



Crystallization of ATO silicoaluminophosphates nanocrystalline spheroids using a phase-transfer synthetic strategy for n-heptane hydroisomerization

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ABSTRACT

Changing size and shape of zeolitic crystals brings about enhanced diffusion properties and related promotion of catalytic performances. This work puts forward a phase-transfer synthetic strategy to generate ATO nanocrystalline silicoaluminophosphates spheroids under tumbling crystallization using aluminum isopropoxide dissolved in toluene and other ingredients (fumed silica/phosphoric acid/Di-n-hexylamine) dissolved in water as precursors. Toluene and aqueous phase formed a Pickering emulsion like structure during hydrothermal crystallization. Highly uniform crystalline spheroids of weighted 55 nm with strong acidity and high surface area were obtained, which exhibited a high isomer yield up to 79% in n-heptane hydroisomerization. Comparisons of product distribution and kinetic studies suggest that monomethyl-branched isomer selectivity is controlled by product shape selectivity, whereas dimethylbranched isomer selectivity is affected by combined transition state and product shape selectivity. The increase in selectivity for ATO spheroids is attributed to an expansion of intrinsic reaction controlled temperature regime and an improved diffusion property.

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1. Introduction

Molecular sieves are widely used as adsorbents, ion-exchangers, or solid acid catalysts in various industrial processes, and new applications in fields such as light emitting, microelectronics, and medical diagnosis, are also reported more recently [1–4]. Among them, aluminophosphates (AlPOs) and silicoaluminophosphates (SAPOs) alongside zeolites are important heterogeneous catalysts for their unique shape selectivity imparted by crystallographically defined micropores, presenting an effective way to tailor product spectrum. AlPOs and SAPOs were first artificially synthesized by researchers in Union Carbide Corporation (UCC) in 1980s [5,6], and new framework topologies as well as new applications are expanding progressively ever since. Afterwards, SAPOs were found to possess intermediate acidity, desired shaped selectivity and catalytic durability, hence, suitable as solid acid catalysts. Representative SAPO-34 (CHA) and SAPO-11 (AEL) are nowadays used as commercial methanol-to-olefin (MTO) and hydroisomerization catalysts, respectively [7–9]. Unidimensional

zeolites and SAPOs, such as ZSM-22(TON) [10], ZSM-23(MTT) [11], ZSM-35(FER) [12], ZSM-48(*MRE) [13], SAPO-11(AEL) [14], SAPO-5(AFI) [15], SAPO-31(ATO) [16] and SAPO-41(AFO) [17], exhibit high hydroisomerization selectivity, owing to their tubular micropores that facilitate formation of monomethylbranched isomers (MBs) and pose constraints to the formation of multi-branched ones that are susceptible to cracking. In particular, SAPO-31 is an attractive acid catalyst for its 12 member ring (MR) circular shaped channel ($5.4 \times 5.4 \text{ \AA}$, running along [0 0 1] axis) that shows high isomer selectivity in n-hexane [18], n-octane [14] and n-hexadecane [19] hydroisomerization, which was attributed to a combined effect of shape selectivity from unidimensional pore structure and enhanced diffusion property from relatively large pore size. Besides, SAPO-31 are also useful catalysts for other reactions, such as Heck reaction of aryl chlorides [20], m-xylene isomerization [21], alkylation of toluene with methanol [22] and so forth. The catalytic performance of SAPOs, including SAPO-31, is not only dependent on the acid properties, but also relies on the morphology-relevant diffusion properties.

Hydroisomerization of n-paraffins is an important process in petrochemical industry. It is used to produce high octane number gasoline [23], to improve cold-flow properties of middle-distillate fuels and lube base oils [24], and also to transform long carbon

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chain wax obtained from Fischer-Tropsch synthesis to high grade fuels [25]. Typical hydroisomerization catalysts comprise a noble metal component serving as (de)hydrogenation centers and an acidic component responsible for skeletal isomerization and are therefore bifunctional [26]. Hydroisomerization of n-alkanes is a sequential reaction, n-alkanes undergo dehydrogenation to the corresponding olefins on metal centers before being protonated by Brønsted acid sites to form n-alkyl carbenium ions. These carbenium ions proceed skeletal rearrangement to produce iso-alkyl carbenium ions such as MBs or dimethylbranched isomers (DBs), which subsequently desorb from acid sites and are hydrogenated to iso-alkanes over metal sites [27–30]. The unwanted byproducts mainly stem from β -scission of DBs or trimethylbranched isomers (TB) that are more susceptible towards cracking [31]. If the two functions are well balanced, (de)hydrogenation reaches equilibrium and selectivities are solely dependent on the acidic components [32,33]. Under such ideal operation conditions, shape selectivity imparted by zeolitic pore structure plays deterministic role towards tailoring product distribution. The origin of shape selectivity in n-alkane hydroisomerization remains debated. Transition state shape selectivity involving cyclopropane intermediates [34,35], diffusion coefficient based product shape selectivity [36,37], combined transition state and product shape selectivity [38,39], as well as pore-mouth and key-lock concepts [40,41] have been proposed to explain hydroisomerization product selectivity. In addition, it has been recognized that hierarchical or nanosized zeolites show enhanced isomer yields than their micron sized counterparts [42]. The influence of architecture can be ascribed to shortening of diffusion path length and thus reduction of residence time of isomers, especially for DBs, inside the micropores, leading to a lowered cracking probability. To overcome the isomer selectivity loss caused by sluggish diffusion, various nano or hierarchical zeolites have been synthesized and employed as acidic components for skeletal rearrangement. Quite typically, to certain degrees, isomer selectivity increments were accomplished [42–45].

Nano or hierarchical zeolites have witnessed tremendous progress in the past two decades [46]. Several low-cost and scalable methods suitable for production of industrially important zeolites have been implemented, hierarchical ZSM-5 [47] and mesoporous FAU zeolite [48] are among the paradigms. In contrast, relatively fewer methods have been explored for the synthesis of SAPOs, and successful synthesis for AEL, AFI, CHA structured SAPOs using hard-template [49], soft-template [50], microwave synthesis [51], dry gel crystallization [52], post-synthetic modification [53], precursor control [8], etc., have been reported recently. Principally, these synthesis strategies can be divided into: (a) Dual templates route, using both an organic structure directing agents (OSDAs) for zeolite synthesis and an additional porogen for the generation of mesopores in the synthesis gel [54], (b) Multifunctional template route, using a single molecule containing structure directing fragments for the generation of both micro- and meso-pores [55], (c) Crystallization process control, generating nanozeolites while avoiding the use of a secondary templates [51], and (d) Post synthetic demetallation routes, introducing auxiliary porosity from pre-made zeolites by selectively leaching one of the framework elements to generate mesopores [56]. Among these, methods (a), (b) and (c) are bottom-up routes and method (d) is regarded as a top-down one. In particular, for hierarchical or nano ATO SAPO synthesis, only a bifunctional OSDA proposed by Ryoo et al [57] is available to generate hierarchical SAPO-31. The bifunctional OSDA, $C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-[CH_2-(C_6H_4)-CH_2-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2]-C_{22}H_{45}(OH^-)_4$, is able to direct the formation of ATO crystals characteristic of nanosheets morphology with precisely controlled thickness down to 3 nm, and a maximum isomer yield of 51% for n-heptane hydroisomerization has been

achieved. Nonetheless, the bifunctional OSDA is prohibitively expensive for industrial use and its preparation is tedious and requires strict anhydrous manipulations, which thereby is less likely to be a practical catalyst. Generating nano SAPO-31 is a promising, but nontrivial issue because common synthetic strategies can hardly be extended for its synthesis, since amorphous as well as competing phases may coexist in the final product [58]. The narrow synthetic window discourages further attempts to fabricate nano or hierarchical SAPO-31, consequently, no facile recipe to generate SAPO-31 nanocrystallites has thus far been reported, to the best of our knowledge.

In the quest for low-cost synthesis of nano SAPOs, herein, we present a single step phase-transfer synthetic concept to fabricate SAPO-31 nano spheroids with improved catalytic selectivity in hydroisomerization of n-heptane. Noteworthy, the method is arguably different from two-liquids syntheses that have been reported to fabricate SAPOs before, for instances, SAPO-5 in a biphasic water/hexanol system [59] or SAPO-11 in $H_2O/CTAB/butanol$ system [60]. These synthesis procedures influenced the final Si environment, modifying the mechanism of silicon incorporation into the framework and the consequent acid properties. Previous syntheses used two immiscible liquids as micelle system, i.e., one discontinuous aqueous phase containing all ingredients for zeolite synthesis enclosed by surfactants was dispersed in a continuous hydrophobic phase, whereby micelles acting as confined space to limit zeolites growth through steric hindrance [61,62]. In this proposed phase-transfer synthesis, conversely, aluminum isopropoxide (AIP) as Al source was dissolved in toluene phase, the rest ingredients such as OSDA, H_3PO_4 , SiO_2 and H_2O were dissolved in a separate aqueous phase, and crystallization was conducted under tumbling. We will disclose, for the first time, that a Pickering emulsion like structure in situ formed is responsible for formation of uniform SAPO-31 spheroids. The catalytic consequence of these spheroids shall be evaluated in n-heptane hydroisomerization. Kinetic studies and catalytic product distribution comparisons permit us to distinguish the origin of shape selectivity for individual isomers. Meanwhile, diffusion influences over cracking products shall be considered by distinguishing the effect of temperature into reaction controlled and diffusion controlled regimes. This investigation is structured into three parts. First, we report the synthesis and structural features for the obtained SAPO-31 spheroids, as shall be revealed with extensive characterization techniques, such as X-ray Diffraction (XRD), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Field-Emission Scanning Electron Microscope (FE-SEM), Transmission Electron Microscope (TEM), N_2 physisorption, Pyridine desorption Fourier-Transform Infrared Spectroscopy (Py-IR), ^{27}Al , ^{31}P , ^{29}Si MAS NMR. Next, the underlying formation mechanism is postulated based on monitoring the crystallization process with XRD, FE-SEM, and elemental composition analyses of both solid and aqueous phases. Through comparison with a standard hydrothermal synthesis, a new confined growth concept will be proposed. In the final part, the influence of crystal size on catalytic n-heptane hydroisomerization will be assessed. A structure-catalysis relationship will be revealed by correlating catalytic properties with kinetic studies, diffusion properties and structural features.

2. Experimental section

2.1. Materials

Samples were prepared from the following materials. Aluminum isopropoxide (AIP, 98%, TCI) was used as aluminum source. Phosphoric acid (85%, Shanghai Lingfeng Chemical Reagent Co. Ltd.) was used as phosphorus source. Fumed silica (Shanghai Kaiyin Chemical Reagent Co. Ltd) was used as silicon source.

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