Postsynthesis of mesoporous MOR-type titanosilicate and its unique catalytic properties in liquid-phase oxidations

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ABSTRACT

Mesoporous titanosilicate with the MOR topology, denoted as Ti-Meso-MOR, was postsynthesized from commercially available mordenite by sequential acid, alkaline, acid, and $TiCl_4$ vapor treatments, and its catalytic oxidation properties were investigated in detail in liquid-phase oxidation reactions with hydrogen peroxide as an oxidant. A controllable acid leaching was first carried out on H-mordenite (Si/Al = 7.8) to induce a partial dealumination to Si/Al = 80, which was suitable for constructing secondary mesopores by subsequent alkaline treatment. Alkaline treatment-induced desilication introduced a large number of intracrystal mesopores. Tetracoordinated Ti species were then inserted into the resultant mesoporous mordenite with a high dealumination degree (Si/Al = 145) through the gas–solid reaction with $TiCl_4$ vapor at elevated temperatures. In comparison with conventional Ti-MOR and TS-1, Ti-Meso-MOR thus prepared exhibited an improved catalytic activity in the hydroxylation of toluene and the ammoximation of cyclohexanone as well. Moreover, Ti-Meso-MOR proved to be a robust catalyst for continuous ammoximation since the mesopores minimized diffusion limitation and suppressed coke formation efficiently.

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1. Introduction

The first titanosilicate of TS-1 has achieved a great success in last decades because it is capable of catalyzing efficiently the oxidation of a variety of substrates using hydrogen peroxide [1,2]. The utilization of H_2O_2 oxidation produces water as the sole byproduct, which already leads to environmentally benign chemical processes in commercial use, i.e., the hydroxylation of phenol [3] and the ammoximation of cyclohexanone [4]. In comparison with conventional non-catalytic oximation process using hydroxylamine sulfate, TS-1-catalyzed ammoximation of cyclohexanone with H_2O_2 and NH_3 produces cleanly cyclohexanone oxime, the key material in nylon-6 manufacturing industry, without coproducing any ammonium sulfate [5]. The titanosilicate/H_2O_2 system is expected to develop green processes for the production of phenol and cresols through one-pot hydroxylation of benzene or toluene [2], while conventional hydroxylation processes usually employ corrosive liquid acid like sulfuric acid as the catalyst and co-produce a large quantity of valueless waste products [6].

The liquid-phase reactions operated under mild conditions and in the presence of water (contained inevitably in aqueous H_2O_2 and coproduced during reactions) usually suffer more problems of kinetic mass transfer than the gas-phase reactions carried out at high temperatures [7]. Moreover, TS-1 with 10-membered ring (MR) window of approximately 5.5 Å in size proposes significant diffusing limitations to the large molecules penetrating into the pores [8]. Additionally, the reaction mechanism of titanosilicate/H_2O_2 catalytic system is postulated to involve the Ti–OOH species or 5-MR intermediate formed via the coordination of Ti site with H_2O_2 and solvent molecules [9]. Once these species are formed, they may narrow the kinetic size of zeolite pores obviously and then hinder the mass transfer therein. Thus, how to enhance the accessibility of substrate molecules to Ti sites turns out to be an important issue in titanosilicate catalysis. With the aim of overcoming the problems encountered by medium-pore TS-1, an alternative way is to develop titanosilicates with larger porosities. In this sense, those with 12-MR pores have been hydrothermally synthesized or postsynthesized, e.g., Ti-MWW [10], Ti-Beta [11], Ti-MTW [12], and Ti-MOR [13]. They are superior to TS-1 especially in the selective oxidation of bulky substrates. On the other hand, for the titanosilicates originating from lamellar precursors, the techniques of phase delamination [14,15], interlayer pillaring [16], and expansion [17] have been developed to improve their porosity and then oxidation ability effectively.

Among larger-pore zeolites, MOR-type aluminosilicate is hydrothermally synthesized easily even in the absence of any organic structure-directing agent, and it serves as an important solid acid catalyst that is widely used in petrochemical processes [18]. Direct synthesis of Ti-MOR, however, is still of a great challenge. This is

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because its specific structure features such as 4-MR make the crystallization of MOR structure impossible under siliceous conditions, let alone in the absence of any alkali source, a critical precondition favored by titanosilicate. Ti-MOR is thus prepared by combined postsynthesis treatments including dealumination and $TiCl_4$ vapor treatment [13]. It is shown to be more active than TS-1 in the hydroxylation of aromatics [19]. However, the one-dimensional (1D) channel system of Ti-MOR is short of interconnectivity, which may make it lack the potential activity possessed by the zeolites with three-dimensionally connected channels. Introducing intercrystal and/or intracrystal mesopores into Ti-MOR are thus expected to minimize the diffusion limitation possibly.

Several techniques have been established to create extra mesopores in microporous zeolite crystals, such as post-treatments of acid leaching [20] or base leaching [21], and direct synthesis with hard [22] or soft templates [23]. All these methods are sorted into two categories, that is, templating and non-templating ways. With respect to templating way, both soft templates of supramolecular organics [23–26] and hard templates of carbon nanoparticles [27], polymer [28], starch [29], and resins [30] have been used successfully to induce mesopores into zeolite crystals during hydrothermal synthesis processes.

As for non-templating route, the nucleation and crystal growth are controlled in synthesis process, which leads to self-assembling of primary particles and formation of intercrystal mesopores [31]. Another feasible approach is to carry out demetallation including streaming, acid, and base treatments. Low silica zeolites are usually steamed and then treated with acid to generate mesoporosity via dealumination process. For example, USY, the main active component in FCC catalysts, is commercially produced in this way for decades.

For high silica zeolites (Si/Al > 5), alkaline treatment-induced desilication is powerful for creating extra mesopores [32]. However, the leaching of silicon from the structures closely depends on the treatment conditions, e.g., concentration of alkaline solution, temperature, and time [33,34]. Moreover, the aluminum content of zeolites alters the desilication process, and the Al content suitable for mesopore formation is reported to be in the Si/Al ratio range of 20–50 in the case of ZSM-5 zeolite [35]. This technique has been applied widely to the preparation of other mesoporous zeolites such as mordenite (MOR) [36], zeolite Y (FAU) [37], β zeolite (BEA) [38], ZSM-22 (MTW) [39], and SSZ-13 (CHA) [40]. Up to date, the researches predominantly focus on the design of solid acid catalysts with larger porosities but rarely deal with the preparation of metallosilicates with unique redox properties.

In this study, mesopores have been introduced into MOR crystals to improve the accessibility to Ti active sites and then oxidation activity. The catalytic performance of postsynthesized Ti-Meso-MOR has been compared with that of conventional Ti-MOR and TS-1 in the hydroxylation of toluene and the ammoximation of cyclohexanone.

2. Experimental

2.1. Zeolite materials

A commercially available H-mordenite with a Si/Al molar ratio of 7.8 was purchased from Shangsi Fine Chemical Co., China. Denoted as Parent-MOR, it was used as-received as the starting material for preparing dealuminated MOR with or without mesopores.

Parent-MOR was first refluxed in 6 M HNO_3 solution at a liquid-to-solid ratio of 1:50 w/w for 20 h. The treated sample was subsequently filtrated and washed with deionized water until the pH value of the filtrate was over 5. It was then dried at 353 K overnight

and further calcined in air at 973 K for 10 h to obtain a partially dealuminated sample (Acid-MOR) with a Si/Al ratio of 80. This sample was subjected to acid refluxing again with 6 M HNO_3 for 20 h following conventional dealumination procedures reported previously [41], which gave a deeply dealuminated sample (C-MOR, Si/Ai = 195).

Alkaline treatment was performed on Acid-MOR to generate mesopores. Following a literature procedure [42], Acid-MOR (9 g) was treated in 270 mL NaOH solution (0.2 M) at 338 K for 0.5 h. The sample was collected by centrifugation, washed with deionized water repeatedly until the pH value reached ca. 7, and finally dried at 353 K overnight. The solid product yield after desilication corresponded to 70.5 wt.%. Then, another acid treatment (6 M HNO_3, refluxing for 20 h) was carried out on the alkaline-treated sample. The ion-exchange into proton form and removal of Al from the framework occurred simultaneously during this process, leading to dealuminated Meso-MOR (Si/Al = 145).

2.2. Preparation of titanosilicates

Ti-containing MOR samples were postsynthesized through a solid–gas reaction between dealuminated MOR and $TiCl_4$ vapor at elevated temperatures [13]. A dealuminated MOR sample (2.0 g) placed in a quartz tube reactor (i.d. 4 cm) was pretreated at 773 K for 2 h in a dry N_2 stream (30 mL min^{-1}). Then, the reactor was brought to a treatment temperature of 673 K, where the N_2 stream went through an anhydrous $TiCl_4$ solution contained in a glass bubbler and maintained at 303 K. The $TiCl_4$ vapor saturated in N_2 flow was carried into the reactor to contact the zeolite bed for a determined period of time. After the treatment, the sample was purged with pure N_2 at the same temperature for 1 h to remove any residual $TiCl_4$ from the zeolite powder. After cooling to room temperature in N_2, the treated sample was washed with deionized water under stirring until chloride ions were not detected in the filtrate by $AgNO_3$ solution. The sample was then dried in air at 353 K overnight. The duration of $TiCl_4$ treatment was varied in the range of 5 min^{-1} h to achieve different Ti incorporation. The Ti-containing samples obtained from Meso-MOR and C-MOR were denoted as Ti-Meso-MOR and Ti-MOR, respectively. Scheme 1 shows graphically the whole procedures for preparing Ti-Meso-MOR.

For control experiment, TS-1 was hydrothermally synthesized from raw materials of tetraethyl orthosilicate (TEOS), tetrabutyl orthotitanate (TBOT), and tetrapropylammonium hydroxide (TPAOH) solution following typical ENI method [43]. The synthetic gel was prepared to have a molar composition of 0.18TPAOH:0.01 or 0.03TiO$_2$:1.0SiO$_2$:18H$_2$O. The gels were transferred into a 120-mL Teflon-lined autoclave and crystallized at 443 K for 3 days under rotation (100 rpm). The two TS-1 samples were recovered by filtration, washed thoroughly by deionized water, dried at 353 K, and calcined in air at 823 K for 10 h, which had Si/Ti ratios of 95 and 35.

2.3. Characterization methods

Powder X-ray diffraction (XRD) was employed to check the structure and crystallinity of the zeolites. The XRD patterns were collected on a Rigaku Ultima IV diffractometer using Cu Kα radiation at 35 kV and 25 mA in the 2θ angle range of 5–35°. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscope to determine the morphology. Transmission electron microscopy (TEM) images were collected on a JEOL JEM-2100 microscope after the samples were deposited onto a holey carbon foil supported on a copper grid. The Ti and Al contents were determined by inductively coupled plasma emission spectrometry (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer