Effects of hydrophobicity on the epoxidation of cyclohexene by *tert*-butyl hydroperoxide on TiO_2–SiO_2 mixed oxides

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The effects of the addition of water to the reaction medium have been investigated for the epoxidation of cyclohexene by *tert*-butyl hydroperoxide catalysed by a series of TiO_2–SiO_2 mixed oxides prepared by a sol–gel procedure in which a fraction F of tetraethoxysilane is substituted by phenyltriethoxysilane. Infrared spectrometry gives a direct evidence of the retention of Si–C bonds by the solid. The substitution of OH groups by phenyls modifies the catalytic properties: for $F = 0$, the solid is hydrophilic, inhibited by water and catalyses the hydrolysis of TBHP as competitive side reaction, whereas the solid obtained for $F = 0.2$ is hydrophobic and not sensitive to a water/TBHP ratio as large as 1.

Keywords: hydrophobic mixed oxides, epoxidation, cyclohexene, t-butyl hydroperoxide, phenyltriethoxysilane

1. Introduction

The importance of hydrophobicity of heterogeneous catalysts for selective epoxidation has been emphasized by Sheldon [1]: this will favour the adsorption of the nonpolar reactants in competition with the polar products, and then will increase both activity and selectivity. Amorphous *microporous* and hydrophobic titania–silica mixed oxides have been obtained by a sol–gel technique using a mixture of tetraethoxysilane and methyltriethoxysilane as source of Si [2]. A previous work showed that *mesoporous* hydrophobic Ti–Si mixed oxides could be obtained using a sol–gel technique in which part of the tetraethoxysilane was replaced by phenyltriethoxysilane [3]. The comparison of the separate adsorptions of n-hexane and water supported the conclusion that the surface was indeed hydrophobic. It is, however, difficult to measure this property: Weitkamp [4] introduced an hydrophobicity index based on the competitive adsorption of octane and water. The best characterization is probably obtained from the adsorption of the real reactants, and we present here results based on the kinetics of epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP) in the presence of water. This determination is a simple one, and more representative of the *in situ* behaviour of the solid.

2. Experimental

Catalysts: the solids have been described in detail in a previous work [3]. They are obtained by conventional sol–gel methods, using Ti isopropoxide and a mixture of tetraethoxysilane and phenyltriethoxysilane. The fraction of tetraethoxysilane substituted by phenyltriethoxysilane in the synthesis was 0 for AP0, 10% for AP10 and 20% for AP20. Drying the solid resulting from sol–gel by CO_2 in supercritical conditions permits to obtain aerogels which are mesoporous solids [5]. This procedure was used here (APx for aerogel and x% phenyl).

The surface area and mean pore diameter obtained from the isotherms of adsorption of nitrogen at 77 K, measured on a Micromeritics ASAP 2000 are reported in table 1. The adsorptions of n-hexane and water determined by gravimetry on a Setaram microbalance are also reported in table 1. The decrease of water adsorption and increase of n-hexane adsorption suggests that the gradual substitution of OH by phenyls due to the synthesis increases hydrophobicity. The lattice vibrations were investigated by FTIR spectrometry using a Bruker IFS-48 instrument, and samples diluted (1%) in KBr.

The kinetics of cyclohexene epoxidation was investigated in a batch reactor, using a three-neck glas flask (20 ml) equipped with a condenser, and swept with a small flow of nitrogen. The reaction mixture was sampled periodically through a septum with a syringe. The temperature was maintained at 348 K by an oil bath. 0.25 g of catalyst were placed in the reactor containing 5 g of solvent and 63 mmol of cyclohexene, the reactor was heated at the reaction temperature under stirring (1000 rpm), then 3.125 mmol of TBHP were added. This moment defined the time zero of the kinetics. Small samples were taken

Table 1
Surface areas, mean pore diameters, adsorptions of water and n-hexane for the catalysts used here.

Sample	Ti (%)	Surface area (m^2/g)	dp[a] (nm)	Adsorption (wt%) Water	Adsorption (wt%) Hexane
AP0	0.74	730	3.4	8	7.6
AP10	0.99	489	3.5	6	10
AP20	0.86	624	3.7	3	14

[a] Pore diameter.

(1 μl) with a syringe at different reaction times through a septum fitted with the flask, diluted in the solvent to which n-decane was added as an internal standard for quantitative analysis. The products were analyzed by gas chromatography (Shimadzu GC 14 B) equipped with a capillary column (Supelcowax 10 TM, 30 m length, 0.25 mm ID and 0.25 μm film thickness) and a flame ionization detector.

3. Results and discussion

The infrared spectra of the gel are given in figure 1. The spectrum relative to the gel obtained from phenyltriethoxysilane shows a band at 1432 cm^{-1} assigned to Si-phenyl [6]. The aryl moiety is then retained as expected. This retention accounts for the lower adsorption of water and higher adsorption of n-hexane reported earlier. Hydrophobicity can be evidenced directly from kinetic measurements.

The results obtained are summarized in table 1. The reaction of cyclohexene with TBHP is very selective and gives mainly epoxycyclohexane with trace amounts of glycol, cyclohex-2-ene-1-ol and cyclohex-2-ene-1-one. The different reactions occurring in the process can be represented by scheme 1.

The initial rate corresponds to the rate of reaction of cyclohexene at low conversion, i.e., in the absence of kinetic effect of the products. In that case the concentration is that of the original reaction mixture.

The yield and selectivities were calculated at the end of the reaction, then at high conversion of TBHP. The selectivity for TBHP was defined as the number of moles of products formed from cyclohexene (i.e., TBHP reacting on the olefin) to the number of moles of TBHP consumed in the

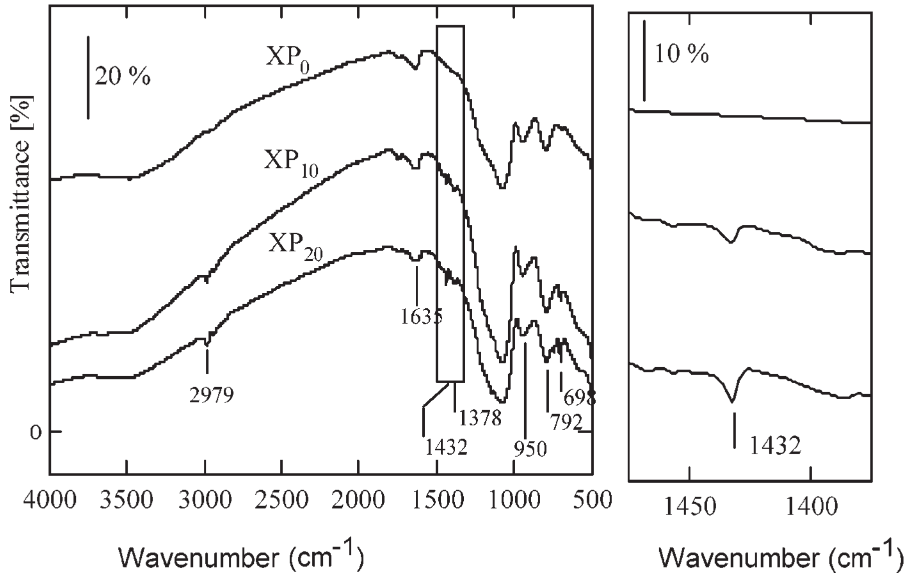
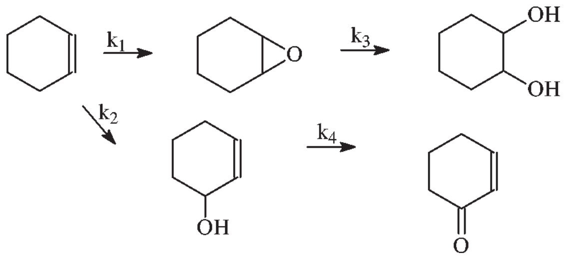


Figure 1. Infrared spectra of the xerogels prepared phenyltriethoxysilane.

Table 2
Effect of water on the catalytic properties of the different catalysts.

H_2O/TBHP	Initial rate	TBHP		Olefin select. (mol%)		Epoxide yield
(mol/mol)	(mmol min^{-1} g^{-1})	Conv. (%)	Select. (mol%)	(C=C) attack	S_{epoxide}	(%)
Hydrophilic gel AP0						
0	2.92	91.0	91.0	88	86.4	80
0.43	1.86	84.0	93.0	90.4	88.0	74
0.70	2.10	75.5	82.6	79.0	77.8	56
1.05	2.12	62.1	68.0	65.3	64.3	40
Semi-hydrophobic sample AP10						
0	1.38	94.0	95.4	91.0	90.6	89.3
0.43	3.12	95.2	100	93.4	93.1	88.6
0.70	1.10	83.0	73.4	65.0	64.0	53.1
1.05	1.60	80.0	80.0	75.2	73.0	58.4
1.75	1.58	75.0	80.0	73.0	70.0	52.5
Hydrophobic sample AP20						
0	2.54	93.0	100	96.5	96.2	90
0.43	2.45	95.5	100	98.0	97.5	93.2
1.05	2.48	95.0	100	97.0	95.0	90.2



Scheme 1.

reaction. This selectivity for TBHP is below 100% in many cases, therefore some decomposition of TBHP occurs.

The nature of the products demonstrates that cyclohexene can suffer either epoxidation yielding epoxycyclohexane and glycol or an allylic attack forming cyclohex-2-ene-1-ol and cyclohex-2-ene-1-one, therefore two selectivities can be defined:

(a) The ratio $(k_1 + k_3)/(k_2 + k_4)$ which represents the selectivity of epoxidation versus allylic oxidation, which is called here selectivity for C=C attack of the olefin.

(b) The ratio $k_1/k_3 + k_1 = S_{\text{epoxide}}$ represents the extent of retention of the epoxide in the process, and $1 - S_{\text{epoxide}}$ the selectivity of hydrolysis of the epoxide to glycol.

The final yield in epoxide integrates the different steps of the reaction and is a function of the conversion and selectivity of decomposition of TBHP, of the selectivities of the allylic attack and hydrolysis of the epoxide. Water can alter many of these reactions, and its effect was then investigated on the different steps of scheme 1, using acetonitrile as solvent.

With the hydrophilic sample AP0, the addition of water to the reaction medium decreases slightly the initial rate of reaction and the final conversion of TBHP. The rate decreases to a plateau suggesting that the Ti sites are partially blocked by water. The selectivity towards TBHP also decreases, then the peroxide is partially lost in that case. Since this reaction occurs upon water addition, it is attributed to an hydrolysis. The selectivity for the epoxide also decreases markedly as a reflect of ring opening to a glycol.

With a sample of intermediate hydrophobicity the effect of water is more complex, since the rate first increases, then goes through a maximum for a ratio H_2O/TBHP = 0.43. This maximum is close to the rate observed on the hydrophilic sample in absence of water. Indeed, it can be noticed that the amount of water also corresponds then to that adsorbed by the AP0 sample, about 8%. If a small amount of water promotes the reaction, a higher concentration inhibits the rate and TBHP is decomposed as in the former case, but this phenomenon appears at higher H_2O concentration.

The most hydrophobic AP20 sample shows a different behaviour since water has no effect at all even for a ratio H_2O/TBHP = 1. This is then a true hydrophobic sample. In that case TBHP is not decomposed at all, which favours the hypothesis of an hydrolytic decomposition of the reagent.

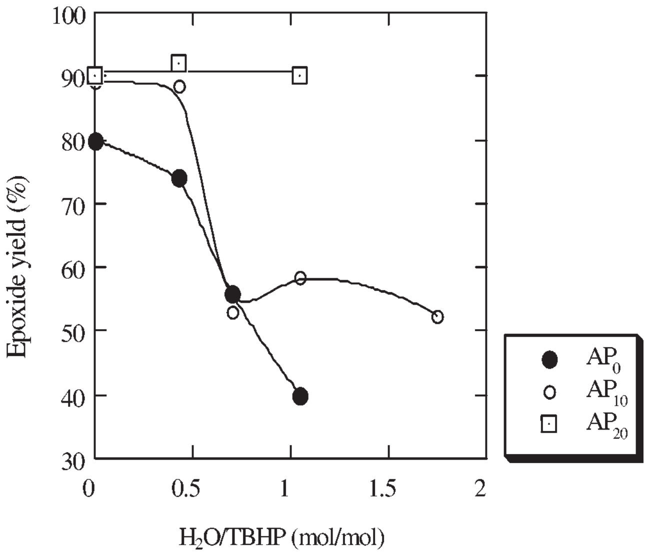


Figure 2. Final yield of epoxide as a function of the amount of water added to the reaction mixture on three representative samples.

The final yields in epoxide are reported in figure 2 as a function of the ratio H_2O/TBHP. Two points appear here:

(a) In the absence of water added to the reaction mixture, the yield is better on hydrophobic solids. This may be attributed to the traces of water contained in the reactants or the catalyst.

(b) The samples prepared from phenyltriethoxysilane are hydrophobic, and can be operated in the presence of water as solvent if necessary. From the practical point of view, the big advantage is that neither the epoxide nor the peroxide are hydrolyzed by water.

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