Synthesis and catalytic performance of Ti-MCM-68 for effective oxidation reactions†

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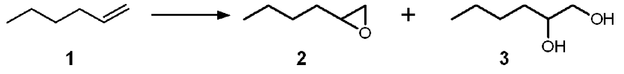
Microporous titanosilicate Ti-MCM-68 (Ti-MSE) was successfully synthesized by post-synthetic isomorphous substitution of Ti for Al and proved to be a high-performance catalyst, in particular showing superior performance to TS-1, Ti-BEA, and Ti-MWW for phenol oxidation using H_2O_2 as an oxidant.

It is well documented that titanosilicates with isolated tetrahedral Ti species in the zeolite framework are highly efficient for the selective oxidation of a wide range of organic substrates using hydrogen peroxide.[1–5] Compared to peracid or alkyl hydroperoxide, hydrogen peroxide is a preferable oxidant for liquid-phase reactions from the environmental points of view.[6] It is able to oxidize organic compounds with an atom efficiency of 47% and with the generation of water as the only theoretical coproduct. Therefore, the combined use of titanosilicate with hydrogen peroxide is a promising way to develop green and sustainable processes. In order to meet the requirements of various reactions and take advantage of various zeolitic crystalline structures, a variety of titanosilicates such as TS-1,[7] TS-2,[8] Ti-beta (Ti-BEA),[9–11] Ti-ZSM-12 (Ti-MTW),[12] Ti-ZSM-48,[13] Ti-mordenite (Ti-MOR),[14] Ti-SSZ-33,[15] Ti-ITQ-7 (Ti-ISV),[16] and Ti-MCM-22 (Ti-MWW)[17–19] have been prepared by the direct hydrothermal synthesis (HTS), direct dry-gel conversion (DGC),[11,19] and post-synthetic isomorphous substitution.[14,15,17,18] It is well known that TS-1 is an industrially useful titanosilicate and effective for processes such as propene epoxidation and phenol oxidation. Due to its ten-membered ring (10-MR) nature, however, the activity for epoxidation is significantly reduced when the substrate is cyclohexene or bulkier olefins. Ti-BEA with 3-D, 12-MR large pores shows higher activity than TS-1 when the substrate is cyclohexene. Wu *et al.* reported the high activity of Ti-MWW and a remarkable enhancement of activity for bulkier olefins by post-synthetic delamination of Ti-MWW.[20] However, both Ti-BEA and Ti-MWW show poor activities in phenol oxidation. Mesoporous titanosilicate such as Ti-MCM-41 containing numerous hydrophilic surface silanol groups suffers the serious disadvantage of Ti leaching in reactions.[5] It is therefore urgent to develop titanosilicate catalysts that are truly more efficient than TS-1 to meet the demands not only from petrochemical industries but also from fine chemical and pharmaceutical industries.

MCM-68 (MSE topology[21]) is a new type of multi-dimensional zeolite with a 12 × 10 × 10-MR pore system where a 12-MR straight channel intersects with two independent twisted 10-MR channels. This material also contains a supercage (18 × 12-MR) that is accessible only through the 10-MR pores. The synthesis and structural elucidation of this zeolite was first achieved by researchers from Mobil,[22,23] and various applications, such as alkylation catalysts[24,25] and hydrocarbon traps,[26] have been reported independently since then.

To date this zeolite has only been synthesized under hydrothermal conditions by using *N*,*N*,*N*′,*N*′-tetraethylbicyclo-[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium diiodide as an organic structure-directing agent (SDA). The gel composition window for the successful crystallization of pure MCM-68 is very narrow and the Si/Al ratio of the product is limited to 9–12. Although we have succeeded in deviating from this limitation very recently by utilizing the "steam-assisted crystalliztion (SAC)" method[27] to obtain a pure-silica version of the MSE topology,[28] direct crystallization of titanosilicate version is still difficult. If dealumination could be easy, however, it would be favorable that the typical MCM-68 contains a relatively large amount of aluminium sites, for the purpose of introducing a sufficient amount of Ti into the framework by isomorphous substitution.

We report herein the synthesis of Ti-MCM-68 (Ti-MSE) by the successful post-synthetic modification (dealumination by acid treatment followed by gas-phase Ti insertion using $TiCl_4$ as a Ti source) of Al-MCM-68 (Al-MSE), physicochemical characterization, and the catalytic performance for the epoxidation of olefins (eqn (1); see also ESI†) as well as the oxidation (hydroxylation) of phenol (eqn (2)) using hydrogen peroxide as an oxidant. Comparative investigations were mainly carried out for TS-1 and Ti-BEA.



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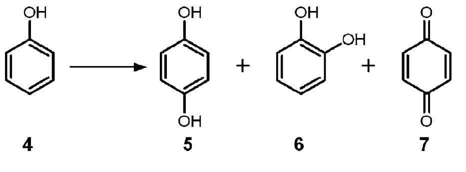

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† Electronic supplementary information (ESI) available: Experimental section, XRD, UV-Vis spectra, water adsorption isotherms, and some of the reaction tables. See DOI: 10.1039/b814286f

In order to generate the vacant site where Ti can be introduced, dealumination by acid treatment was carried out from calcined Al-MSE. The samples dealuminated with refluxing 6.0 M and 13.4 M nitric acid solutions were designated as deAl-MSE-A and deAl-MSE-B, respectively. It was confirmed by X-ray diffraction (XRD) that the framework structure was retained after acid treatment. Ti insertion was carried out into the frameworks of deAl-MSE-A and deAl-MSE-B samples to give titanosilicates Ti-MSE-A and Ti-MSE-B, respectively. These were further calcined at 600 °C and designated as Ti-MSE-A-cal and Ti-MSE-B-cal, respectively (for details see ESI†). After introducing Ti by post-synthetic treatment and the subsequent calcination, the framework structure was still unchanged as shown in Fig. S1. †It was also confirmed by UV-Vis spectroscopy that Ti was more efficiently introduced into the framework at a temperature as high as 600 °C. There was a tendency that the acid treatment with more concentrated nitric acid gave the sample with larger amount of Ti and the smaller amount of Al. In fact, Ti-MSE-B-cal contains more Ti and less Al than Ti-MSE-A-cal (Tables 1, 2, S2, and S3†). UV-Vis spectra indicate that titanosilicate MSE materials contain almost single tetrahedral sites (Fig. S2†).

Table 1 shows the result of epoxidation of 1-hexene (**1**) with hydrogen peroxide. The catalyst that was dealuminated with more concentrated acid (*i.e.* Ti-MSE-B-cal) gave higher conversion of **1** and higher turnover number (TON) than Ti-MSE-A-cal. It should be noted that the calcination step after introducing Ti into the framework significantly improved the catalytic performance (*e.g.* Ti-MSE-A *vs.* Ti-MSE-A-cal in Table 1). This was the common tendency that was also observed in all the following reactions and this effect was more prominent in the case of phenol oxidation. Water adsorption measurements suggested that this improvement was due to the increase in hydrophobicity (Fig. S3†). Ti-MSE was found to be more active than TS-1 and Ti-BEA, although the activity for olefin epoxidation did not exceed that of optimized Ti-MWW-type catalysts reported by Wu *et al.*[20] However, Ti-MWW was not suitable for phenol oxidation (*vide infra*).

The spent Ti-MSE-A was regenerated by calcination at 600 °C for 4 h. After a third repeated run, surprisingly unchanged catalytic performance was observed (Table S1†).

In the epoxidation of 2-hexene, Ti-MSE gave higher conversion, TON, and the efficiency of H_2O_2 utilization than TS-1 and Ti-BEA (Table S2†). It is interesting to note that the Ti-MSE showed high *cis* selectivity. We used 2-hexene with *cis* : *trans* ratio of 32 : 68 and obtained epoxide with a *cis* : *trans* ratio of 79 : 21–72 : 28 over the Ti-MSE. The same trend was observed for TS-1 and Ti-BEA, suggesting that *cis*-2-hexene is more reactive over the titanosilicates used. The absence of the interconversion of *cis*- and *trans*-epoxide was confirmed by carrying out the reaction starting from pure *cis*-2-hexene. Epoxide selectivities of >98% and *cis* : *trans* epoxide ratios of 100 : 0 were observed when started from *cis*-2-hexene for all titanosilicates listed in Table S2.† Conversion and TON were higher when the reaction started from *cis*-2-hexene. The high *cis*-selectivity has been common for TS-1 and Ti-BEA. Wu and Tatsumi reported the exceptional unique *trans*-selectivity of Ti-MWW that originated mainly from its sinusoidal 10-MR channels.[29] In this work, Ti-MSE proved to have common *cis*-selective nature like TS-1 and Ti-BEA.

Table S3† shows the catalytic results for the oxidation of cyclohexene. Ti-MSE gave higher conversion and epoxide selectivity than TS-1. In the case of Ti-MSE, it is easy for epoxide of 6-MR cyclic alkenes to diffuse in the 12-MR pores, whereas the molecules cannot easily enter into 10-MR pores of TS-1 making the reaction take place on the external surface. Ti-MSE showed higher TON and the efficiency of H_2O_2 utilization than Ti-BEA although conversion was lower than Ti-BEA. It is noteworthy that the Ti-MSE catalysts successfully suppressed the formation of hydrolysed product, 1,2-cyclohexanediol (see ESI for details†).

In the phenol oxidation, activity of Ti-MSE was much higher than other titanosilicates tested, and *para* selectivity of Ti-MSE was prominent (Table 2 and Fig. 1). The 12-MR of this catalyst should be suitable for the diffusion of a molecule of a single aromatic ring compound with the assistance of intersected 10-MRs. At the same time, there is no large cavity at the intersection. These factors may contribute to the high *para*-selectivity in the phenol oxidation. In sharp contrast, Ti-BEA and Ti-MWW, which are moderate to excellent catalysts for olefin epoxidation, proved to be very poor catalysts for phenol oxidation. Lack of robustness of the active sites in the Ti-BEA and Ti-MWW may be a factor. These results imply that Ti-MSE-type materials are near-almighty catalysts for the oxidation reactions that utilize H_2O_2 as an oxidant. Decrease in the yield after a long duration of the reaction, as shown in Fig. 1, may be due to polymerization such as tar formation.

In summary, a new type of microporous titanosilicate Ti-MSE was synthesized by post-synthetic isomorphous substitution of Ti for Al. The calcination after Ti-insertion significantly enhanced the catalytic performance of Ti-MSE mainly

Table 1 Oxidation of 1-hexene (**1**) with H_2O_2 over various titanosilicates[a]

				Selectivity (%)			H_2O_2	
Catalyst	Si/Al ratio[b]	Si/Ti ratio[b]	Conversion (%)	Epoxide **2**	Diol **3**	TON[c]	Conv. (%)	Eff. (%)[d]
Ti-MSE-A	480	95	28.8	>99	0	337	26.8	>99
Ti-MSE-A-cal	534	91	32.4	>99	0	359	27.5	>99
Ti-MSE-B-cal	979	67	55.7	>99	0	409	58.5	99
TS-1	∞	43	10.1	>99	0	54	16.5	61
Ti-BEA	∞	45	18.6	>99	0	104	31.0	60

[a] Reaction conditions: 1-hexene (**1**), 5.0 mmol; catalyst, 25 mg; solvent (CH_3CN), 5.0 ml; H_2O_2, 5.0 mmol; temperature, 60 °C; time, 2.0 h. [b] Determined by ICP analysis. [c] Turnover number (moles of [epoxide **2** + diol **3**] per mole of Ti site). [d] Efficiency of H_2O_2 utilization (moles of [epoxide **2** + diol **3**] per mole of H_2O_2 converted).

Table 2 Oxidation of phenol (**4**) with H_2O_2 over various titanosilicate[a]

Catalyst	Time/min	Si/Al ratio[b]	Si/Ti ratio[b]	TON[c]	Yield (%)[d]				*Para*/*ortho* ratio[e]	H_2O_2	
					Total	**5**	**6**	**7**		Conv. (%)	Eff. (%)[f]
Ti-MSE-A-cal	15	534	91	489	82.5	63.9	18.1	0.5	3.6	97.1	84.9
Ti-MSE-B-cal	10	979	67	307	69.1	55.5	13.6	0	4.1	100	69.1
TS-1	20	∞	43	166	57.5	29.1	27.2	1.2	1.1	90.0	63.9
Ti-BEA	5	∞	45	5	1.7	0.3	0.7	0.7	1.4	54.6	3.0
Ti-MWW	20	∞	42	11	4.0	0.6	2.1	1.3	0.9	55.0	7.2

[a] Reaction conditions: phenol (**4**), 21.25 mmol; catalyst, 40 mg; H_2O_2, 4.25 mmol; temperature, 100 °C. [b] Determined by ICP analysis. [c] Turnover number (moles of [hydroquinone (**5**) + catechol (**6**) + benzoquinone (**7**)] per mole of Ti site). [d] Product yield based on added H_2O_2. [e] Moles of [**5** + **7**] per mole of **6**. [f] Efficiency of H_2O_2 utilization (moles of [**5** + **6** + **7**] per mole of H_2O_2 converted).

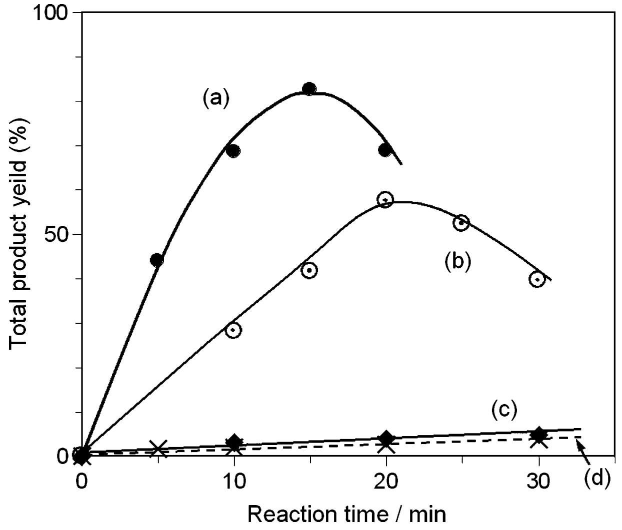

Fig. 1 Time-course of phenol oxidation using H_2O_2 as an oxidant and catalyzed by various titanosilicates. (a) Ti-MSE-A-cal, (b) TS-1, (c) Ti-MWW, and (d) Ti-BEA.

due to the increase in hydrophobic nature inside pores. Optimized Ti-MSE type catalyst showed superior performance to TS-1, Ti-BEA for olefin epoxidation, and to these two catalysts as well as Ti-MWW for phenol oxidation, using H_2O_2 as an oxidant. In particular, the use of calcined Ti-MSE for the latter reaction resulted in high yield and high efficiency of H_2O_2 utilization in a short reaction time, as compared to industrially useful TS-1. The high activity and *para*-selective nature of Ti-MSE were ascribed to higher diffusivity in 12-MR over 10-MR channels and the absence of a large cavity inside, respectively.

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