Synthesis of Ti-beta Zeolite with High Oxidation Activity by a Dry-gel Conversion Technique

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A new method of synthesizing zeolite Ti-beta has been developed based on a dry-gel conversion technique. The obtained Ti-beta samples exhibited high activity for oxidation of cyclohexene with H_2O_2, irrespective of the presence of sodium.

Camblor *et al.*[1] firstly reported the synthesis and oxidation activity of large-pore Ti-beta zeolite with low Si/Al ratio (≦ 150) and low zeolite yield. Because of a three-dimensional large-pore channel system, zeolite Ti-beta is more active than the medium-pore TS-1 catalyst for the oxidation of cyclic and branched alkenes and alkanes with aqueous hydrogen peroxide.[2] In contrast with TS-1, the crystallization of zeolite beta requires some Al as a framework constituent when tetraethylammonium (TEA) ion is used as structure-directing agent. This leads to a detrimental effect on the activity and selectivity of Ti-beta catalysts in the oxidations using H_2O_2. The Al-free beta structure is thought to be an unstable kinetic phase which crystallizes merely under very specific conditions.[3] To obtain Ti-beta possessing high oxidation activity in high zeolite yield, a variety of methods have been developed, such as cogel method,[4] seeding techniques,[5] and gas-solid[3,6] and liquid-solid[7] isomorphous substitutions as well as conventional hydrothermal syntheses.[1-3] Vapor-phase transport (VPT) has recently proved to be an efficient method for the crystallization of zeolites.[8-10] Recently, Rao and Matsukata[11] developed a similar new effective technique designated as dry-gel conversion (DGC) for the synthesis of zeolite beta with high SiO_2/Al_2O_3 molar ratio up to 900; zeolite beta of good quality was directly crystallized in the presence of TEAOH and steam at the temperature as high as 453 K. Here we report a new procedure based on the DGC method affording very high yield of Ti-beta zeolite with high oxidation activity.

Typically, Ti-beta was synthesized according to the following procedure: tetrabutyl orthotitanate (97 wt%) was added to distilled water and H_2O_2 (31 wt%) and the mixture was stirred at room temperature for 2 h. Anhydrous $NaAlO_2$ and NaOH was dissolved in TEAOH (40 wt% in water) at room temperature while stirring. After 1 h, the aluminum-containing solution was added to the peroxo titanate solution and stirring was continued for 1.5 h, and then was added fumed silica (Aerosil 200, TEAOH/SiO_2 = 0.44) under vigorous stirring. A clear homogeneous solution obtained after 2 h was heated to 353 K while stirring. When the gel became dry, it was ground into fine powder and transferred into a special autoclave with water in its bottom. The crystallization was carried out under different temperature programs (Table 1). Amorphous SiO_2-TiO_2 was prepared by drying and calcining a mixture of fumed silica, $NaAlO_2$, NaOH, peroxo titanate and water. TS-1 was synthesized by a method reported in the literature.[12]

As shown in Table 1, procedure A gave Ti-beta with the Si/Al ratio higher than 350 in >90% zeolite yield (based on total silica). X-ray powder patterns of sample 1 are typically shown in Figure 1. Starting with a higher temperature (procedure C), however, resulted in no crystalline products. We presume that the low temperature in the initial stage is favorable for the nucleation of Ti-beta and that the high temperature is beneficial to the crystal growth. It is noteworthy that aluminosilicate beta was synthesized at a higher temperature (353 K).[11] Procedure B was not advantageous owing to the low zeolite yield. We have found that when neither Al nor Na was added to the synthesis gel and no water was poured into the bottom of the autoclave, the products were always amorphous. It was reported that in the presence of alkaline cations the hydrothermal synthesis of Ti-beta gave rise to solids with low crystallinity.[1]

The Ti-beta zeolite calcined at 793 K displayed the typical UV-Vis spectroscopic features of Ti-containing zeolite: the narrow diffuse reflectance UV band at 205-225 nm attributed to isolated framework Ti.[1,5,7] Neither anatase nor rutile was detected in the calcined Ti-beta. By the treatment with 1 M H_2SO_4 at room temperature,[13] the content of Al and Na in the samples 1, 2 and 4 remarkably decreased, and the Ti content also slightly decreased (Table 1).

We studied cyclohexene oxidation with H_2O_2 over several catalysts obtained. As shown in Table 2, all of the calcined (H_2SO_4-unwashed) Ti-beta catalysts showed sizable catalytic

Table 1. Synthesis of Ti-beta zeolites[a]

Sample	Gel			Calcined				H_2SO_4-Washed		
(Procedure)	Si/Ti	Si/Al	Si/Na	Si/Ti	Si/Al	Si/Na	ZY[b]	Si/Ti	Si/Al	Si/Na
1(A)	30.4	331	98.4	31.3	352	94.4	95	36.6	652	533
2(A)	30.2	332	49.9	28.4	324	49.3	92	30.5	708	313
3(A)	58.3	332	98.3	55.5	463	93.3	93		n.d	
4(A)	89.4	330	97.2	78.4	378	93.5	90	92.4	682	630
5(B)	58.3	330	98.2	56.4	341	94.3	39		n.d.	
6(C)	58.3	330	99.0		amorphous				n.d.	
Amorphous	30.1	477	143.9		n.d.					
TS-1	79.0	>5000	∞		n.d.					

[a] Procedure A: at 403 K for 96 h, subsequently at 448 K for 18 h; B: at 403 K for 120 h; C: at 448 K for 24 -120 h. Elemental analysis was made by ICP. n.d.: not determined. [b] Yield of zeolite (wt%) based on silica.

Table 2. Activity of Ti-containing catalysts in the oxidation of cyclohexene with H_2O_2[a]

Sample	Calcined							H$_2$SO$_4$-Washed						
No.	H_2O_2/%		Yield[b]/	TON[c]	Selectivity/%[d]			H_2O_2/%		Yield[b]/	TON[c]	Selectivity/%[d]		
	Conv.	Selec.	%		EP	GLYS	CHO	Conv.	Selec.	%		EP	GLYS	CHO
1	100	100	30.4	98.1	1.2	95.9	2.9	98	96.1	28.6	106.9	0.1	97.2	2.7
2	76	91.2	21.0	61.9	22.7	72.1	5.2	72	97.4	21.3	66.7	0.3	95.0	4.7
3	54	98.7	16.2	97.5	19.5	75.8	4.7				n.d.			
4	47	71.4	10.2	80.9	12.3	82.2	5.5	26	98.8	7.8	72.5	0.5	96.4	3.1
5	78	95.0	22.5	117.5	25.8	70.0	4.2				n.d.			
Amorph[e]	8	32.9	0.8	2.5	9.9	83.0	7.1				n.d.			
TS-1	10	59.4	1.8	14.3	88.0	6.9	5.2				n.d.			

[a] Reaction conditions: catalyst 200 mg, cyclohexene 33 mmol, H_2O_2 10 mmol, methanol (solvent) 20 ml, temperature 333 K, duration time 3 h. [b] (total moles of products/moles of substrates) x 100%. [c] moles of products/moles of Ti in the catalyst. [d] EP: epoxide, GLYS: glycol and glycol ether, CHO: 2-cyclohexene-1-ol and 2-cyclohexene-1-one. [e] Amorphous TiO_2-SiO_2 (Si/Ti = 30.1).

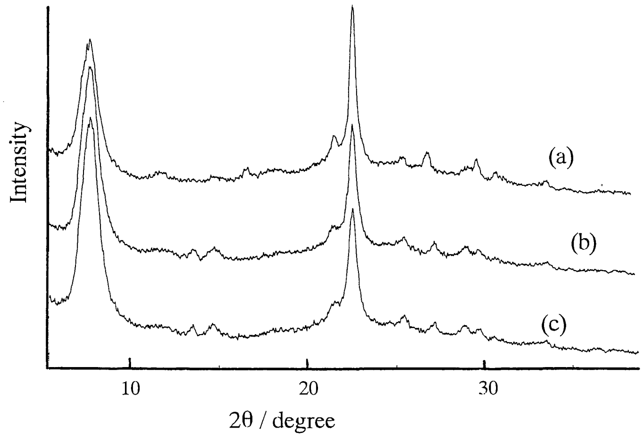

Figure 1. X-ray diffraction patterns of Ti-beta; (a) as-synthesized, (b) calcined at 793 K, (c) treated with 1 M H_2SO_4.

activity. Particularly, the performance of the calcined sample 1 was the best at the level of about 100% in the conversion and selectivity of H_2O_2 to the products. The relatively low turnover number for sample 2 may be due to the low Si/Na ratio in the gel, as was found for TS-1 by Khouw and Davis.[13] The activity of TS-1 for this reaction was negligible, probably because cyclohexene is too large to easily diffuse into the channel of TS-1. By washing with H_2SO_4, the turnover number (TON) of Ti-beta catalysts slightly increased for the samples 1 and 2; however, the yield of the oxidized products decreased except for the sample 2 since the Ti content was decreased. The presence of Al in these catalysts resulted in the production of glycols, but the catalysts with higher Na content exhibited higher selectivity to the epoxide. Without exception, the washed Ti-beta catalysts preferred glycols. Procedure A is advantageous considering the zeolite yield and its catalytic activity. It is important to note that the crystal size of the Ti-beta zeolites synthesized in the present way was in the range of 20-50 nm, suggesting that very small crystal size may be partially responsible for the high oxidation activity of Ti-beta. Larger crystals were formed when colloidal silica was used as a silica source.

In conclusion, we have developed an effective method for the synthesis of Ti-beta zeolite with high oxidation activity. It has been reported that the presence of alkaline metals, even in very small amounts, retards the catalytic activity of TS-1, suggesting that alkaline metal ions present in the synthesis gel prevent the insertion of titanium into the silicalite framework.[12,14] Our results show that the presence of small amount of Na is not a real hindrance to the insertion of Ti into beta framework but a requisite to the crystallization of Ti-beta. Furthermore, the presence of Na in small amounts has no significant effects on the catalytic activity for alkene oxidation.

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