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Preparation of hierarchical MWW-type titanosilicate by interlayer silylation with dimeric silane

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Dedicated to Dr. Michael Stöcker on the occasion of his retirement as Editor-in-Chief of Microporous and Mesoporous Materials.

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ABSTRACT

An interlayer expanded zeolite structure with dimeric silane as the pillars was constructed by a combination of pre-swelling and silylation. The pre-swelling process was carried out on the lamellar precursor of MWW-type borosilicate, which created enough interlayer space for accommodating the dimeric silane molecules with a relatively large molecular dimension. An appropriate amount of dimeric silane was important to prepare an ordered interlayer expanded structure pillared by monomolecular silane agent. The *d*-spacing of interlayer expanded MWW zeolite by dimeric silane reached 30.9 Å, which is larger than that of the conventional 3-dimentional (3D) MWW (25.0 Å) as well as the silylated sample pillared by monomeric silane (27.5 Å). Ti cations were isomorphously incorporated into the interlayer expanded MWW zeolite pillared by dimeric silane. The obtained titanosilicate was highly active in the epoxidation of alkenes with hydrogen peroxide, especially in the case of cyclohexene.

1. Introduction

Zeolites, with well-defined micropores and strong acidity, have found important applications in adsorption, separation and catalysis [1]. The pore size of zeolites is mainly around 1 nm, which has the ability to control the access and egress of specific reactants and products. Similarly, the inner space formed by cages preferentially accommodate certain transition states while exclude others [2]. This kind of recognition at molecular level is defined as “shape selectivity”, which contributes remarkable reactivity and selectivity as catalysts. Zeolites made up of tetrahedral SiO_4 and AlO_4 units may serve as solid acid catalysts. The marked performance of zeolites in acid catalysis inspired researchers to introduce other active sites into the framework such as Ti [3], Sn [4], and Zr [5], opening up new catalytic applications in selective oxidation reactions.

With the increasing demands from petrochemical industry, the small pore size of zeolites, also called “1 nm prison”, has become a bottleneck for their application in catalysis as well as separation. Introducing another level of porosity either by direct synthesis or postsynthesis is a useful way to release the diffusion constrains inside zeolite crystals. Introducing mesopores with the size of 2–50 nm is a good choice, which can increase largely the accessibility of active sites in the zeolite framework. Direct synthesis of zeolite with two-level porosity can be achieved by hard-template [6], soft-template [7] and non-template [8] methods. In addition, post-synthesis method is a more general way to introduce mesopores. Metal leaching including dealumination and desilication has achieved great success in the postsynthesis of many mesopore-containing zeolites, such as ZSM-5 [9], MOR [10], Beta [11], ZSM-22 [12]. Structural modification of zeolitic lamellar precursors is another useful postsynthesis method.

Lamellar zeolites, with over 20 members, are becoming an important branch of zeolite materials. Different from conventional 3-dimensional (3D) zeolite with rigid structure, 2-dimensional layered zeolites with hydrogen bonds between two neighboring layers exhibit a structural diversity. The interlayer hydrogen bond is relatively weak and can be cleaved easily, which is also the premise for post modifications including swelling [13], delamination [14], and pillaring [15]. Swelling, always carried out before delamination and pillaring, is achieved in an alkaline solution combined with surfactant molecules, which has a long hydrophobic tail intercalating into the interlayer space and enlarges the *d*-spacing. Swelling treatment was firstly carried out at high temperature of 353 K, which caused a significant desilication and degradation of zeolite layers [16,17]. Then, more mild condition was proposed to swell the lamellar zeolite precursors at room temperature, largely preserving the layer structure [18]. Recently, a special swelling mixture containing F^- and Cl^- ions was applied to break the interlayer hydrogen bonds under nearly neutral conditions and successfully avoided metal leaching aroused by conventional alkaline solution [19,20]. Ultra sound treatment and pillaring then can be carried out on swollen materials to construct delaminated and pillared structures. The large interlayer space created by swelling

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would disappear upon calcination. Pillaring then constructs permanent inorganic pillars between zeolite layers forming mesopores in the interlayer space. Silylation is a kind of acute pillaring with specially chosen silanes to react with the silanols on the surface and connect the up-and-down layers leaving newly formed mesopore channels in the interlayer space [21,22].

Lamellar zeolite MCM-22(P) was at first successful silylated with a pre-swelling treatment resulting in an interlayer expanded structure with 12-member ring (12-MR) channels in the interlayer space other than the 10 MR pore channels of 3D MWW structure. To avoid the complex swelling and silylation procedure, Wu et al. proposed a facial one-step silylation, which relays on the interlayer space large enough to let the monomeric silanes in [21]. This one-step method was then expanded to many other lamellar zeolites including PLS-1 [23], PLS-4 [24], PREFER [25], RUB-36 [26] and RUB-39 [27], and it was proved to be a general method. To further increase the interlayer space, dimeric silane with larger molecular size was adopted to connect the up-and-down layers. Corma et al. applied dimeric silane 1,4-*bis*(triethoxysilyl)benzene to prepare a inorganic/organic multifunctional material, with acid sites in the zeolite inorganic layers and base sites in the organic layer of interlayer props. The *d*-spacing of the interlayer expanded structure was about 40 Å and the interlayer props were believed to be made up of two condensed BTEB molecules [28].

Ti-MWW zeolite is a useful oxidation catalyst and prepared from a lamellar zeolite. Its catalytic performance was enhanced a lot after it was silylated into IEZ-Ti-MWW with interlayer expanded structure through one-step silylation process [21,22], because the newly formed 12-MR channels increase the accessibility of reactants to the active sites. In this study, dimeric silanes were applied to serve as pillars between the MWW layers, and then larger interlayer space was expected to be created, which would provide more open entrance for reactants and decrease the diffusion constrains in oxidation reactions.

2. Experimental

2.1. Synthesis of MWW lamellar precursor

The synthesis of B-containing MWW lamellar precursor was performed according to previous report [29]. Firstly, boric acid was dissolved in aqueous solution of hexamethyleneimine (HMI) under vigorous stirring till a clear solution was formed. Then, colloidal silica (30 wt.%) was added into the above clear solution under stirring to form a synthesis gel with the composition of 1.0 SiO_2:1.4 HMI:0.67 B_2O_3:19 H_2O. The resulting gel was transferred into a Teflon-lined autoclave and heated with a stirring rate of 100 rpm at 443 K for 6 days. After cooling, the solid product was filtered off and washed with deionized water thoroughly. The product was then dried at 323 K for 1 day and denoted as MWW-P. The lamellar precursor was calcined at 823 K for 6 h to form a 3D structure denoted as 3D-MWW.

2.2. Swelling of MWW lamellar precursor

A mild procedure was carried out to swell MWW-P in order to preserve the layer structure [18]. The swelling mixture composed of swelling agent hexadecyltrimethyl ammonium bromide (CTAB) and alkaline source tetrapropylammonium hydroxide (TPAOH) was prepared in advance and then MWW-P was added into the mixture, the weight ratio of which was 1.0 MWW-P:5.7 CTAB:2.5 TPAOH:21.5 H_2O. The mixture was kept stirring at room temperature for 16 h after which the product was recovered by repeated centrifugation and water washing. Then swollen MWW (denoted as MWW-S) was finally obtained after drying at 323 K overnight.

2.3. Interlayer expansion of swollen MWW

Interlayer expanded MWW structure was obtained by silylation of MWW-S with dimeric silanes $Cl(CH_3)_2Si–Si(CH_3)_2Cl$ or $Cl(CH_3)_2$-Si–O–$Si(CH_3)_2Cl$. In a typical run, swollen MWW powder (1.0 g) was suspended in the 50 mL HNO_3 (or HCl) aqueous (2 M), and then a desirable amount of dimeric silane was added. The mixture was stirring at room temperature for 0.5 h. The silylation process was performed at 423 K in an autoclave or at 373 K under reflux condition for 20 h. The interlayer expanded product was filtrated, washed with deionized water and dried at 353 K overnight. The interlayer expanded zeolites (IEZ) obtained by silylation with $Cl(CH_3)_2Si–Si(CH_3)_2Cl$ was denoted as IEZ-MWW(SiSi), while denoted as IEZ-MWW(SiOSi) in the case of silylation with $Cl(CH_3)_2$-$SiOSi(CH_3)_2Cl$. Then calcination treatment was carried out to burn the organic species introduced by swelling and silylation to obtain IEZ-MWW(SiSi)-cal*x* or IEZ-MWW(SiOSi)-cal*x*, where *x* indicates the calcination temperature.

2.4. Insertion of titanium into interlayer expanded MWW structure by liquid-solid reaction

The synthesis of titanium-containing interlayer expanded MWW materials was realized by a liquid-solid reaction with H_2TiF_6 as the titanium source. Typically, 0.6 g calcined zeolite was suspended in 60 mL deionized water, and then a desirable amount of H_2TiF_6, corresponding to Si/Ti ratio of 5, was added into the mixture. The whole procedure was carried out in a Teflon bottle at 308 K under stirring for 5 h. The product was collected by filtration and washing, and then dried at 353 K overnight, denoted as Ti-IEZ-MWW(SiSi).

For control experiment, conventional Ti-MWW zeolite was prepared by hydrothermal method according to the report [29]. Another expanded structure silylated by monomeric silane $Cl_2(CH_3)_2Si$ was prepared with one-step silylation procedure without swelling and denoted as IEZ-MWW(Si). According to the literature [21], 1 g B-MWW zeolite was immersed in 50 mL HNO_3 aqueous (2 M) and 0.15 g $Cl_2(CH_3)_2Si$ was then added. The mixture was transferred into a Teflon-lined autoclave and heated at 443 K for 20 h. After cooling, the solid product was washed to yield IEZ-MWW(Si). Ti cations were also introduced into IEZ-MWW(Si) by the above mentioned liquid-solid reaction. Before Ti insertion, calcination treatment at 773 K was carried out to remove the organic molecules. The Si/Ti ratio was also set as 5 when preparing Ti-IEZ-MWW(Si)-cal773.

2.5. 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 RigakuUltima IV diffractometer using CuKα radiation at 35 kV and 25 mA in the 2θ angle range of 2–30° using a step size of 0.04° and at a scanning speed of 10° min^{-1}. UV–visible diffuse reflectance spectra were recorded on a PerkinElmer Lamda 35 UV/VIS spectrometer using $BaSO_4$ as a reference.The adsorption isotherms of N_2 were measured at on a BELSORP-MAX instrument equipped with a precise sensor for low pressure measurement at 77 K. The samples were activated at 573 K under vacuum for at least 3 h before adsorption. The ^{29}Si MAS NMR spectra were measured on a VARIANVNMRS 400WB NMR spectrometer using single pulse method at a frequency of 79.43 MHz, a spinning rate of