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Preparation of B-free Ti-MWW through reversible structural conversion

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B-free titanosilicate with the MWW topology, Ti-MWW, has been successfully prepared from its highly siliceous analogue through structural interconversion and simultaneous titanium incorporation in the presence of piperidine or hexamethyleneimine.

The successes of the versatile liquid-phase oxidation catalyst TS-1[1] have encouraged researchers to synthesize other titanosilicates for the purpose of making full use of their zeolite structures. Ti-Beta (Al-containing or free),[2,3] Ti-MOR,[4] and Ti-ITQ-7[5] have been prepared either by direct hydrothermal synthesis or by postsynthesis methods. Very recently, the incorporation of titanium into MWW zeolite (typically known as MCM-22[6]) has attracted a preminum of research attention because MWW zeolite possesses structural diversity in the sense that its has two independent 10-membered ring (MR) channels one of which composes the supercages, and also 12 MR side pockets on the crystal exterior.

MWW metallosilicates containing transition metal elements are seldom reported probably because the more special synthesis conditions required such as alkali-free media and high silica gels. Consequently, the postsynthesis method had been the only way to obtain Ti-containing MCM-22[7] or its delaminated form, Ti-ITQ-2.[8] We developed, for the first time, hydrothermal synthesis procedures for MWW titanosilicate in which boric acid is used as a structure-supporting agent and alkali-free conditions are adopted.[9] [Ti,B]-MWW proves to be an active and selective catalyst in the epoxidation of both linear and cyclic alkenes,[10] and exhibits unique stereoselectivity in the epoxidation of *cis*/*trans* alkene isomers.[11] Nevertheless, the coexisting framework boron species would develop Brønsted acid sites, which although weak in acidity, increase the electronegativity of zeolite framework and lead to a detrimental influence on the product selectivity and the specific activity of Ti. We present here the preparation of B-free Ti-MWW by a postsynthesis method fundamentally different from the conventional process. More importantly, this novel method might be applicale to the preparation of other MWW metallosilicates which are scarcely synthesized hydrothermally.

The synthesis of pure silica Ti-MWW involved the preparation of highly siliceous MWW zeolite and the incorporation of Ti. MWW borosilicate was synthesized using piperidine (PI) or hexamethyleneimine (HM) as a structure-directing agent (SDA) following previous procedures.[9] The borosilicate was deboronated by calcination at 873 K followed by reflux in 6 M HNO_3 solution. This treatment was repeated to remove nearly all the boron and resulted in a highly siliceous sample (Si/B ratio > 1000). This silicate was then treated with tetrabutyl orthotitanate (TBOT), which was hydrolyzed in an aqueous solution of cyclic amines such as PI, HM, pyridine, piperazine, *etc.* A typical molar composition of the mixture corresponded to the formula 1.0 SiO_2 : 0.03 TiO_2 : 1.0 amine : 19 H_2O. The mixture was tumbled and heated in a Teflon stainless-steel autoclave at 448 K for 7 days. The solid product otained in 95 wt% yield based on SiO_2, was collected by filtration and washed thoroughly with deionized water.

Fig. 1 shows representative structure changes during the deboronation and the postsynthesis of Ti-MWW. The as-synthesized borosilicate is a typical MWW lamellar precursor which showed the characteristic 001 and 002 X-ray diffraction (XRD) peaks due to the layer structure (Fig. 1a). The combination of calcination and acid treatment not only totally removed the framework boron but also converted the lamellar precursor into a three-dimensional MWW silicate as evidenced by the disappearance of 001 and 002 peaks together with clear changes in the diffraction patterns at high 2θ values (Fig. 1b). When this deboronated MWW was treated with TBOT in PI solution, incorporation of Ti was achieved and more interestingly, the lamellar structure was simultaneously restored (Fig. 1c). Extraction of the extraframework Ti species by acid treatment (see next section) followed by subsequent calcination caused the layers to dehydroxylate, resulting in B-free Ti-MWW (Fig. 1d).

When the amount of TBOT initially added was changed in the Si/Ti ratio range of 20–100, nearly all the Ti was incorporated into the solid product, indicating this postsynthesis method was highly effective for Ti introduction. Such an effective Ti insertion could be related to the reversible interchange between three-dimensional and lamellar structures during the posttreatment. It should be noted that this structural conversion occurred only in the presence of PI and HM, the two typical SDAs for the MWW zeolite,[9] but was never caused by pyridine and piperazine although these cyclic amines have similar molecular shapes. This means there is a 'fingerprint recognition' between the MWW structure and amine molecules. This kind of structural change occurred after heating at 448 K for 1 day at amine/SiO_2 molar ratios over 0.5.

The inserted PI or HM molecules would slightly open the MWW interlayer spacing, *i.e.* the 10 MR channels with supercages, and then make the Ti species more accessible to the vacancies developed as a result of deboronation and structural connectivity defects. Since both the 10 MR channels of MWW structure share the same tetrahedral framework element, a uniform Ti incorporation would be reached once one of these is opened. Therefore, the present method is assumed to overcome the problems encountered by the solid–gas reaction using $TiCl_4$[7] (6.7 × 6.7 Å) or by the solid–liquid reaction using more

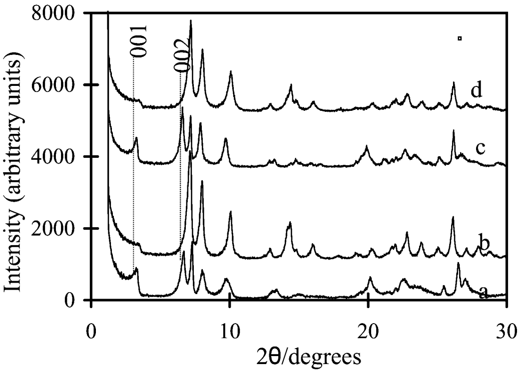

Fig. 1 X-Ray diffraction patterns of as-synthesized B-MWW (Si/B = 11) (a), deboronated MWW (Si/B > 1000) (b), Ti-MWW (Si/Ti = 30) precursor (c), and sample c treated with 2 M HNO_3 and calcined (d).

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Table 1 Epoxidation of alkenes over various titanosilicates[a]

Entry	Cat.	Si/Ti	Substrate	Reaction time/h	Conv.[b] (mol%)	TON/ mol(mol-Ti)$^{-1}$	Product sel. (mol%) Epoxide	Others[c]	H_2O_2 Efficiency (mol%)
1	Ti-MWW	43	Cyclohexene	2	9.9	53	75.5	25.5	91
			Allyl alcohol	0.5	95.9	510	99.7	0.3	98
2	[Ti,B]-MWW[d]	46	Cyclohexene	2	6.3	35	35.7	64.3	88
			Allyl alcohol	0.5	77.1	440	99.0	1.0	96
3	TS-1	52	Cyclohexene	2	0.7	0	36.4	63.6	65
			Allyl alcohol	0.5	39.1	249	75.6	24.4	85
4	Ti-Beta[e]	42	Cyclohexene	2	16.2	81	48.2	52.8	76
			Allyl alcohol	0.5	13.9	70	75.4	24.6	75

[a] *Reaction conditions*: bath reactor; cat., 50 mg; substrate, 10 mmol; H_2O_2, 10 mmol for allyl alcohol, 5 mmol for cyclohexene; MeCN (for Ti-MWW, [Ti,B]-MWW and Ti-Beta) or MeOH (for TS-1), 5 ml for allyl alcohol and 10 ml for cyclohexene; temp., 333 K; time, 2 h. [b] Based on the substrate. [c] Diols and allylic oxidation products particularly for cyclohexene. [d] See ref. 9, Si/B = 49. [e] Hydrothermally synthesized according to ref. 2

bulky titanocene dichloride.[8] Both Ti precursors are expected to suffer serious steric restriction when penetrating the 10 MR pores (4.0 × 5.9 Å, 4.0 × 5.4 Å) of MWW and then might give rise to uneven Ti distribution.

UV-visible spectra verified that the Ti species in the as-synthesized Ti-MWW were located in both tetrahedral and octahedral coordination states as evidenced by bands at 220 and 260 nm, respectively (Fig. 2a and b). The presence of octahedral Ti species was independent of the Si/Ti ratio, which was very similar to hydrothermally synthesized [Ti,B]-MWW.[9] This has been suggested to be closely related to the lamellar structure of MWW zeolite whose layers possess a number of silanol groups for incorporation of octahedral species. The absence of a 330 nm band excluded the possibility of the anatase phase. When the TBOT-treated sample was directly calcined at 823 K, the layers underwent recrystallization along the *c* axis and a part of octahedral Ti species located there were condensed to the anatase phase which gave a UV band around 330 nm (Fig. 2c). The anatase phase was extremely stable and not removed by the acid treatment even under reflux conditions. In contrast, when the TBOT-treated sample was acid-treated, the extraframework octahedral Ti species were effectively and selectively extracted, while the tetrahedral Ti species remained even after subsequent calcination (Fig. 2d and e). Isomorphously incorporated Ti species in the framework were also confirmed by IR spectra which showed the fingerprint stretching band around 960 cm^{-1}. Thus, pure silica Ti-MWW, containing only tetrahedral framework Ti species, has been successfully prepared by combining a novel postsynthesis method and acid treatment technique.

The activity and selectivity of B-free Ti-MWW in the selective epoxidation of various alkenes with H_2O_2 were tested and compared to the performance of [Ti,B]-MWW, TS-1 and Al-free Ti-Beta with a comparable Ti content (Table 1). The reactions were carried out in a suitable solvent (acetonitrile) for [Ti,B]-MWW, B-free Ti-MWW and Ti-Beta, while in the best solvent (methanol) in the case of TS-1. Compared to [Ti,B]-MWW, B-free Ti-MWW showed improved specific catalytic activity, *i.e.* turnover number (TON), and epoxide selectivity in the epoxidation of both bulky cyclohexene and linear allyl alcohol (Table 1, entries 1 and 2). This is assumed to be a result of decrease in B-related acidity and framework electronegativity. Ti-MWW was obviously a more active epoxidation catalyst than TS-1, a well-known effective oxidation catalyst for small substrates. Compared to three-dimensional large pore Ti-Beta, Ti-MWW reasonably showed somewhat lower TON in the epoxidation of cyclohexene, because this reaction is confirmed to take place mainly on the Ti species within the side pockets and supercages of the MWW structure, while its 10 MR channel is not available for bulky cyclohexene.[10] Ti-MWW catalyzed the epoxidation of allyl alcohol, which is hydrophilic in nature, to the corresponding glycidol within a rather short reaction time very selectively and actively. It seems that Ti-MWW does not suffer the important problem of hydrophilicity/hydrophobicity imposed by Ti-Beta with crystal defects. Furthermore, when the used Ti-MWW catalyst was regenerated by calcination in air at 773 K for 5 h and reused for the epoxidation of allyl alcohol, it maintained the conversion and did not lose Ti species even after five reaction–regeneration cycles, indicating Ti-MWW is stable against the Ti leaching.

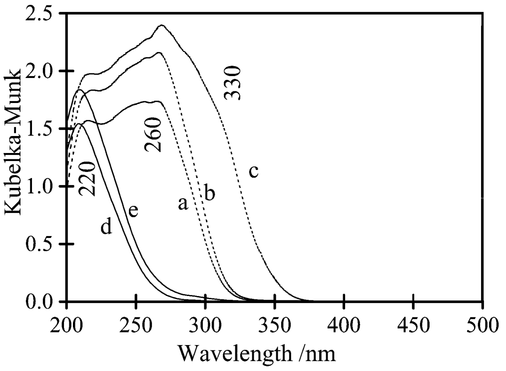

Fig. 2 UV-visible spectra of as-synthesized Ti-MWW with Si/Ti ratio of 45 (a), 30 (b), as b calcined at 823 K for 10 h (c), as a treated with 2 M HNO_3 and calcined (d), and as b treated with 2 M HNO_3 and calcined (e).

Since the incorporation of framework transition elements into the MWW structure is a relatively unexplored research area, this novel postsynthesis method is expected to be applicable to the preparation of other MWW metallosilicates as new catalytic materials.

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