Crystallization of TS-1 in the presence of alcohols: influence on Ti incorporation and catalytic activity

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Received 15 October 1997; accepted 14 January 1998

TS-1 has been synthesized following various recipes of the literature in the presence of alcohols, i.e., from gels that were not evaporated prior to crystallization, which considerably reduces the preparation time of the zeolites. When samples are prepared following a method adapted from the original patent, extra-framework species are observed even for low Ti contents. In contrast, when hydrolysis of the Si and Ti sources is performed in the presence of isopropyl alcohol, all Ti in the zeolite is incorporated in the lattice. However, incorporation is limited to about 1.9 Ti/u.c., even when catalysts are crystallized from gels with relatively high Ti concentrations. These samples are active in the hydroxylation of phenol with H_2O_2 and their activity is comparable with that of conventional catalysts obtained from alcohol-free gels.

Keywords: TS-1, titanium, incorporation, hydrogen peroxide

1. Introduction

Titanium-substituted silicalite-1 (TS-1) has received great attention in both the patent and open literature over the past years due to its remarkable properties as catalyst in the oxidation of small organic substrates with dilute H_2O_2 solutions [1]. TS-1 was originally synthesized following two different routes [2] and the best catalysts were obtained by careful hydrolysis of a mixture of silicon and titanium ethoxides with aqueous tetrapropylammonium hydroxide (TPAOH) [3]. The low stability of titanium ethoxide (TEOT) in the presence of water encouraged researches to develop new synthesis procedures using more stable compounds like titanium butoxide (TBOT) [4] or TiF_4 [5]. In all cases, preparation of the zeolite involves hydrolysis of silicon ethoxide (TEOS) and eventually TEOT or TBOT, which makes that the precursor gel contains large amounts of alcohol. Typically, the alcohol/SiO_2 ratio is EtOH/$SiO_2 = 4$ when syntheses are performed with TEOT or TiF_4 and $(EtOH + BuOH + i\text{PrOH})/SiO_2 \approx 5.5$ when TBOT is used. In the latter case, TBOT is dissolved in dry isopropyl alcohol (iPrOH) prior to addition to the silica source [4]. Alcohol is usually removed by heating gels at ca. 80 °C for a few hours. Whilst this step can be relatively easily performed at a laboratory scale when small amounts of gel are concerned, it may be a source of difficulties and additional cost in large preparation plants. Moreover, water is also evaporated upon heating and the real water concentration in the final gel is hard to control. For these reasons, crystallization of TS-1 in the presence of alcohols would not only facilitate its preparation but also afford significant advantages in terms of time and energy.

To date, the influence of alcohol on the crystallization of TS-1 has never been a matter of discussion in the literature. In the present paper, we report on the synthesis of TS-1 using various preparation routes in the presence of alcohols, i.e., from gels that were not evaporated prior to their transfer into the autoclave. Physico-chemical characteristics as well as catalytic properties in the hydroxylation of phenol with H_2O_2 of the obtained zeolites are reported and compared with those of conventional catalysts obtained from alcohol-free gels.

2. Experimental

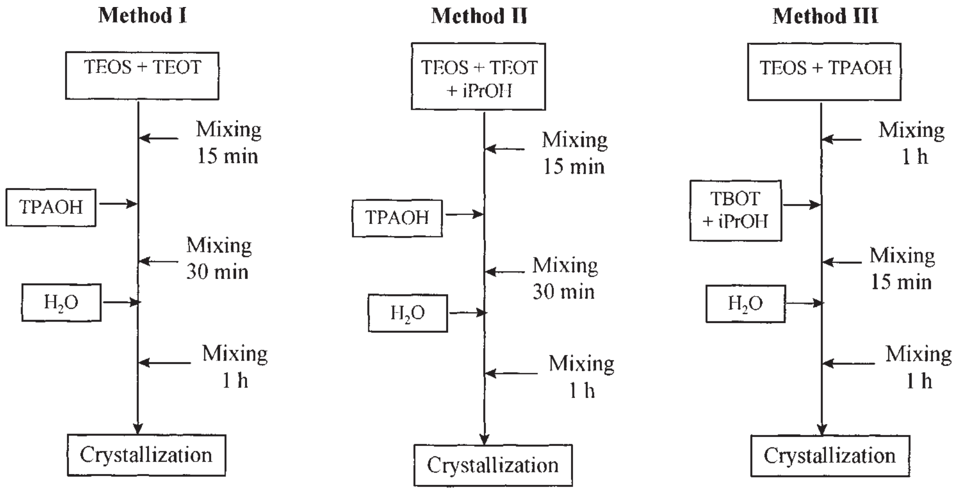
TS-1 samples were synthesized following methods adapted from literature procedures [2,4]. In *method I* adapted from the original patent, silicon and titanium ethoxides are first mixed together for 15 min (scheme 1). Then an aqueous solution of TPAOH is added dropwise and the mixture is stirred for 30 min. Water is then added and the gel, with the following composition:

$$SiO_2\text{–}x TiO_2\text{–}0.4TPAOH\text{–}4EtOH\text{–}30H_2O$$
$$0.01 < x < 0.05$$

is stirred at room temperature for 1 h before crystallization in a stainless steel Teflon-lined autoclave under static conditions at 170 °C for 48 h.

Method II is similar to method I except that TEOT is added to a mixture of TEOS (0.1 mol) and iPrOH (0.13 mol).

Method III is similar to that reported by Thangaraj et al. [4]. TEOS is preliminary hydrolyzed with TPAOH. Then TBOT in dry isopropyl alcohol is added, followed by distilled water. The gel with the composition:



Scheme 1.

$$SiO_2\text{–}x TiO_2\text{–}0.4TPAOH\text{–}4EtOH\text{–}1.3iPrOH\text{–}30H_2O$$
$$0.01 < x < 0.05$$

is stirred for 1 h at room temperature and crystallization is performed as in method I.

From these methods, standard catalysts are obtained by heating the gel at about 80 °C for 3 h prior to its transfer into the autoclave.

After crystallization, zeolites were recovered by centrifugation, washed with distilled water, dried at 110 °C for 12 h and finally calcined in air at 550 °C for 10 h. The Ti content was obtained by ICP after solubilization of the samples in HF:HCl solutions. Catalysts were characterized by X-ray diffraction (Philips PW 1710 diffractometer, SiO_2 as external standard) and UV/Vis spectroscopy. For each sample, unit cell parameters and volume were calculated using Rietveld refinement of the X-ray pattern in the $20° \leqslant 2\theta \leqslant 50°$ angular range. Zeolites were calcined and rehydrated for 48 h prior to analysis. SEM pictures were obtained on a Jeol 2010 microscope.

The hydroxylation of phenol was performed in a round flask equipped with a condenser and magnetically stirred. Phenol (0.1 mol), methanol (0.35 mol) and TS-1 (0.5 g) were stirred together and the mixture was heated at 60 °C. Then H_2O_2 (0.02 mol, 35 wt% in water) was added in one lot. Products of the reaction were analyzed by gas chromatography using a nickel column packed with Tenax GC 60/80 (Alltech). The reaction was stopped after 3 h and the amount of unreacted oxidant was measured by titration with KI.

3. Results and discussion

All methods give highly crystalline solids with the MFI structure type as evidenced by X-ray diffraction. As a general trend, we observe that the Ti content in calcined solids is similar for the three methods used (table 1). For low Ti contents (Si/Ti > 50), Si/Ti ratios in the zeolite are similar to those of the precursor gel, indicating that all Ti and Si originally introduced are in the solid phase (the yield of zeolite is typically >90%). For higher Ti loading, a deviation is observed (figure 1) and the Ti/(Si + Ti) ratio in the catalysts reaches a maximum corresponding to approximately 1.9 Ti/u.c. which is independent of the gel composition. This strongly contrasts with data obtained on zeolites prepared following the original patent [2] with alcohol removal prior to crystallization. In this case, solids with Ti/(Si + Ti) ratios up to 4.5 wt% can be obtained, of which the composition reflects quite well that of the corresponding gel. However, incorporation is limited to approximately 2.4 Ti/u.c., and samples prepared with an excess of titanium contain extra-framework TiO_2 species. Since crystallization of TS-1 is almost complete (yields > 90%), some part of the Ti species are not incorporated in the zeolite and remain in solution when the synthesis is performed in the presence of alcohol. Such a limitation in Ti incorporation

Table 1
Chemical composition and unit cell volumes of the various TS-1 samples.

Sample[a]	Ti/(Si + Ti) (%) gel	Ti/(Si + Ti) (%) zeolite[c]	u.c.[b] (Å^3)
TS(I)-1	1	1.12	5359.5(8)
		[1.07]	5362.0(8)
TS(I)-2	2	1.67	5370.0(9)
		[1.91]	5379.5(8)
TS(I)-3	3	2.07	5371.1(9)
		[2.85]	5390.0(9)
TS(I)-4	5	2.1	5373.2(10)
		[4.51]	5389.4(9)
TS(II)-1	1	1.03	5361.2(8)
TS(II)-2	2	1.64	5374.0(9)
TS(II)-3	3	2.07	5383.2(8)
TS(II)-4	5	2.06	5383.0(8)
TS(III)-1	1	0.98	5360.1(9)
TS(III)-2	2	1.57	5372.3(9)
TS(III)-3	3	1.94	5380.4(10)
TS(III)-4	5	2.03	5382.3(10)

[a] (I), (II) and (III) refer to the synthesis method described in section 2.
[b] e.s.d's between parentheses.
[c] Data between brackets refer to samples obtained after evaporation of alcohol.

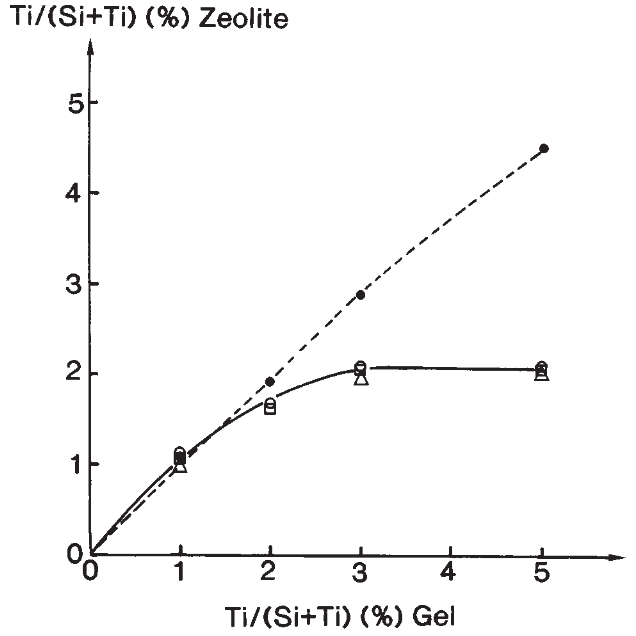


Figure 1. Ti content in the zeolites versus Ti content in the gel for gels prepared following (○) method I, (□) method II, (△) method III and (●) method I after evaporation of alcohol before crystallization.

was already reported by Huybrechts et al. [3] for materials prepared following example 2 of the original patent, i.e., using tetrapropylammonium peroxytitanate as Ti precursor. For Ti/(Si + Ti) ratios in the gel between 1 and 6%, these authors showed that the amount of Ti incorporated corresponded to approximately 1.5 mol%, which is in harmony with our results.

The various TS-1 materials are in the form of small crystallites of ca. 0.3–0.4 μm diameter, similar to those obtained in the absence of alcohol [6], indicating that the latter does not significantly influence the crystallization process. UV/Vis spectra of the calcined materials show that samples obtained by method I contain extra-framework Ti species, even at low Ti loading (figure 2). By contrast, when alcohol is evaporated by heating the gel before crystallization, extra-framework species are only detected for high Ti loadings, typically for samples with more than 2.5 Ti/u.c. A ^{29}Si NMR examination of the various gels prepared by method I shows that monomeric $Si(OH)_4$ species are in the majority and that polymeric species are not yet formed in large amounts (figure 3). Under such conditions, heating the gel under static conditions at high temperature, leads to the formation of extra-framework TiO_2. By contrast, when the gel is heated at 80 °C to remove alcohol, the NMR line corresponding to monomers Q^0 has disappeared and oligomerized species (mainly Q^3) are observed. This demonstrates that heating the precursor gel greatly increases the polycondensation rate, which improves Ti incorporation in the silicalite framework. As a consequence, the presence of extra-lattice TiO_2, evidenced by a UV/Vis absorption around 330 nm, is probably not due to the presence of alcohol in the gel but rather to an incomplete condensation of titano-silicate species before hydrothermal crystallization.

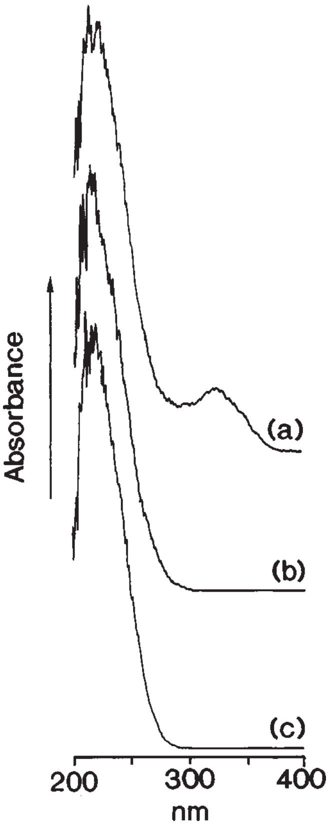


Figure 2. UV/Vis spectra of calcined zeolites prepared with Ti/(Si + Ti) = 0.02 in the gel following method I (a), method II (b) and method III (c).

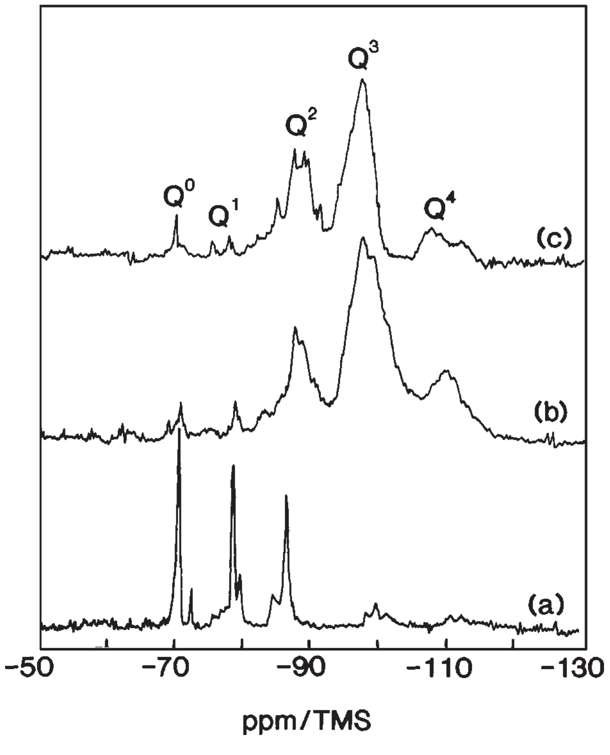


Figure 3. ^{29}Si NMR spectra of gels prepared with Ti/(Si + Ti) = 0.02 following method I (a), method I after evaporation of alcohol at 80 °C (b) and method II (c). Spectra were recorded on a Bruker DSX 400 spectrometer.

This is confirmed by the following experiment: a gel with Si/Ti $= 50$ is prepared following method I, heated at 80 °C for 3 h and ethanol (corresponding to $EtOH/SiO_2 = 4$) is added before crystallization. The zeolite obtained contains 1.6 Ti/u.c. and does not show any UV/Vis signal above 280 nm.

In contrast to method I, methods II and III yield zeolites for which no signal is observed above 300 nm in UV/Vis spectra, which indicates the absence of extra-lattice species. However, it was reported that the absence of signals characteristic of TiO_2-like species could not be taken as a real proof for Ti incorporation [7]. Very small domains of oxide species may indeed give UV/Vis signals at relatively high energies, due to quantum size effects [8]. For this reason, the extent of Ti incorporation in our samples has been measured by calculating unit cell parameters from X-ray diffraction patterns. Rietveld refinement is the only method capable of discriminating between framework and extra-framework species, the unit cell parameters being proportional to the Ti fraction up to $Ti/(Si + Ti) = 0.025$ [7]. As already suggested by UV/Vis spectroscopy, samples obtained by method I possess a unit cell volume significantly smaller than those of pure TS-1 having the same Ti content and where all Ti are at framework positions (table 1). Comparison between X-ray data and chemical analysis shows that approximately 25% of the Ti species are not incorporated for sample TS(I)-3 prepared with $Ti/(Si + Ti) = 0.03$ in the gel. By contrast, for samples prepared by methods II and III, the unit cell volume is in good agreement with chemical composition, demonstrating the absence of extra-framework species (table 1). For these samples, the major difference with method I is that hydrolysis of the precursors is performed in the presence of isopropyl alcohol. Thangaraj and Sivasanker [9] as well as our group [10] have already reported that isopropyl alcohol greatly increases the rate of polymerization of titano-silicate species in the precursor gel, even at room temperature. As an example, figure 3 shows that the ^{29}Si NMR spectrum of a synthesis gel prepared by method II is similar to that of the same gel prepared by method I after evaporation of ethanol at 80 °C. Therefore, heating gels obtained by methods II and III will result in the evaporation of alcohol but will not greatly improve the degree of oligomerization. The presence of titano-silicate oligomers in solution before crystallization seems thus to be a condition to prevent the formation of Ti–O–Ti linkages during hydrothermal treatment.

All zeolites were tested as catalyst in the hydroxylation of phenol with aqueous H_2O_2. Table 2 shows that for all zeolites H_2O_2 is totally consumed after 3 h reaction. However, catalysts prepared following method I give lower yields in dihydroxybenzenes (catechol and hydroquinone) as compared to catalysts obtained by the two other methods. This is particularly evident for samples TS(I)-3 and TS(I)-4 prepared with relatively high Ti concentrations in the gel. Since all zeolites possess small crystallites of typically 0.3–0.4 μm size, the lower activity of these solids cannot be attributed to additional diffusion limitations. It is actually a direct consequence of the presence of extra-framework Ti species that are known to decompose hydrogen peroxide and therefore decrease the yield of oxygenated products.

Table 2
Hydroxylation of phenol over the various catalysts.[a]

Sample	$C_{H_2O_2}$[b] (%)	S_{DHB}[c] (%) phenol	H_2O_2	H/C[d]
TS(I)-1	99	85	82	1.8
	(100)[e]	89	(93)	(2.0)
TS(I)-2	98	87	85	1.8
TS(I)-3	100	79	78	1.7
TS(I)-4	99	81	71	1.5
	(98)	93	(92)	(2.1)
TS(II)-1	99	91	92	1.9
TS(II)-2	97	93	90	2.0
TS(II)-3	98	89	90	2.0
TS(II)-4	100	90	96	1.9
TS(III)-1	100	94	93	2.1
TS(III)-2	100	91	92	2.0
TS(III)-3	98	91	92	2.0
TS(III)-4	99	93	93	1.9

[a] Reaction conditions: 0.5 g TS-1, 0.1 mol phenol, 0.35 mol ethanol, phenol/$H_2O_2 = 5$, $T = 60$ °C. Data obtained after 3 h reaction.

[b] H_2O_2 conversion.

[c] Selectivity in dihydroxybenzenes based on H_2O_2 (phenol) and defined as (moles of dihydroxybenzenes formed)/(moles of H_2O_2 (phenol) consumed)$\times$100.

[d] Hydroquinone/catechol molar ratio (p/o ratio).

[e] Data in parentheses were obtained on conventional catalysts obtained after evaporation of the alcohol.

All catalysts obtained by methods II and III are very active in phenol hydroxylation and selectivities in dihydroxybenzenes as well as the para/ortho ratio at the end of the reaction are similar to those obtained over a conventional TS-1 prepared in an alcohol-free medium.

4. Conclusion

TS-1 can be synthesized from alcohol-containing mixtures, i.e., from non-evaporated gels obtained following literature procedures. In contrast to standard catalysts obtained from alcohol-free media, the Ti content in the zeolite is limited to ca. 1.9 Ti/u.c., even when the precursor gel contains higher Ti concentrations. When TS-1 is prepared by a method derived from that of the original patent, extra-framework Ti species are observed, even for low Ti loading. In contrast, when hydrolyses of the silicon and the titanium sources are performed in the presence of isopropyl alcohol, all Ti atoms are incorporated. The presence of alcohol during crystallization does not influence the crystal size and the zeolites obtained possess an activity comparable to that of standard TS-1 in the hydroxylation of phenol with H_2O_2. This method does not only considerably reduce the preparation time and cost of the catalysts but it also provides zeolites free from extra-framework species, even when they are crystallized from gels with relatively high Ti concentrations.

References

[1] B. Notari, Catal. Today 18 (1993) 163.

[2] M. Taramasso, G. Perego and B. Notari, US Patent 4,410,501 (1983).

[3] D.R.C. Huybrechts, P.L. Buskens and P.A. Jacobs, J. Mol. Catal. 71 (1992) 129.

[4] A. Thangaraj, R. Kumar, S.P. Mirajkar and P. Ratnasamy, J. Catal. 130 (1991) 1.

[5] E. Jorda, A. Tuel, R. Teissier and J. Kervennal, Zeolites, in press.

[6] A.J.H.P. van der Pol and J.H.C. van Hooff, Appl. Catal. A 92 (1992) 93.

[7] R. Millini, E. Previde Massara, G. Perego and G. Bellussi, J. Catal. 137 (1992) 497.

[8] S. Klein, B.M. Weckhuysen, J.A. Martens, W.F. Maier and P.A. Jacobs, J. Catal. 163 (1996) 489.

[9] A. Thangaraj and S. Sivasanker, J. Chem. Soc. Chem. Commun. (1992) 123.

[10] A. Tuel and Y. Ben Taârit, Appl. Catal. A 110 (1994) 137.