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Synthesis and morphology research of framework Ti-rich TS-1 containing no extraframework Ti species in the presence of CO_2

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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 μm were formed via introduction of CO_2. The catalytic activity of TS-1 is remarkably enhanced compared with the conventional synthesis.

Ti-silicalite-1 (TS-1) is a very active and versatile oxidation catalyst in particular using diluted H_2O_2 as oxidant in various catalytic oxy-reductive 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^{4+} 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 $(NH_4)_2CO_3$ 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 well-controlled 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_2, 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_2: 0.026 TiO_2: 0.40 TPAOH: 4.39 H_2O_2: 47 H_2O, 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_2O_2 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.

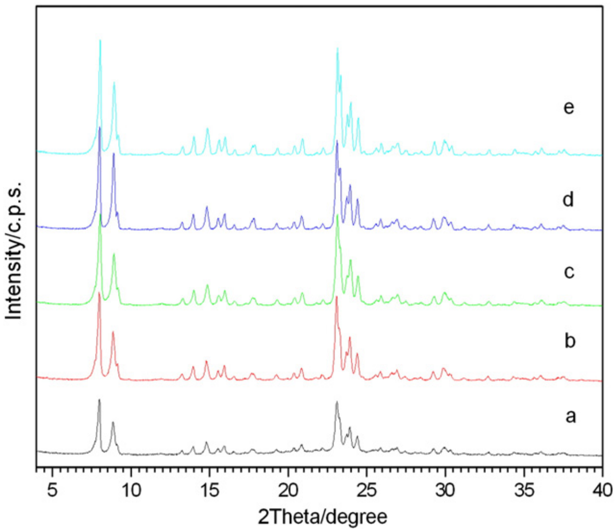

Fig. 1. XRD patterns of (a) TS-1-a, (b) TS-1-b, (c) TS-1-c, (d) TS-1-d, and (e) TS-1-e.

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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 $2\theta = 7.9°$, 8.8°, 23.1°, 23.9° and 24.4°, 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_2 (from TS-1-a to TS-1-e). On the other hand, the crystallinity varies little when the amount of the CO_2 arrived 5 M and more (not reported here), which is probably caused by the saturation dissolvation of CO_2 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_2. In TS-1-e, almost all crystals are double interpenetrated hexagonal with a twinning angle close to 90° in approximate dimensions of $1 * 0.3 * 2$ μm ($a * b * c$). We believe that the addition of CO_2 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_2 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_2 (TS-1-e), the prepared gel

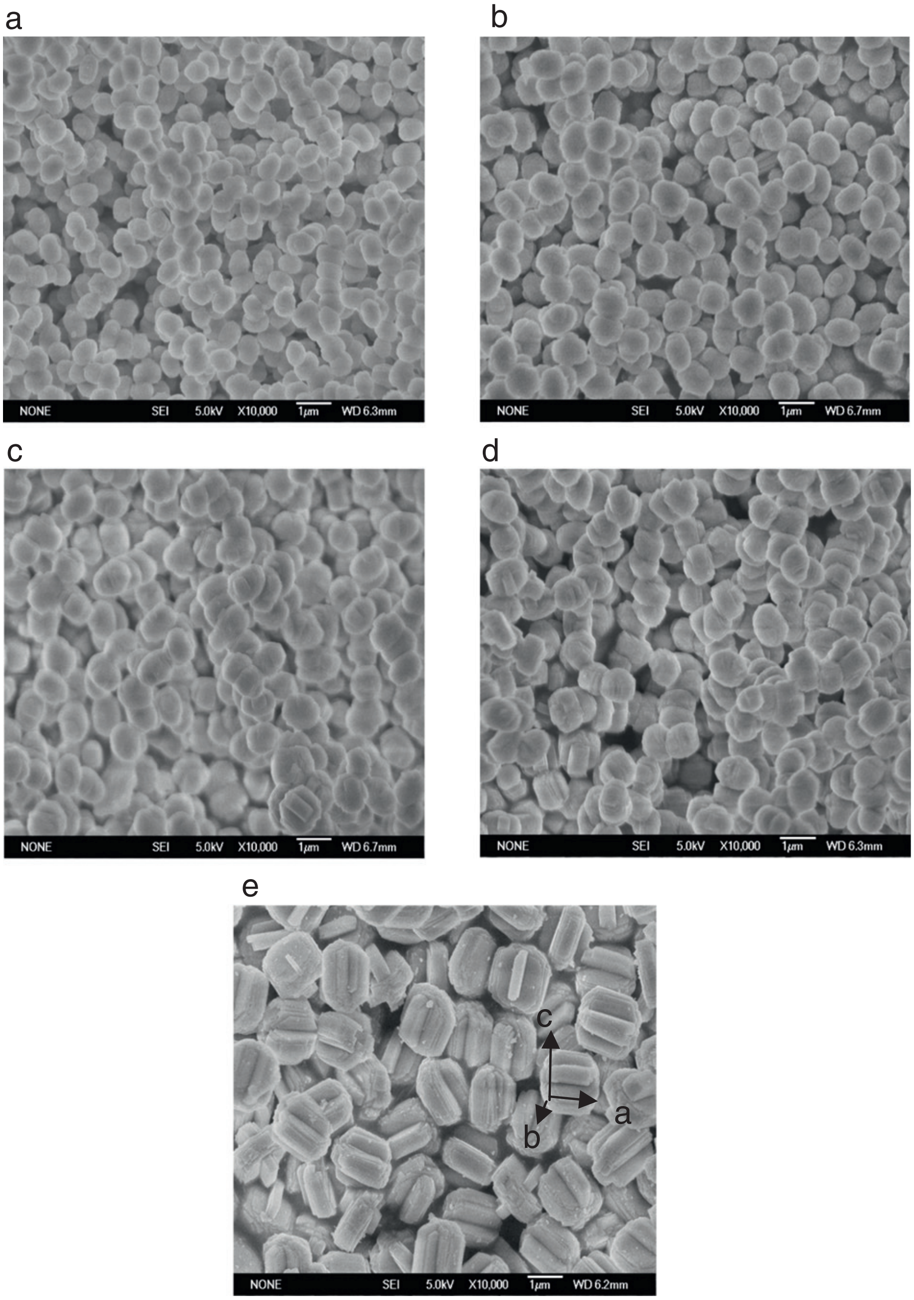

Fig. 2. SEM micrographs of (a) TS-1-a, (b) TS-1-b, (c) TS-1-c, (d) TS-1-d, and (e) TS-1-e.