



# Anionic polymer as a quasi-neutral medium for low-cost synthesis of titanosilicate molecular sieves in the presence of high-concentration alkali metal ions



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## ABSTRACT

Titanosilicate molecular sieve (TS-1) is an important commercial catalyst for green production of oxy-functionalized chemicals such as alcohols, ketones, epoxides, and oximes. Active TS-1 can normally be achieved in the synthetic media strictly free of alkali metal cations (e.g., Na<sup>+</sup> and K<sup>+</sup>). This condition severely raises the purity demands of starting reagents, which greatly increases the production cost. Herein, we developed a method to achieve highly active titanosilicates in the presence of high-concentration alkali metal cations using anionic polymer-based quasi-neutral media. This synthetic route could effectively inhibit the adverse influence of alkali metal cations on the incorporation of active titanium(IV) sites into the framework of titanosilicate, directly affording the maximal framework titanium content (2.0 wt.%) with almost 100% yield. This development shows a great commercial potential and opens the possibility of preparing silica-based molecular sieves/zeolites in non-fluoride neutral media.

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## 1. Introduction

Increasing attention has been paid to develop sustainable processes to produce chemicals without wastes and by-products [1,2]. Notably, the discovery of effective catalysts that lead to the desired product as directly as possible is a research focus in this field [3,4]. One of the greatest breakthroughs in the last few decades is the discovery of TS-1 titanosilicate [5], a titanium-containing MFI-type (MFI is a zeolite framework code by International Zeolite Association) silica zeolite. TS-1 exhibits high activity, selectivity, and atomic efficiency (about 47%) for selective oxidation of industrially important organic compounds such as alkanes [6,7], alkenes [8,9], alcohols [10] and many others [11–13] in the presence of H<sub>2</sub>O<sub>2</sub> with only water as the co-product. The eco-friendly processes based on TS-1/H<sub>2</sub>O<sub>2</sub> have been successfully applied to industry-scale production of diphenols from phenol, cyclohexanone oxime from cyclohexanone, and propylene oxide

from propylene [14,15]. It has been proven that the catalytic activity of TS-1 mainly depends on the framework Ti content [5,7–16,6]. However, the synthesis of titanium-rich TS-1 is still difficult even in the laboratory, because bigger ion radius of Ti than that of silicon [17–20] leads to the difficulty in the incorporation of Ti into the molecular sieve framework [21]. In practical synthesis process, many factors could influence the incorporation of Ti into the titanosilicate framework, including the poisoning effect of alkali metal cations, formation of TiO<sub>2</sub> tiny particles before the crystallization, crystallization temperature, category and amount of template, pH value, agitation, and so on [5,10,22]. Among them, the presence of alkali metal cations and the formation of TiO<sub>2</sub> are the most difficult factors to control. To prevent the formation of TiO<sub>2</sub> tiny particles, some effective techniques have been developed by either carefully controlling the hydrolysis process of the titanium source or changing the titanium source [23–26]. For the adverse influence of alkali metal cations, unfortunately, no effective strategy has been discovered so far. In fact, scientists and engineers have spent great efforts on this issue and finally made a conclusion that active TS-1 can only be obtained from the medium in the presence of a very small amount of alkali metal cations (<0.1 wt.%) [23,27–30]. Although some methods were used to synthesize highly crystalline TS-1 in the presence of high-concentration alkali

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metal cations, the catalytic activity of synthesized TS-1 was not tested or very low [31]. In the current methods, synthetic systems without alkali metal cations are needed to produce TS-1 and even other titanosilicates [32–38]. Such methods dramatically increase the production cost of TS-1 due to the requirement of expensive high-purity starting materials free of alkali metal cations. Meanwhile, these methods show significant decreases of the product activity, yield, and reproducibility on account of inevitable contamination of alkali metal cations especially in industrial processes. Thus, it is highly desired and significant to develop an effective way to synthesize TS-1 in the presence of alkali metal cations from both academic and industrial point of view.

Davis and co-workers studied the effect of alkali metal cations on the synthesis of TS-1 in detail [28], and they found that a strong base, e.g. NaOH, was required to introduce sodium cation into TS-1 by reacting with silanols or breaking Si–O–Ti bonds, while a neutral NaNO<sub>3</sub> solution could not afford. This observation suggests that the synthesis under a neutral condition is a possible route to produce highly active TS-1 in the presence of alkali metal cations. Thus, we firstly tried to synthesize TS-1 in the presence of alkali metal cations under a neutral fluoride medium [39] that was the only neutral synthetic system discovered for the preparation of silica-based molecular sieves so far. But, we could not obtain high-performance TS-1 due to big size of the TS-1 crystals obtained as well as adverse effect of fluoride on the activity of TS-1 [40]. In our previous studies [41], we discovered that the crystalline zeolites could be synthesized in a high-concentration anionic polymer medium with a pH value of about 7. Herein, we employed this quasi-neutral medium to challenge the synthesis of titanosilicate TS-1 in the presence of high-concentration alkali metal cations.

## 2. Experimental

### 2.1. Synthesis and characterization of TS-1

Firstly, titanium tetra-*n*-butoxide was added to H<sub>2</sub>O<sub>2</sub> aqueous solution to form a stable Ti source of Ti-peroxo complex. Then, an aqueous solution of tetrapropylammonium hydroxide containing alkali metal cations (Na<sup>+</sup> and/or K<sup>+</sup>) was added into above Ti solution followed by the addition of tetraethylorthosilicate under stirring. After 0.5 h, the resultant solution was heated to 353 K to evaporate alcohol generated during the hydrolysis of the Ti and Si precursors. After completely evaporating alcohol, the clear solution was cooled down, and anionic polymer poly(acrylic acid) (PAA) was added. The molar composition of the final mixture was given in Table 1. The final mixture was transferred into an autoclave and treated at 443 K for 2 days. The solid product was centrifuged, washed with distilled water, and dried at 373 K. The obtained product was treated under the calcination at 823 K for 6 h to remove the organic templates. The preparation of TS-1 under conventional synthetic route without PAA was also conducted as the control experiment.

Powder X-ray diffraction (PXRD) measurements were performed on a Bruker Powder D8 Advance diffractometer at 40 kV

and 40 mA using CuK $\alpha$  radiation ( $\lambda = 1.5418$  Angstrom). Diffuse reflectance ultraviolet–visible (DRUV/Vis) spectra were recorded on a SHIMADZU UV-2450 spectrophotometer at 298 K using BaSO<sub>4</sub> as a reference. IR spectra were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer. The samples were dried at 473 K for 4 h before the DRUV/Vis and IR measurements. Raman spectra were obtained using a Thermo SCIENTIFIC DXR Raman microscope with an excitation wavelength at 532 nm. Elemental analyses (Si, Ti, Na and K) were performed on an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer ICP Optima 2000DV). Field-emission scanning electron microscope (SEM) images were obtained on a JEOL JSM-7600F microscope operated at 5 kV. Transmission electron microscopy (TEM) observations were performed on a JEOL JEM-1400 TEM microscope working at 100 kV. All samples subjected to TEM measurements were dispersed in ethanol ultrasonically and then dropped on copper grids.

### 2.2. Catalytic reactions

Oxidation reactions were performed in a 20 mL glass reactor immersed in a temperature-controlled oil bath in the presence of H<sub>2</sub>O<sub>2</sub> (35 wt.% in water). The typical reaction mixture consisting of TS-1 catalyst (25 mg) in methanol (5 mL) with 1-hexene (5 mmol) was first placed in the temperature-controlled oil bath for 10 min to reach the desired temperature, and then added with H<sub>2</sub>O<sub>2</sub> (5 mmol) to start the reaction. Samples were taken at various times using a syringe, and analyzed by gas chromatography. The amount of unconverted H<sub>2</sub>O<sub>2</sub> was determined by titrating with Ce(SO<sub>4</sub>)<sub>2</sub> aqueous solution (0.25 M).

## 3. Results and discussion

### 3.1. Synthetic conditions and compositions of final TS-1 samples

The synthetic conditions and compositions of the final TS-1 samples are summarized in Table 1. The yield of TS-1 was almost 100% in nearly neutral PAA medium (pH = 7.4), but only ~70% in conventional basic condition (pH = 12.3). Importantly, the titanium content of the final TS-1 products was not affected by alkali metal cations in the PAA medium, while an obvious decrease in the conventional route was observed. Moreover, this novel PAA medium could significantly decrease the content of alkali metal cations in the final TS-1 product by one order of magnitude when comparing TS-1-PAA-K0.1 (TS-1 prepared under PAA medium containing 0.1 molar ratio of K<sup>+</sup>/Si) with TS-1-con-K0.1 (TS-1 prepared under conventional route containing 0.1 molar ratio of K<sup>+</sup>/Si).

### 3.2. Catalyst characterizations

PXRD patterns (Fig. 1) show that all the samples prepared from both conventional route and PAA medium had pure MFI-type structure with high crystallinity, belonging to the topology struc-

**Table 1**  
Synthetic conditions and compositions of final TS-1 samples.

Samples	Gel composition <sup>a</sup>				Final product	
	Si/Ti (mol/mol)	PAA(unit)/Si (mol/mol)	Alkali Metal	Alkali Metal/Si (mol/mol)	Si/Ti (mol/mol)	Alkali Metal/Si (mol/mol)
TS-1-con	40	n.a.	n.a.	–	51	n.d.
TS-1-con-Na0.02	40	n.a.	Na	0.02	71	0.0047
TS-1-con-K0.1	40	n.a.	K	0.1	56	0.024
TS-1-PAA	40	0.45	n.a.	–	40	n.d.
TS-1-PAA-Na0.02	40	0.45	Na	0.02	42	0.0014
TS-1-PAA-K0.1	40	0.45	K	0.1	40	0.0027

<sup>a</sup> Other compositions: TPAOH/SiO<sub>2</sub> = 0.45, H<sub>2</sub>O/SiO<sub>2</sub> = 35. The abbreviation of n.a. means no addition. The abbreviation of n.d. means not determined.

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