Large Pore Bifunctional Titanium–Aluminosilicates: the Inorganic Non-enzymatic Version of the Epoxidase Conversion of Linalool to Cyclic Ethers

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Bifunctional aluminosilicate catalysts containing framework Ti are prepared, with two different topologies and pore sizes; these samples contain both acid and oxidizing catalytic sites and are highly selective for carrying out multistep reactions with selectivities close to those obtained with epoxidases, this is shown to occur for the oxidation of linalool to cyclic hydroxy ethers.

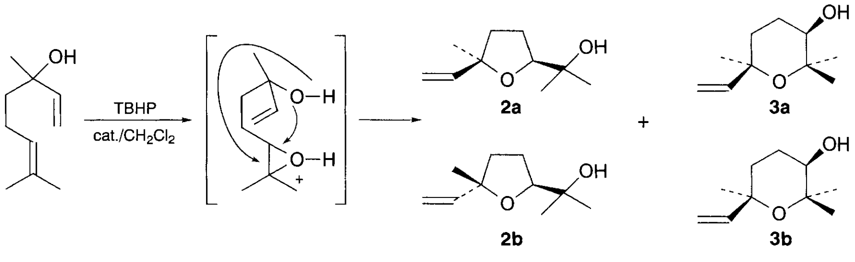
The increasing demand for 'natural' flavours has rendered the natural sources no longer sufficient. To overcome this limitation, studies on biogenetic flavour formation have been performed[1–4] and new biocatalytic ways of production using plant cell, microorganisms or enzymes are being thought.[5,6]

In the case of linalool, chemical routes for the production of furans **2** and pyrans **3** hydroxy ethers involve refluxing of a large excess of H_2O_2 in 40% formic acid in H_2O_2,[7] or oxidation of linalool with monoperephthalic acid and heating in the presence of trifluoroacetic acid.[8] Besides the unfriendliness of the reaction systems, yields lower than 70% are obtained. The epoxidase enzyme is able to convert linalool selectively to the corresponding intensely rose sented furans **2** and pyrans hydroxy ethers **3** (Scheme 1). In order to explain the formation of products **2**–**3**, the isomers of 6,7-epoxylinalool and the corresponding triol have been assumed as natural precursors.[8–10]

If this is true, then an epoxidating and an acidic function could be introduced on a solid catalyst in a suitable environment, to perform the transformation of linalool to the hydroxy ethers **2**–**3** in one pot reaction with the advantage that the inorganic catalyst will work under a broader range of experimental conditions and be recyclable. In this sense a zeolite Beta and an MCM-41 material containing Ti^{4+} as oxidation sites, and Al^{3+}, which has an associated H^+ as the complementary cation are shown here to convert linalool to the hydroxy derivatives with 100% selectivity.

The titaniumsilicoaluminate isomorphous to zeolite Beta[11] has been prepared in the following way: Tetraethylammonium hydroxide (TEAOH) (Aldrich) was added to the required amount of water containing tetraethyl orthotitanate (Alfa) and aerosil (Aerosil 200, Degussa) at room temp. with stirring. Then, a solution of aluminium nitrate was also added. The resulting gels were heated at 408 K in poly(tetrafluoroethylene)-lined stainless steel autoclaves, while they were rotated at 60 rpm. After cooling the autoclave, the sample was centrifugated at 1000 rpm and the recovered solids were washed until pH 9 dried at 353 K and calcined at 853 K. The Ti-MCM-41 sample was prepared[12] using amorphous silica (aerosil 200, Degussa), 25% aqueous solution tetramethyl ammonium hydroxide (Aldrich, containing less than 1 and 3 ppm of K^+ and Na^+, respectively, and an aqueous solution of hydroxide and bromide of hexadecyltrimethyl-ammonium (Merck). The source of Ti was $(C_2H_5O)_4Ti$ (Alfa). The molar composition of the starting gel was $1:SiO_2$; $0.0025:Al_2O_3$; 0.17 : cetyl trimethyl ammonium hydroxide (CTMAOH); 0.21 : CTMABr; 0.26 : tetramethyl ammonium hydroxide; $24.3:H_2O$; $0.0167:TiO_2$ and the final product contains 1.8% TiO_2 and 0.4% Al_2O_3. The isomorphous substitution of Si by Ti in zeolite Beta and MCM-41 framework, was assessed by means of powder X-ray diffraction (XRD) (Cu-Kα radiation) in the former, and by mid-IR characterization in both samples. The higher covalent radius of Ti compared with Si causes an increase in the interplanar d-spacing of the zeolite Beta, as measured by the change in position of the most intense XRD peak (2θ *ca.* 22.4°), after dehydration at 383 K for 1 h, and rehydration overnight over a $CaCl_2$ saturated solution. Both samples showed a band at about 960 cm^{-1} in the IR spectrum (KBr pellet), which has been assigned to Ti=O or Si–O–(Ti) groups in the zeolite framework[13] and is usually taken as evidence of the isomorphous substitution of Si by Ti.[14] The UV–VIS spectrum of the samples do not show the band at 300 nm characteristic of the anatase, but bands at 210–230 nm which indicate that Ti is in a 4–6 coordination in both materials. Finally, the Brønsted acidity of the samples has been determined by adsorption–desorption of pyridine and IR spectroscopy.[15] The pyridinium band appeared at 1545 cm^{-1} and remained visible after desorption at 523 K and 10^{-4} Torr vacuum, indicating that strong acid site are present in both titanoaluminosilicate samples.

These samples were used as a catalyst (100 mg) for the transformation of linalool (462 mg, 3 mmol) by *tert*-butylhydroperoxide (TBHP) (3.3 mmol) and MeCN (30 ml) in a glass reactor at 353 K. Conversion is defined here as moles of linalool converted per 100 moles of linalool fed, and selectivity to pyrans plus furans is defined as the moles of these products formed, per 100 moles of linalool converted. When the reaction was carried out using as catalyst the acid form non-Ti containing catalysts no oxidized products, but traces of linalool isomers, were found after 40 h reaction time. In the presence of *p*-toluenesulfonic acid no oxidized products were formed, but only products such as nerol, geraniol, terpineol, which are formed by isomerization of the linalool, catalysed by acid sites. In the case of the Ti-containing catalysts, the results presented



Scheme 1

in Table 1 show that both catalysts are active for the oxidation of linalool to hydroxy ethers (furanoid and pyranoid forms) (**2**–**3**). The ratio **2**/**3** found changes very little with conversion, indicating that as with the epoxidase enzyme, they are produced by parallel reactions, through a common intermediate, and not through and isomerization process. Thus, we postulate that in our systems the reaction involves firstly the epoxidation of the trisubstituted double bond on the Ti sites, followed by the intramolecular opening of the epoxide ring by the 3-hydroxy group at positions 6 or 7; this reaction being catalysed by the acid sites of the Ti aluminosilicates.

The catalysts are very selective and no other reaction products have been detected. The activity of Ti-MCM-41 is higher than that of Ti-Beta. This cannot be due to a higher intrinsic activity of the Ti sites in the former, since we have presented that Ti-Beta is intrinsically more active than Ti-MCM-41 for epoxidation of lineal olefins.[12] Thus, the activity results have to be explained on the basis of a faster diffusion of the reactants and products through the larger pores of the MCM-41 structure.

The **2**/**3** ratios obtained by epoxidase are lower than one,[16] while the **2**/**3** ratio obtained on the large pore Ti-Beta is always greater than one, and an enrichment of the furan derivatives occurs owing to shape selectivity effects. On the other hand, **2**/**3** ratios lower than one are obtained on Ti-MCM-41 where there are not geometrical constraints and those values are close to those obtained by analysis of wines, and are closely related to epoxidase conversion of linalool. The **2**/**3** ratios obtained using the Ti bifunctional catalysts are much lower than the values obtained by the chemical routes described above[7,8] and which yield **2**/**3** ratios up to 9.0.

Finally, the selectivity observed with respect to the C=C double bond attack (trisubstituted *vs.* the vinyl moiety) is reverse of that attained by other homogeneous oxidation catalysts such as salen complexes or Sharpless titanates, where a precoordination of hydroxy group takes place before oxygen transfer.

Table 1 Catalytic oxidation of linalool with Bu^{t}OOH on Ti-Beta

t/h	Conversion (%)	Furans **2**	Pyrans **3**	**2/3**
3	21.7	13.2	8.5	1.55
5	30.4	18.6	11.8	1.57
12	58.3	34.7	23.6	1.47
24	73.4	45.4	28.0	1.62

Table 2 Catalytic oxidation of linalool with Bu^{t}OOH on Ti-MCM-41 zeolite

t/h	Conversion (%)	Furans **2**	Pyrans **3**	**2/3**
2	28.4	13.6	14.8	0.92
4	36.1	17.2	18.9	0.91
10	50.9	24.7	26.2	0.94
24	80.1	37.8	42.3	0.89

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