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# Synthesis and morphology research of framework Ti-rich TS-1 containing no extraframework Ti species in the presence of CO<sub>2</sub>



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## ABSTRACT

A new method to synthesis TS-1 has been developed using the carbon dioxide ( $CO_2$ ) as an alkalinity regulator that resulted in the increased framework Ti contents. The prepared catalyst had a Si/Ti ratio as low as 40 in contrast to the ratio of 56 prepared through conventional synthesis. The twin crystals with the length of 2  $\mu$ m were formed via introduction of CO<sub>2</sub>. The catalytic activity of TS-1 is remarkably enhanced compared with the conventional synthesis.

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Ti-silicalite-1 (TS-1) is a very active and versatile oxidation catalyst in particular using diluted H<sub>2</sub>O<sub>2</sub> as oxidant in various catalytic oxyreductive processes, such as selective oxidation of olefins to epoxies, hydroxylations of aromatics, and ammoximation of cyclohexanone [1]. The major problem often encountered is during the synthesis of TS-1, the presence of anatase reduces significantly the catalytic performance of TS-1, due to its promotion to the decomposition of  $H_2O_2$  [2], and the maximum amount of Ti<sup>4+</sup> that can be incorporated in framework positions in TS-1. It is known that the more framework Ti, the TS-1, contains the higher catalytic performance it would present, e.g. Weibin Fan and co-workers [3] have reported a new route to synthesis TS-1 using (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> as a crystallization-mediating agent, by which the framework Ti content had been significantly improved without forming extraframework Ti species. Also, it is well-known, zeolites with wellcontrolled morphology are of great importance as devices and catalysts in many applications [4-6]. However, most TS-1 materials reported show poor crystal morphologies, mainly sphere-like, and morphology modulation by adjusting alkalinity of the gel is absent. Therefore, developing synthetic strategies to regulate crystal size and morphology of TS-1 with more framework Ti is more concerned. Herein, we present a facile method for preparation of framework Ti-rich TS-1 in the presence of CO<sub>2</sub>, with the controllable crystal size and morphology.

Synthesis of TS-1 via various procedures—Procedure A. In a conventional synthesis, the molar composition of the reaction mixture was SiO<sub>2</sub>: 0.026 TiO<sub>2</sub>: 0.40 TPAOH: 4.39 H<sub>2</sub>O<sub>2</sub>: 47 H<sub>2</sub>O, 8 g of TPAOH and 5 g of TEOS were dissolved in 5 g of deionized water, and 0.2 g TBOT dissolved in 11 g of 30% aqueous H<sub>2</sub>O<sub>2</sub> solution was added dropwise. After stirring at room temperature for 24 h, the resulted gel was

transferred into a 50 ml Teflon-lined autoclave and subjected to a hydrothermal crystallization at 453 K for 3 days. Finally, the solid product was recovered by centrifugation, washed, dried, and calcined at 823 K for 6 h. This specimen is denoted by TS-1-a.

Procedure B. In contrast to Procedure A, after the resulted gel was transferred into a Teflon-lined autoclave, the autoclave was pressurized with  $CO_2$  up to comfortable pressure (1 M, 2 M, 3 M, 5 M) with high-pressure liquid pump under stirring, agitating for 5 min and a certain amount of  $CO_2$  was added in the gel, then the pressure was released.



Fig. 1. XRD patterns of (a) TS-1-a, (b) TS-1-b, (c) TS-1-c, (d) TS-1-d, and (e) TS-1-e.

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The corresponding pHs of gel are 10.7, 9.5, and 8.8, and when the  $CO_2$  pressure is 5 M, pH cannot be determined due to the gel solidifying. The following treating procedure was in accord with above for TS-1-a (without  $CO_2$ ), and these specimens are denoted as TS-1-b (1 M), TS-1-c (2 M), TS-1-d (3 M), and TS-1-e (5 M).

The characterization and catalytic measurements of samples are described in Supporting Information.

As it is shown in Fig. 1 of the XRD patterns, all the specimens are crystalline with a set of diffraction peaks at  $2\theta = 7.9^{\circ}$ ,  $8.8^{\circ}$ ,  $23.1^{\circ}$ ,  $23.9^{\circ}$  and  $24.4^{\circ}$ , indicating the characteristic of MFI topological structure [7]. It is clear that the crystallinity of materials was promoted along with the increasing addition of the CO<sub>2</sub> (from TS-1-a to TS-1-e). On the other hand, the crystallinity varies little when the amount of the CO<sub>2</sub> arrived 5 M and more (not reported here), which is probably caused by the saturation dissolvation of CO<sub>2</sub> in the gel.

To certify the morphology of prepared materials, SEM micrographs were taken and shown in Fig. 2. Generally speaking, from TS-1-a to TS-1-d, the regular spheroid morphologies are popular with an approximate diameter of 400–800 nm, and particle sizes become larger upon the increasing amount of the CO<sub>2</sub>. In TS-1-e, almost all crystals are double interpenetrated hexagonal with a twinning angle close to 90° in approximate dimensions of  $1 * 0.3 * 2 \mu m$  (a \* b \* c). We believe that the addition of CO<sub>2</sub> to the synthesis gel lead to the changes of morphology and crystal size as a result of decreasing the alkalinity of the crystallization mixtures. It is well proved that more nuclei are formed in higher alkalinity in the preparation of MFI type silicalite-1 [8], which results in the formation of smaller crystals. While CO<sub>2</sub> was used as the alkalinity regulator, the TS-1 formation would exhibit a quite different behavior. We speculate the twin crystal formation mechanism as follows: with the increased addition of CO<sub>2</sub> (TS-1-e), the prepared gel



Fig. 2. SEM micrographs of (a) TS-1-a, (b) TS-1-b, (c) TS-1-c, (d) TS-1-d, and (e) TS-1-e.



Fig. 3. The FT-IR spectra of (a) TS-1-a, (b) TS-1-b, (c) TS-1-c, (d) TS-1-d, and (e) TS-1-e.

Fig. 4. The UV-vis spectra of (a) TS-1-a, (b) TS-1-b, (c) TS-1-c, (d) TS-1-d, and (e) TS-1-e.

was solidified, the massive dry-gel aggregation was formed, and the dissociation and rearrangement/restructuring of this initial solid gel resulted in a secondary gel [9,10]. In crystallization process, nucleation and crystal growth occur at the interface of gel particles and liquid, TPA<sup>+</sup> diffuses from solution to the crystal/gel interface, inducing the crystal growth which was preferentially along certain planes, finally gave twin crystals.

The infrared spectra of calcined specimens were shown in Fig. 3, and the MFI structure was certified as well. The peak at 960  $\text{cm}^{-1}$  is often referred to Ti-O-Si band and is taken as good indication of titanium substitution into the zeolite framework [11]. The bands at 550 and 800 cm<sup>-1</sup> are assigned to  $\delta(Si - O - Si)$  and  $\nu(Si - O - Si)$ , respectively. The relative intensity of the 960–800 cm<sup>-1</sup> peak has often been used to estimate the titanium incorporation in TS-1 specimens [12]. In another word, the larger the relative intensity (I960/I800) presents, the higher framework Ti contains. It is clear in Table 1 that the framework Ti content is the highest in the TS-1-d and TS-1-e, which indicates that CO<sub>2</sub> helps in increasing the amount of Ti incorporated into framework of TS-1. It is also in agreement to the results of ICP-AES (characterizations of Ti contents in the specimens). From data of IR (Table 1), we can find out that the TS-1-d and TS-1-e prepared is with highest framework Ti content. From Fig. 2 and Table 1, it is in accordance with the results reported by Cundy et al. that incorporation of more Ti into the framework resulted in the formation of larger crystals [13].

Fig. 4 shows the UV–vis spectra of the five specimens. All specimens show a main absorption around 210 nm, substantiating the existence of framework Ti [14]. The band at 250–280 nm is considered as a charge-transfer process in isolated [TiO<sub>4</sub>] or [HOTiO<sub>3</sub>] units, which are assigned to the amorphous Ti species. The absorption at 330 nm originated from the anatase phase. Comparing the spectrum of TS-1-a, d with those of b–e, it is obvious that extraframework Ti species are present in the specimen b–e, especially anatase TiO<sub>2</sub>. Although TS-1-a and d cannot be

Table 1	
The chemical compositions and values of I960/I804 of specimens.	

Specimens	Molar ratio Si/Ti in TS-1	1960/1800
TS-1-a	56	1.7
TS-1-b	44	1.8
TS-1-c	40	1.7
TS-1-d	43	2.0
TS-1-e	40	2.0

Ratios I960/I800 for the 960 and 800 cm<sup>-1</sup> absorption bands in the FT-IR spectra of specimens.

excluded the possibility of the presence of amorphous Ti species, it is undoubtedly accepted that most of the Ti species present in the specimens have been incorporated into the framework. The sample a has the lowest extraframework Ti species, because optimal alkalinity can inhibit extraframework Ti species [3]. As for sample d, we speculate that it is caused by the combined action of alkalinity and CO<sub>2</sub> pressure. We have made the relevant experiment about the effect of CO<sub>2</sub> pressure. When the autoclave was pressurized with CO<sub>2</sub> up to comfortable pressure (6 MPa, 8 MPa, 10 MPa, 15 MPa) with high-pressure liquid pump, it is obvious that extra-framework Ti species are present in the specimens. It showed that the greater pressure has a negative effect on inhibiting extraframework Ti species. So the sample TS-1-e (5 M) has more extraframework Ti species.

The catalytic activities of the specimens from TS-1-a to TS-1-e have been evaluated by the phenol hydroxylation with hydrogen peroxide and the result is listed in Table 2. The catalytic performance of TS-1-a is the worst, while the catalytic ability of TS-1-d is the best. It is likely that the framework Ti content in TS-1-d is highest. Although the framework Ti in TS-1-e is similar with TS-1-d, due to the higher concentration of anatase TiO<sub>2</sub>, as well as the larger size of crystals, the catalytic performance of TS-1-e is reduced.

In the present work, we have characterized that through alkalinity reduction of the initial gel, not only promotion on the crystallization of TS-1, favorable incorporation of Ti into the framework and altering morphology of the crystal, from small spheroid to larger twin crystals were achieved, but also enhancing the catalytic activities of TS-1. The optimum cooperation of alkalinity and CO<sub>2</sub> pressure (TS-1-d) can inhibit extraframework Ti species, in particular the formation of anatase TiO<sub>2</sub>, the catalytic activity of the specimen TS-1-d is the best. We have provided a promising method to study the positive effect of alkalinity for the synthesis of transition metal-rich zeolite.

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Comparison of catalytic performances over specimens TS-1-a-TS-1-e.

Specimens	Conversion (mol%)	Selectivity	Selectivity (mol%)		
	PHE	CAT	HQ	PBQ	
TS-1-a	19.66	51.22	48.63	0.15	
TS-1-b	22.80	44.06	55.28	0.66	
TS-1-c	21.23	46.03	52.50	1.47	
TS-1-d	26.10	48.11	51.78	0.11	
TS-1-e	20.88	48.63	50.64	1.73	

Reaction conditions: Phenol/ $H_2O_2 = 2/1$  (molar ratio); catalyst/phenol = 10% (weight ratio); temp = 80 °C; time = 5 h; acetone as a solvent. PHE = phenol; CAT = catechol; HQ = hydroquinone; PBQ = para-benzoquinone.



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