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Co-templated synthesis of polymorph A-enriched zeolite beta

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ABSTRACT

The initial mixture containing fully hydrolysed tetraethyl orthosilicate (TEOS) and tetraethylammonium hydroxide (TEAOH) solution was treated either by heating at 80 °C or by freeze-drying. After adding an appropriate amount of concentrated hydrofluoric acid, the resulting mixture was crystallized at 150 °C. The heating treated mixture produced polymorph A-enriched zeolite beta while freeze-drying treated mixture gave only normal zeolite beta. The ^{13}C magic angle spinning nuclear magnetic resonance (MAS NMR) analysis and thermogravimetric analysis (TGA) indicated that a partial decomposition of TEAOH to generate triethylamine (TEA) occurred during the heating dehydration process, which was the only difference compared with the freeze-drying process. Together with the reduced TEAOH, different monoamines as a co-template directed the polymorph A-enriched zeolite beta with the freeze-drying process. Diamines as a co-template directed only the normal zeolite beta. The synthesis cost of polymorph A-enriched zeolite beta can be significantly reduced by lowering the usage of expensive TEAOH and using cheaper monoamines.

1. Introduction

Zeolite beta was first synthesized by Mobil using tetraethylammonium hydroxide (TEAOH) as a structure directing agent (SDA) in 1967 [1]. The structure of zeolite beta was determined independently in 1988 by Newsam and Higgins as a random intergrowth of two closely related polymorphs, named polymorph A and polymorph B, which were in a ratio of 44:56 [2,3]. Polymorph A belongs to the space group $P4_122$ or $P4_322$, and polymorph B belongs to the space group $C2/c$. Polymorph A has two enantiomorphs containing a helical pore along the c-axis, whereas polymorph B does not show chirality. A homochiral form or one enantiomorph of polymorph A could be used for asymmetric catalysis and chiral separations because the constrained geometry of its framework could eventually control the stereoselectivity of chiral catalytic reactions or result in enantioselective sorption or separation processes [4]. However, synthesis of a pure form of the chiral polymorph A remains a significant goal in zeolite synthesis, as well as one of the most difficult challenges.

Several attempts have been made to synthesize pure polymorph A. Davis and Lobo reported developing an unspecified chiral template with appropriate size and sufficient thermal stability in 1992 [5]. According to the comparison of the experimental X-ray diffraction (XRD) pattern with the simulated one of the pure polymorph A, the authors claimed that the product has more polymorph A than the normal zeolite beta and could yield a low enantiomeric excess (5%) under enantioselective adsorption and catalysis. Later, Camblor et al. presented the unseeded synthesis of all-silica zeolite beta in fluoride media in 1996 [6]. The XRD pattern of the all-silica zeolite beta suggested that polymorph A was predominant (~50%). In 2003, Xia et al. synthesized a series of metal incorporated zeolite beta; the majority of these materials consisted of polymorph A (~50%) and yielded an appreciable enantiomeric excess value of approximately 9–11% when applied to the asymmetric hydrogenation of tiglic acid [7]. In 2008, Takagi et al. reported the crystallization of zeolite beta in the presence of chiral amine or rhodium complexes [8]. Afterwards, Taborda et al. reported the synthesis of all-silica zeolite beta by an ageing-drying method in 2011 [9]. They evaluated the ratio of polymorphs independently by a peak-differentiating and imitating method and claimed that the zeolite beta they obtained was somewhat enriched in polymorph A. However, the profiles of the experimental XRD patterns they reported were very similar to those of the normal

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zeolite beta, suggesting that the percentage of polymorph A was no more than 50%.

Recently, Tong et al. reported the crystallization process of all-silica zeolite beta with enriched polymorph A (approximately 66%) under concentrated hydrothermal conditions [10]. It was found that the amount of water in the initial mixture was the key in the enrichment of polymorph A. They dehydrated the initial mixture in an 80 °C oven, which resulted in a partial decomposition of TEAOH via Hofmann degradation to form triethylamine (TEA). Later, Guo et al. reported the synthesis of polymorph A enriched zeolite beta in the presence of two new quaternary ammonium bases under the same concentrated hydrothermal conditions [11]. However, the preparation of these organic molecules remains fairly expensive. Very recently, Tong et al. reported a generalized, extremely concentrated fluoride route for the synthesis of polymorph A-enriched zeolite beta [12]. The initial mixture was dehydrated at 80 °C before it was loaded into the autoclave, which also resulted in a partial decomposition of TEAOH via Hofmann degradation to form TEA. According to the single pulse ^{13}C MAS NMR data, it was determined that the molar ratio of TEAOH/TEA in the dehydrated mixture was approximately 2/3 (0.61), implying that the triethylamine might play an important role in the enrichment of polymorph A. In this work, we experimentally confirmed that speculation by control experiments. We developed a co-template strategy to synthesize polymorph A-enriched zeolite beta for the first time, which can significantly reduce the usage of the expensive TEAOH template. With this strategy, we screened several mono- and diamines as the second structure-directing agent (co-template) and found that only monoamines can direct the polymorph A-enriched zeolite beta. The synthesis cost of polymorph A-enriched zeolite beta can be significantly reduced by lowering the usage of expensive TEAOH and using cheaper monoamines.

2. Experimental section

2.1. Materials

All reagents were used without purification. Tetraethyl orthosilicate (TEOS), diethylamine (DEA), ethylenediamine (en) and n-butylamine (BA) were obtained from the Tianjin Fuchen Chemical Reagent Factory. Tetraethylammonium hydroxide (TEAOH, 35 wt%) was supplied by Alfa Aesar Company. Hydrogen fluoride (HF, 40 wt %) was obtained from the Beijing Chemical Reagent Factory. Triethylamine (TEA) was obtained from Tianjin Fuyu Fine Chemical Co., Ltd. 1,2-diaminopropane (DPA) was obtained from the Aladdin Chemical Reagent Company. Cyclohexylamine (CHA) and ethylamine (EA) were obtained from the Tianjin Guangfu Fine Chemical Reagent Company. The n-propylamine (PA) was obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Dehydrated mixture preparation and hydrothermal synthesis

Our earlier work showed that dehydration of the initial mixture was the key in the synthesis of the polymorph A-enriched zeolite beta [12]. In this work, dehydration was conducted either by heating or by freeze-drying. The initial mixture was prepared as follows: 6 g TEOS was added to a solution of 5.89 g TEAOH solution (35 wt% in water) under stirring. After the hydrolysis of TEOS for 5 h, the resulting mixture was stirred for a further 8 h until a uniform, viscous mixture was formed. The resulting mixture was placed either in an 80 °C oven for 5 days (heating dehydration process) or in a freeze-drier for 5 days (freeze-drying dehydration) until the weight of the mixture reached 3.8 g. The dehydrated mixture was ground into fine powder, and 605 μL of hydrofluoric acid (HF, 40 wt%) was subsequently added dropwise while stirring. The resulting mixture was then loaded into an autoclave and heated at 150 °C for 7 days. The autoclave was quenched with cold water, and the solid product was washed thoroughly with deionized water (DI) via filtration and dried at 100 °C overnight.

2.3. Co-templated synthesis with freeze-drying dehydration

Typically, 4.5 g of TEOS, 4 g of deionized water, and 2.21 g of TEAOH were added to a plastic beaker. After the hydrolysis of TEOS for 5 h, the resulting mixture was stirred for a further 8 h and then freeze-dried for several days until the weight of the mixture reached 2.15 g. The dehydrated mixture was ground into fine powder. Subsequently, an appropriate amount of the second amine (SDA_2) and 450 μL of HF solution were added while stirring. The molar composition of the final mixture was SiO_2/0.25 TEAOH/0.25 SDA_2/0.5 HF, where the SDA_2 could be triethylamine (TEA), diethylamine (DEA), n-butylamine (BA), n-propylamine (PA), cyclohexylamine (CHA), or ethylamine (EA). In addition to the monoamines, diamines such as ethylenediamine (en) and 1,2-diaminopropane (DPA) were also used. The final mixture was crystallized in an autoclave at 150 °C for 7 days. The solid product was washed thoroughly with water via filtration and dried at 100 °C overnight. The template was removed by calcination in air at 550 °C for 6 h.

2.4. Characterization

Powder XRD patterns were recorded on a Rigaku D/MAX-2550 diffractometer equipped with a graphite monochromator using Cu Kα radiation ($\lambda = 1.5418$ Å) and operated at 50 kV and 200 mA. The samples were scanned in the 2θ range from 4° to 40° with step size of 0.02°. SEM images were collected on a JEOL JSM-6510 microscope. Thermogravimetric analysis (TGA) with a heating rate of 10 °C/min was performed in air using a TGA Q500 analyser from TA Instruments. Nitrogen adsorption–desorption measurements were carried out on a Micromeritics 2020 analyser at 77.35 K after the sample had degassed at 200 °C under vacuum. The ^{13}C CP MAS NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probe head with the X channel tuned to 100.62 MHz for ^{13}C and the other channel tuned to 400.18 MHz for broad band ^{1}H decoupling using a magnetic field of 9.39 T at 297 K. The dried and finely powdered samples were packed in the ZrO_2 rotor closed with Kel-F cap and were spun at 8 kHz. The experiments were conducted at a contact time of 2 ms. A total of 5000 scans were recorded with a 3 s recycle delay for each sample. All ^{13}C CP MAS chemical shifts are referenced to the resonances of an adamantane ($C_{10}H_{16}$) standard ($\delta_{CH2} = 38.4$).

3. Results and discussion

3.1. Crystallization of zeolite beta from heating and freeze-drying treated initial mixtures

3.1.1. X-ray diffraction investigation

The percentage of polymorph A in zeolite beta is usually estimated by comparing an experimental powder XRD pattern with the simulated XRD patterns with different A/B polymorph ratios. The simulation is commonly performed using the DIFFaX program developed by Treacy and co-workers [2]. Fig. 1 shows the experimental powder XRD patterns of the zeolite beta crystallized from the initial mixtures dehydrated by heating and freeze-drying and the corresponding simulated XRD patterns with polymorph ratios A/B of 50/50, 60/40, and 70/30. The shape of the first low angle peak of zeolite beta was affected by the A/B polymorph ratios [8]. By