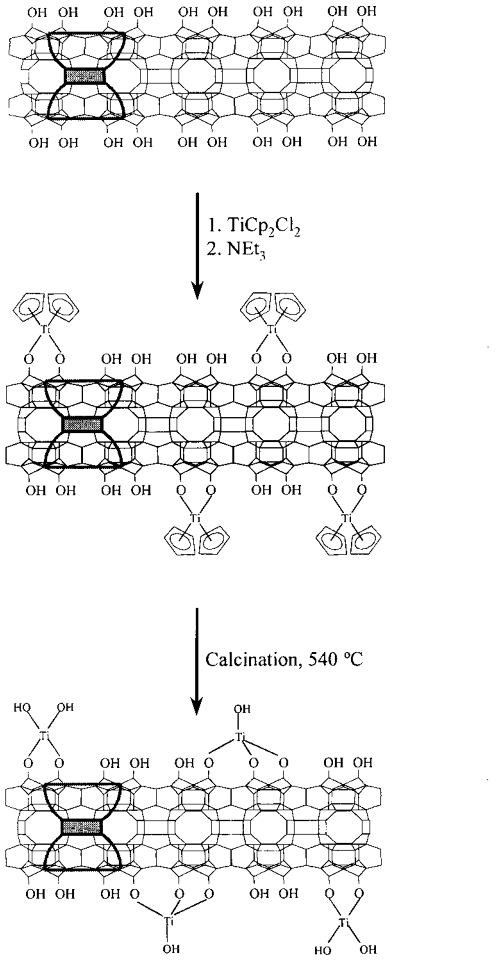

Fig. 1 Schematic grafting of titanocene on the ITQ-2 surface.

Table 1 Cyclohexene conversion and selectivity after 120 min reaction time, and initial rate of reaction for Ti containing samples

Sample	Conversion (%)	Selectivity (%)	r_c/mol g_{cat}^{-1} h^{-1}	r_c/mol mol_{Ti}^{-1} min^{-1}
0.125%TiO_2/ITQ-2	71.7	98.3	0.044	46.9
0.25%TiO_2/ITQ-2	75.1	97.8	0.047	25.0
0.5%TiO_2/ITQ-2	70.8	95.4	0.049	13.1
1%TiO_2/ITQ-2	68.2	91.6	0.045	7.5
0.125%TiO_2/ITQ-2/sil.	73.4	99.4	0.049	64.7
1%TiO_2/ITQ-2/sil.	85.3	99.0	0.070	11.7
Ti/MCM-41[a,7]			0.18	2.1
TiO_2-SiO_2 co-gel[b,18]			0.50	3.3

[a] TBHP/cyclohexene = 1.2, 8 wt% cyclohexene in $CHCl_3$; reaction temperature = 40 °C. [b] Using cumene hydroperoxide (CHP) as oxidant (12 wt% in cumene). Cyclohexene/CHP = 4, 4 wt% of catalyst, reaction temperature = 60 °C.

in N_2 and then 6 h in air was carried out in order to remove all the organics. The resultant materials (Ti/ITQ-2) have the same textural and structural characteristics as ITQ-2, and present in their UV–VIS spectrum only a narrow band located below 220 nm assigned to the formation of monomeric Ti^{IV} species.[11,12] The presence of monomeric Ti species has been further established by the presence of a very intense pre-edge peak in the XANES spectrum of the dehydrated Ti/ITQ-2 sample with an intensity of 0.74, close to the intensities found for Ti-zeolites possessing Ti isomorphically substituted in the framework,[13,14] and higher than those reported for Ti-MCM-41[15,16] and Ti grafted on MCM-41.[15,16,7] This is clear evidence for the presence of Ti linked through O bridges to the siliceous ITQ-2 framework, in the absence of polymeric species of titanium.

Ti/ITQ-2 (295 mg) was used as a catalyst for epoxidation of cyclohexene (4.648 g) with *tert*-butyl hydroperoxide (TBHP) (cyclohexene/TBHP = 4.0) at 60 °C. Results are given in Table 1 where it is evident that the activity and selectivity of all the Ti/ITQ-2 materials to the epoxide are excellent. It is clear that the selectivity to the epoxide decreases as the Ti content increases. This is an indication of the presence of some weak acid sites which are responsible for the opening of the epoxide ring to form the corresponding glycols. Recently, we have reported that the presence of glycols in the reaction medium deactivates the catalysts.[17] The selectivity to the epoxide can be improved, and therefore the formation of glycols reduced, by modifying the adsorption properties of the Ti/ITQ-2 catalysts by silylation. This can be done by contacting 10 g of dehydrated Ti/ITQ-2 with a solution of 6.33 g of $SiMe_3Cl$ in 90 g of $CHCl_3$, and subsequently with a solution of 4.27 g of NEt_3 in 10 g of $CHCl_3$. The catalytic performance of two silylated Ti/ITQ-2 catalysts containing different loadings of Ti is also given in Table 1 where a strong improvement in the activity and selectivity is observed. Also, it is noticeable that Ti/ITQ-2 containing 1 wt% TiO_2 shows a higher activity and similar selectivity to a 0.125 wt% TiO_2 catalyst, indicating that when no deactivation occurs, the higher the Ti content, the higher the catalytic activity.

In order to obtain comparative estimates of the catalytic performances of the different Ti/ITQ-2 catalysts, Table 1 lists catalytic conversion of cyclohexene and the selectivity to the corresponding peroxide. Also, the turnover number and the kinetic rate obtained on Ti/ITQ-2 is compared to literature values for other Ti-containing catalysts (Ti grafted on MCM-41 and Ti mesoporous materials obtained by a co-gel procedure).[18] Ti/ITQ-2 shows the best performance per Ti atom.

However, as important as the activity and selectivity of the catalysts are their stability towards Ti leaching. In order to study this, we have recycled the Ti-ITQ-2 silylated catalysts (METIQ-2) (1wt% TiO_2) three times, and the conversion obtained remained practically the same indicating the good stability of this catalyst.

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