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Short communication

Gas-phase dehydration of glycerol over hierarchical silicoaluminophosphate SAPO-40

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ABSTRACT

Hierarchical silicoaluminophosphate SAPO-40 was synthetized using an organosilane acting as additional porogen agent. The structural, textural and acid properties of the new material were evaluated using XRD, ^{29}Si and ^{27}Al MAS NMR, SEM, N_2 adsorption, pyridine adsorption followed by IR spectroscopy and thermal analyses. The evaluation of the catalytic performance in the dehydration of glycerol has evidenced a high activity and a very low deactivation rate. When compared with the conventional SAPO-40, this catalyst shows higher acrolein selectivity and a significantly longer catalytic lifetime.

1. Introduction

Glycerol is a chemical product with a paramount importance in a variety of applications that include the pharmaceutical, cosmetic and food industries. Nevertheless, this compound is the main by-product of the biodiesel industry and due to the continuous demand for bio-fuels its production has increased significantly, which tends to reduce the market price. The conversion of glycerol into value-added products is thus an important variable to consider in order to improve the biodiesel economic viability [1–3].

One of the most studied routes to the conversion of glycerol is its conversion to acrolein that has important uses in the polymer and detergents industries. Glycerol can be converted to acrolein by an acid-catalyzed dehydration reaction in liquid or gas-phase using a large variety of catalysts. The gas-phase process is considered more advantageous due to the environmental and operational issues usually associated with the liquid-phase route. Different types of catalysts have been reported for this reaction in gas-phase that include zeolites, heteropolyacids, metal oxides and modified mesoporous silica materials [4–11]. This reaction has been shown to be highly dependent on the textural and acid properties of the catalyst [7,11–13]. The formation of acrolein is favored in presence of medium to strong Brönsted acid sites (Supplementary data, Scheme SD1), however, in these conditions the formation of coke will also increase, giving rise to a faster deactivation of the catalyst. The presence of large pores in the catalyst reduces the constraints to the mass transfer and usually improves the performance by facilitating both the access of the reactants to the active sites and the diffusion of reaction products.

SAPO-40 is a microporous silicoaluminophosphate, first reported by Lok et al. in 1984 [14]. This material has a large pore structure with 12-membered rings channels running parallel to the c-axis with a free diameter of 6.7 Å and 8-membered rings forming channels parallel to the b-axis with a free diameter of 3.8 Å that intercept to form a two-dimensional pore structure (AFR topology) [15]. AFR-based materials have proved to be highly resistant to thermal and hydrothermal treatments, although this may depend to some extent on the composition [16,17]. This high stability is a key-point when considering a catalyst for the dehydration of glycerol to acrolein since the reaction is usually carried out at high temperature and in presence of a large amount of water.

In a previous work [18] we have demonstrated the superior performance of SAPO-40 material as catalyst for the gas-phase conversion of glycerol towards acrolein, when compared with other silicoaluminophosphates (SAPO-34 and SAPO-11). This catalyst has shown high catalytic activity and hydrothermal stability, nevertheless, its catalytic performance would benefit from a larger porosity, as the deactivation seems to be mainly due to the coke formation. Fewer constraints to the mass transfer may facilitate both the access to the inner active sites and the diffusion of the reaction products thus allowing a lower reaction temperature and an improved lifetime of the catalyst [4,7,11].

Introduction of hierarchical porosity in microporous catalysts has gained a renewed interest due the superior performance in a large

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variety of chemical reactions [19–21]. To attain this objective, several strategies have been developed including the use of soft and hard co-templates and post-synthesis treatments such as alkaline desilication [22]. In the case of silicoaluminophosphates, although post-treatments may be used to create porosity [23], other strategies using organosilane surfactants in the conventional synthesis procedure [24–26] have been attempted and proved successful for selected structures.

In this work, we have introduced an additional porosity in SAPO-40 using [3-(trimethoxysilyl)propyl]-octadecyldimethyl-ammonium as secondary template. Its catalytic performance was compared with the conventionally prepared SAPO-40 in the gas-phase dehydration of glycerol.

2. Experimental

2.1. Synthesis

Pseudoboehmite (Pural SB, Condea, 74% Al_2O_3), fumed silica (Cab-OSil M5, Fluka), ortho-phosphoric acid (85% Merck) and tetrapropylammonium hydroxide (40% aq. sol., Alfa) were used to prepare SAPO-40 according to the method described by N. Dumont et al. [27], which comprises the preparation of two solutions. Briefly, for the preparation of solution A, 10.53 g of pseudoboehmite was mixed with 12.30 g of water and 17.63 g of ortho-phosphoric acid. The mixture was left under magnetic stirring for 4 h. A second solution, solution B, was prepared by mixing 9.88 g of water, 20.0 g of tetrapropylammonium hydroxide and 0.77 g of fumed silica. After stirring for 2 h, 9.73 g of solution A were added to solution B and the final mixture was aged for 2 h. The gel, with a molar composition of $0.93Al_2O_3/0.93P_2O_5/0.65SiO_2/2TPAOH/74H_2O$ was submitted to a hydrothermal treatment at 200 °C during 144 h in static conditions.

Mesoporous SAPO-40 (mSAPO-40) was prepared following closely the method used for the preparation of SAPO-40, replacing part of the silica source (Cab-OSil-M5) in the synthesis gel by [3-(trimethoxysilyl)propyl]-octadecyldimethyl-ammonium chloride (Aldrich, 78%) (TPOAC) and adjusting the other quantities (amount of solution A and water). The required amount of TPOAC was mixed with part of the water and let to hydrolyze overnight before mixing with TPAOH and the silica. The final gel composition was $0.98Al_2O_3/0.98P_2O_5/0.5SiO_2/0.15TPOAC/2TPAOH/120H_2O$. The final mixture was submitted to a hydrothermal treatment at 200 °C during 144 h.

Both samples were calcined at 550 °C for 12 h under a flux of dry air. This procedure assures the complete removal of the organic moieties.

2.2. Characterization

All the samples were checked for phase purity and crystallinity by powder X-ray diffraction on a Panalytical X'Pert Pro diffractometer using Cu Kα radiation filtered by Ni and an X'Celerator detector. ^{29}Si MAS NMR spectra were recorded on a Bruker Avance III 400 (9.4 T) multinuclear spectrometer. ^{27}Al MAS NMR spectra were recorded on a Bruker Avance III HD 700 (16.4 T) multinuclear spectrometer. SEM micrographs were obtained on a JEOL JSM-7001F equipment equipped with an Oxford light elements EDS detector. Pyridine (Py) adsorption was followed by FTIR spectroscopy using a home-made quartz cell allowing sample vacuum and temperature pretreatment and subsequent Py adsorption at 150 °C. Quantitative measurements were done as described elsewhere [28]. Thermogravimetric data (TG) were obtained with a TG92 Setaram apparatus, under air at a heating rate of 10 °C/min. Nitrogen sorption experiments were performed using an ASAP 2010 series equipment from Micromeritics. Prior to measurements, samples were outgassed first at 90 °C and then at 350 °C, during 1 and 4 h, respectively.

2.3. Catalytic tests

Dehydration of glycerol was performed at 320 °C under atmospheric pressure, in a fixed-bed quartz reactor (i.d. 1.5 cm) using 300 mg of catalyst.

Before each test, the catalyst was maintained for 2 h at 500 °C under a flux of dry nitrogen (30 $mL\cdot min^{-1}$). The reaction feed, an aqueous solution containing 10 wt% of glycerol, was introduced into the reactor by a syringe pump KD Scientific at a WHSV of 0.85 h^{-1} and diluted in a flow of dry nitrogen (30 $mL\cdot min^{-1}$). The reaction products were collected in an ice trap followed by two additional water traps. The reaction products were analyzed on a Chrompack CP9001 gas chromatograph equipped with a 25 m OPTIMA FFAP Macherey Nagel capillary column and a FID detector. For quantitative measurements 1-propanol (for low boiling point products) and 1,4-butanediol (for glycerol) were used as internal standards.

The conversion and selectivity were calculated as follows:

$$\%\text{Conv} = \frac{ng_{total} - ng_t}{ng_{total}} \times 100$$

$$\%\text{Sel}_i = \frac{ng_{i,t}}{ng_{total} - ng_t} \times 100$$

where ng_{total} is the total number of moles of glycerol injected into the reactor during the time on stream t, ng_t the number of moles of glycerol in the products recovered at time on stream *t* and $ng_{i,t}$ the number of moles of glycerol converted to the product *i* during the time on stream *t*. In order to obtain a significant amount of products, each analysis corresponds to the products usually recovered for 3 h. The products obtained for the first hour were rejected due to a poor mass balance. The time on stream indicated in Table 2 and Figs. 4 and 5 correspond to the middle point of the recovering time interval.

3. Results and discussion

Fig. 1 shows the XRD patterns obtained for as-prepared SAPO-40 and mSAPO-40. The patterns agree with the presence of the AFR as the sole crystalline phase (ICDD PDF2 # 01-087-1146). Although the pattern of mSAPO-40 is perfectly defined, the shape of the baseline also suggests the presence of some amorphous phase, which is confirmed by SEM (Supplementary data, Fig. SD1). In what concerns the crystal morphology, mSAPO-40 sample shows interconnected plate-like crystal aggregates which contrasts with the isolated plate-like crystals typical of SAPO-40 [18].

The structural and textural parameters of the samples mSAPO-40 and SAPO-40 are presented in Table 1. When compared with SAPO-40,

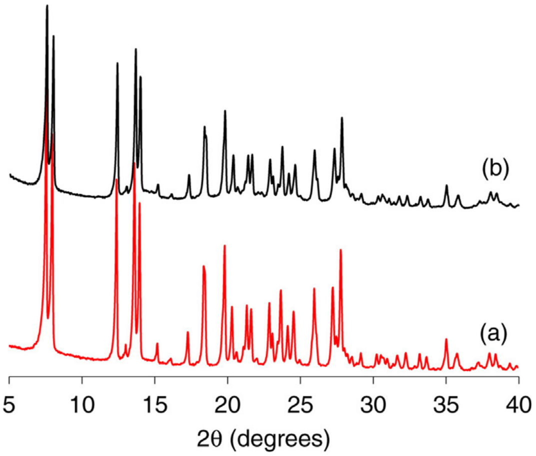

Fig. 1. XRD patterns of as-synthetized SAPO-40 (a) and mSAPO-40 (b).