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Methanol-to-olefin reaction on SAPO-35 catalysts synthesized with controlled crystal size and using mesoporogen additives

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ABSTRACT

SAPO-35 molecular sieves have been synthesized using different additives. Monosaccharides were employed in order to decrease the crystal size and classical mesoporogen agents (carbon black and chitosan) were combined with the sugar additives to generate small crystals of SAPO-35 with intracrystalline mesoporosity. This synthesis strategy produces silicoaluminophosphate materials with larger non-microporous surface area, which facilitates the mass transfer within the catalyst. Thus, the use of these synthesis additives allows to retard catalyst deactivation in the methanol-to-olefin process.

1. Introduction

Short chain olefins constitute one of the most important petrochemical classes, being the global production of ethylene and propylene in the range of 200 million tons/year. They are primarily obtained by thermal cracking of naphtha, but there is a growing need to develop processes to produce lower olefins from alternative, non-petroleum sources. The technology for converting methanol into hydrocarbons, developed by Mobil Oil Company in 1976 [1], was initially considered a powerful method to make high quality gasoline from coal. However, almost any kind of hydrocarbon, including light olefins, can be obtained from methanol depending on the catalyst and operation conditions employed. Thus, this process provides a way to produce high-value petrochemicals from non-traditional row materials, as methanol can be obtained via intermediate syngas production by reforming of natural gas or from any gasifiable carbon-based feedstock, including coal [2] or biomass [3], as well as by chemical recycling of carbon dioxide [4,5]. Due to the steady increase in the global demand of ethylene and propene, the transformation of methanol into light olefins (MTO process) is getting a renewed interest. The MTO technology is ready now for commercial operation [6] and first commercial plants started up in China in 2010.

Small pore silicoaluminophosphate (SAPO) molecular sieves are efficient MTO catalysts [7–9]. The small apertures of pore cages in these SAPO materials restrict the diffusion of branched and heavy hydrocarbons by real shape-selectivity, leading to exceptionally high selectivity towards C2-C4 olefins.

The cage-based silicoaluminophosphate SAPO-34 is one of the most promising materials as catalyst for this process [8–11]. SAPO-34 structure, analogous to the zeolite chabazite, consists of large cages accessible through 8-ring (8R) windows with dimensions 3.8×3.8 Å that form a 3-directional system of channels [12]. The MTO reaction over SAPO-34 catalysts has been found to be dominated by the so-called hydrocarbon pool mechanism [13–15]. According to this mechanism, methanol is dehydrated to dimethylether that is subsequently dehydrated producing hydrocarbon molecules encapsulated within SAPO cavities. Among these products, the main intermediate species are polymethylbenzenes that interact with the oxygenated reactants (methanol or dimethylether) generating a sequence of steps that results in the production of olefins and the regeneration of the original hydrocarbon species, thus completing the cycle. The main drawback of these materials as catalyst in the MTO reaction is the rapid deactivation they suffer under reaction conditions, caused by the deposition of high molecular weight hydrocarbons on the pore entrances, which restricts the diffusion of reactants and products [16,17].

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Other small-pore zeolitic topologies have been tested as MTO catalysts [18–22], and the important role of the structural characteristics of the catalyst has been demonstrated [14,23]. The size and shape of the cages and channels may determine the kind of organic molecules that can be formed inside the catalyst and those that can diffuse out from it. Thus, framework topology controls the final selectivity towards different hydrocarbon products. SAPO-35, which is a small-pore molecular sieve analogous to the zeolite levinite, is made up of Levine cages connected through six-rings (6R) and double six-rings (D6R). These cages are accessible through 8R windows of dimensions 3.6 × 4.8 Å [12]. This silicoaluminophosphate has been tested previously in the MTO reaction [19,24,25] and showed to produce high selectivity to C2-C4 olefins with high initial reaction rate, but with shorter lifetime compared to other related materials as SAPO-18 or SAPO-34 [23]. Various studies indicate that crystallites size and morphology affect directly to the catalyst performance. There is a clear benefit of increasing the external surface area on the lifetime of SAPO catalysts in methanol-to-olefin reaction. Several strategies, such as creating mesoporosity in the sample by the addition of mesoporogen additives or reducing the crystal size, can be adopted in order to increase the non-microporous (external or mesopore) surface of the samples, improving methanol conversion efficiency and prolonging the lifetime [26–33]. Carbon-black and chitosan have been demonstrated to be efficient mesoporogen additives [34–36]. On the other hand, in a previous work, the amino sugar glucosamine was found to show a crystal growth modifier effect in the synthesis of SAPO-35 [37]. Even if it was initially proposed as a mesoporogen additive, glucosamine acted indeed blocking the crystal growth of SAPO-35 nuclei. It was postulated that glucosamine molecules may interact with the hydrophilic surface of SAPO-35 growing crystals, surrounding them and hindering their growth.

As the external surface area value (meaning all the non-microporous surface area, that is, the sum of both the actual external surface of crystals and the area of mesopores) is strongly influenced by the size of the crystals and also by the presence of mesopores, in the present study our goal was to modify both properties in SAPO-35 samples by using a combination of crystal growth modifier and mesopore modifier additives. Highly crystalline SAPO-35 samples with controlled crystal size were obtained varying the amount of glucosamine added to the synthesis gel. A combination of glucosamine and chitosan or carbon black additives was employed in order to obtain small crystals of mesopore-modified SAPO-35, aiming to shorten the diffusion path of reactants and products inside the crystals and thus increase the lifetime of the catalyst in the MTO reaction.

2. Experimental

2.1. Synthesis of SAPO materials

Hydrothermal synthesis of SAPO-35 samples was carried out using hexamethyleneimine (HMI, Sigma–Aldrich, 99%) to template the zeotype topology. Aluminum hydroxide hydrate (Sigma–Aldrich), ortophosphoric acid (Riedel-de-Häen, 85%) and fumed silica (Aerosil 200, Degussa) were used as sources of the framework-forming elements. Gels with molar composition Al_2O_3: P_2O_5: 0.6 SiO_2: 1.5HMI: 55 H_2O were prepared, to which different modifiers were added. D-(+)-glucosamine hydrochloride (GluN, Sigma–Aldrich, 99%) or D(+)-glucose (GluC, Panreac) were added to the gels as crystal growth modifier additives. In order to generate mesoporosity in the samples, chitosan (CH, medium molecular weight 75–85% deacetylated chitin, Sigma–Aldrich) and carbon black (CB, BP2000, CABOT Corporation, particle size: 12 nm) were incorporated to the synthesis. Table 1 summarizes the concentration of additives (in grams per 100 g of gel) used in each synthesis. All the samples were prepared by hydrothermal synthesis in a convection oven at 473 K and autogeneous pressure for 24 h. These conditions were adjusted previously for the reference sample (synthesized without additives) in order to obtain pure LEV phase crystals. In a typical procedure to synthesize SAPO-35, a solution containing the orthophosphoric acid and 44% of the total weight of water was added dropwise onto a dispersion of aluminum hydroxide in 34% of the total weight of water. The mixture was vigorously stirred for 2 h in order to obtain a uniform gel. Then, the silicon source dispersed in 22% of the total weight of water was added to the gel. After stirring vigorously for around 30 min, HMI was added dropwise and the gel was stirred to make it perfectly homogeneous. All the additives except chitosan were added to the gels after the incorporation of the organic template except chitosan that was incorporated dissolved in the orthophosphoric acid solution. The gels obtained were transferred into Teflon-lined stainless steel autoclaves with and internal capacity of 40 cm^3, which were heated under the mentioned crystallization conditions. The resulting solids were collected by centrifugation, washed several times with ethanol and water and dried at 338 K overnight. Prior to catalytic testing, the organic template and additives trapped within the pores of the silicoaluminophosphate were removed by calcination under air flow (100 mL/min) at 823 K. The duration of the thermal treatment required to achieve complete removal of these compounds was 7 h for the reference sample, 8 h for samples prepared with glucosamine or glucose and 16 h for samples prepared with glucosamine and chitosan or carbon black.

2.2. Characterization

Powder X-ray diffraction patterns of the as-synthesized and calcined samples were recorded with a PANalytical X'Pert Pro diffractometer using CuKα radiation with a nickel filter. The organic content of the samples was determined by thermogravimetric analyses (TGA) using a PerkinElmer TGA7 instrument. The TGA analyses were performed at a heating rate of 20 K/min under air flow. Textural properties (pore volume and surface area) of the calcined samples were determined by nitrogen adsorption/desorption measurements at 77 K employing a Micrometrics ASAP 2010 volumetric apparatus. Previous to analysis, the samples were degassed at 632 K for 20 h. Chemical composition of the inorganic solids after calcination was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a PerkinElmer 3300DV instrument. Samples were dissolved by alkaline fusion prior to the analysis. ^{29}Si CP/MAS NMR spectra were recorded at room temperature using a Bruker AV 400-WB spectrometer operating at 79.5 MHz, with a 4 mm probe spinning at 10 kHz. A $\pi/2$ pulse of 3 μs, contact time of 6 ms and recycle delay of 5 s were used. The chemical shifts were referenced to tetramethylsilane (TMS). Ammonia temperature programmed desorption (NH_3-TPD) was performed using a Micrometrics Autochem II chemisorption analysis equipment. Typically, 100 mg of sample pellets (30–40 mesh) were pretreated at 823 K for 1 h in helium flow (25 mL/min) and then cooled to the adsorption temperature (450 K). A gas mixture of 5.0 vol% NH_3 in He was then allowed to flow over the sample for 4 h at a rate of 15 mL/min. Afterwards a 25 mL/min helium flow was passed over the sample while maintaining the temperature at 450 K for 30 min to remove weakly adsorbed NH_3, and finally the temperature was increased to 823 K at a rate of 10 K/min. The crystal size and morphologyof the SAPO-35 samples were studied by scanning electron microscopy (SEM) using a Hitachi TM-1000 microscope operating at 15 kV with a solid state backscattering detector (BSE) and a FEI Nova NanoSEM 230 microscope operating at 5 kV with a vCD detector.

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