Hydrothermal Synthesis of a Novel Titanosilicate with MWW Topology

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A novel titanosilicate with the MWW topology hydrothermally synthesized in the presence of boron shows catalytic activity for the liquid-phase oxidation reaction of cyclohexene after removal of the extraframework Ti species by an acid treatment.

The discovery of titanium containing silicate with the MFI structure (TS-1) has developed a new research field in the zeolite catalysis since it is able to catalyze the selective oxidation of various organic substrates using hydrogen peroxide as an oxidant.[1] However, the medium-size pore of TS-1 restricts its utilization to the substrates and the oxidants with small molecular diameters. To overcome this limitation, Ti-containing crystalline silicates having 12-ring channels such as Ti-Beta,[2,3] TAPSO-5,[4] Ti-ZSM-12[5] and Ti-MOR[6] have been prepared by hydrothermal synthesis or post-synthesis methods. A crystal structure of the MWW topology (typically known as MCM-22),[7] formed from a lamellar precursor through a dehydroxylation between layered sheets during calcination, is expected to supply the possibilities for preparing oxidation catalysts containing highly stable and accessible Ti species. The super cage (0.7 × 0.7 × 1.8 nm) within the MWW crystals and the "cup" (0.7 × 0.7 nm) moiety of a supercage,[8] penetrated into the crystal from the external surface have already been proved to serve as open reaction space in the disproportionation of toluene[9] and in the alkylation of benzene.[10] Furthermore, the lamellar precursor can be converted into a micro-mesoporous hybrid, MCM-36,[11] by swelling with organic surfactant followed by pillaring with polymeric silica, and can also be delaminated into a material composed of thin sheets, ITQ-2,[12] by forcing apart the swollen precursor with ultrasound. Both MCM-36 and ITQ-2 have extremely high surface area and are highly accessible for reactants. In spite of the diversity of the MWW structure, its synthesis has been focused on trivalent cations but little on Ti. An only report on this issue is the post-synthesis of Ti/ITQ-2 by grafting titanocene onto the surface of pure silica ITQ-2.[13] We report here for the first time the direct synthesis of Ti-containing MWW zeolite (Ti-MWW) using boron as a structure-supporting agent and its catalytic activity in the liquid-phase oxidation of alkenes.

The precursor of Ti-MWW was synthesized from fumed silica (Cab-o-sil M7D), tetrabutyl orthotitanate (TBOT), boric acid and piperidine (PI). By modifying the procedures for preparing MWW type borosilicate,[14] the present synthesis was carried out as follows. An aqueous solution prepared by dissolving PI in deionized water was divided into two equal parts. Desirable amount of TBOT or boric acid was added to each PI solution under vigorous stirring. Silica was also divided into two equal parts and added gradually to the solutions containing Ti and B, respectively. A further stirring for 1 h allowed to form two homogeneous gels. The gels were then mixed together and stirred for 1.5 h to obtain a gel with a molar composition of 1 SiO_2 : 0.01–0.05 TiO_2 : 0.67 B_2O_3 : 1.4 PI : 19 H_2O. The crystallization of the resultant gel was carried out at a stirring rate of 100 rpm at 403 K and then 423 K each for 1 day, and further at 443 K for 5 days. The solid product after filtering off and washing with deionized water was dried at 323 K for 1 day. To remove B and extraframework Ti species, an acid treatment with 2 M HNO_3 solution was performed at 373 K for 20 h at a solid to liquid ratio of 1 g to 20 ml. The samples were calcined at 803 K to burn off the remaining organic species. In some cases, the acid treatment was repeated.

The XRD pattern of as-synthesized sample (Si/Ti = 50) was consistent with that reported for the lamellar precursor of MWW zeolite (Figure 1a). It showed the characteristic 001 and 002 peaks at $2\theta = 3–7°$ due to the lamellar structure and peaks due to the crystalline layers.[11] The calcination led to the dehydroxylation and recrystallization between the layers. The diffraction peaks due to the lamellar structure disappeared and the XRD pattern turned to be that of the MWW structure (Figure 1b). In agreement with the results reported for MWW type borosili-

Table 1. Acid treatment and catalytic properties of Ti-MWW

No.	Sample	Si/B	Si/Ti	Cyclohexene oxidation with H_2O_2[a]							Cyclohexene oxidation with TBHP[a]				
				Cyclohexene		Product sel. /%			H_2O_2 /%		Cyclohexene		Product sel. /%		
				Conv. /%	TON[b]	Oxide	Glycols	Others[c]	Conv.	Sel.	Conv. /%	TON[b]	Oxide	Glycols	Others[c]
1	Ti-MWW1[d]	11	51	2.0	13	10	82	8	6	67	1.4	9	69	14	17
2	Ti-MWW2[e]	39	72	4.7	42	68	28	4	10	94	4.2	38	85	4	11
3	Ti-MWW3[f]	543	107	4.3	55	60	34	6	9	96	-	-	-	-	-
4	Ti-MWW4[g]	54	38	7.1	34	34	63	3	15	95	5.7	27	84	7	9
5	Ti-β[h]	71[i]	40	11.9	56	68	30	2	34	70	4.3	20	89	8	3

[a]Conditions: cat., 50 mg; cyclohexene, 10 mmol; H_2O_2 or TBHP, 5 mmol; acetonitrile, 10 ml; temp., 333 K; time, 2 h. [b]TON in mol (mol-Ti)$^{-1}$. [c]2-Cyclohexene-1-ol and 2- cyclohexene-1-one. [d]Synthesized from a gel of Si/Ti=50. [e]No. 1 acid-treated. [f]No. 2 further acid-treated. [g]As-synthesized sample of Si/Ti=20 acid-treated. [h]Hydrothermally synthesized according to Ref. 2. [i]Si/Al ratio.

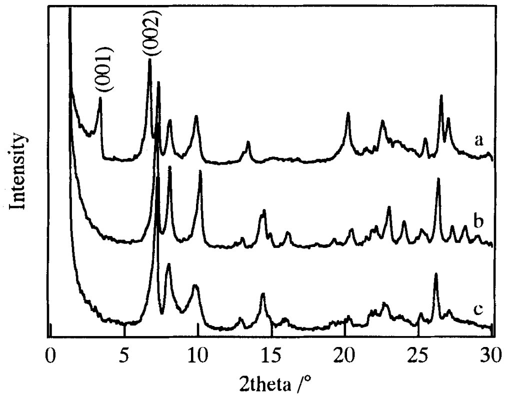

Figure 1. XRD patterns of (a) as synthesized sample (Si/Ti=50), (b) (a) calcined, and (c) (a) treated with 2 M HNO_3 and then calcined.

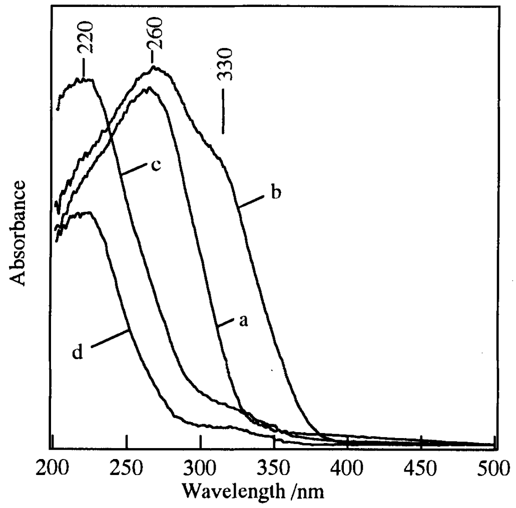

Figure 2. UV-visible spectra of (a) as-synthesized sample (Si/Ti=50); (b) (a) calcined, (c) (a) treated with 2 M HNO_3 and then calcined and (d) (c) further treated with 2 M HNO_3.

cate,[14] the amount of boron incorporated into the product corresponded to an Si/B molar ratio of 11 in spite of 0.75 in the gel (No. 1 in Table 1). Almost all the Ti added (corresponding to Si/Ti = 50), however, was incorporated into the product. The as-synthesized sample before calcination showed in the UV–visible spectrum a main band at 260 nm and a weak shoulder around 220 nm (Figure 2a). The 260 nm band attributed to octahedral Ti species was always observed before calcination even when increasing the Si/Ti ratio to 100. These Ti species are probably related firmly to the lamellar structure of the MWW precursor. A part of Ti species may prefer to deposit on the external surface of sheets to have 6-coordinated states. These Ti species were partially aggregated upon calcination to form the anatase phase which showed a band at 330 nm (Figure 2b). Once the stable anatase was formed, it was hardly removed by acid treatment (data not shown). Nevertheless, these octahedral Ti species were easily removed by the acid treatment on the as-synthesized samples. As shown in Figure 2 c and d, after the calcination only the narrow 220 nm band due to monomeric tetrahedral Ti species was observed for the samples pretreated with acid. The acid treatment extracted both B and Ti from the precursor. The amount of B extracted by acid was larger (No. 2 in Table 1). A further acid treatment of the acid-treated and subsequently calcined sample resulted in a sharp decrease in the amount of B to a nearly B-free sample, while the amount of Ti kept a certain level (No. 3 in Table 1). IR measurements further verified that the B-free sample showed the 960 cm^{-1} band assigned to the Si–O–Ti stretching of framework Ti. The MWW structure was totally maintained after the acid treatment as shown by XRD (Figure 1c). Therefore, it is concluded that a novel MWW titanosilicate with isolated Ti within the framework has been prepared by combining the present hydrothermal synthesis with the acid treatment.

The resultant samples were used as catalysts for cyclohexene oxidation with H_2O_2 or TBHP (Table 1). Besides the epoxide, other products, mainly the glycols, were also obtained. The sample without acid treatment showed lower conversion for cyclohexene and lower efficiency of oxidant as expected because of the presence of anatase. Both the specific activity per Ti site (TON) and the oxidant efficiency increased greatly after removing the extraframework Ti species by the acid treatment. The selectivity for epoxide product also increased when the framework B atoms was removed, because they would act as weak acid sites which may accelerate the ring opening of the epoxide to glycols.[15]

To confirm whether Ti-MWW servers as an open reaction space, its catalytic activity was compared with Ti-β at a similar Ti content (Nos. 4 and 5 in Table 1). Although Ti-MWW showed somewhat lower TON than Ti-β in the case of H_2O_2, it was slightly more active when using the bulky oxidant, TBHP. These results strongly suggest that the external cup moieties of supercages of Ti-MWW would make it a catalyst for the oxidation of relatively bulky reactants. Furthermore, no significant decrease both in the Ti amount and in TON was observed after reusing Ti-MWW for five times, which indicates this material is excellently stable towards Ti leaching. As a result, a novel titanosilicate with the MWW topology, both catalytically active in the oxidation and stable in the Ti species, has been prepared by the hydrothermal synthesis combined with a post-synthesis modification.

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