



Template-controlled acidity and catalytic activity of ferrierite crystals

A.B. Pinar, C. Márquez-Álvarez, M. Grande-Casas, J. Pérez-Pariente*

Instituto de Catálisis y Petroquímica (CSIC), c/ Marie Curie 2, Cantoblanco, 28049-Madrid, Spain

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ABSTRACT

A synthesis strategy to tailor the acid sites location in ferrierite crystals has been developed. The zeolite catalysts were synthesised in fluoride medium using different combinations of organic structure directing agents (SDAs) in the absence of inorganic cations. Therefore, the negative charge associated to the incorporation of aluminium to the framework was compensated exclusively by the positive charge of the organic SDAs. In this way, Al siting in the zeolite framework was driven by the specific location of the different SDA molecules within the zeolite void volume. Following this synthesis strategy, it has been found that the distribution of strongly acidic hydroxyl groups in the proton form of the zeolites obtained after removal of the organic templates was dependent on the combination of organic molecules used as SDAs. Moreover, the catalytic activity of the zeolites in *m*-xylene and 1-butene isomerisation increased as the relative population of strong Brønsted acid groups in sterically constrained sites inside the ferrierite cavity decreased.

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1. Introduction

Activity and selectivity patterns of a particular acid zeolite in different catalytic reactions are recognised to depend upon the combination of several factors, the number and distribution of acid sites in the framework among them. Controlling the distribution of framework aluminium atoms, and hence that of the acid sites, in zeolites is a much sought objective in zeolite research, as it would have a strong impact on catalytic activity and selectivity. Indeed, it has been shown for ZSM-5 [1–3] and MCM-22 [4] that Al distribution is dependent on the Si/Al ratio and on the synthesis procedure.

The presence of different types of cavities for a given zeolite topology introduces a high degree of complexity in the distribution of acid sites. Many interesting zeolite catalysts possess precisely the complex void architecture that makes them suitable candidates for the development of specific synthesis strategies envisaging to control the aluminium siting and hence the acidity of the structure. Ferrierite is one of such materials. Its structure consists of channels of 10-membered rings (10-MR, a ring constituted by 10 T atoms linked through T–O–T bonds, where “T” represents a Si or an Al atom tetrahedrally coordinated to 4 oxygen atoms) running parallel to the crystallographic [001] direction, which are intersected by 8-MR channels parallel to the [010] direction. In addition, 6-MR

channels run along the [001] direction. The intersection of these 6-MR channels with the above mentioned 8-MR channels leads to the formation of the “ferrierite cavity”, a [8²6²6⁴5⁸] cage accessible through 8-MR windows [5]. The ferrierite framework was first determined in the space group *Immm* [6] although reductions of symmetry have been reported [7–9]. In Fig. 1 a representation of the structure can be seen, showing the 4 non-equivalent T atoms (in space group *Immm*) and their accessibility from the 10-MR channel and the cage. It has been shown before [10–12] that this zeolite can be conveniently synthesised in the absence of alkaline cations by using an appropriate combination of small and large structure directing agents (SDA). In particular, the hydrothermal treatment of synthesis gels containing both 1-benzyl-1-methylpyrrolidinium (bmp) and tetramethylammonium (TMA) cations in fluoride medium allows the crystallisation of zeolite ferrierite. Furthermore, computational studies reveal that TMA cations are located inside the small cages, while the large and elongated bmp cations are placed in the 10-MR straight channel. Hence, both cations cooperate to build up the ferrierite structure. Moreover, in the absence of either bmp or TMA, ferrierite was not obtained, thus showing the key role of both cations in the crystallisation of this zeolite in these synthesis conditions. As far as no alkaline cations are present in the structure, the charge compensation of the aluminium atoms located in the framework is due to the cationic SDA only. Using CP-MAS NMR and heteronuclear correlation NMR, Lobo et al. [13] found that the positively charged fragment of the SDA is preferentially ordered near the negative frame-

* Corresponding author. Fax: +34 91 5854760.

E-mail address: jperez@icp.csic.es (J. Pérez-Pariente).

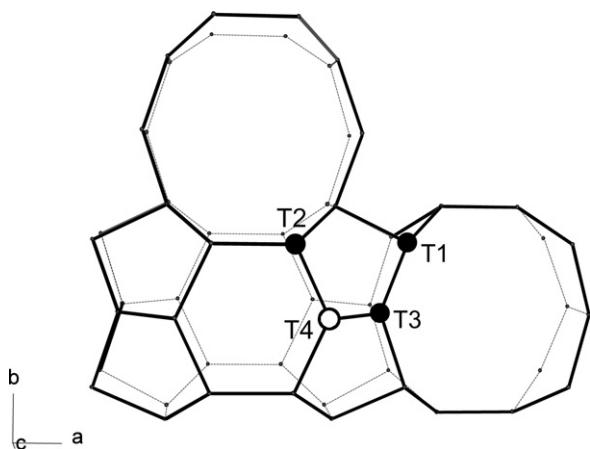


Fig. 1. Framework structure of FER showing the 4 non-equivalent T-atoms (in space group *Immm*). T1, T2 and T3 (black atoms) are accessible from the 10-MR channel and from the FER cavity. T4 (white atom) is accessible only from the cavity. Bridging oxygen atoms have been omitted for clarity.

work charge in ZSM-12, and suggested that the location of acid sites in the zeolite might be controlled by the charge distribution of the SDA. It could be then conceived that the framework sites occupied by aluminium in ferrierite would be eventually dependent upon the specific combination of SDAs used in the synthesis. Moreover, it has been evidenced that the extra-framework charge-compensating cation distribution in ferrierite zeolites changes as a function of their Si/Al ratio [14], and from this feature it has been concluded that the Al distribution among the different T sites is affected as well.

Based upon these previous studies, we report in this work a new approach aiming to influence the aluminium location in ferrierite. Our hypothesis is that the use of a combination of organic molecules as SDAs can influence the distribution of acid sites of the zeolite obtained, i.e., the particular combination of SDAs employed in each case could have an effect on the population of aluminium in the different T sites of the zeolite. Therefore, our synthesis strategy consists on the use of a combination of different organic molecules acting as co-structure directing agents, in the absence of sodium cations. This is an important aspect, as the negative charge associated to the incorporation of aluminium to the tetrahedral sites by isomorphic substitution of silicon will be compensated exclusively by the positive charge of the organic SDAs. Following the previous synthesis approach using bmp and TMA as SDAs, ferrierite samples have been obtained from gels in which the bulky bmp cation has been substituted by pyrrolidine (pyrr) and then both bmp and TMA have been replaced by pyrrolidine, i.e., only pyrrolidine has been used as SDA, always maintaining a constant total concentration of organic compounds. For comparison purposes, a ferrierite sample has been prepared by using pyrrolidine at high pH in presence of sodium cations [15]. The acidity of the calcined materials has been investigated by FTIR spectroscopy and pyridine adsorption, and their catalytic activity in *m*-xylene and 1-butene isomerisation has also been determined.

2. Experimental and methods

2.1. Synthesis of the SDAs

The synthesis of bmp was carried out by methylation of benzylpyrrolidine as reported earlier [10]. The purity of the tertiary amine was assessed by thin layer chromatography (hexane/ethyl acetate as solvent) and chemical analysis (calculated values, in wt%: C 82.0; N 8.7; H 9.3; found: C 81.5; N 8.7; H 9.9).

Benzylpyrrolidine was methylated with methyl iodide (50% molar excess, Fluka) in ethanol. The stirring was maintained for 5 days at room temperature and ethanol was then removed under vacuum at 60 °C. The resulting solid benzylmethylpyrrolidinium iodide was exhaustively washed with diethyl ether until the resulting liquid was colourless. The composition of the collected yellow solid was determined by chemical analysis (calculated values, in wt%: C 47.5; N 4.6; H 5.9; found: C 47.3; N 4.7; H 5.8), while ¹³C CP MAS-NMR confirmed the integrity of the benzylmethylpyrrolidinium cation (bmp). The iodide salt was then converted into the corresponding hydroxide salt (bmpOH) by ion exchange through an Amberlyst IRN78 resin (exch. cap.: 4 meq/g, Supelco). The obtained solution of bmpOH was filtered to remove the resin and titrated with 0.05 M HCl (Panreac) using phenolphthalein (Aldrich) as an indicator.

2.2. Synthesis of the zeolites

Zeolite products synthesised in fluoride medium were obtained following the synthesis procedure reported earlier [10] from synthesis gels in which the molar ratio organic/T atoms was kept constant. The molar gel composition for the samples with bmp and TMA as SDAs was: 0.969 SiO₂:0.031 Al₂O₃:0.06 TMAOH:0.48 bmpOH:0.48 HF:4.6 H₂O. For the samples prepared with TMA and pyrrolidine as SDAs, the same gel composition was employed, substituting bmp by pyrrolidine. For the samples prepared in the presence of pyrrolidine as the only SDA the same molar composition was used but with molar ratio pyrr:(Si + Al) = 0.54, thus maintaining the ratio organic compounds/T atoms constant. The Si/Al ratio in the gel was 15.7 in all the cases. In the synthesis gels in which TMA is one of the SDAs, the ratio TMA/Al was 1.

All these samples underwent a post-synthesis treatment in order to get their catalytically active form. They were heated in nitrogen flow up to 200 °C and kept at this temperature for 2 h, followed by a treatment with a flow of oxygen enriched in ozone (60 mL/min, ca. 2 vol% ozone) at 200 °C to remove, in mild conditions, the organic molecules employed as SDAs. An ECO-5 ozone generator (Salveco Proyectos, S.L.) was employed to produce the ozone-enriched oxygen stream. In the final step prior to their use as catalysts the samples were heated in an air flow for 2 h up to 550 °C and kept at this temperature for 2 additional hours.

The sample synthesised in alkaline medium following the conventional procedure, FER1, crystallised from a gel with the following molar composition: 0.969 SiO₂:0.031 Al₂O₃:0.323 pyrrolidine:0.049 Na₂O:11.95 H₂O. The gel was heated at 175 °C and autogeneous pressure for selected periods of time, and then it was filtrated, washed and dried overnight. The same treatment in an ozone-enriched stream was applied to remove the organic material occluded within the zeolite. The calcined product was subsequently ion-exchanged with a 1 M ammonium chloride solution (Probus, 99.5 wt%) to eliminate Na⁺ cations, which were substituted by ammonium cations in this process. For this purpose the zeolite was placed in a round-bottomed flask with the ammonium chloride solution (1 g zeolite/100 mL solution) and it was stirred at 80 °C for 8 h under reflux. Then the solid was recovered by filtration and washed exhaustively with deionised water to eliminate chloride and sodium ions. This procedure was repeated twice, maintaining the stirring for 12 and 24 h, respectively. Complete removal of chlorine ions was confirmed by the absence of AgCl (white solid precipitated) when adding silver acetate solution to the filtrate. The sample was dried overnight and calcined in an air atmosphere for 3 h at 350 °C and 3 h at 550 °C to decompose ammonium ions, thus obtaining the zeolite in its proton form.

Hereafter, the ferrierite samples will be denoted making reference to the organic cations employed as SDAs in their synthesis, separated by a dash if two different molecules are em-

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