Synthesis of titanium containing silica ZSM-48 (TS-48) using hexamethonium hydroxide as template

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Titanium containing silica analog of ZSM-48 (TS-48) has been synthesized by a new method using hexamethonium hydroxide as a template. Titanium incorporation in the framework was evidenced from unit cell volume expansion, framework IR spectra and diffuse reflectance UV–Vis spectra.

Keywords: Titanium silica-ZSM-48; TS-48; hexamethonium hydroxide; titanium incorporation

With the growth of the interest in the utilization of framework-modified zeolites as catalysts, more attention has been devoted to the introduction of various elements as substitutes for lattice silicon or aluminum. This effort has led to the development of many new catalysts by substitution of elements such as B, Fe, Ga, Ti, V etc. in different zeolite lattices. Such substitution may be achieved either during synthesis or by post-synthesis procedures. Kaliaguine et al. [1] reviewed the structure and catalytic properties of some chemically modified ZSM-5 zeolites.

In 1983, Taramasso et al. [2] reported the hydrothermal synthesis of titanium substituted derivative of pure silica ZSM-5 (TS-1). TS-1 was found to be a remarkable catalyst for the oxygenation of a variety of organic compounds with aqueous hydrogen peroxide as oxidant [3–5]. Since then, there has been a sustained interest for the synthesis of titanium containing pure silica zeolites. Reddy et al. [6] reported another titanium silicalite, TS-2, with ZSM-11 topology, where the synthesis procedure was similar to the one used for TS-1 except that tetrabutyl ammonium hydroxide was used as template instead of tetrapropyl ammonium hydroxide. The catalytic activity was also found to be somewhat similar to TS-1 [6,7]. Though the catalytic properties of titanium silicalites were shown to be due to the Ti species engaged into the zeolite framework, the Ti environment and its bonding in the framework are still a matter of debate. Recently, Ti sites in TS-2 have

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been investigated by near-edge and extended X-ray absorption fine structure techniques [8]. It was observed that the Ti and Si tetrahedra are linked through an edge rather than via the usual corner-sharing mode [8].

The problems in synthesizing TS-1 and the influence of synthesis parameters were investigated extensively [9]. Several methods to make suitable gels for the synthesis of TS-1 using different titanium and silica sources with the same organic template were developed [2]. Titanium silicalite gels made from tetraethyl orthosilicate as Si source and tetrabutyl orthotitanate as Ti source produced well crystalline materials with relatively high level of titanium incorporation [2,10]. It was also observed that materials produced by this method had excellent catalytic properties [11].

Recently, the titanium containing silica analog of ZSM-48 has also been synthesized [12] using fumed silica as Si source, peroxytitanate as Ti source (prepared from aqueous hydrogen peroxide and hydrous TiO_2) and diamino octane as an organic template. We found that TS-48 produced by the above method is not fully crystalline and shows no activity for the hydroxylation of phenol using hydrogen peroxide [13], which is a characteristic reaction for titanium silicalites (TS-1 and TS-2) [7]. ZSM-48 is a uni-dimensional, medium pore high silica zeolite [14] synthesized by Chu [15] using alkylamines as templates. ZSM-48 was later synthesized by various methods in presence of a number of organic templates [16–18]. Here we report a new method for the synthesis of titanium containing all-silica ZSM-48 (TS-48) and the characterization of this solid.

The materials used in this synthesis were tetraethyl orthosilicate (TEOS), tetrabutyl orthotitanate ($Ti(OBu)_4$) and hexamethonium hydroxide ($OH^-(CH_3)_3N^+$–CH_2–$(CH_2)_4$–CH_2–$N^+(CH_3)_3OH^-$; $HM(OH)_2$) as a template. $HM(OH)_2$ was prepared from a solution of $HMBr_2$ in water through reaction with Ag_2O. In a typical procedure, 25 g of aqueous $HM(OH)_2$ (0.6 M solution) and 9 g of water were slowly added to 17.38 g of TEOS. The mixture was stirred for 30 min at room temperature. To the resultant mixture a solution of 0.33 g $Ti(OBu)_4$ in 5 g of dry isopropyl alcohol was added very slowly under vigorous stirring. The clear liquid mixture was stirred at room temperature for about 1 h. Then, 12.66 g of $HM(OH)_2$ solution was added and the stirring was continued for another 2 h. Finally 50 g of water was added and the mixture was stirred for 30 min. The resultant clear liquid was transferred into a teflon lined autoclave and heated at 473 K for 7 days. During the crystallization, autoclaves were rotated continuously at 40 rpm. The obtained crystalline solid was filtered, washed thoroughly with deionised water, dried at 373 K for 6–8 h and calcined at 833 K overnight in dry air. As this sample contains about 1 wt% Ti, it will be labelled as 1TS-48. Samples 0TS-48 and 2TS-48 containing zero and about 2 wt% Ti, respectively were synthesized in a similar way.

X-ray diffraction patterns of all above samples matched well with that of pure silica ZSM-48 without any extra peaks. Using silicon as an internal standard, XRD peak positions were indexed for orthorhombic cell. Then unit cell parameters were calculated. Table 1 shows that the unit cell volume increases as the Ti content

Table 1
Properties of TS-48 samples

Sample	Si/Ti in gel	Si/Ti in product [a]	Unit cell volume [b] (Å^3)
0TS-48	–	–	2397
1TS-48	86	60	2416
2TS-48	42	35	2440

[a] Molar ratio calculated from bulk chemical analysis by atomic absorption.

[b] Calculated from X-ray powder diffraction data.

increases. The replacement of Si by the larger Ti ions grafted in the framework brought about an increase in these parameters and hence the unit cell volume. Table 1 also shows that it is possible to synthesize TS-48 with different Ti contents. The Ti content in the product was found to be higher than in the initial gel. This is in agreement with similar findings for TS-1 and TS-2 systems [6].

Fig. 1 illustrates the framework IR spectra of all these samples. An absorption band at around 960 wavenumbers was observed for samples 1TS-48 and 2TS-48 but not for 0TS-48. The band at around 960 wavenumbers in titanium silicalites was attributed to the vibrations of a silica tetrahedron perturbed by interaction with a neighbouring Ti atom linked to the framework [19]. According to a recent assignment by Corma et al. [20], the IR band at 960 wavenumbers is due to Si–O$^-$ defect groups generated upon titanium incorporation in the framework. The intensity of this band increased with the Ti content linked to the framework.

Additional evidence for framework grafting of Ti is given in fig. 2, which depicts

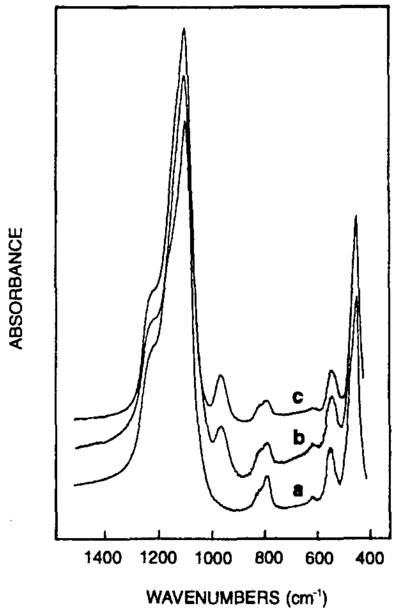

Fig. 1. Framework IR spectra of (a) pure silica ZSM-48 (0TS-48), (b) 1TS-48, and (c) 2TS-48.

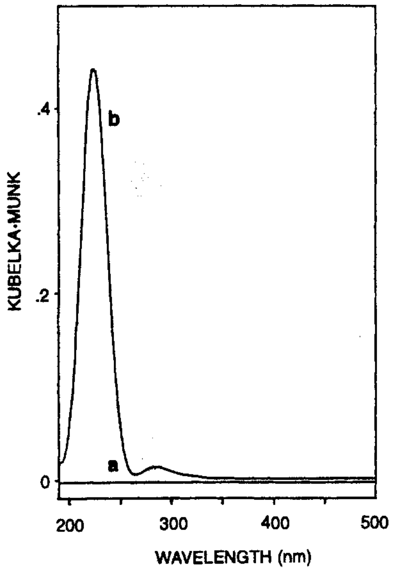

Fig. 2. Diffuse reflectance UV–Vis spectra of (a) pure silica ZSM-48 (0TS-48) and (b) 1TS-48.

the diffuse reflectance UV–Vis spectra of samples 0TS-48 and 1TS-48. A very strong band at around 220 nm along with a very small band at around 300 nm were present in the 1TS-48 spectrum but not in the spectrum of 0TS-48. The 300 nm band which was also observed for pure anatase (TiO_2) [19] was attributed to octahedral Ti and the one at around 220 nm to tetrahedral Ti. The presence of the 300 nm band indicates the presence of extraframework titanium species. Fig. 2 shows that the 300 nm band is hardly perceptible in 1TS-48 indicating that at low Ti content, all the Ti is grafted to the framework.

In conclusion, titanium containing ZSM-48 (TS-48) has been synthesized by a new method using a different template and different sources of Si and Ti from previously reported synthesis method [12]. A more detailed characterization study of TS-48 is underway.

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