



# Comparison of the structure-directing effect of ephedrine and pseudoephedrine during crystallization of nanoporous aluminophosphates



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## ABSTRACT

We present here a systematic study about the behavior of two diastereomeric chiral organic molecules, (1R,2S)-ephedrine and (1S,2S)-pseudoephedrine, for directing the crystallization of crystalline nanoporous aluminophosphates. We apply a combination of extensive synthetic experiments, characterization and molecular simulations in order to relate the different structure-directing effects of the two isomers experimentally observed with their particular molecular structure. Our results show a higher efficiency of pseudoephedrine to direct the crystallization of AFI materials: in contrast, ephedrine tends to give a layered-like phase with a strong supramolecular aggregation together with AFI materials. In addition, aggregation of ephedrine within the AFI channels is stronger than that of pseudoephedrine. Molecular simulations show a different conformational behavior for the two diastereoisomers, which is manifested in a different supramolecular behavior, and as a consequence a different structure-directing behavior. This multi-level study shows the intricacy between the absolute configuration of the structure-directing agents, and hence their molecular structure which results in the development of distinct intramolecular H-bonds, the molecular conformational space, the supramolecular chemistry associated, and the structure-directing mode of action during the crystallization of AFI-aluminophosphate materials, providing a molecular-level understanding of the structure-directing phenomena of these molecules.

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## 1. Introduction

Since life works in an asymmetric fashion, with only particular enantiomers of chiral building-blocks, L-aminoacids and D-sugars, making up the essential biological macromolecules, proteins and nucleic acids, chirality is fundamental for the correct functioning of living beings [1]. As a consequence, the metabolism of living beings differentiates between enantiomers of chiral compounds, very frequently having only one enantiomer the desired therapeutic effect [2]. In this context, the design of chiral solids able to discriminate between enantiomers of a chiral compound, either during separation or catalytic processes, represents one of the greatest challenges in contemporary chemical research [3,4]. In the quest for chiral functional solids, zeolites and crystalline

nanoporous materials in general have been proposed as ideal candidates since they could potentially combine their high surface area and characteristic shape-selectivity with a potential enantioselectivity that might be enhanced by the confinement effect [5–8]. Several chiral zeolites do actually exist and have been recognized as such [9], like polymorph A of zeolite Beta [10], the chiral zincophosphate CZP [11], the mesoporous chiral ITQ-37 zeolite [12] and HPM-1 [13], the silica-form of the chiral SU-32 silicogermanate [14]. However, almost always these nanoporous materials crystallize as racemic crystals, and consequently these solids cannot be used for asymmetric operations.

The traditional strategy to induce chirality in zeolite frameworks has been the use of chiral molecules as organic structure-directing agents (SDAs). These organic SDAs organize the inorganic tetrahedral units in a particular geometry from which crystallization of a particular framework takes place [15]. Despite the successful use of several chiral organic molecules as SDAs for the synthesis of zeolite materials, even some of them leading to chiral frameworks [6], the

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occurrence of racemic crystals evidences a lack of transfer of chirality from the organic molecule to the framework. In order to produce chiral solids, we have argued that self-assembling molecules that can develop supramolecular long-ranged chiral arrangements, more suitable to fit to the chiral dimension of zeolite frameworks which is manifested also at long-range, are more likely to promote such transfer of chirality. In this context, we have recently proposed the use of chiral (1R,2S)-ephedrine and (1S,2S)-pseudoephedrine as organic SDAs (see Fig. 1). The selection of these chiral precursors is four-folded, they have i) an aromatic ring which triggers the formation of supramolecular dimers through  $\pi$ - $\pi$  type interactions, ii) two stereogenic centers that will impart a strong asymmetric molecular structure, iii) H-bond donor and acceptor groups that will promote the formation of strong interactions between consecutive dimers, potentially leading to long-range chiral orderings, and iv) R-NH<sub>2</sub><sup>+</sup>-R' positively-charged groups that will develop strong electrostatic interactions with the negative charge associated to the isomorphic substitution of Al<sup>3+</sup> by divalent dopants (typical of nanoporous aluminophosphates). Such special features of these chiral molecules would potentially enable a transfer of chirality from the supramolecular long-range chiral ordering of the molecules not only to the overall framework itself, but also to the spatial distribution of dopants, leading potentially to solids with chirally-ordered distributions of dopants, representing a new concept of chirality in zeolite materials [16,17].

In recent works, we reported the structure-directing ability of (1R,2S)-ephedrine towards the crystallization of the AFI aluminophosphate framework in the presence of different dopants, showing a strong trend to self-assemble as  $\pi$ - $\pi$  stacked dimers when confined within the AFI framework [18,19]. A complementary study based on molecular simulations [20] suggested that ephedrine dimers tend to pack within the AFI channels developing a helicoidal ordering within the AFI channels, which might be transferred to the spatial distribution of dopants through H-bonds [21] and electrostatic interactions. On the other hand, we have recently reported a notably different supramolecular aggregation behavior of the two diastereoisomers, ephedrine and pseudoephedrine, during the crystallization of nanoporous aluminophosphates, which was explained with the aid of molecular simulations in terms of a different conformational behavior because of the occurrence of distinct intramolecular H-bonds in aqueous solution [22]. Due to the interest and novelty on the use of this type of chiral self-assembling molecules as SDAs, here we

report an extensive and systematic study about the structure-directing phenomena of (1R,2S)-ephedrine and (1S,2S)-pseudoephedrine during the crystallization of nanoporous aluminophosphates in the presence of different dopants and under very different synthesis conditions, paying special attention to their supramolecular aggregation behavior when confined within the porous materials. The experimental and characterization work is complemented with molecular simulations in order to understand from a molecular level the experimentally observed trends.

## 2. Methodology

### 2.1. Experimental details

Mg, Zn, Co and Si-doped AFI aluminophosphate materials were synthesized by hydrothermal methods using (1R,2S)-Ephedrine (EPH) (Sigma Aldrich, 98%) or (1S,2S)-Pseudoephedrine (PsEPH) (Sigma Aldrich, 98%) as organic structure-directing agents. Four different gel molar compositions were studied, 1R:xMeO:(1-x/2)Al<sub>2</sub>O<sub>3</sub>:1P<sub>2</sub>O<sub>5</sub>:100H<sub>2</sub>O, 2R:xMeO:(1-x/2)Al<sub>2</sub>O<sub>3</sub>:1P<sub>2</sub>O<sub>5</sub>:100H<sub>2</sub>O, 1R:xMeO:(1-x/2)Al<sub>2</sub>O<sub>3</sub>:1P<sub>2</sub>O<sub>5</sub>:50H<sub>2</sub>O and 2R:xMeO:(1-x/2)Al<sub>2</sub>O<sub>3</sub>:1P<sub>2</sub>O<sub>5</sub>:50H<sub>2</sub>O, where x was 0.11, 0.22, or 0.32; R stands for the organic SDA (EPH or PsEPH), and Me for the dopant (Mg, Zn, Co or Si). Pseudoboehmite (Pural SB-1 77.5% Al<sub>2</sub>O<sub>3</sub>, Sasol), phosphoric acid (Sigma-Aldrich, 85%), magnesium acetate Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (Sigma-Aldrich, 99%), zinc acetate Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (Sigma-Aldrich, 98%), cobalt acetate Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (Sigma-Aldrich, 98%) and tetraethylorthosilicate TEOS (Si(CH<sub>3</sub>CH<sub>2</sub>O)<sub>4</sub>, Merck 99%) were used as sources of Al, P, Mg, Zn, Co and Si, respectively. The gels were transferred into Teflon-lined stainless steel autoclaves with a capacity of 14 mL, which were heated statically at temperatures between 140 and 180 °C under autogeneous pressure for 24 h. The resulting solids were collected by filtration, washed thoroughly with ethanol and water and dried at room temperature.

### 2.2. Characterization

The obtained solids were characterized by powder X-Ray Diffraction (XRD), using a Philips X'PERT diffractometer with CuK<sub>α</sub> radiation with a Ni filter. Thermogravimetric analyses (TGA) were registered using a Perkin-Elmer TGA7 instrument (heating rate = 20°C/min) under air flow. UV-Visible diffuse reflectance spectroscopy was recorded with a UV-Vis Cary 5000 Varian

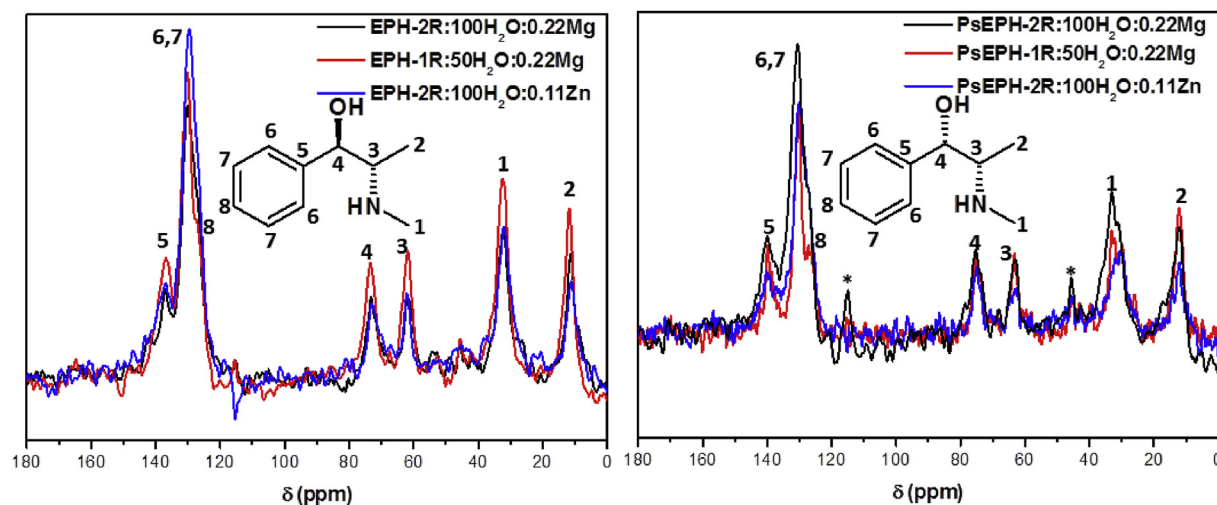


Fig. 1. <sup>13</sup>C CP NMR spectra of several AFI samples obtained at 180 °C with ephedrine (left) and pseudoephedrine (right). Bands assigned to degradation products are indicated by asterisks.

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