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ScienceDirect

Microporous and Mesoporous Materials 112 (2008) 178–186

MICROPOROUS AND MESOPOROUS MATERIALS

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Crystal size control of transition metal ion-incorporated aluminophosphate molecular sieves: Effect of ramping rate in the syntheses

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Received 6 December 2006; received in revised form 30 August 2007; accepted 22 September 2007
Available online 1 October 2007

Abstract

Several aluminophosphate (AlPO) molecular sieves (AEL and AFI structures) containing Co, V or Fe are synthesized in various ramping rates (reciprocal of the time needed to reach the reaction temperature from room temperature) in order to understand the effect of the rates on the crystal size of the molecular sieves. As the ramping rate increases, the crystal size decreases probably because the nucleation rate is higher than the crystal growth rate when the reaction temperature increases rapidly. The small crystals obtained by rapid heating adsorb benzene rapidly, offering potential application in catalysis and separation. The suggested method to control a crystal size is very simple (does not require additive materials, different precursors or pH modifier, etc.), reproducible and applicable in the synthesis of various porous materials.

Keywords: Crystal size; Ramping rate; Nucleation rate; Crystal growth rate; Molecular sieve

1. Introduction

Porous materials including zeolites and aluminophosphate molecular sieves (AlPO) are widely used in catalysis and separation, and are still being developed for new applications such as membranes, sensors, optics, etc. [1]. The AEL type molecular sieve (AEL) [2] such as AlPO-11, SAPO-11 and CoAPO-11 has orthorhombic symmetry and is composed of one-dimensional channel of 0.4 nm * 0.65 nm (delineated by 10-membered ring). The AEL has been widely studied for catalysts or catalyst supports for hydroisomerization [3,4], NO decomposition [5], iso-dewaxing [6], isomerization [7], alkylation reaction [8], etc. AFI type molecular sieve (AFI) [2] such as AlPO-5, SAPO-5 and CoAPO-5 with one-dimensional channel of 0.73 nm (delineated by 12-membered ring) has been widely studied in catalysis [9], a carrier for nanomaterials [10], etc.

Metal-containing molecular sieves such as cobalt, titanium, iron, manganese and vanadium incorporated molecular sieves are very interesting since they show remarkable performances in the redox-, photo- and acid-catalysis [11–13]. Especially, cobalt-containing molecular sieves are very attractive catalysts in the oxyfunctionalization of hydrocarbons with air or oxygen [14]. Therefore, there have been considerable attempts [11,15] to substitute a framework element by a metal ion including transition metal ions (TMI).

The shape and size of a molecular sieve are very important for applications such as membrane, catalysis and separation [16,17]. Several advantages, reported in the field of catalysis using small crystals are [16,17]: (a) catalysis is more effective; (b) coke deposition is less severe; (c) diffusion limitation is less severe; (d) template extraction and cation exchange are easier; (e) regeneration of used catalyst

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1387-1811/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2007.09.039

is less difficult for small crystals. On the contrary, larger crystals are more suitable for shape selective catalysis, filtration and recovery of crystals [16,17].

Studies have been often undertaken to reveal the effect of crystal size on catalytic reactions. Chen et al. have reported that the crystal size of SAPO-34 has a remarkable effect in the methanol conversion to olefins [18]. Medium sized crystals (0.4–0.5 μm) are effective to obtain olefins due to the diffusion limitation of dimethylether (DME). On the contrary, small (0.25 μm) and large (2.5 μm) SAPO-34s lead to the formation of high concentrations of DME and coke, respectively, because of the relative diffusivities of DME and methanol [18]. Selectivity for isoparaffins is high over Pt/SAPO-41 [19] or Pt/beta zeolite [20] prepared from small SAPO-41 or beta zeolite in a hydroisomerization of *n*-decane or *n*-heptane. It may be noted that higher activity using small catalysts (due to increased diffusivity of a reactant or a product) has been reported to some extent [3,21–23]. For example, the conversion of polyethylene wax into oil increases as the crystal size of MFI zeolite decreases. Deactivation and coke formation are prohibited [24] and resistance to sulfur poisoning is also increased [20] if small porous materials are used in various catalytic reactions. Nevertheless, the catalysts used in the studies mentioned above are not so diverse in size and have not been synthesized so systematically for various sizes; instead, the catalysts were separated from each fraction by sieving [18] the catalyst or the catalysts were obtained from changing reaction conditions.

Moreover, because many emerging applications of porous materials require well-defined crystal size and morphology, controlling crystal shape and size is also important for special applications [25,26]. Large single crystals with a well-defined orientation and structure are necessary for the development of novel optical, electronic and magnetic materials [25]. Crystals of a specific size and shape are also useful to fabricate membranes and sensor devices [25].

The shape and size of porous materials have been controlled by various methods [16,17], mainly by optimizing the nucleation rate and crystal growth rate. For example, smaller crystals are obtained at lower temperature after aging (below the synthesis temperature) due to high nucleation rate compared with that of low crystal growth. Stirring a reaction mixture is also helpful to decrease the crystal size. On the other hand, large crystals can be obtained by using a nucleation suppressor, fluoride, clear solution and alcoholic solution, etc [17]. However, the morphology has been generally changed by modifying the chemical composition of reactant mixtures (for example, addition of auxiliary compounds, using different precursors and changing pH) [27].

To the best of our knowledge, control of crystal size by optimizing the ramping rate (reciprocal of the time needed to reach the reaction temperature from room temperature) is not known. Herein, we report the facile and reproducible method, by controlling the ramping rate, to control the crystal size of metal-incorporated AlPO molecular sieves such as CoAPO-11, VAPO-11, FAPO-11, CoAPO-5 and FAPO-5 etc. The crystal size of CoAPO-11 decreases with increasing ramping rate and ranges from 4.8 to 28.2 μm (in length) by changing the ramping rate from 275.0 to 2.4 °C/min. The reaction was performed by both microwave (MW) and conventional electric (CE) heating methods for rapid and slow heat-up, respectively, because the synthesis of materials by microwave method has the advantages such as rapid heat-up and fast crystallization [28].

2. Experimental section

AEL and AFI type molecular sieves such as CoAPO-11, AlPO-11, VAPO-11, FAPO-11, CoAPO-5 and FAPO-5 were synthesized from pseudoboehmite (Catapal A, Vista), phosphoric acid (85 wt.%, Aldrich), a template, a metal ion source and deionized water similar to the previous methods [2,8,29]. Di-*n*-Propylamine (Aldrich, 99%, DPA) and triethylamine (Aldrich, 98%, TEA) were used as template molecules for AEL and AFI molecular sieves, respectively. Cobalt acetate tetrahydrate ($Co(OAc)_2 \cdot 4H_2O$, Aldrich, 98%), vanadium pentoxide (V_2O_5, Aldrich, 99.6%) and iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, Aldrich, 99%) were employed as the sources of the incorporated metals for CoAPO, VAPO and FAPO molecular sieves, respectively. Phosphoric acid was diluted with deionized water and metal sources, if any, were dissolved in the diluted solution. While stirring, pseudoboehmite and template were added successively to the mixture, which was stirred to a uniform reaction mixture. The reactant compositions for AEL and AFI were Al_2O_3: $1.0P_2O_5$: (0–0.2)MeO: 1.5DPA: $100H_2O$ and Al_2O_3: $1.0P_2O_5$: 0.2MeO: 1.5TEA: $100H_2O$ (Me: Co, V or Fe), respectively.

The gel of 40 g was loaded in a 100 ml Teflon autoclave, which was sealed and placed in a microwave oven (Mars-5, CEM, maximum power of 1200 W) for rapid heating. The autoclave was heated in 0.6–5 min to the reaction temperature of 190 °C (for AEL) or 170–180 °C (for AFI) and kept for a predetermined time. The ramping time was changed by controlling the power of microwave irradiation during the heat-up stage. Unless otherwise specified, the heating time to the reaction temperature was 2 min. The microwave power was 300 W during the synthesis step (at constant temperature) excluding the heat-up stage. The reaction temperature was controlled using EST-300 Plus system (Electronic sensor – temperature) that monitored and controlled temperature conditions inside sample vessels. More detailed information on the microwave methods including the temperature measurement is described elsewhere [30].

For conventional electric crystallization for slow heating, the gel was loaded in a Teflon lined autoclave and put in a preheated electric oven and maintained the temperature same as that of microwave synthesis for a fixed time. Unless otherwise specified, the ramping time was about 70 min. For some cases, the preset temperature of the oven was increased in order to increase the ramping rate. The