

Hydrothermal Synthesis of Hexamethyleneimine-templated TS-1 Supported by Active Seeds

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The titanosilicate of TS-1 is skillfully hydrothermally synthesized from an inorganic silica source and a cheaper structure-directing agent (SDA) of hexamethyleneimine (HMI) with the assistant of active seeds of TS-1 precursor.

The discovery of MFI-type titanosilicate (TS-1) has opened up new environmentally benign oxidation processes. TS-1 effectively catalyzes the selective oxidation of various organic substrates under mild conditions with H_2O_2 as an oxidant.¹ Particularly, the TS-1/ H_2O_2 catalytic system has been commercialized successfully in the ammoxidation of cyclohexanone by Sumitomo and SINOPEC in 2003. Moreover, BASF has announced that an innovative process will be established in 2008 for the clean synthesis of propylene oxide with a scale of 300,000 metric tons.

Regardless of its importance as well as potential applications, it should be noted that TS-1 is facing a dilemma that its too high manufacturing cost may retard more extensive industrializations. Many endeavors thus have been made to synthesize cheaper TS-1 with good cost performance in last two decades. The synthesis and characterization of TS-1 will still be challenging and attractive research subjects.

Catalytically effective TS-1 usually requires stringent crystallization conditions. It first prefers a synthetic gel free of any alkali-metal cations in order to avoid condensing Ti species to insoluble oxides in the gel and poisoning the Ti active sites as well.¹ Secondary, TS-1 favors an organic Si source of tetraethoxysilane (TEOS). A troublesome step is then required to eliminate the ethanol formed from the hydrolysis of TEOS. Moreover, it requires an extremely expensive quaternary ammonium salt, tetrapropylammonium hydroxide (TPAOH) which serves as SDA and mineralizer and supplies also a basic media when without alkali cations. These strict conditions make the manufacturing cost of TS-1 pile up, which may hinder and/or delay its further industrial applications.

It is thus a great challenge to find new synthesis methods for preparing TS-1 in a cheaper way. Since the high price of TS-1 is mainly due to employing expensive alkali-free SDA of TPAOH, it is very desirable to look for a cheaper substitute. TPA halides have been shown to be substitutable SDAs for the crystallization of TS-1 when being used together with aqueous ammonia.^{2,3} The other approaches have been the coemployment of TPABr and a nonalkali base of methylamine⁴ or hexanediamine.⁵ The combination of tetraethylammonium chloride or tetrabutylammonium chloride with aqueous ammonia has also been reported.⁶ On the other hand, TS-1 is synthesized in fluoride media with TPABr⁷ or amines⁸ as SDAs. No matter what modification has been attempted, the key SDAs have always been the quaternary ammonium salts in all cases. New synthesis systems for TS-1 are thus still urgently expected though using budget amine SDAs instead

of costly quaternary ammonium ions.

We present here a new approach to the synthesis of TS-1 in the absence of alkali ions from a cheaper SDA of HMI and a fumed silica source with the supporting of active seeds of TS-1 precursor. To the best of our knowledge, there have been no reports on the synthesis of TS-1 using such a secondary amine solely, although HMI is well known to be useful in the synthesis of MWW-type^{9,10} and UTM-1 zeolites.¹¹

A typical synthesis of TS-1 with HMI was as follows. First, the seed solution was prepared by suspending the white cake of incompletely crystallized TS-1 precursor after heating the gel ($1SiO_2:0.02TBOT:0.15TPAOH:35H_2O$) at 443 K for 12 h. Tetrabutyl orthotitanate (TBOT) was carefully hydrolyzed in an aqueous HMI solution to obtain a clear solution, into which the fumed silica (Cab-o-sil M5) and the above-mentioned seed solution of TS-1 precursor were then added. The mixture was stirred continuously to obtain a homogeneous gel with a molar composition of $1SiO_2:0.01-0.05TBOT:1HMI:12H_2O$. The amount of seed added corresponded to a proportion of 5 wt % dry silica relative to the total amount of silica in the gel.

By crystallizing the above synthetic gels in autoclaves under autogeneous pressure and rotation conditions at 443 K for 6 days, highly crystalline TS-1 samples with various Ti contents were obtained (Figure 1). This is the first example of TS-1 synthesized only by using a secondary amine as an SDA.

A detailed investigation of crystallization conditions indicated that the involvement of so-called "active" seeds of TS-1 precursor was essential for the crystallization (Table 1 and Supporting Information).¹² Highly crystalline TS-1 was readily synthesized with the presence of seeds of TS-1 precursor, while only amorphous product was obtained in the absence of

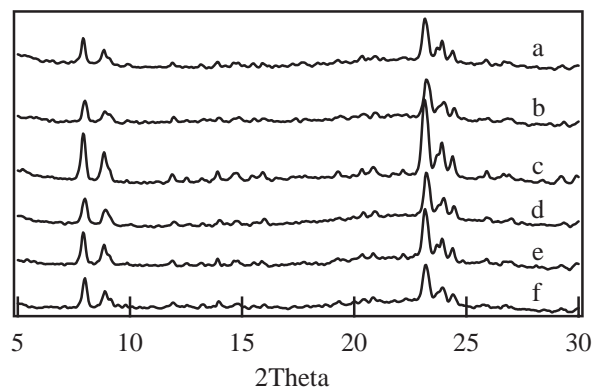


Figure 1. XRD patterns of as-synthesized TS-1 crystallized at a Si/Ti molar ratio of 20 (a), 30 (b), 40 (c), 50 (d), 70 (e), and 100 (f). Crystallization conditions: $1SiO_2:0.01-0.05TBOT:1HMI:12H_2O$; 443 K; 6 days under rotation; with 5 wt % TS-1 precursor suspension.

Table 1. Effects of various conditions on the crystallization of TS-1 in the HMI system^a

No.	Si source	Seed	Product
1	Fumed silica	TS-1 precursor ^b	Crystalline TS-1
2	Fumed silica	no	Amorphous
3	Fumed silica	TS-1 precursor ^c	Amorphous
4	Fumed silica	TS-1 precursor ^d	Amorphous
5	Fumed silica	TS-1 precursor ^e	Poor TS-1
6 ^f	Fumed silica	no	Amorphous
7	TEOS	TS-1 precursor ^b	Amorphous
8	Colloidal silica	TS-1 precursor ^b	Poor TS-1
9	Particle silica gel	TS-1 precursor ^b	Poor TS-1

^aGel composition, 1SiO₂:0.02TBOT:1HMI:12H₂O; crystallization, 443 K, 6 days. ^b5 wt % TS-1 precursor suspension. ^c5 wt % TS-1 precursor dried at 373 K. ^d5 wt % TS-1 precursor calcined at 773 K. ^e5 wt % TS-1 precursor silylated with Me₂SiCl₂ (suspension). ^fA same amount of TPAOH as that in 5 wt % TS-1 precursor was added.

seeds (Nos. 1 and 2). When the TS-1 precursor was centrifuged and further dried at 373 K or calcined at 773 K to obtain a powder, only amorphous products were produced in the synthesis of HMI system with these kinds of seeds (Nos. 3 and 4). Moreover, when the TS-1 precursor was silylated with dichlorodimethylsilane (Me₂SiCl₂), but without drying or calcination, this organofunctionalization made the seeding effect retard greatly, leading to a TS-1 with an extremely poor crystallinity (No. 5 and Figure 1S).¹² To exclude the possibility of structure-directing effect of TPA⁺ cations within the TS-1 precursor seeds, the synthesis has been tried by adding a same amount of TPAOH as that in seeds. Such an amount of TPA⁺ was not enough to lead to an effective crystallization even with the coexistence of HMI, but only resulted in an amorphous product (No. 6).

Above results indicate that a synergism between the SDA effect of HMI and the seeding effect of precursor is important to cause a full crystallization of TS-1. Furthermore, it seems that to initiate the nucleation and then the crystallization in the HMI system, the TS-1 precursor seeds should be active, that is, possess at external surface the active silanol groups available for interaction with HMI and silica source.

To synthesize highly crystalline TS-1, the HMI synthetic system preferred fumed silica to the other Si sources of TEOS, colloidal silica and particle silica gel (Nos. 7–9, Figure 2S).¹² Supported by the active seeds of precursor, high quality TS-1 products were prepared readily at optimized conditions of HMI/SiO₂ of 1.0, H₂O/SiO₂ of 12 and crystallization time of 6 days at 443 K (Figures 3S–5S).¹²

TS-1 structurally directed by HMI exhibited aggregated particles (0.5–1.0 μm) consisting of plate-shaped primary crystals, which was much larger than that of conventional TS-1 in uniformly round shape (0.2–0.3 μm) (Figure 2). The larger crystal size of the former is presumably attributed to less nucleation centers and lower crystallization rate in HMI with a weaker basity in comparison to more basic TPAOH.

TS-1 prepared with HMI contained essentially the tetrahedral Ti species in the framework as evidenced by the 220-nm adsorption and 960-cm⁻¹ stretching band in UV–visible and IR spectra, respectively (Figures 6S and 7S).¹² Because of its too large crystal size resulting in much slower diffusion rates for both the substrates and products within its confined channels, TS-1–HMI was reasonably somewhat less active than conventional TS-1–TPA. However, it did serve as an active catalyst

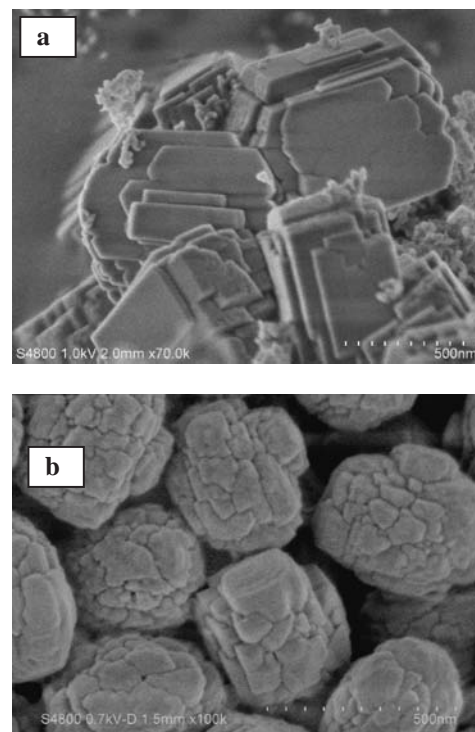


Figure 2. Representative SEM images of TS-1 synthesized with HMI (a) and TPAOH (b) as an SDA. The scale bar was 500 nm in both cases.

in the epoxidation of 1-hexene with H₂O₂ (Table S1).¹²

As a result, a new method has been developed for synthesizing TS-1 in a cheaper way from a secondary amine of HMI and a fumed silica source with the assistant of active seeds of TS-1 precursor. This strategy may be applicable to the synthesis of metallosilicates with the MFI structure or others.

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