Synthesis and Catalytic Properties of Titanium-substituted Silicoaluminophosphate TAPSO-5

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Titanium-substituted silicoaluminophosphates with the AFI structure are synthesized hydrothermally and are found to be active as catalysts in oxidation reactions with alkyl peroxides.

Titanium silicalite-1 (TS-1) is a zeolite of the pentasil family with the MFI structure, the framework of which contains isolated tetrahedrally coordinated titanium atoms.[1] TS-1 has proved to be an excellent catalyst in oxidation reactions at mild temperatures involving hydrogen peroxide as the oxidant.[2] However, these reactions were usually limited to small reactants, because of the relatively small pore openings of the MFI stucture (*ca.* 5.5 Å). In particular, substituted aromatics like phenol could be easily hydroxylated,[3] whereas the formation of cresols from toluene or the epoxidation of cyclohexene were very difficult.[4]

Therefore, many attempts have been made to incorporate titanium in other microporous materials, particularly large pore zeolites, that were expected to catalyse the oxidation of larger molecules. However, the synthesis of Ti-containing materials is relatively difficult. Indeed, they have to be prepared in the absence of alkali cations since these have been reported to favour the formation of extra-framework titanium species.[5] Recently, the titanium β-zeolite has been synthesized.[6] In contrast to TS-1, the zeolite could not be prepared in the absence of aluminium, but only with Si : Al < 400 in the precursor gel. This zeolite was found to be active in the epoxidation of cyclohexene with hydrogen peroxide.[4] Very recently, two mesoporous materials,[7] namely Ti-HMS and Ti-MCM-41, have been prepared. Catalytic data for these solids seem to be very promising, especially for polysubstituted aromatics.

We report here on the synthesis and catalytic properties of the new titanium-containing molecular sieve TAPSO-5.

SAPO-5 is a silicoaluminophosphate molecular sieve with a 12-membered ring monodimensional micropore system.[8] Depending on the synthesis procedure, it can be prepared within a large composition range. For high Si fractions in the gel, silica or aluminosilicate domains are generated inside the AlPO-5 framework. If titanium is carefully added to the gel mixture, we may expect Ti^{4+} ions to substitute for Si^{4+} atoms in the siliceous domains, thus giving a material with properties similar to those of Ti-substituted zeolites. In particular, TAPSO-5 may contain Ti–O–Si bridges, which seem to be very important in the catalytic process.[9]

Table 1 Chemical composition of the different gels and products[a]

	x		Ti/Si		y/z	
Sample	Gel	Product	Gel	Product	Gel	Product
1	0.2	0.17	0	0	1	1.18
2	0.2	0.17	0.01	0.018	1	1.07
3	0.2	0.165	0.05	0.079	1	1.17
4	0.3	0.27	0	0	1	1.21
5	0.3	0.265	0.01	0.019	1	1.15
6	0.3	0.26	0.05	0.077	1	1.25

[a] The general formula adopted for TAPSO-5 samples was $(Ti_wSi_xAl_yP_z)O_2$.

A typical synthesis of TAPSO-5 was as follows. Titanium butoxide (0.63 g) was hydrolysed with distilled water (17 ml). To the white homogeneous suspension thus obtained, aqueous hydrogen peroxide (1.05 ml, 30% m/m) was added, and the clear orange solution was stirred for about 2 h. Then Ludox AS-40 (Dupont) (13.85 g) was added and stirring was maintained for 2 h before the addition of cyclohexylamine (5.22 ml). The resulting mixture (solution A) was stirred for about 2 h. Aluminium isopropoxide (22 g) was slowly hydrolysed in a solution containing orthophosphoric acid (8.97 g) and distilled water (40 ml) for about 3 h at room temp. (solution B). Solution A was then slowly added to solution B under vigorous stirring. The homogeneous gel was transferred to a PTFE flask and crystallized at 190 °C for two days under stirring (100 rpm).

Various samples were prepared, with different Si and Ti contents. In order to have a high probability for Ti^{4+} ions to be located inside the siliceous domains, samples with relatively high Si fractions in the precursor gel were synthesized. Table 1 lists the chemical composition of the gels and the corresponding products. The ratio Al : P is generally >1 in as synthesized samples, reflecting the substitution of some of the Si^{4+} for P^{5+} in the framework. Moreover, for all samples, the Ti : Si ratio was higher in the product than in the gel, indicating that not all the silica was involved in the crystallization process. A similar trend was previously observed by different authors for titanium silicates. The pure AlPO-5 structure type was obtained for Si fractions up to 0.3 in the precursor gel. For higher fractions ($x > 0.3$), co-crystallization of AlPO-44 was observed in the X-ray diffraction pattern. For $x = 0.3$, samples with Ti : Si = 0.05 in the gel could be prepared without formation of extra-framework species. Indeed, the UV–VIS spectra of the samples showed a single line centred on *ca.* 230 nm, characteristic of Ti^{4+} ions in a tetrahedral coordination.[10] IR spectra of the samples (Fig. 1) showed the typical absorption bands of the SAPO-5 materials, particularly the absorption at 800 cm^{-1} characteristic of SiO_2 domains.

Table 2 Catalytic activity of TAPSO-5 (sample 6) in the epoxidation of cyclohexene[a]

		Selectivity/%				
Catalyst	ROOH	Cyclohexene oxide	Cyclohexenol	Cyclohexenone	1,2-cyclohexenediol	S(ROOH)[b]
TAPSO-5	H_2O_2	0.0	20.0	21.0	59.0	82.5
	Bu^tOOH	79.0	2.60	9.0	9.0	87.0
TS-1[c]	H_2O_2	91	—	—	9.0	11.5[d]

[a] Reaction conditions: 1 g catalyst, 20 ml cyclohexene, 20 ml acetone, ROOH : cyclohexene = 0.2, $T = 70$ °C. [b] S(ROOH) is the peroxide selectivity in (cyclohexene oxide + cyclohexenol + cyclohexenone + cyclohexenediol). [c] The TS-1 sample used for comparison was synthesized following the recipe given in ref. 1. The Ti content was about 1.7% m/m. [d] Composition of the mixture after 5 h reaction.

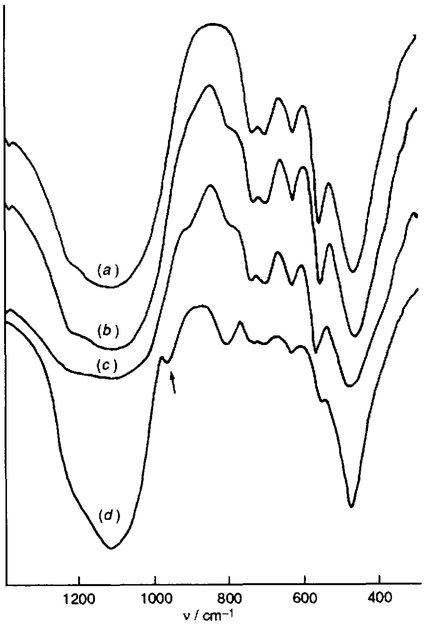

Fig. 1 Framework IR spectra of (*a*) AlPO-5, (*b*) SAPO-5 sample 4, (*c*) TAPSO-5 sample 6 as synthesized and (*d*) TAPSO-5 sample 6 calcined

Samples with titanium in the framework also showed an additional band around 970 cm^{-1}. This band is good evidence for the presence of Si-O$^-$ defects in the siliceous domains, created by the presence of Ti atoms. Indeed, it was already observed in the IR spectra of various metal-containing molecular sieves.[11]

The ^{27}Al, ^{31}P and ^{29}Si NMR spectra of TAPSO-5 were similar to those of pure SAPO-5, suggesting that the presence of titanium in the gel did not influence the distribution of silicon species in the product.

SEM pictures revealed that TAPSO-5 was in the form of spherical irregular particles of 4–6 μm diameter, slightly smaller than those of pure SAPO-5 materials.

TAPSO-5 has been used as a catalyst for the liquid phase epoxidation of cyclohexene. In contrast to highly siliceous zeolites, the framework of aluminophosphate molecular sieves is hydrophilic, and oxidation reactions are usually carried out with *tert*-butyl hydroperoxide (Bu^{t}OOH). Because of the presence of large SiO_2 domains in the framework of TAPSO-5, the hydrophobicity of the product is considerably increased and aqueous H_2O_2 can also be used as the oxidant.

Table 2 shows the results of the oxidation of cyclohexene over TAPSO-5 using either H_2O_2 or Bu^{t}OOH as the oxidant. For comparison, results obtained over a titanium silicalite-1 have also been reported. With both peroxides, the major products formed are cyclohexene oxide, cyclohexenol, cyclohexenone and 1,2-cyclohexenediol. Using H_2O_2 leads to the preferential formation of 1,2-cyclohexenediol. Indeed, at the end of the reaction the diol selectivity is close to 60%. When Bu^{t}OOH is used as the oxidant, Table 2 shows that the epoxide is formed very selectively. These results confirm that the epoxide formed is readily converted to the corresponding diol with aqueous hydrogen peroxide. Another important difference between this reaction and that carried out with H_2O_2 is that total conversion is only achieved after 12 h instead of 5 h. Moreover, traces of bicyclohexenyl were detected at the beginning of the reaction. Similar reactions carried out in the absence of catalyst gave very low conversions for the same reaction times. Table 2 also shows that the cyclohexene conversion was very low over TS-1, probably because of the steric restrictions in the channels.

The nature of the products at the end of the reaction strongly suggests different oxidation mechanisms with hydrogen peroxide and Bu^{t}OOH. A similar behaviour had already been reported for the oxidation of substituted aromatics over vanadium-containing molecular sieves.[12]

Received, 14th April 1994; Com. 4/02230K

References

1 M. Taramasso, G. Perego and B. Notari, *US Pat.* 4 410 501, 1983.
2 U. Romano, A. Esposito, F. Maspero, C. Neri and M. G. Clerici, in *New Developments in Selective Oxidation*, ed. G. Centi and F. Trifiro, Elsevier Science Publishers, 1990, 33.
3 A. Tuel, S. Moussa-Khouzami, Y. Ben Taârit and C. Naccache, *J. Mol. Catal.*, 1991, **68**, 45.
4 A. Corma, M. A. Camblor, P. Esteve, A. Martinez and J. Perez-Parienté, *J. Catal.*, 1994, **45**, 151.
5 C. B. Khouw, H. X. Li, C. B. Dartt and M. E. Davis, in *Catalytic Selective Oxidation*, ACS Symp. Ser. ed. S. T. Oyama and J. W. Hightower, 1992, **523**, 273.
6 M. A. Camblor, A. Corma and J. Perez-Parienté, *Zeolites*, 1993, **13**, 82.
7 P. T. Tanev, M. Chibwe and T. J. Pinnavala, *Nature*, 1994, **368**, 321.
8 B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan and E. M. Flanigen, *US Pat.* 4 440 871, 1984.
9 B. Notari, *Catal. Today*, 1993, **18**, 163.
10 M. R. Boccuti, K. M. Rao, A. Zecchina, G. Leofanti and G. Petrini, in *Structure and Reactivity of Surfaces*, ed. C. Morterra, A. Zecchina and G. Costa, Elsevier B.V., 1989, 133.
11 M. A. Camblor, A. Cortma and J. Perez-Parienté, *J. Chem. Soc., Chem. Commun.*, 1993, 557.
12 M. S. Rigutto and H. van Bekkum, *J. Mol. Catal.*, 1993, **81**, 77.