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The influence of L-lysine and PDADMA on the crystal size and porosity of zeolite Y material

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ABSTRACT

The influence of L-lysine, one of the most basic amino acids, and poly(diallyldimethylammonium) (PDADMA) poly(cations) with different molecular weights on the zeolite Y crystal size and porosity was evaluated by using a high-throughput experiment (HTE) approach, allowing the exploration of a wide range of organic compound concentrations under the same experimental conditions. Depending on their nature and molecular weight, the increased concentration of these organic compounds into the synthesis gel gradually delays the crystallization of the zeolite Y. An intermediate molar content of the amino acid (1 L-lysine:9 SiO_2) led to slight decrease of the crystallization rate and a significant reduction of the crystal size down to 300 nm. Thus, the L-lysine is assumed to act as a growth inhibitor. The addition of poly(cations) to the synthesis gel results in the creation of silica-rich mesoporous particles forming aggregates. The PDADMA is mainly located in the silica-rich particles and favor their formation along with their mesoporosity. The larger crystal size is attributed to the inhibition of the nucleation process by the poly(cations).

1. Introduction

Zeolites, crystalline materials with a controlled porosity, are obtained by the polymeric combination of TO_4 tetrahedra, T being either silicon or aluminum elements. The incorporation of the latter element into zeolite frameworks induces the generation of an intrinsic Brönsted acidity which, coupled with a typical high thermal stability, are responsible for their interesting adsorption, diffusion and catalytic properties [1]. Over the past century about 200 different zeolite structures were discovered, but so far only a few have found an industrial application [2–6]. It is the case of zeolite Y, exhibiting a FAU-type structure with a three dimensional porosity, 12 membered rings windows and a silicon to aluminum molar ratio (Z) in the range of $1.5 \leqslant Z \leqslant 2.5$. Its pseudo-linear channels facilitate the diffusion of bulk hydrocarbons while its supercages act as nanoreactors adapted for hydrocarbon cracking. Still, important diffusion restrictions occur inside its porosity, motivating both industry and research fields to find new stable zeolite structures with larger pores and to improve the diffusion inside existing zeolite crystals [7].

There are two ways to improve this diffusion: the first is to generate an intracrystalline mesoporosity under acidic conditions or hydrothermal treatments (dealumination), under basic conditions (desilication) or by using sacrificial templates with a controlled size during the zeolite synthesis [8–11]. The second and most effective way is to decrease the typically micrometric crystals size below 100 nm. Such materials have an exalted specific surface area and an increased accessibility of their inner acid sites which, in turn, implies enhanced catalytic properties [12–20]. By shortening 10 times the diffusional pathway of a zeolite, one may multiply the hydrocarbon diffusion coefficient by a factor comprised between 3 and 10 and thus, inhibit the overcracking [21].

To obtain nanozeolites, the nucleation step should prevail on the growth step. Several synthesis methods were developed for this purpose over the last years. The most outlined is the clear solution method, where high water/hydroxide anion molar ratio and large quantities of structure-directing agents in their hydroxide form are used to avoid the gelification of the synthesis solution, and thus the condensation of nuclei in solution [12,22–24]. It allows the formation of well-distributed nanocrystals, but the yield is typically low, below 12 wt% in the case of FAU-type zeolites. At the opposite, it is also possible to provoke a burst of nucleation, at the expense of the growth step, by using low water/hydroxide anion molar ratio but the crystal size distribution is broader, and crystal agglomeration occurs [12,25–26]. The temperature of those two methods is usually moderated, to favor the nucleation. A third method, based on the synthesis of zeolites in confined space such

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as mesoporous materials, thermoreversible polymers or different inverse microemulsion systems, allows to recover nanocrystals with a tailorable maximal size [27–29]. But as before, agglomeration of crystals with a broad size distribution is observed. Thus, zeolite nanocrystals synthesis did not reach yet ripeness and numerous problems persist, restraining their use at the industrial scale.

Generally, organic compounds are widely used, sometimes even in industry, to finely control the morphology, polymorphism, agglomeration or size of several mineral particles [30–32]. In zeolite synthesis, organic compounds are mostly used to specifically direct the formation of one crystalline structure: in that case, they are called structure-directing agents. Sometimes they can also have the opposite effect, blocking the crystallization of one or several undesired structure types. Thus, a low concentration of hexamethonium cations can inhibit the crystallization of a MFI-type zeolite, and some of the organic dyes, such as crystal violet or acriflavine, can be adsorbed specifically at the surface of crystals from an initial mixture of zeolites A (LTA), P (GIS), X and Y (FAU), directing the formation of a unique structure [33,34]. But so far, a systematic study of their effect on zeolites, particularly for size control, was rarely performed or was concluded in a low impact [35–37].

L-lysine is an amino acid with two amino groups, which makes it one of the most basic of the 22 amino acids. It was successfully used to inhibit the size of silica nanoparticles above 10 nm by adsorption on their surface [38,39]. Very recently, L-lysine also led to a size control of silicalite-1 (MFI) crystals between 50 and 100 nm [40]. To our knowledge, this amino acid was never used during the synthesis of an aluminosilicate such as zeolite Y (FAU), although that its strong affinity with FAU-type zeolite frameworks was already reported, giving a clue of a possible growth inhibitor effect [41,42].

Zeolite films are usually produced from a layer-by-layer assembly of zeolite seeds or nanocrystals, bounded by strong electrostatic interactions generated by poly(cations) [43,44]. One of these poly(cations), the poly(diallyldimethylammonium) chloride (PDADMA), was also used during the synthesis of a FAU-type zeolite X in a previous study [45]. The authors observed the generation of a mesoporosity which would result from the auto-assembly of zeolite X nanocrystals, the complete aggregation being limited by the presence of the poly(cation) between the nanocrystals. Nevertheless, only a proof of a surface mesoporosity was supplied.

Thus, this study aims to better understand the influence of both L-lysine and PDADMA on zeolite Y crystal size and mesoporosity, by using a high-throughput experiment (HTE) approach allowing the exploration of a wide range of organic compound concentrations in parallel and in the same conditions.

2. Experimental

2.1. Synthesis of zeolite Y

L-lysine (Alfa Aesar, 98%) and poly(diallyldimethylammonium) chloride of various molecular weights (Aldrich) were used as purchased. Hereafter the different PDADMA will be named PDADMA-1 (molecular weight below 100.000 g/mol), PDADMA-2 (100.000–200.000 g/mol), PDADMA-3 (200.000–350.000 g/mol) and PDADMA-4 (400.000–500.000 g/mol) for convenience. The gel preparations and hydrothermal syntheses were performed using a Tecan Freedom EVO liquid handling robot and a Top Industry high-throughput heated and stirred multi-autoclave unit (100 Monel autoclaves, 5 mL), respectively. First, an appropriate amount of organic compound was homogenized in 0.37 mL of deionized water, in the autoclave. 1.057 mL of a 20 wt% aqueous solution of sodium hydroxide (Prolabo, 99%), followed by 0.756 mL of a 4 wt% aqueous solution of sodium aluminate (Carlo Erba, 56% Al_2O_3, 37% Na_2O) were then added under magnetic stirring. Finally, 0.817 mL of a Ludox AS-40 colloidal silica (Aldrich, 40% in water) was added dropwise to the mixture, giving the following gel molar composition: 9 SiO_2:0.4 Al_2O_3:6 Na_2O:x OC:150 H_2O ; with $x = 0.05–2$ when OC (organic compound) = L-lysine and $x = 1.10^{-4}–1.10^{-2}$ when OC = PDADMA. The gel was stirred at 200 rpm during 18 h, prior to be heated at 100 °C for 6 h under static conditions. After synthesis the product was filtrated, washed with deionized water several times and dried overnight at 100 °C. The organic compounds were finally removed by calcination in a muffle furnace at 550 °C during 8 h in air.

2.2. Characterization

Wide-angle powder X-ray diffraction patterns were collected on a Bruker D4 Endeavor diffractometer equipped with $CuK_{\alpha 1}$ monochromatic radiation source (40 kV, 40 mA). Diffraction patterns in the 5°–40° region were recorded with a 0.02° step size (step time = 1 s) and a variable slit mode. The intensity distribution was recalculated to simulate a fixed slit mode. Here, the crystallization rate (τ) is defined as the difference between diffraction peak intensities of the as-synthesized powder in the 19°–32° 2θ range (d_{hkl} (FAU) = 440, 533, 642 and 555) and those of one zeolite Y sample fully crystallized and synthesized without organic compound under the same experimental conditions. The accuracy is ±5%. The refinement of the unit cell parameters was performed using the Eva Solid Solutions v 16.0 software and knowing that FAU-type zeolites crystallize in a cubic system. The formula proposed by Fitchner–Schmittler et al. [46], linking the unit cell parameter of a FAU-type zeolite to its silicon to aluminum molar ratio, was applied. The synthesized materials were also analyzed using a Jeol JSM-6340F scanning electron microscope, under an acceleration voltage of 1 kV. Samples were prepared by depositing a drop of solution containing the sample in ethanol on an aluminum mounting. Transmission electron microscopy images were realized using a Jeol JEM-2100F microscope equipped with a JEOL EX-2300-BU energy dispersive spectrometer under an acceleration voltage of 200 kV. For EDX mapping, the sample was tilted by 7° and the analysis lasted 30 s. The samples were embedded in an epoxide-type resin (EPON) block and cured at 60 °C during 48 h. The block was then sliced up by a microtome to produce 70 nm-thick sections following a method reported elsewhere [47]. Thermogravimetric analysis was carried out using a TA Instrument SDT 2960 thermoanalyzer between the room temperature and 800 °C, at a heating rate of 5 °C/min. Reconstituted air (80% N_2 and 20% O_2) with a flow rate of 1 L/h was used during measurement. Nitrogen sorption measurements were performed at −196 °C on a Micromeretics ASAP 2010 apparatus. Samples were degassed at 350 °C during 10 h prior analysis. Surface area was calculated according to the BET method. Pore volume and external surface were determined using the *t*-plot method.

3. Results and discussion

The Table 1 shows the relation between the molar content of the different organic compounds in the synthesis gel and the crystallization rate of the material obtained. This molar content was slightly increased between the experiments, until an initial decline of the material crystallization rate (= 70–80%) was observed. At this point, the organic compounds reach a critical molar content ($x = 0.001$ for PDADMA and $x = 1$ for L-lysine) impacting the nucleation process. Interestingly, a good correlation is observed between the use of PDADMA poly(cations) at different molar