



Effect of ammonium salts on the synthesis and catalytic properties of TS-1

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ABSTRACT

Effects of ammonium salts on the synthesis and characteristics of TS-1 were studied by adding different ammonium salts (NH_4F , NH_4Cl , NH_4Br , NH_4I , $\text{CH}_3\text{COONH}_4$, NH_4NO_3 , $(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_3\text{PO}_4$) to the synthesis gel. It was shown that the fine structure and crystal morphology of the synthesized materials depended on the type of ammonium salts. Except for NH_4F , the ammonium salts, and particularly $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_3\text{PO}_4$ significantly decreased the crystallization rate as a result of remarkably reducing the pH value of the crystallization mixture. Nevertheless, all of these ammonium salts were favorable for the incorporation of Ti in the framework, and the beneficial effect was dependent on the type of ammonium salts. In addition, the ammonium salt also has a strong influence on the catalytic properties of the prepared catalyst. It is worth noting that the catalytic performance of TS-1 was closely related to the substrate molecules. TS-1 catalyst prepared in the presence of $(\text{NH}_4)_2\text{SO}_4$ gave the highest conversion in the epoxidation of 1-hexene, whereas that prepared with $(\text{NH}_4)_2\text{CO}_3$ was suitable for the oxidation of phenol.

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1. Introduction

Zeolites and related materials have been widely synthesized with the assistance of alkali cations and/or organic amines. These organic amines play a templating and/or structure-directing role, while alkali cations serve as counterions to balance negative charges of the framework and sometimes as structure-directing agents as well. The effects of alkali cations on the crystallization of molecular sieves have been investigated by many researchers [1–4]. This is because alkali cations directly influence the nucleation and growth of crystals, and consequently the characteristics of zeolites by their structure-forming or structure-breaking characters. In contrast, few of work contributes to the study of the effects of anions although there are a lot of researches on the synthesis of zeolites in the presence of fluoride ions (F^-) because this ion is an effective mineralizer and/or a structure-directing molecule. As a matter of fact, other anions also have a great effect on the synthesis of zeolites [5–7]. Kumar et al. reported that addition of a small amount of ClO_4^- , PO_4^{3-} , NO_3^- , SO_4^{2-} , CO_3^{2-} , AsO_4^{3-} , BrO_3^- and IO_3^- significantly promoted the crystallization process of a variety of zeolites,

such as NU-1, FER, MFI, ZSM-48, MTW, BEA, and even TS-1 and iron silicates, by speeding up the condensation process [8]. We also found that anions, like F^- , Cl^- , Br^- and I^- , influenced not only the nucleation rate, and thus the crystal morphology of ZSM-48, but also the framework Si/Al ratio and the catalytic performance for CO hydrogenation to light olefins [9].

Titanosilicate molecular sieves have been proved to be highly efficient and clean catalysts for the oxidation of alcohols, aromatics and alkenes [10,11]. It was found that the presence of alkali cations in the synthesis system not only inhibited the incorporation of Ti into the framework, but also led to a drastic reduction in activity [12]. Up to now, however, nobody systematically investigated the effect of different anions except for F^- and CO_3^{2-} on the synthesis and catalytic performance of titanosilicates [13–15]. The presence of F^- in Ti-Beta drastically decreased the activity for epoxidation of alkenes [13,14]. In contrast, addition of an appropriate amount of ammonium carbonate to the crystallization mixture resulted in a great increase in the framework Ti content and the hydrophobicity of TS-1, and thus, an increase in the catalytic activity for oxidation of a variety of organic substrates [15]. This suggests that the type of anions may significantly influence the catalytic performance of titanosilicates, and some of them could increase the catalytic activity of titanosilicates for oxidation of certain substrates. Thus, it would be useful to investigate the effects of different anions on the synthesis and catalytic properties of titanosilicates. Since the

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existence of alkali cations must be avoided in the synthesis of titanosilicates, it would be judicious to use ammonium salt as anion source to study the effect. In this paper, the influences of various anions, including F^- , Cl^- , Br^- , I^- , CH_3COO^- , PO_4^{3-} , NO_3^- , SO_4^{2-} , CO_3^{2-} , on the crystallization and characteristics of TS-1 are explored.

2. Experimental

2.1. Synthesis of samples

All samples were synthesized according to the Enicem method with a modified procedure [14]. The gel started from the mixture with a composition of $0.5TPAOH:(0.1-0.5)(NH_4)_nM:SiO_2:(0.0125-0.05)TiO_2:0.2H_2O_2:35H_2O$ ($n = 1-3$; $M = F^-, Cl^-, Br^-, I^-, NO_3^-, CO_3^{2-}, CH_3COO^-, SO_4^{2-}$ and PO_4^{3-}). First, a certain amount of water was added to titanium tetra-*n*-butoxide. Then, H_2O_2 was quickly added and stirred for 30 min to convert Ti into a monomeric peroxide species. This was followed by addition of aqueous tetrapropylammonium (TPAOH) solution. The clear solution was stirred for 10–15 min, and tetraethyl orthosilicate (TEOS) was then introduced. The resultant solution was kept at 50–60 °C for 4 h under stirring conditions. Occasionally, distilled water was added to compensate for evaporation loss. Afterwards, an aqueous solution of ammonium salt was added into the above mixture at ambient temperature, and the resultant mixture was stirred for another 30 min. The final gel was autoclaved at 170 °C for 2–7 d. For comparison, conventional TS-1 catalyst was prepared by the Enicem method [14].

2.2. Characterization of samples

The X-ray diffraction patterns (XRD) were recorded on a MAC Science M3X 1030 X-ray diffractometer with Cu $K\alpha$ radiation (40 kV, 20 mA) to identify the crystalline phase and estimate the crystallinity. Scanning electron microscopy (SEM) images were collected on a JEOL JSM 6300 microscope. The titanium coordination states of the as-synthesized and calcined materials were investigated by diffuse reflectance (DR) UV–vis spectroscopy (Jasco V-550 UV–vis spectrophotometer equipped with an integration sphere). Framework infrared (IR) spectra were measured on a PE-1600 FTIR spectrometer. Before the measurement, all samples were evacuated at 500 °C for 2 h at about 1 Pa. N_2 adsorption measurements were carried out at –196 °C on a Belsorp 28SCA apparatus. The chemical composition of the samples was determined by an inductively coupled plasma-atomic emission spectrometer (Shimadzu ICPS-8000E).

2.3. Catalytic measurements

The liquid-phase oxidation of 1-hexene with H_2O_2 was carried out at 60 °C for 2 h under stirring conditions in a batch reactor of

a round-bottom flask (20 mL) equipped with a condenser. The temperature was controlled with a water bath. Unless specified, the reaction mixture was as follows: 0.05 g catalyst, 10 mL acetonitrile as solvent, 10 mmol 1-hexene and 10 mmol H_2O_2 (31% in aqueous solution) as oxidant. The product was analyzed on a Shimadzu GC-14B gas chromatograph equipped with a 50-m OV-1 capillary column and a flame ionization detector. The amount of the unconverted H_2O_2 was determined by titrating with 0.1 M $Ce(SO_4)_2$ aqueous solution.

The liquid-phase hydroxylation of phenol was conducted in a similar manner. The reaction conditions were as follows: 60 °C, 1.5 h, 0.05 g catalyst, 10 mL water as solvent, 5 mmol phenol, 2.5 mmol H_2O_2 (30% in aqueous solution). The product was analyzed on a GC-9A gas chromatograph equipped with a 60-m SE-30 capillary column and a flame ionization detector.

3. Results and discussion

3.1. XRD characterization

Table 1 gives the sample notations (designated as TS-1-*x*-*y*-*z* with *x*, *y* and *z* representing anion, anion/SiO₂ and Si/Ti ratios in the synthesis gel, respectively), the pH values of the crystallization mixtures and the physical property data of the prepared TS-1 catalysts. The XRD patterns of all the samples synthesized in the presence of different ammonium salts show the typical diffraction lines of MFI-type structure without contamination of impure phases (Fig. 1). Nevertheless, two types of XRD patterns were observed. One is for the materials synthesized in the presence of NH_4F , NH_4Cl , NH_4Br , NH_4I , NH_4NO_3 , $(NH_4)_2CO_3$ or CH_3COONH_4 (NH_4Ac). This type is the same as that of the sample prepared in the absence of ammonium salts, and in agreement with the literatures reported when only TPAOH was used as a templating molecule [16]. The other is characteristic of the samples synthesized in the presence of $(NH_4)_2SO_4$ or $(NH_4)_3PO_4$. The primary difference between them is in the relative intensities of diffraction lines, particularly of those corresponding to $(0k0)$ reflections. This difference was still retained after calcination, indicating that it was not due to the occlusion of different ammonium salts in the channels. It was rather attributed to the presence of preferential planes in the crystals. This is supported by the systematic increase in the intensities of $(0k0)$ diffraction lines with increasing $(NH_4)_2SO_4$ content in the synthesis gel (Fig. 2). The intensity ratio of the (020) reflection to the (101) one was about 0.65, 1.19 and 1.58 for the samples synthesized with the gel having a SO_4^{2-}/SiO_2 ratio of 0.1, 0.3 and 0.5, respectively. This phenomenon seems to be independent of the Si/Ti ratio in the synthesis gel since no apparent change was observed with respect to the relative line intensity when the Si/Ti ratio was increased from 33 to 80.

The ammonium salts also have a strong effect on the crystallization rate of TS-1. Except for ammonium fluoride, addition of a certain amount of other ammonium salts to the synthesis gel did not

Table 1
Physical properties of the prepared TS-1 catalysts.

Sample	pH value of the crystallization mixture	S_{BET} ($m^2 g^{-1}$)	$S_{Langmuir}$ ($m^2 g^{-1}$)	$S_{External}^a$ ($m^2 g^{-1}$)	Si/Ti
TS-1-non-50	11.90	399.0	601.4	36.1	77.5
TS-1-F-0.3-50	10.62	422.9	619.6	15.6	52.4
TS-1-Cl-0.3-50	10.60	436.8	650.3	13.3	58.5
TS-1-Br-0.3-50	10.66	427.5	641.5	14.6	67.0
TS-1-I-0.3-50	10.65	421.1	614.7	12.5	71.0
TS-1-Ac-0.3-50	10.64	440.9	663.5	17.4	57.1
TS-1-NO ₃ -0.3-50	10.70	425.0	626.3	11.3	55.7
TS-1-CO ₃ -0.3-50	10.58	390.0	567.1	11.4	56.1
TS-1-SO ₄ -0.3-50	10.18	361.0	508.5	10.2	61.8
TS-1-PO ₄ -0.3-50	10.22	359.1	518.5	9.7	61.0

^a Estimated by the t-plot method.

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