SYNTHESIS OF FERRIERITE FROM GELS CONTAINING A MIXTURE OF TWO TEMPLATES

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday.

Ferrierite synthesis from gels containing a mixture of two template molecules, in the absence of inorganic cations and in fluoride media, is described. One of them is a bulky structure-directing agent (SDA), 1-benzyl-1-methylpyrrolidinium cation (bmp), and the other one is a small organic cation acting as a co-template. We present here the results obtained with tetramethylammonium (TMA) and quinuclidinium (Qui) compounds as co-templates in a gel containing bmp cation as SDA. It has been observed that in both cases co-templates exert a marked effect on the nature of the synthesis products.

Keywords: Ferrierite; Mordenite; Template mixture; Tetramethylammonium; Quinuclidinium; Fluoride media; Zeolites; Mesoporous materials; Crystallization; IR spectroscopy.

The crystallization of zeolite-like materials under the conditions generally prevalent in the synthesis systems is rather slow. This process usually requires the presence of organic molecules (templates), which are assumed to organize tetrahedral TO_4 units around them to form the building blocks for the nucleation and growth of a particular zeolitic phase[1]. Bulky templates are preferentially used in attempts to obtain large-pore structures, but this likely imposes the necessity of assembling a large number of TO_4 units during the nucleation step, in agreement with the long induction period generally observed during crystallization. Under these conditions, the crystallization process may not be energetically favourable, leading to the formation of amorphous materials or, eventually and very often, to mixtures of phases. The presence of small species in the synthesis gel could aid the crystallization process by helping to overcome the energy barrier of the nucleation. The arrangement of tetrahedral TO_4 units around a less bulky structure-directing agent (SDA) to form organized inorganic entities would not require such an increase in the structural ordering of the system. It

would make the system more flexible since these small inorganic entities could be gradually assembled around the main SDA, thus opening the possibilities of the crystallization of more complex structures. The building-up process of crystal structures would hence be favored by creating a "soup" rich in organic compounds, which could contain inorganic cations as well. This could be defined as a cooperative structure-directing effect of both the small molecule, which will be referred to as co-template, and the bulky SDA.

Based upon those grounds, a systematic study is currently being undertaken in our laboratory to investigate the cooperative structure-directing effect of mixtures of two SDAs and their influence both in the nucleation kinetics and in the nature of the zeolitic phases obtained. We have employed 1-benzyl-1-methylpyrrolidinium cation (bmp) as the large SDA, used either as the only SDA or together with a co-template. Experimental work showed that a mixture of phases was obtained when using bmp alone as a SDA [2]. Of all the co-templates explored, the combination of the bmp cation with tetramethylammonium (TMA) or quinuclidinium (Qui) has yielded a particularly interesting product from both the academic and applied point of view: ferrierite zeolite (FER).

Ferrierite is a naturally occurring aluminosilicate zeolite that can be synthesized in both pure silica and aluminosilicate forms. It is a medium-pore-type zeolite whose structure (natural single crystal) was first determined in orthorhombic space group *Immm* [3]. The space group has been the subject of some discussion, and a reduction of symmetry to *Pmnn* has been reported [4–6]. The FER framework is based on chains of five-membered rings, which are linked to give [5^4] polyhedral units. There are two types of perpendicularly intersecting channels in the structure. The main channel is parallel to the orthorhombic *c*-axis of the crystal, and is outlined by elliptical ten-membered rings (4.3 × 5.5 Å in diameter), while the side channel, along the *b*-axis, is formed by an eight-membered ring (3.4 × 4.8 Å in diameter). The structure contains oval cavities (6–7 Å in diameter) named FER cage [7], formed by the intersection of the eight-membered ring channels and the six-membered ring channels (parallel to the *c*-axis).

This medium-pore zeolite is of current interest because of its exceptional selectivity in the skeletal isomerization of n-butene to 2-methylpropene (isobutene). The latter is an important raw material for the production of *tert*-butyl methyl ether (MTBE) which is widely used as a major octane-enhancer in reformulated gasoline. However, the current supply of isobutene from the catalytic cracking of petroleum is not sufficient to meet the increasing demand for MTBE. Therefore, considerable interest has been

devoted to finding a new isobutene source via skeletal isomerization of n-butene[8].

More than forty years ago, Barrer and Marshall[9] reported the synthesis of a FER-type material from a fully inorganic synthesis gel, whose composition was $(SrO)(Al_2O_3)(SiO_2)_9(H_2O)_{485}$. Autoclaving at unusually high temperature (340 °C) gave a ferrierite-type zeolite after 10 days. Seeding and the simultaneous use of different alkaline earth metal hydroxides as a source of basicity reduces the synthesis time to one day[10]. The first quaternary ammonium cation used for the synthesis of ferrierite was tetramethyl-ammonium[11]. Since then, many N-containing compounds as well as oxygenated hydrocarbons (THF [12], pentane-2,4-dione[13]) have been used in its synthesis. Among N-containing compounds, cyclic amines, such as pyrrolidine[14,15] and piperidine[16], have been frequently used, all of them in alkaline aqueous media in the presence of inorganic cations (usually Na⁺). Aliphatic amines have also been employed as structure-directing agents of ferrierite, for instance diethanolamine[17], propane-1,3-diamine[18], butane-1,4-diamine[18], ethylenediamine[19]. To our knowledge, there is only one reference for the synthesis of ferrierite in alkaline media in the absence of inorganic cations[20]. Kim et al. reported in that paper the synthesis of ferrierite with butane-1,4-diamine, ethylenediamine and pyrrolidine, but in all cases the synthesis showed serious drawbacks with respect to the systems with Na⁺: the synthesis conditions were very restrictive, ZSM-5 was often obtained as an impurity, the induction period was quite long and the amount of organics required in the synthesis gel was considerably high. The crystallization of ferrierite has also been carried out in fluoride media, using an HF/pyridine solvent system in the presence of propylamine and excess pyridine[21].

In this work, we report a new route to synthesize ferrierite from a gel containing two organic compounds acting as SDAs. We describe here the results of synthesis and characterization of zeolites obtained in the presence of the bmp cation in combination with the co-templates previously mentioned, TMA and Qui, showing a strong effect on the nature of the synthesis products.

EXPERIMENTAL

Tertiary Amine Synthesis

The reagents used in the synthesis of 1-benzylpyrrolidine (bp) were: pyrrolidine, benzyl chloride, potassium carbonate (all Sigma–Aldrich, 99 wt.%) and ethanol. The reagents were used without purification. The detailed procedure of synthesis to prepare 73.0 g of bp was

the following: 78.2 g of benzyl chloride were added dropwise to a solution of 65.9 g of pyrrolidine (50% molar excess) in ethanol (200 ml) in a round-bottomed flask. Then 128.1 g of K_2CO_3 were added and the resulting solution was maintained under magnetic stirring at reflux for 48 h. The tertiary amine was filtered to remove K_2CO_3, and washed with ethanol. Ethanol was then removed under vacuum at 60 °C and 1-benzylpyrrolidine was purified by vacuum distillation (110 °C at 17 mm Hg, 74% yield). The purity of the amine was assessed by chemical analysis.

Quaternary Ammonium Cation Synthesis

The reagents used in the synthesis of 1-benzyl-1-methylpyrrolidinium (bmp) hydroxide were: bp, methyl iodide (Fluka, >99 wt.%), ethanol, diethyl ether (stabilized with 6 ppm BHT, Panreac) and ion-exchange resin Amberlyst IRN78 (exchange capacity 4 meq/g, Supelco). The detailed procedure to obtain 99.4 g of 1-benzyl-1-methylpyrrolidinium iodide (bmpI) was the following: a solution of 92.9 g of CH_3I (50% molar excess) in 200 ml of ethanol was prepared in a round-bottomed flask. Then 73.0 g of bp were added to the stirred solution and placed in an ice-water bath for ca. 30 min. Then, the reaction mixture was stirred at room temperature for 5 days. Ethanol was then removed under vacuum at 60 °C, and the orange solid product obtained was thoroughly washed with diethyl ether until the washings were colorless. The solid was dried at room temperature (to evaporate ether). BmpI was obtained as a yellow solid (72% yield). It was characterized by chemical analysis and ^{13}C CP MAS NMR. The iodide was converted to the corresponding hydroxide by ion exchange. A 2 M solution of solid bmpI (99.4 g) in water was placed in a PP bottle and 328 g of ion exchange resin were added (four times the stoichiometric quantity). After 3-days stirring at room temperature, the resulting solution was filtered and titrated with 0.05 M HCl (Panreac) using phenolphthalein (Aldrich) as indicator to signal the completion of the acid-base reaction. The amount of bmpOH obtained in aqueous solution was 50.7 g (80% yield). This solution was concentrated by evaporating a part of the water under vacuum at moderate temperature (lower than 55 °C) to prevent bmpOH from degradation. By following this procedure, a 65 wt.% aqueous solution of bmpOH was obtained.

Preparation of the Synthesis Gel

Zeolite products were obtained from synthesis gels with molar composition: x AOH : $(0.54 - x)$ bmpOH : 0.48 HF : 0.03 Al_2O_3 : 0.94 SiO_2 : 4.65 H_2O, where AOH stands for the corresponding co-template and x was 0.06 for TMA and Qui as co-templates and 0 for the non-co-templated system (TMA-bmp, Qui-bmp and bmp). The reagents used were: tetraethyl orthosilicate (TEOS, Merck, 98 wt.%), aluminium isopropoxide (Fluka, 97 wt.%), tetramethylammonium hydroxide (TMAOH Aldrich, 25 wt.% aqueous solution), 1-benzyl-1-methylpyrrolidinium hydroxide (bmpOH, 65 wt.% solution in water), quinuclidine hydrochloride (Aldrich, 97 wt.%) and hydrofluoric acid (HF, Panreac, 48 wt.%). The reagents were used without purification. The detailed procedure to prepare 58.7 g of gel was the following: 49.20 g of TEOS and 2.91 g of aluminium isopropoxide were added to a solution containing 32.86 g of bmpOH and the corresponding co-template (5.09 g of TMAOH or 2.08 g of quinuclidine hydrochloride) in a polypropylene flask. The solution was stirred until ethanol and excess water were evaporated. Subsequently, HF was added dropwise. The resulting thick gel was homogenized manually (pH ca. 10) and introduced into 20-ml Teflon-lined stainless steel autoclaves which were heated without stirring at 150 °C and autogenous pressure for

selected periods of time. The solid products were recovered by filtration, washed first with water, next with ethanol and finally with water again, and dried at room temperature overnight.

Characterization

The solid products were characterized by XRD (Seifert XRD 3000P diffractometer, CuKα radiation), FTIR spectroscopy using the KBr pellet technique (Nicolet 5ZDX FTIR spectrometer provided with an MCT detector), SEM and EDX (Jeol JSM 6400 Philips XL30 operating at 20 kV), MAS NMR (Bruker AV 400 spectrometer using a BL7 probe for ^{29}Si and ^{13}C, and a BL2.5 probe for ^{19}F), TEM (JEOL-2000FX microscope), ICP-OES (Optima 3300 DV Perkin–Elmer), TGA (Perkin–Elmer TGA7 instrument, heating rate 20 °C/min, air flow 30 ml/min) and CHN analysis (Perkin–Elmer 2400 CHN analyzer).

RESULTS AND DISCUSSION

TMA as a Co-template

Addition of co-templates clearly influences the nature of final products of synthesis. When bmp was used as the only SDA, a mixture of up to four phases was obtained, in accord with SAED-TEM results. On the contrary, XRD patterns of the TMA-bmp preparations at selected heating times (Fig. 1 and Table I) indicate that ferrierite was obtained as the only product, showing the stability of this phase, whose crystallinity increases with heating
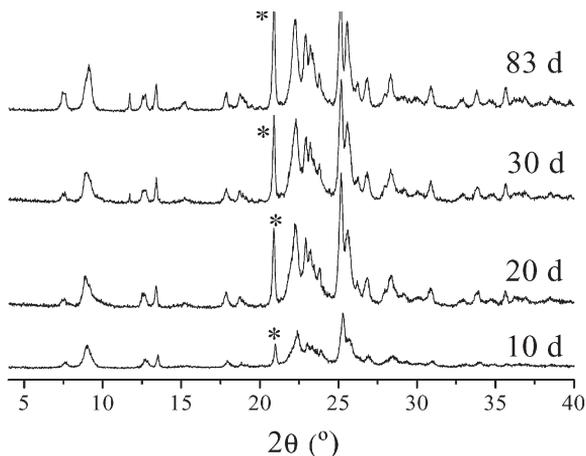

FIG. 1
XRD patterns of TMA-bmp samples obtained at 150 °C at 10, 20, 30 and 83 days. The peak highlighted with * corresponds to quartz

time. The presence of ferrierite was further confirmed by TEM studies. In these preparations, ferrierite crystallized as isolated elongated needles, the length of which was of the order of 10 μm, with a well-defined shape as revealed by SEM. Remarkably, ferrierite is not obtained in the absence of co-template. This result evidences the fundamental role of TMA in crystallizing this new phase rather than promoting the crystallization of one of the phases present in the mixture obtained when bmp is used as the only SDA.

Chemical analysis (ICP-AES) showed that the Si/Al ratio of the samples is around 15.6, very close to the Si/Al ratio of the synthesis gel.

The TGA analysis in air of the TMA-bmp sample obtained after 20 days of hydrothermal treatment is shown in Fig. 2. Three weight losses are found, the first and last at around 330 and 680 °C, respectively, and the most intense one at ca. 520 °C. The samples are remarkably water-free (TG loss < 0.5 wt.% at $T < 150$ °C) as obtained in many other high-silica zeolites synthesized in the presence of F^- anion. According to TGA results, the organic content of TMA-bmp samples is, on average, 13 wt.%, similar to the amount of occluded organics commonly reported for ferrierite[6,22] and slightly lower than the result obtained from chemical analysis. It can be ob-

TABLE I
Summary of the syntheses performed at 150 °C for gels of composition: x AOH : $(0.54 – x)$ bmpOH : 0.48 HF : 0.03 Al_2O_3 : 0.94 SiO_2 : 4.65 H_2O, where AOH stands for the corresponding co-template and x was 0.06 for TMA and Qui as co-templates and 0 for the non-co-templated system (TMA-bmp, Qui-bmp and bmp, respectively)

System	Co-template	t, days	Product	C/N ratio
bmp	–	10	amorphous	–
		45	MF*	–
		98	MF*	–
TMA-bmp	TMA	10	FER	6.1
		20	FER	6.3
		30	FER	6.2
		83	FER	6.0
Qui-bmp	Qui	10	FER	7.7
		20	FER+MOR	7.8
		30	FER+MOR	7.9

FER, ferrierite; MOR, mordenite; MF*, unidentified mixture of phases.

served in the figure that even at 850 °C, not all organics are removed, presumably due to diffusion restriction for the organics to leave the zeolitic structure. This is probably the reason for the underestimation of the C content as measured by chemical analysis. Moreover, the C/N ratio of the sample for which the TGA is shown, was found to be 6.3, without substantial differences between the samples obtained at other heating times. This ratio is between the ratios of the two compounds employed as SDAs, bmp (C/N = 12) and TMA (C/N = 4), thus suggesting that both cations are incorporated within the zeolitic structure.
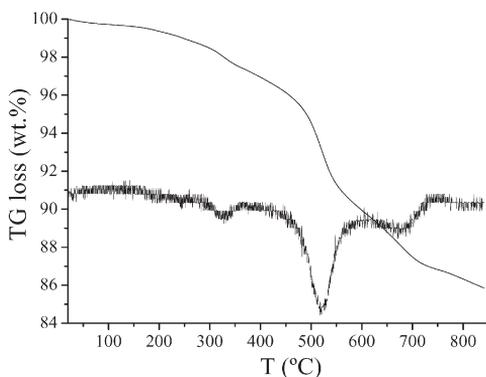

Fig. 2
TGA (air) of TMA-bmp sample obtained after 20 days of hydrothermal treatment

To assess the incorporation of both organic molecules, TMA-bmp samples were further characterized by FTIR and ^{13}C MAS NMR. FTIR spectra of these samples are shown in Fig. 3. The spectrum of TMA occluded in faujasite zeolite is also shown as a reference. The spectra of the TMA-bmp samples contain two bands in the CH stretching region, at 3070 and 3042 cm^{-1}, assigned to the aromatic ring of the bmp cation. Characteristic methyl and methylene stretching and bending bands are observed in the regions 2850–3100 and 1400–1500 cm^{-1}, respectively. The former are assigned to the pyrrolidine ring with the methyl group linked to the nitrogen, and to the TMA cation. The band at 1485 cm^{-1}, due to the methyl bending, appears at wavenumbers slightly lower in the TMA-bmp samples than in the TMA reference spectrum. The reason could be that in the samples this band is the result of two contributions: of the methyl groups of TMA cations and of the methyl group linked to the nitrogen atom of the pyrrolidine ring. Therefore, it can be concluded that the two compounds employed as templates are occluded within the ferrierite framework.
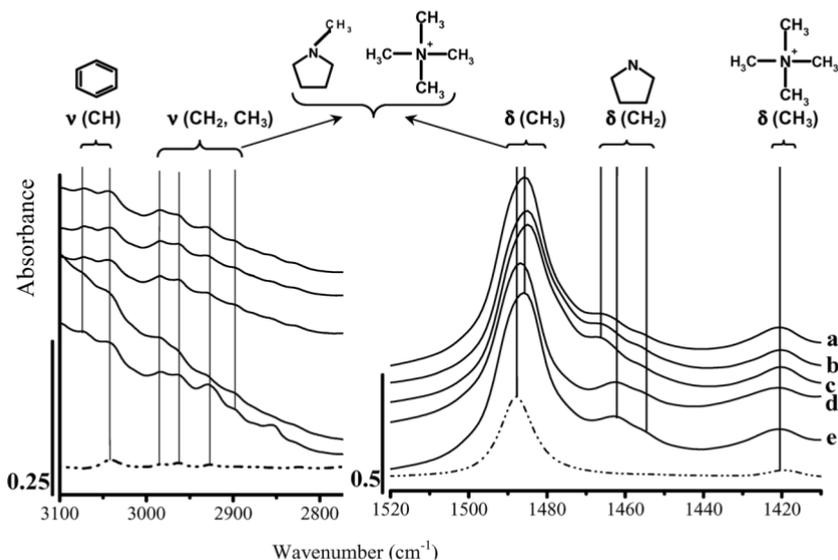
Fɪɢ. 3
IR spectra of TMA-bmp samples (solid lines) treated at 150 °C for 10 (a), 20 (b) and 30 (c) days, and at 135 °C for 10 (d) and 20 (e) days. TMA/FAU spectrum (dash and dotted line) as a reference

The incorporation of the two organic molecules was assessed by ^{13}C CP MAS NMR. The spectrum (not shown) reveals the presence of all the signals corresponding to the free bmp cation and an additional signal, which appears in the typical range of the TMA cations trapped in zeolitic cages[23].

Quinuclidinium as a Co-template

XRD pattern of the synthesis products obtained with Qui as a co-template are shown in Fig. 4 and the results are summarized in Table I. After 10 days of heating at 150 °C, the product shows a pattern with resemblance to that of a ferrierite-type structure but characterized by very broad diffraction peaks and a high background base line, thus indicating poor crystallinity of the sample. Prolonging the heating to 20 days led to the appearance of competing phases. The X-ray diffraction pattern of this solid exhibits the diffractions of the ferrierite-type structure mentioned above, plus the characteristic diffractions of the zeolite mordenite (MOR). The sample heated at 150 °C for 30 days shows a similar but more defined diffraction pattern, with an additional very sharp reflection at 2θ ~ 20.9°, assigned to quartz.
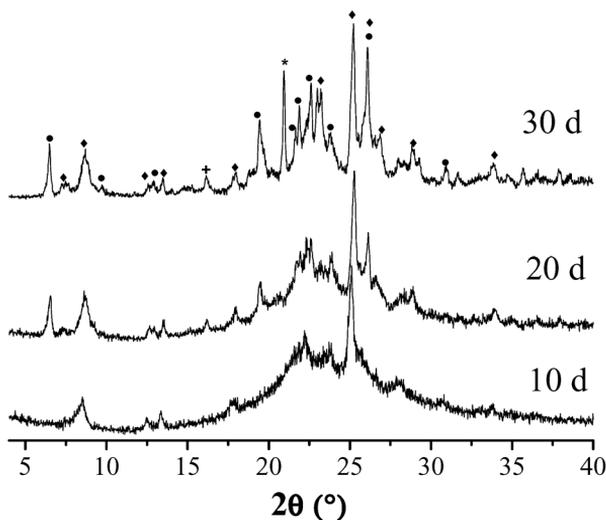
XRD patterns of Qui-bmp samples obtained at 150 °C at 10, 20 and 30 days. Symbols indicate the phases present in the products: mordenite (●), ferrierite (◆), α-quartz (*), unidentified phase (+)

The zeolites mordenite and ferrierite show some structural similarities, such as an abundant proportion of five-membered rings within their frameworks. These rings are directly connected in ferrierite forming a saw chain (in the [001] projection), whereas, in mordenite, they are connected through four-membered rings (Fig. 5). Because of this, the channels parallel to the *c*-axis of mordenite, consisting of twelve- and eight-membered rings, are bigger than those in ferrierite (ten- and six-membered rings)[7]. Cavities are also present in the mordenite framework. They are formed by the intersection of the sinusoidal eight-membered ring channel parallel to the *b*-axis with the twelve- and eight-membered ring channels.

Due to this close structural relation, mixtures of ferrierite and mordenite are commonly obtained. In particular, Jongkind et al.[14] reported various saturated cyclic amines to direct the synthesis of mordenite, ferrierite and mixtures of both. In these preparations, the products of synthesis were influenced by the ring size of the cyclic amine used as structure directing agent. Piperidine was shown to yield a mixture of mordenite and ferrierite, while the smaller cyclic amine, pyrrolidine, directed the synthesis of ferrierite and the use of amines with a larger ring, such as hexamethyleneimine and heptamethyleneimine, directed the synthesis of mordenite.
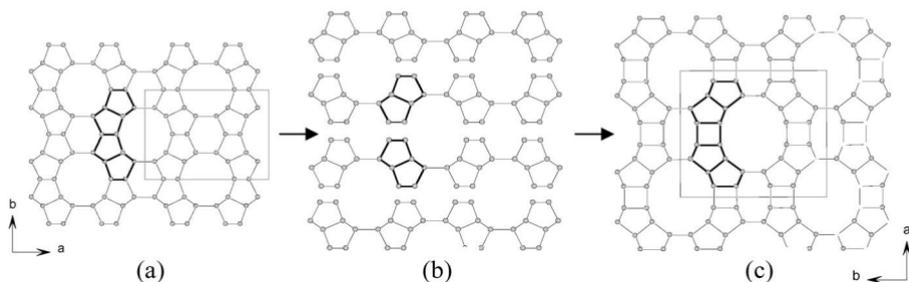
FIG. 5
Scheme showing the structural relationship between the frameworks of ferrierite (a) and mordenite (c). Picture (b) remarks that by connecting the five-membered rings in ferrierite through four-membered rings, the structure of mordenite can be built up

The products were further characterized by SEM. The sample of poorest crystallinity (10-day heating) was shown to be a mixture of amorphous material and some small needle-like crystals of ferrierite, as indicated by the XRD pattern of this product. In contrast, a different situation was found for the sample heated for 20 and, in particular, for 30 days (Fig. 6). Two different types of crystals, needle-like crystals of ferrierite and big hexagonal aggregates made up of smaller thin plates of mordenite, can be distinguished in this preparation. This is not a common morphology for mordenite crystals, although mordenite present different morphologies depending on the crystallization conditions[24]. Moreover, EDX analysis performed in both types of crystals shows that the Si/Al ratio of the hexagonal aggregates is
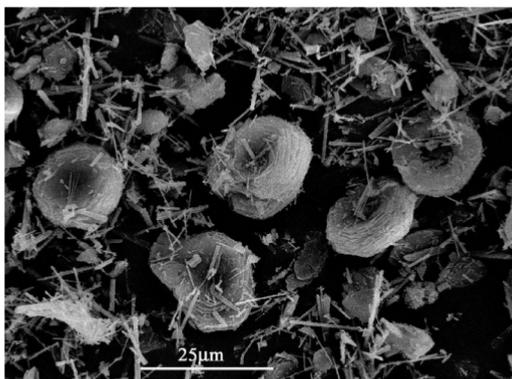

FIG. 6
SEM micrograph of sample crystallized at 150 °C for 30 days

close to the nominal value of gel (Si/Al molar ratio 16 and 18, for samples heated at 20 and 30 days, respectively) whereas the needles were shown to be depleted of aluminium.

The CHN analysis of the sample obtained after 10 days of heating revealed a very low value for the C/N ratio, close to that of quinuclidine (C/N = 7) rather than to the C/N ratio of the bigger bmp (C/N = 12). Assuming that both organics were occluded within the solids, a rough estimation indicates that, for the sample heated for 10 days, the 86 molar % of the total organic content would be quinuclidine and only 14% would be due to the bmp SDA. Similar results were found for the products obtained after 20 and 30 days of heating. Therefore, further characterization by FTIR spectroscopy was carried out with these samples in order to assess the incorporation of the organic bmp cation within the solids. The spectra of the Qui-bmp samples (Fig. 7) show the bands in the CH stretching region, at 3070 and 3042 cm^{-1}, characteristic of the aromatic ring of the bmp cation (Fig. 3). This suggests that the organic bmp is also present in the crystals.
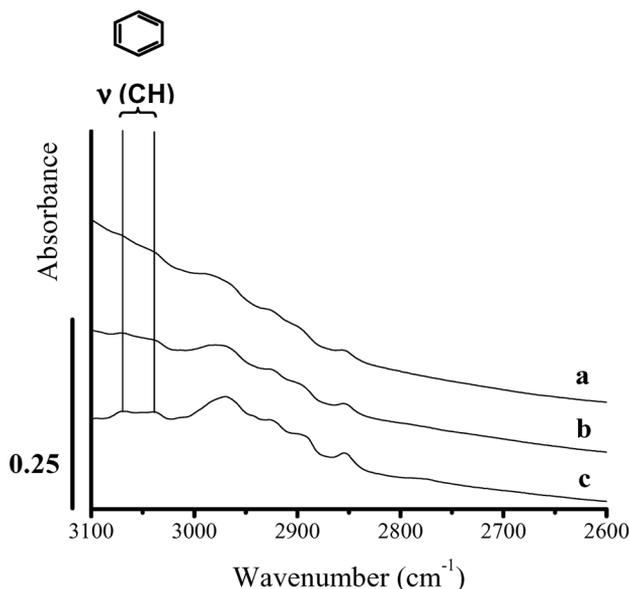

Fig. 7

IR spectra of Qui-bmp samples treated at 150 °C for 10 (a), 20 (b) and 30 (c) days, showing the bands assigned to the aromatic ring of the bmp cation

Comparison of Qui-bmp and TMA-bmp Samples

From the results above, it seems clear that the TMA-bmp system is more adequate to direct the synthesis of the FER-type structure than the Qui cation combined with bmp. In the presence of TMA, ferrierite is obtained after 10 days of hydrothermal treating, and no other structure appears after 83 days of heating, thus demonstrating the thermodynamic stability of this phase. In contrast, when Qui cation was used as a co-template, the ferrierite structure obtained after 10 days of heating transformed into a mixture of zeolites ferrierite and mordenite after 20 days. Therefore, it appears that ferrierite is formed in the reaction steps where the system is under kinetic control, whereas, at longer times, it is more favourable for the amorphous material to transform into mordenite than to ferrierite. As observed from XRD patterns, the crystallinity of ferrierite slightly increases with the heating time; so, in the period of time we have studied, mordenite does not seem to crystallize at the expense of ferrierite dissolution, but from the amorphous material still present in the synthesis mixture. Therefore, since the large organic cation bmp is present in both preparations, the co-template added in each case plays a critical role in the nucleation and growth of the ferrierite phase. TMA cation has a better template ability to direct the synthesis of ferrierite whereas Qui cation, though nucleating ferrierite, tends to form the structurally related mordenite, with a slightly larger pore size, probably in order to fit better the steric requirements of the bulkier quinuclidine as compared with TMA. This suggests that TMA cation, under the synthesis conditions described in this work, is a very specific SDA for the ferrierite framework.

CONCLUSIONS

A novel synthesis route has been described to obtain ferrierite zeolite in the presence of a mixture of two SDAs, bmp and TMA cations. Ferrierite crystallized at short heating times and was stable to prolonged hydrothermal treatment. In contrast, when Qui cation was used as a co-template, mordenite competed with ferrierite at long crystallization times. This evidences the strong effect that the addition of a co-template has on the nature of the synthesis products. While the TMA cation combined with bmp proved to be a suitable SDA to direct the synthesis of ferrierite under the synthesis conditions, the Qui-bmp system is less specific to promote crystallization of this structure.

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