Tailoring the acid strength of microporous silicoaluminophosphates through the use of mixtures of templates: Control of the silicon incorporation mechanism

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ABSTRACT

SAPO-5 samples have been synthesized with triethylamine (TEA), benzylpyrrolidine (BP) and mixtures of them as structure directing agents (SDAs). It has been observed that in the as-synthesised materials the concentration of SDAs (molecules per unit cell) and the Si content are similar. According to the different molecular size of both SDAs, the samples exhibit higher organic weight and lower water content as the molar fraction of BP in the synthesis gel increases. These differences in selectivity for organic/water incorporation influences the mechanism of Si substitution in the AlPO lattice: the higher organic content obtained at higher BP/TEA ratio leads to the formation of large Si islands, while the higher water content of the sample obtained with TEA enhances the formation of isolated $Si(OAl)_4$ environments. Interestingly, it has been found that these two opposite trends can be tailored to a certain point by using mixtures of both SDAs, TEA and BP, in the required ratio. The catalytic activity of the samples has been tested in the isomerisation of m-xylene. It has been observed a higher activity of samples obtained with BP as the main SDA, thus evidencing the better performance of large Si islands in this reaction.

1. Introduction

Since the discovery of microporous aluminophosphates (AlPO) in 1982 by Wilson et al. [1], the synthesis of these materials has been widely studied, yielding a diversity of structural types comparable to that of the previously known aluminosilicate-based zeolites [2]. Known microporous AlPO structures include polymorphs that are common to both SiO_2 and AlPO compositions, but also structures that have no zeolitic counterpart. In these AlPO materials, there is a strict alternation of Al^{3+} and P^{5+} ions; nevertheless, both ions can be isomorphically replaced by heteroatoms through different substitution mechanisms. The most common one is the replacement of Al by a divalent metal that gives a negative charge to the framework, which is usually charge-balanced by the organic cationic molecules that act as structure directing agents. However, Si^{4+} can also be incorporated in AlPO networks, giving place to acid catalysts with very interesting properties. Silicoaluminophosphates (SAPOs) have attracted considerable attention due to potential industrial applications; SAPOs have been tested for several acid-catalysed reactions such as isomerisation of xylenes [3–5], transalkylation [6], isomerisation of 1-pentene [7], isopropylation of benzene [8], methanol-to-hydrocarbons reaction [9] and oligomerisation of propylene [10].

The incorporation of silicon in AlPO frameworks is a special case where two different substitution mechanisms can simultaneously occur [11,12]. Silicon (Si^{4+}) can be incorporated via SM2 (Substitution Mechanism 2), that consists in the substitution of a single phosphorus ion (P^{5+}) for one Si (Si^{4+}), giving a negative charge per Si in the framework that is usually balanced by the positive charge of the organic molecules occluded within the microporous structure. This substitution mechanism gives an environment of Si surrounded by 4 Al atoms (in the second coordination shell, $Si(OAl)_4$). In the other mechanism (SM3), the incorporation of Si occurs via a simultaneous substitution of a pair of adjacent Al^{3+} and P^{5+} ions by two Si^{4+} ions, giving no net charge. Due to the instability of Si–O–P bonds, the latter mechanism is always accompanied by a certain extent of SM2 in order to prevent the formation of those unstable bonds, thus giving rise to silica domains (commonly referred to as Si islands) in the AlPO network. The simultaneous occurrence of both mechanisms results in the presence of different Si environments ($Si(OAl)_n(OSi)_{4-n}$, where n varies between 1 and 3). These environments are located at the border of the Si island, at the interface between the islands and the Al–O–P framework. Depending on the ratio of SM3 to SM2 substitutions, the size and concentration of the Si islands will be different.

In SAPO materials, Brønsted acidity rises when the negative charge of the framework (induced by the incorporation of Si through the SM2) is compensated by H^+, usually after calcination or ionic exchange of the cationic organic molecules. In the Si

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islands, the acidity is generated at the border, associated to the presence of $Si(OAl)_n(OSi)_{4-n}$ environments. It has been observed that the strength of the acid sites generated at the border of the Si islands is usually higher than that of the acid sites created by the isolated Si atoms ($Si(OAl)_4$), and increases as the value of n in those environments decreases [13]. In addition, it is generally accepted that the strength of the acid sites generated at the border of the Si islands increases with the island size. In summary, a higher number of acid sites are generated through SM2, while SM2 + SM3 yields less but stronger acid sites. Therefore, controlling the incorporation of Si through the different mechanisms would enable a control of the acidity of the materials, what would be very desirable for designing new and efficient catalysts for selected reactions. Following this aim, there have been many works on potential ways of controlling the Si incorporation into AlPO networks, especially by modifying the synthesis parameters [14,15]. An important improvement in the catalytic activity of SAPO materials was provided by the use of non-aqueous solvents (hexanol) and surfactants in the synthesis gels, which produced higher dispersion of Si in the crystals and smaller particles [4]. In our case, we aimed to control the Si incorporation via the rational use of the organic structure directing agents.

The synthesis of microporous materials involves the use of hydrothermal methods, where the source of the inorganic ions, water and, generally, an organic molecule, are heated in an autoclave for a certain period of time. The inclusion of organic molecules is usually required to direct the crystallization of a certain microporous structure, and so they are called structure directing agents (SDAs). The role of these organic molecules has been traditionally described as a "template effect" [16] to indicate that the organic molecules organize the inorganic tetrahedral units into a particular topology around themselves during the nucleation process, providing the initial building blocks from which crystallization of the microporous structures will take place. Nevertheless, the action of the SDA molecules is not limited to their role in structure directing the crystallization of the microporous structure, but they can also influence the substitution mechanisms by which Si is incorporated in the AlPO frameworks. Barthomeuf and coworkers studied the role of the SDA molecules in directing the Si incorporation in the network of SAPO-34 [17]. They observed that the occurrence of the different mechanisms whereby Si is incorporated depends on the organic SDA employed in the synthesis. It was concluded that Si substitution is governed by the number and charge of the SDA molecules that can be packed within the structure in order to charge-balance the negative charge generated by the inclusion of Si through SM2. A recent work has also evidenced the influence of the organic SDA employed in the synthesis over the distribution of Si in the AEL structure [18], leading to SAPO-11 materials with different catalytic activities. These works suggest that, at least in principle, the Si incorporation, and thus the acid strength of SAPO materials, could be controlled by a rational use of the organic molecules that structure-direct the crystallization of the microporous material. In a recent work we studied the structure directing effect in the presence of water of three different SDA molecules, triethylamine (TEA), benzylpyrrolidine (BP) and (S)-(−)-N-benzylpyrrolidine-2-methanol (BPM), in the synthesis of AlPO-5 (AFI type structure) [19]; this is a large-pore microporous structure composed of one-dimensional 12 membered ring (MR) channels with a diameter of 7.3 Å [2]. In that work we observed an important and complementary role that water molecules play in the structure direction of the microporous structure. Interestingly, we observed a higher water occlusion within the AFI structure when the synthesis was performed with TEA as the SDA, while the use of the aromatic molecules (BP and BPM) led to a lower water occlusion, specially in the material obtained with BPM. Such a difference in the water/organic occlusion would in principle lead

to a notable distinction in the hydrophilic/hydrophobic character of the channels of the microporous material. In last term, this could eventually lead to a different incorporation of Si in the AFI structure, since the incorporation of Si as Si islands would impart a more hydrophobic character to the network, while the predominance of SM2 mechanism would result in more hydrophilic materials. Based upon these grounds, we wondered whether the use of these different SDAs, and thus the different hydrophilicity of the resulting AFI materials, could provide a control over the Si incorporation, and would thus afford a fine-tuning of the acid strength of the obtained catalysts. Due to the high cost associated to the use of BPM as SDA, and thus the low interest of this molecule to be used in potential applications, only TEA and BP molecules will be studied in this work. Not only samples obtained with pure TEA and pure BP will be prepared, but also materials in which mixtures of both SDAs are used, in order to determine whether the features promoted by the use of the different SDAs can be modulated in this way.

2. Experimental details

Triethylamine (TEA, 99%) was purchased from Sigma–Aldrich. The synthesis of benzylpyrrolidine (BP) was carried out by reacting pyrrolidine (Sigma–Aldrich, 99%) with benzyl chloride (Sigma–Aldrich, 99%) in ethanol (90 °C, 24 h) in the presence of potassium carbonate (Sigma–Aldrich, 99%). The tertiary amine was extracted with chloroform and purified by vacuum distillation. The purity of the amine and its chemical formula was assessed by thin layer chromatography (hexane/ethyl acetate as solvent) and CHN chemical analysis (Perkin–Elmer 2400 CHN analyzer).

The synthesis gels were prepared with the following molar composition: x TEA:y BP:1.0 P_2O_5:1.0 Al_2O_3:0.5 SiO_2:40 H_2O, keeping a constant total SDA (TEA + BP) concentration of 1.5 ($x + y$ = 1.5). 1.5, 1.0, 0.5 and 0 values for 'x' (0, 0.5, 1.0 and 1.5 for 'y', respectively) were studied. The gels were prepared by adding the aluminium source, pseudoboehmite (Catapal Pural SB, 75.3% wt Al_2O_3), to a solution of phosphoric acid (Riedel-de Haen, 85 wt%) and water and stirred for 1h in a closed recipient (having a hole for the stirrer). The corresponding necessary amount of organic was then added (taking into account the addition of organic for the hydrolysis of TEOS, see below), and the stirring maintained for 2 h. The silicon source (tetraethylorthosilicate, TEOS, Merck, 99%) was previously hydrolysed in the presence of water and the organic molecule (40% of the necessary amounts) in a different vessel and the solution stirred until all the ethanol coming up from the hydrolysis of TEOS was evaporated; then it was added to the synthesis gels in the last step (after the addition of the remaining organic), and stirred for two more hours. The pH of the resulting gels was in a range between 3.5 and 4.1. The gels were introduced into 60 ml teflon lined stainless steel autoclaves and heated statically at 170 °C for 16 h. The resulting solids were separated by filtration, washed with ethanol and water and dried at 60 °C overnight.

Calcination of the samples was carried out by passing an oxygen stream enriched in ozone (3–4%) at 200 °C for 24 h. Complete removal of the organic molecule was assessed by TGA.

The crystallization of the AFI structure as a pure phase was assessed by X-ray diffraction (Seifert XRD 3000P diffractometer, Cu Kα radiation). Nitrogen adsorption–desorption isotherms were measured at −193 °C using a Micrometrics ASAP 2010 volumetric apparatus. All the samples exhibited isotherms characteristic of microporous solids, with a micropore volume (t-plot method, using the Halsey equation) of ca. 0.09 cm^3/g, total pore volume in the range 0.17–0.23 cm^3/g, BET surface area in the range 330–350 m^2/g, and external surface area ranging from 90 to 120 cm^3/g.

The organic content of the samples was studied by chemical CHN analysis (Perkin–Elmer 2400 CHN analyzer) and thermogravi-