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*Review*

# Synthesis of Zeolites Using Imidazolium Cations as Organic Structure-Directing Agents

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**Featured Application: This mini-review presents a case study about the research performed on zeolite synthesis with imidazolium derivatives as OSDAs at the Molecular Sieves Laboratory (LABPEMOL, Federal University of Rio Grande do Norte-UFRN). To do so, we first describe a quick overview of imidazolium derivatives and what is being done in other laboratories, after which we summarize the main results obtained at LABPEMOL. Readers will find a bibliography to deepen their knowledge of synthesis and characterization techniques and to help design new projects involving the synthesis or application of the obtained materials based on the know-how reviewed here.**

**Abstract:** Imidazolium-derivative cations are very interesting molecules used as organic structure-directing agents (OSDAs) for zeolite synthesis, widening the possibilities of new materials and applications in this research area. In this review, the studies performed at LABPEMOL using this kind of compound are presented after a quick overview on imidazolium derivatives. The first zeolite synthesis results that started this research study were obtained with 1-butyl-3-methylimidazolium chloride. Then, the design of new OSDAs based on the imidazolium cation, such as 1,2,3-triethylimidazolium, 2-ethyl-1,3-dimethylimidazolium and 1,2,3-triethyl-4-methylimidazolium, is reported. Afterwards, the structure-direction effect caused by the introduction of heteroatoms with already-published imidazolium derivatives (for example, the $Al^{3+}$ insertion into zeolite frameworks with two different OSDAs and the silico aluminophosphate (SAPO) synthesis using 2-ethyl-1,3,4 trimethylimidazolium cations) is discussed. Finally, we also present a quick overview of some achievements of other laboratories.

**Keywords:** zeolite synthesis; imidazolium derivatives; structure-directing agent

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## 1. Introduction

The first synthetic zeolite obtained marked a milestone in the study of porous materials [1,2]. Since then, scientists have attempted to design quick and reliable routes for synthesizing analogues of the existing natural zeolitic topologies [3,4]. However, this scientific marathon did not end here, as another ongoing major effort has been made to find new structures [5–7]. The question this poses is how this challenge is faced. To answer this question, we need to go back to that first synthesis procedure performed with hydrothermal technology [3]. This procedure uses a mixture of silicon and aluminum sources that are dissolved in an aqueous medium (*hydro*, the solvent) to later undergo a high temperature treatment (*thermal*). These reagents were (and are) difficult to dissolve in water, which is the reason for alkali and alkaline-earth metal hydroxides addition, giving rise to the need for a mineralizing agent and basic media to synthesize zeolites. In addition, different combinations of these reagents were tested, and different zeolitic topologies were obtained [1,8]. At the same time, zeolitic scientists observed that changing the cation of the hydroxide in the same synthesis (e.g., replacing sodium hydroxide with potassium hydroxide) forced variations in the crystal parameters of the final material, even to the point of synthesizing a completely different topology. This behavior justified the incorporation of the concepts *templates*, *structure-directing agents* (SDAs), and *pore-fillers*, which were differentiated based on the type of interactions present in the structure [9].

Over time, scientists began to study the addition of organic compounds to the synthesis procedure [10–14]. However, what popularized these organic compounds was the synthesis with HF (hydrofluoric media) to replace the hydroxides. Zeolites such as pure silica sodalite, ZSM-5, silicalite-1, and silicalite-2 were obtained. Since then and until now, these compounds have been studied for synthesis applications.

A very interesting type of organic compound is ionic liquids. These molecules are characterized by a low melting temperature and low vapor pressure [15]. It is precisely these properties that justify their application for synthesizing zeolites. Ionic liquids can act as an SDA and solvent. Then, we can use ionic liquids in hydrothermal synthesis with water as the solvent and, also, in a new type of synthesis method, the ionothermal, in which the ionic liquid role is twofold, an SDA and a solvent [16,17]. This mini-review is focused on that first situation, but we recommend reading other reviews or book chapters, such as those from the Morris group, regarding the second type of synthesis [18,19].

Among the various ionic liquids there are the imidazolium derivatives, which are usually synthesized via the quaternization of one of the Ns of the corresponding imidazole derivative [20,21]. These compounds have a certain degree of hydrophobicity, which helps to explain the role they represent in synthesis, as for example described in the articles by Rojas et al. and Variani et al. [22,23]. Ionic liquids are also easy to use and possible to recycle. Ionic liquids possess diverse possible substituents and, as a consequence, wide synthetic possibilities [24–26]. In the first example, an ionic liquid was used to synthesize an extra-large pore zeolite by adjusting the supramolecular chemistry, possibly thanks to the use of imidazolium derivatives. Subsequently, the second example showed how an imidazolium derivative helped produce a high silica zeolite Y thanks to the interactions of the OSDA-framework. The last example described a fast ZSM-22 synthesis procedure. For these reasons, great interest has been generated.

The use of ionic liquids in the synthesis of zeolites began with the group of Prof. Dr. Morris, and they currently continue to carry out studies in this regard [27,28]. Ultimately, these materials led to the synthesis of more germanosilicates using imidazolium derivatives, as reported by Prof. Dr. Davis's group and Prof. Dr. Corma and collaborators [6,29,30], and in turn, these ionic liquids were studied by Prof. Dr. Morris' group to achieve a new synthesis route: ADOR (assembly-disassembly-organization-reassembly) [31,32]. Through this process, some of the hypothetical structures that were once called unfeasible have been synthesized, which was not possible through traditional methodologies [33].

Returning to the pure silica composition, we find that Prof. Dr. Camblor's group also excels in this type of synthesis, managing to stabilize the chiral topology of STW, which is also thanks to the use of the hydrofluoric medium [7]. Afterwards, we will describe a study on introducing aluminum into this structure, which was performed at LABPEMOL [34]. Note that further studies about the germanosilicate STW zeolite were published by Prof. Dr. Camblor's group [35,36]. Furthermore, this topology led to a major breakthrough in zeolite synthesis by the enantiomeric resolution achieved by Prof Dr. Davis's group [37].

Another study that have also helped to understand the performance of imidazolium derivatives (and other OSDAs) used in synthesis was that conducted by Prof. Dr. Pérez-Pariente's group. Through computational experiments, this group was able to predict dimeric OSDA aggregates formed in the course of the zeolite synthesis by helping to direct toward one or another topology [23,38,39]. We interject here to highlight the importance of computational studies in the field of zeolites [40].

Computational studies have been applied to try to predict and/or explain some of the behaviors found during synthesis and in applications. There are studies that model nucleation and template mechanisms [41,42], template interactions that occur when forming dimers [39], and adsorption isotherms [43]. It is worth noting there are studies that predict new structures, such as those used to collect the database of hypothetical structures, as mentioned previously [44]. Finally, the latest attempt to explain interzeolitic transformations and intergrowth has recently been published by Schwalbe-Koda et al. using graph theory [45]. In short, these types of studies are important to explain behaviors and help define new experiments.

There are several other groups working with imidazolium derivatives [46–49], but still, there is much more to do. Due to the results obtained with this kind of compound, Prof. Dr. Corma and collaborators proceeded to study P-containing [50–52] and As-containing [53] OSDAs and initiated new lines of study that have much to offer.

Thus, in this review, we will describe a case study about the establishment of a research line on using imidazolium derivatives for synthesizing zeolites at LABPEMOL. Without elaborating on the general aspects of these compounds, which was previously described in a general review from our laboratory [54], we will carry out a comparative description of our work to help the reader, whether they belong to a university or industry, to develop research on the synthesis with and/or application of these compounds.

## 2. LABPEMOL Case Study: First Synthesis Method Using Imidazolium Derivatives

The first attempt to synthesize zeolites with compounds derived from the imidazolium cation culminated in the publication of an article in 2009 in collaboration with the Porto Alegre (Brazil) group led by Dr. Roberto F. de Souza and Dr. Katia Bernando-Gusmão [55]. This article described the use of 1-butyl-3 methylimidazole chloride (Figure 1) as the OSDA and basic media as the mineralizing agent. The ZSM-5 zeolite belonging to the MFI topology, possessing an interesting spherical morphology (Figure 2) and was synthesized in 3 days using a high Si/Al ratio (SAR, 50 or 100) and high temperatures (180 °C). However, a lower SAR (20) and temperature (150 °C) directed the structure toward a beta zeolite, corresponding to the *BEA topology (Figure 3). Both topologies feature three-dimensional channel systems and similar pore sizes (between 5.1 and 5.6 Å) [8]. However, the MFI topology, in addition to being orthorhombic and not tetragonal like the *BEA topology, has a higher framework density (FD; MFI = 18.4 T/1000 Å$^3$, *BEA = 15.3 T/1000 Å$^3$). Precisely, this high FD was favored by the higher temperature used and followed the same tendency observed when synthesizing without an OSDA, as published by Maldonado et al. [56]. In addition to this, when introducing more aluminum cations into the framework, more crystallographic distortion should occur due to the difference between the ionic radii of the aluminum and silicon cations [57].

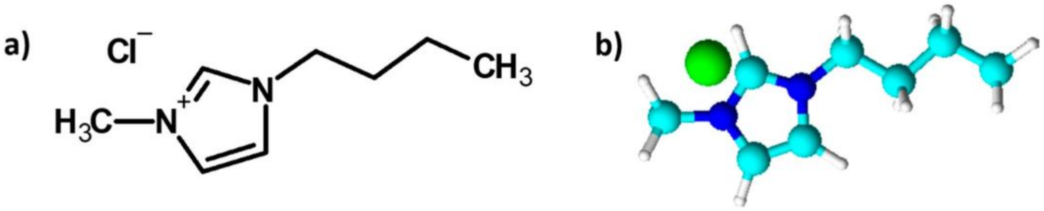
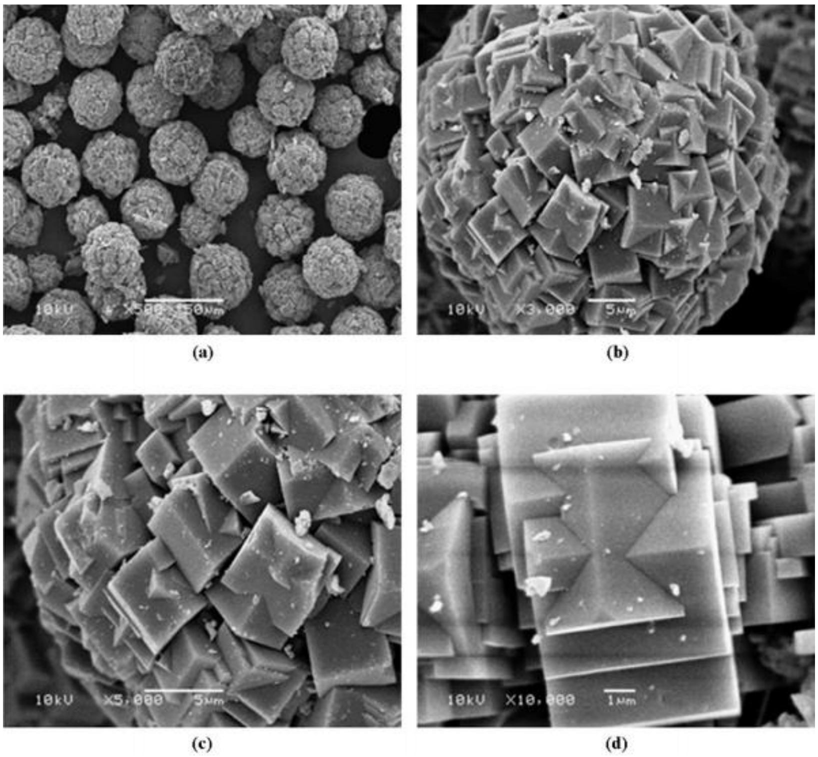


**Figure 1.** (**a**) Chemical representation of the OSDA 1-butyl-3-methylimidazolium chloride and its (**b**) 3D representation obtained using the freeware programs ChemSketch (ACD/Labs 2017.2.1, copyright 1994–2018) and ACD/3D Viewer (ACD/Labs 2017.2.1, copyright 1997–2017).



(a) (b) (c) (d)

**Figure 2.** SEM micrographs of the ZSM-5 samples with an Si/Al ratio of 100 and different magnifications: (**a**) 500×, (**b**) 3K×, (**c**) 5K×, and (**d**) 10K× (Reprinted from Applied Catalysis A: General, v. 374, issues 1-2, M. L. Mignoni, M. O. de Souza, S. B. C. Pergher, R. F. de Souza, K. Bernardo-Gusmão, Nickel oligomerization catalysts heterogenized on zeolites obtained using ionic liquids as templates, pp. 23–30, Copyright (2009), with permission from Elsevier B. V.) [55].

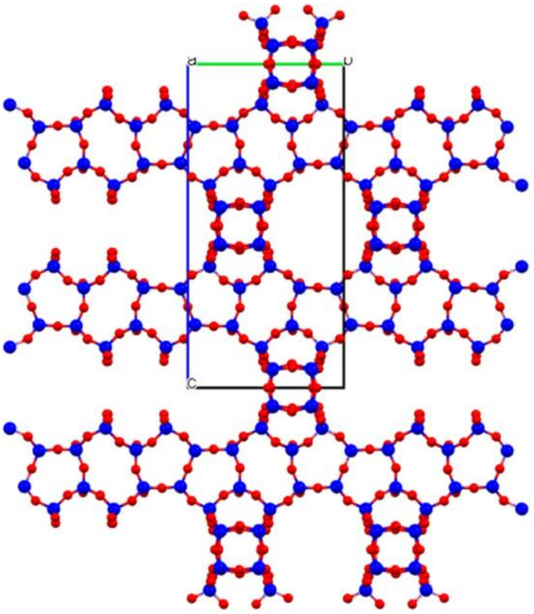


**Figure 3.** *BEA topology represented with the program Mercury from the CIF, which was provided by the International Zeolite Association (IZA) [8,58]. The oxygen atoms are red, and the silicon/aluminum atoms are in blue.

With the same OSDA and fixing the temperature (160 °C) and the $H_2O/Si$ ratio (25), the synthesis studies continued to use basic media and obtained the pure silica TON zeolite and the hetero-substituted

Ti-TON [59]. The samples were synthesized both in static and in rotation and were completely crystalline after 1 day of synthesis (Figure 4). This work showed for the first time that titanium cations were introduced into the TON framework in basic media, resulting in a breakthrough for LABPEMOL.

In comparison with the MFI structure of the previous publication, we observed a similar FD (18.1 T/1000 Å$^3$) and the same crystallographic system (orthorhombic). However, the TON topology has a structure with a one-dimensional channel system. Most likely, some kind of relationship can be established with the amount of OSDA molecules found per unit cell, but unfortunately we lack the data presented in these two articles to make that comparison.

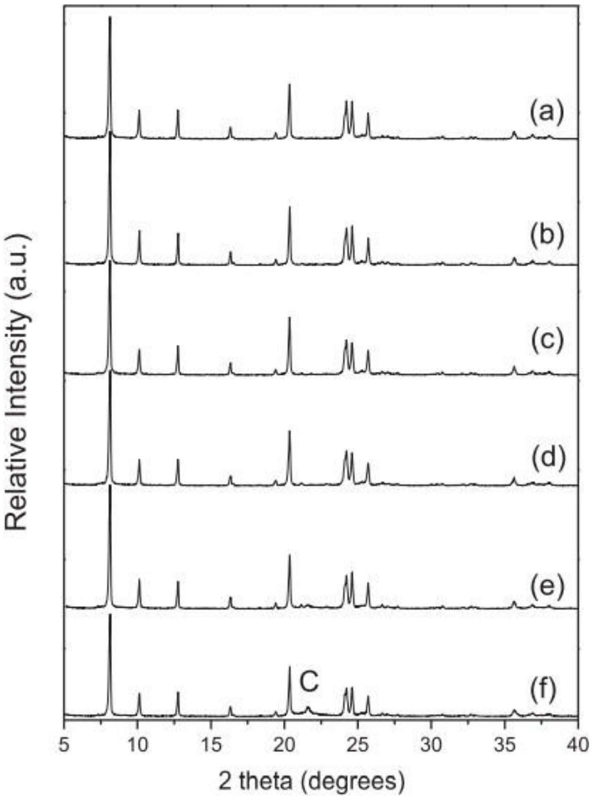


**Figure 4.** X-ray diffractograms of the Ti-TON zeolite prepared with reaction times of (**a**) 1 day, (**b**) 3 days, and (**c**) 7 days with stirring, and (**d**) 1 day, (**e**) 3 days, and (**f**) 7 days in static mode (Reprinted from Microporous and Mesoporous Materials, v. 213, C. L. Lopes, P. H. Finger, M. L. Mignoni, D. J. Emmerich, F. M. T. Mendes, S. Amorim, S. B. C. Pergher, $TiO_2$-TON zeolite synthesis using an ionic liquid as a structure-directing agent, pp. 78–84, Copyright (2015), with permission from Elsevier B. V.) [59].

Completing the experiments with this organic cation, Pergher's group decided to combine the knowledge acquired for the first synthesis attempts in hydrofluoric media with the history of LABPEMOL [60]. To do this, the organic cation had to be exchanged with its hydroxyl form. Once this was achieved, the synthesis was performed at 160 °C, and the pure silica TON topology was obtained with a $H_2O$/Si ratio of 14. However, by introducing Ti under the same synthetic conditions, only amorphous products were identified, even when using seeds. A zeolitic material, Ti-MFI, was only obtained by decreasing the $H_2O$/Si ratio to 7. This result was explained with Villaescusa's rule, which states that concentrated gels lead to less dense zeolitic topologies [61]. Even so, there remains an unknown if Ti-TON would have been obtained in a hydrofluoric medium with the same ratio that was used in the basic medium ($H_2O$/Si = 25).

As a novelty, this last work also incorporated the first study in cooperation with Dr. Luis Gómez-Hortigüela, showing that the more stable location of the OSDA positioned the aromatic ring at the channel intersections, and that the alkyl chains were located in the sinusoidal channels (interaction energy −328.2 kcal/mol per unit cell).

## 3. LABPEMOL Case Study: New OSDAs Based on the Imidazolium Cation

The latest work carried out with the OSDA 1-butyl-3-methylimidazolium opened a plethora of synthetic possibilities at LABPEMOL, which led to a change in course, now focusing on synthesizing zeolites in hydrofluoric media. The direction experiments were started using pure-silica zeolite conditions and concentrated gels, and the hydroxylic forms of the OSDAs 1,2,3-triethylimidazolium, 2-ethyl-1,3-dimethylimidazolium, and 1,2,3-triethyl-4-methylimidazolium (Figure 5) were studied [23]. The STF topology was primarily obtained with all of the OSDAs, while the MFI topology was only identified when using the cation 1,2,3-triethylimidazolium (Figure 6). Dense tridymite-like phases were also found with the cation 1,2,3-triethyl-4-methylimidazolium. These results also followed Villaescusa's rule; however, in this case, what was acting as the second variable was the OSDA (where the first variable was the $H_2O$/Si ratio).

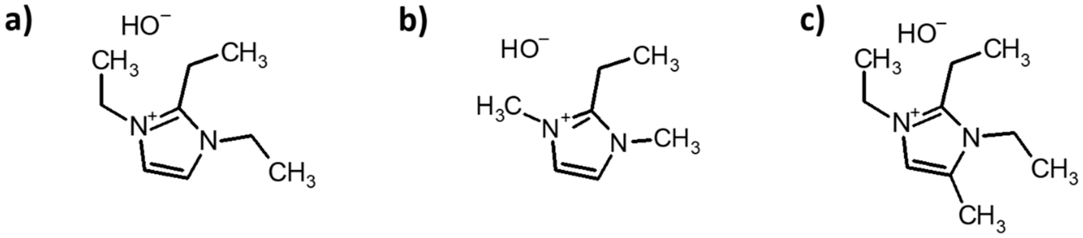


**Figure 5.** Chemical representation of the OSDAs (**a**) 1,2,3-triethylimidazolium hydroxide, (**b**) 2-ethyl-1,3-dimethylimidazolium hydroxide, and (**c**) 1,2,3-triethyl-4-methylimidazolium hydroxide, using the freeware program ChemSketch (ACD/Labs 2017.2.1, copyright 1994–2018).

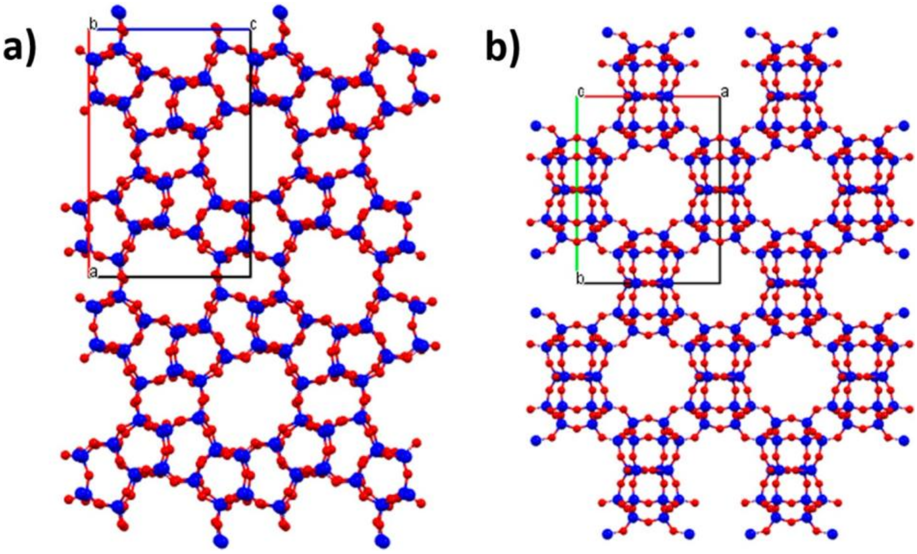


**Figure 6.** (**a**) MFI and (**b**) STF topologies represented with the program Mercury obtained from the CIF and provided by the International Zeolite Association (IZA) [8,58]. The oxygen atoms are in red, and the silicon/aluminum atoms are in blue.

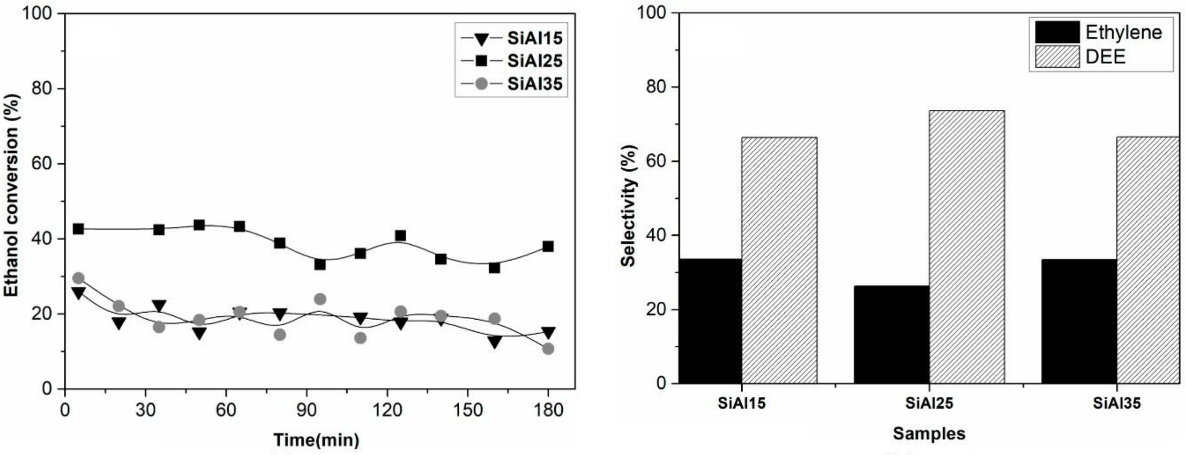
Another difference that was observed was the number of OSDA molecules per unit cell. Regardless of the chosen cation, the STF topology featured 2 imidazolium cations per unit cell, while for the MFI topology there were 4 imidazolium per unit cell. With these data and again in collaboration with Dr. Luis Gómez-Hortigüela, a more comprehensive computational study was carried out. This study began by studying the different isolated cations to determine the most stable conformations. Then, the interactions of the different cations with the crystalline MFI and STF topologies were studied, regardless of whether or not that phase was obtained with all the OSDAs. An interesting result was how the symmetry required by each cation in the MFI structure varied, allowing some combinations to be discarded based on the incompatibility of some of the symmetries with this topology. This was not found when studying the cation-STF topology interactions, which explained the direction strength of each OSDA based on their sizes.

Following the initial reasoning of the works with 1-butyl-3-methylimidazolium, the effect of titanium incorporation on the synthesis method was studied with the OSDA 1,2,3-triethyl- 4-methylimidazolium, which was chosen for directing only the STF topology [62]. The resulting products also belonged to the same zeolitic topology, regardless of the chosen Si/Ti ratio. Nevertheless, we cannot conclude that Ti only directs toward the STF, as the only $H_2O$/Si ratio tested was 3.5. Further study is still needed.

## 4. LABPEMOL Case Study: Al Insertion into the Zeolitic Framework

Zeolitic aluminosilicates were studied again, but this time from a different perspective. The research works that followed focused on the introduction of $Al^{3+}$ cations into known structures synthesized with imidazolium derivatives in hydrofluoric media.

The tests initially started with the STW topology, particularly the HPM-1 zeolite [34]. The great interest generated by this chiral zeolite led us to perform a more advanced characterization through the reaction of ethanol dehydration. The great advantage of this model reaction is that the catalysis products indicate the acidic and/or basic characteristic of the zeolite used [2]. If the zeolite has acidic sites, ethylene and diethyl ether are obtained, whereas a basic material produces acetaldehyde. In our work, which introduced $Al^{3+}$ into HPM-1, we only observed products from acidic sites and a greater selectivity to diethyl ether (Figure 7).



(**a**) (**b**)

**Figure 7.** (**a**) Ethanol conversion of the calcined [Al] HPM-1 samples as a function of time at 250 °C and (**b**) product selectivity (Reprinted from [34]).

This work also marked the beginning of a collaboration with Dr. Enrique Rodríguez-Castellón, a specialist in X-ray photoelectron spectroscopy (XPS) and HPDEC MAS NMR. Thus, we managed to carry out some interesting studies on differentiating the SAR between the bulk ($SAR_{NMR}$) and surface ($SAR_{XPS}$). The work describing the introduction of $Al^{3+}$ into the STF structure was where we most clearly appreciated the differences (Table 1), and we noted that much of the tetrahedral aluminum that was located in the outermost layer of the zeolitic crystals did not observe large differences between the calcined and non-calcined samples, in this regard.

**Table 1.** SAR calculated using the XPS and HPDEC MAS NMR results of the different Al STF samples (Reprinted from Catalysis Today, v. 2019, P. Vinaches, E. C. Gonçalves, Y. Variani, A. Rojas, E. Rodríguez-Castellón, S. B. C. Pergher, Aluminum introduction on the STF zeolite synthesized with the organic structure-directing agent 123TE4MI, in press, Copyright (2019), with permission from Elsevier
B. V.) [63].

| Sample | $SAR_{NMR}$ | $SAR_{XPS}$ |
|---|---|---|
| SA12T11 | 52.7 | 15.6 |
| SA12T11C | 56.5 | 19.0 |
| SA23T11 | 45.9 | 25.3 |
| SA23T11C | 49.6 | 33.3 |
| SA45T11 | 79.8 | 32.3 |
| SA45T11C | 83.8 | 40.3 |

## 5. LABPEMOL Case Study: SAPO Synthesis Using Imidazolium Derivatives

Until that moment at LABPEMOL, aluminosilicates, titanosilicates, and pure silica zeolites were studied in both basic and hydrofluoric media. As shown in the literature, there were some studies with imidazolium derivatives that gave interesting results in the synthesis of silicoaluminophosphates (SAPOs), and we performed a series of experiments in this regard [64]. As the OSDA, we chose the compound 2-ethyl-1,3,4-trimethylimidazolium hydroxide, and we chose hydrofluoric acid as the mineralizing agent. This combination already produced interesting results when a pure silica composition was selected, as the chiral zeolite STW was obtained [7,37]. However, as an SAPO, we obtained two different topologies: CHA and LTA. The SAPO-CHA possesses *t-hpr* tilings, among others, and SAPO-LTA possesses *t-cub* tilings, also among others. Both types of natural tilings are directed by fluoride anions. Apart from that fact, these two SAPO types have no other structural similarities. Then, to understand the results, we performed a statistical study, showing some results regarding the SAPO-CHA in Figure 8.

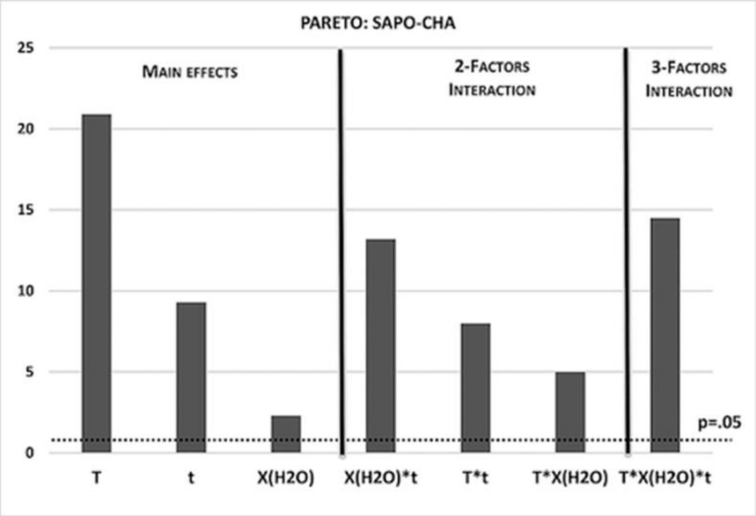


**Figure 8.** Pareto chart referring to the conditions used to synthesize SAPO-CHA (Reprinted from European Journal of Inorganic Chemistry, v. 2018, P. Vinaches, S. B. C. Pergher, Organic structure-directing agents in SAPO synthesis: the case of 2-ethyl-1,3,4-trimethylimidazolium, pp. 123–130, Copyright (2018), with permission from Wiley-VCH Verlag GmbH & Co.) [64].

In the Pareto chart, we observed that the temperature (T) was a decisive parameter for obtaining the SAPO-CHA and had the strongest effect when the water ratio ($xH_2O$) was combined with the synthesis time (t). For the SAPO-LTA, we were unable to quantify the effects due to the small amount of material that was obtained.

Returning to the SAPO-CHA, an interesting fact was the presence of hexacoordinated aluminum in the structure (Figure 9), which was probably due to the interactions of the aluminum cations with the fluoride anions. Concluding this study, it was shown that there is a need to deepen the understanding of the LTA topology, including when the LTA contains phosphor, and the statistical studies used for the structure-direction analysis were very useful.

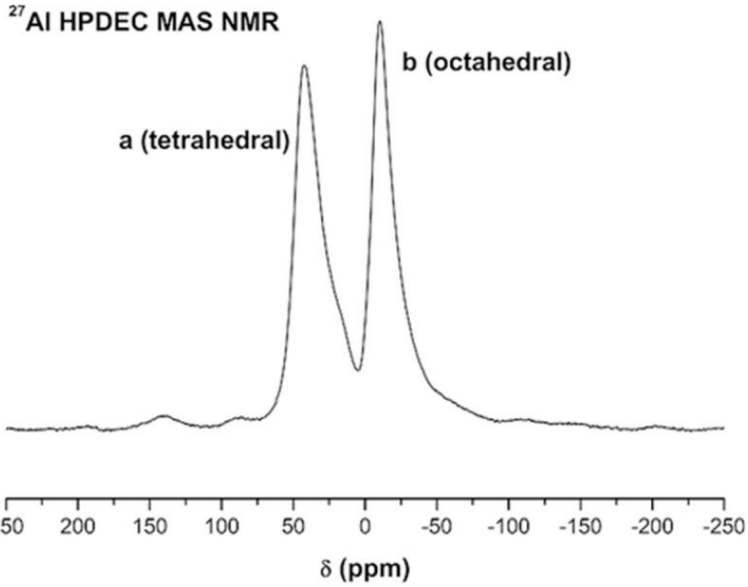


**Figure 9.** $^{27}$Al high-power decoupled (HPDEC) magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectrum of the SAPO-CHA (Reprinted from European Journal of Inorganic Chemistry, v. 2018, P. Vinaches, S. B. C. Pergher, Organic structure-directing agents in SAPO synthesis: the case of 2-ethyl-1,3,4-trimethylimidazolium, pp. 123–130, Copyright (2018), with permission from Wiley-VCH Verlag GmbH & Co.) [64].

## 6. Conclusions and Prospects

Imidazolium cation derivatives are promising compounds both in the search for new zeolitic structures and in the synthesis of the already known ones. The ease of using and recovering imidazolium cation derivatives highlights their potential in zeolite synthesis research. In this review, we have shown several study possibilities that were carried out by establishing this research line at LABPEMOL. There is a need for systematization in order to study the products resulting from the different synthesis methods with imidazolium derivatives. The use of statistical methods, such as that performed with the SAPOs, or of computational studie (for example those used to study the new OSDAs), may help in this sense. Further studies of the zeolite chirality are needed to translate this knowledge into industry. It is also interesting to perform experiments in relation to the recovery of the OSDAs and the use of cheaper alternative silica and aluminum sources. Finally, new OSDAs and new synthetic methods are needed to achieve other hypothetical topologies that are still waiting to be synthesized. We hope that showing the history of the laboratory, in this regard, will help other research groups begin similar studies.

## 7. Patents

R. F. de Souza, M. O. de Souza, K. Bernardo-Gusmão, S. B. C. Pergher, M. L. Mignoni. PI 1001211-7 B1 Processo de preparação de zeólitas utilizando líquidos iônicos como agentes direcionadores de estrutura. Brazil; deposit date 04/19/2010; issued 05/08/2018.

S. B. C. Pergher, M. L. Mignoni, D. J. Emmerich, C. W. Lopes. BR1020140164294 Proccesso de obtenção da zeólita LPM-2, um titanosilicato zeolítico de topologia TON, utilizando líquidos iônicos como agentes direcionadores de estrutura. Brazil; deposit date 05/30/2014; publication date 12/29/2015.

S. B. C. Pergher, Y. M. Variani, A. E. Rojas-Nunes. BR1020160061385 Processo de obtenção da zeólita LPM-5, um titanossilicato possuindo topologia STF, utilizando cátions orgânicos à base de um anel imidazólio como agentes direcionadores de estrutura. Brazil; deposit date 03/21/2016; publication date 09/26/2017.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Mintova, S.; Barrier, N. *Verified Synthesis of Zeolitic Materials*, 3rd ed.; Elsevier (on behalf of the Synthesis Commission of the International Zeolite Association): Amsterdam, The Netherlands, 2016; ISBN 978-0-692-68539-6.
2. Pace, G.G. *Zeolitas: Características, Propriedades e Aplicaciones Industriales*, 2nd ed.; Editorial Innovación Tecnológica, Facultad de Ingeniería, UCV: Caracas, Venezuela, 2000.
3. Cundy, C.S.; Cox, P.A. The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time. *Chem. Rev.* **2003**, *103*, 663–702. [CrossRef]
4. Davis, M.E. Zeolites from a Materials Chemistry Perspective. *Chem. Mater.* **2014**, *26*, 239–245. [CrossRef]
5. Bieseki, L.; Simancas, R.; Jordá, J.L.; Bereciartua, P.J.; Cantín, Á.; Simancas, J.; Pergher, S.B.; Valencia, S.; Rey, F.; Corma, A. Synthesis and structure determination via ultra-fast electron diffraction of the new microporous zeolitic germanosilicate ITQ-62. *Chem. Commun.* **2018**, *54*, 2122–2125. [CrossRef] [PubMed]
6. Kang, J.H.; Xie, D.; Zones, S.I.; Smeets, S.; McCusker, L.B.; Davis, M.E. Synthesis and Characterization of CIT-13, a Germanosilicate Molecular Sieve with Extra-Large Pore Openings. *Chem. Mater.* **2016**, *28*, 6250–6259. [CrossRef]
7. Rojas, A.; Arteaga, O.; Kahr, B.; Camblor, M.A. Synthesis, Structure, and Optical Activity of HPM-1, a Pure Silica Chiral Zeolite. *J. Am. Chem. Soc.* **2013**, *135*, 11975–11984. [CrossRef] [PubMed]
8. Baerlocher, C.; McCusker, L.B.; Olson, D.H. *Atlas of Zeolite Framework Types*, 6th ed.; Atlas of Zeolite Framework Types; Elsevier: Amsterdam, The Netherlands, 2007; ISBN 978-0-08-055434-1.
9. Lobo, R.F.; Zones, S.I.; Davis, M.E. Structure-direction in zeolite synthesis. *J. Incl. Phenom. Mol. Recognit. Chem.* **1995**, *21*, 47–78.
10. Moliner, M. Design of Zeolites with Specific Architectures Using Self-Assembled Aromatic Organic Structure Directing Agents. *Top. Catal.* **2015**, *58*, 502–512. [CrossRef]
11. Moliner, M.; Rey, F.; Corma, A. Towards the Rational Design of Efficient Organic Structure-Directing Agents for Zeolite Synthesis. *Angew. Chem. Int. Ed.* **2013**, *52*, 13880–13889. [CrossRef]
12. Bibby, D.M.; Dale, M.P. Synthesis of silica-sodalite from non-aqueous systems. *Nature* **1985**, *317*, 157–158. [CrossRef]
13. Kokotailo, G.T.; Lawton, S.L.; Olson, D.H.; Meier, W.M. Structure of synthetic zeolite ZSM-5. *Nature* **1978**, *272*, 437–438. [CrossRef]
14. Flanigen, E.M.; Bennett, J.M.; Grose, R.W.; Cohen, J.P.; Patton, R.L.; Kirchner, R.M.; Smith, J.V. Silicalite, a new hydrophobic crystalline silica molecular sieve. *Nature* **1978**, *271*, 512–516. [CrossRef]
15. Katritzky, A.R.; Ramsden, C.A.; Joule, J.A.; Zhdankin, V.V. *Handbook of Heterocyclic Chemistry*, 3rd ed.; Elsevier Science: Amsterdam, The Netherlands, 2010; ISBN 978-0-08-095844-6.
16. Cooper, E.R.; Andrews, C.D.; Wheatley, P.S.; Webb, P.B.; Wormald, P.; Morris, R.E. Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues. *Nature* **2004**, *430*, 1012–1016. [CrossRef]
17. Morris, R.E. Ionothermal synthesis—Ionic liquids as functional solvents in the preparation of crystalline materials. *Chem. Commun.* **2009**, 2990–2998. [CrossRef] [PubMed]
18. Parnham, E.R.; Morris, R.E. Ionothermal Synthesis of Zeolites, Metal–Organic Frameworks, and Inorganic–Organic Hybrids. *Acc. Chem. Res.* **2007**, *40*, 1005–1013. [CrossRef] [PubMed]

19. Aidoudi, F.H.; Morris, R.E. CHAPTER 10 Ionothermal Synthesis. In *Catalysis in Ionic Liquids: From Catalyst Synthesis to Application*; The Royal Society of Chemistry: London, England, 2014; pp. 508–536, ISBN 978-1-84973-603-9.
20. Dong, L.; Zheng, D.X.; Wei, Z.; Wu, X.H. Synthesis of 1,3-Dimethylimidazolium Chloride and Volumetric Property Investigations of Its Aqueous Solution. *Int. J. Thermophys.* **2009**, *30*, 1480. [CrossRef]
21. Joule, J.A.; Mills, K. 1,2-Azoles and 1,3-Azoles. In *Heterocyclic Chemistry at a Glance*; John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 2012; pp. 107–121, ISBN 978-1-118-38020-8.
22. Rojas, A.; Gómez-Hortigüela, L.; Camblor, M.A. Benzylimidazolium cations as zeolite structure-directing agents. Differences in performance brought about by a small change in size. *Dalton Trans.* **2013**, *42*, 2562–2571. [CrossRef] [PubMed]
23. Variani, Y.M.; Rojas, A.; Gómez-Hortigüela, L.; Pergher, S.B.C. Study of the performance of imidazolium-derived cations as structure directing agents in the synthesis of zeolites in fluoride media. *New J. Chem.* **2016**, *40*, 7968–7977. [CrossRef]
24. Gao, Z.-H.; Chen, F.-J.; Xu, L.; Sun, L.; Xu, Y.; Du, H.-B. A Stable Extra-Large-Pore Zeolite with Intersecting 14- and 10-Membered-Ring Channels. *Chem. A Eur. J.* **2016**, *22*, 14367–14372. [CrossRef]
25. Yuan, D.; He, D.; Xu, S.; Song, Z.; Zhang, M.; Wei, Y.; He, Y.; Xu, S.; Liu, Z.; Xu, Y. Imidazolium-based ionic liquids as novel organic SDA to synthesize high-silica Y zeolite. *Microporous Mesoporous Mater.* **2015**, *204*, 1–7. [CrossRef]
26. Lu, P.; Chen, L.; Zhang, Y.; Yuan, Y.; Xu, L.; Zhang, X.; Xu, L. Rapid synthesis of ZSM-22 zeolites using imidazolium-based ionic liquids as OSDAs in fluoride media. *Microporous Mesoporous Mater.* **2016**, *236*, 193–201. [CrossRef]
27. Wheatley, P.S.; Allan, P.K.; Teat, S.J.; Ashbrook, S.E.; Morris, R.E. Task specific ionic liquids for the ionothermal synthesis of siliceous zeolites. *Chem. Sci.* **2010**, *1*, 483–487. [CrossRef]
28. Tian, Y.; McPherson, M.J.; Wheatley, P.S.; Morris, R.E. Ionic Liquid assisted Synthesis of Zeolite-TON. *Z. Anorg. Allg. Chem.* **2014**, *640*, 1177–1181. [CrossRef] [PubMed]
29. Boal, B.W.; Deem, M.W.; Xie, D.; Kang, J.H.; Davis, M.E.; Zones, S.I. Synthesis of Germanosilicate Molecular Sieves from Mono- and Di-Quaternary Ammonium OSDAs Constructed from Benzyl Imidazolium Derivatives: Stabilization of Large Micropore Volumes Including New Molecular Sieve CIT-13. *Chem. Mater.* **2016**, *28*, 2158–2164. [CrossRef]
30. Blasco, T.; Corma, A.; Díaz-Cabañas, M.J.; Rey, F.; Vidal-Moya, J.A.; Zicovich-Wilson, C.M. Preferential Location of Ge in the Double Four-Membered Ring Units of ITQ-7 Zeolite. *J. Phys. Chem. B* **2002**, *106*, 2634–2642. [CrossRef]
31. Henkelis, S.E.; Mazur, M.; Rice, C.M.; Bignami, G.P.M.; Wheatley, P.S.; Ashbrook, S.E.; Čejka, J.; Morris, R.E.
    A procedure for identifying possible products in the assembly–disassembly–organization–reassembly (ADOR) synthesis of zeolites. *Nat. Protoc.* **2019**, *14*, 781–794. [CrossRef] [PubMed]
32. Shamzhy, M.; Opanasenko, M.; Tian, Y.; Konysheva, K.; Shvets, O.; Morris, R.E.; Čejka, J. Germanosilicate Precursors of ADORable Zeolites Obtained by Disassembly of ITH, ITR, and IWR Zeolites. *Chem. Mater.* **2014**, *26*, 5789–5798. [CrossRef]
33. Mazur, M.; Wheatley, P.S.; Navarro, M.; Roth, W.J.; Položij, M.; Mayoral, A.; Eliášová, P.; Nachtigall, P.; Čejka, J.; Morris, R.E. Synthesis of 'unfeasible' zeolites. *Nat. Chem.* **2015**, *8*, 58–62. [CrossRef]
34. Vinaches, P.; Rojas, A.; de Alencar, A.E.V.; Rodríguez-Castellón, E.; Braga, T.; Pergher, S.B.C. Introduction of Al into the HPM-1 Framework by In Situ Generated Seeds as an Alternative Methodology. *Appl. Sci.* **2018**, *8*, 1634. [CrossRef]
35. Lu, P.; Gómez-Hortigüela, L.; Xu, L.; Camblor, M.A. Synthesis of STW zeolites using imidazolium-based dications of varying length. *J. Mater. Chem. A* **2018**, *6*, 1485–1495. [CrossRef]
36. Lu, P.; Mayoral, A.; Gómez-Hortigüela, L.; Zhang, Y.; Camblor, M.A. Synthesis of 3D Large-Pore Germanosilicate Zeolites Using Imidazolium-Based Long Dications. *Chem. Mater.* **2019**, *31*, 5484–5493. [CrossRef]
37. Brand, S.K.; Schmidt, J.E.; Deem, M.W.; Daeyaert, F.; Ma, Y.; Terasaki, O.; Orazov, M.; Davis, M.E. Enantiomerically enriched, polycrystalline molecular sieves. *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 5101–5106. [CrossRef]

38. Bernardo-Maestro, B.; López-Arbeloa, F.; Pérez-Pariente, J.; Gómez-Hortigüela, L. Supramolecular Chemistry Controlled by Conformational Space during Structure Direction of Nanoporous Materials: Self-Assembly of Ephedrine and Pseudoephedrine. *J. Phys. Chem. C* **2015**, *119*, 28214–28225. [CrossRef]
39. Gómez-Hortigüela, L.; Hamad, S.; López-Arbeloa, F.; Pinar, A.B.; Pérez-Pariente, J.; Corà, F. Molecular Insights into the Self-Aggregation of Aromatic Molecules in the Synthesis of Nanoporous Aluminophosphates: A Multilevel Approach. *J. Am. Chem. Soc.* **2009**, *131*, 16509–16524. [CrossRef] [PubMed]
40. Martínez, C.; Pariente, J.P. *Zeolites and Ordered Porous Solids: Fundamentals and Applications*; Universitat Politècnica de València: Valencia, Spain, 2011; ISBN 978-84-8363-707-4.
41. Catlow, C.R.A.; Coombes, D.S.; Lewis, D.W.; Pereira, J.C.G. Computer Modeling of Nucleation, Growth, and Templating in Hydrothermal Synthesis. *Chem. Mater.* **1998**, *10*, 3249–3265. [CrossRef]
42. Lewis, D.W.; Freeman, C.M.; Catlow, C.R.A. Predicting the Templating Ability of Organic Additives for the Synthesis of Microporous Materials. *J. Phys. Chem.* **1995**, *99*, 11194–11202. [CrossRef]
43. Chen, H.; Wang, W.; Ding, J.; Wei, X.; Lu, J. $CO_2$ Adsorption Capacity of FAU Zeolites in Presence of $H_2O$: A Monte Carlo Simulation Study. *Energy Procedia* **2017**, *105*, 4370–4376. [CrossRef]
44. Earl, D.J.; Deem, M.W. Toward a Database of Hypothetical Zeolite Structures. *Ind. Eng. Chem. Res.* **2006**, *45*, 5449–5454. [CrossRef]
45. Schwalbe-Koda, D.; Jensen, Z.; Olivetti, E.; Gómez-Bombarelli, R. Graph similarity drives zeolite diffusionless transformations and intergrowth. *Nat. Mater.* **2019**, *18*, 1177–1181. [CrossRef]
46. Lorgouilloux, Y.; Dodin, M.; Paillaud, J.-L.; Caullet, P.; Michelin, L.; Josien, L.; Ersen, O.; Bats, N. IM-16: A new microporous germanosilicate with a novel framework topology containing d4r and mtw composite building units. *J. Solid State Chem.* **2009**, *182*, 622–629. [CrossRef]
47. Khoo, D.Y.; Awala, H.; Mintova, S.; Ng, E.-P. Synthesis of AlPO-5 with diol-substituted imidazolium-based organic template. *Microporous Mesoporous Mater.* **2014**, *194*, 200–207. [CrossRef]
48. Martínez Blanes, J.M.; Szyja, B.M.; Romero-Sarria, F.; Centeno, M.Á.; Hensen, E.J.M.; Odriozola, J.A.; Ivanova, S. Multiple Zeolite Structures from One Ionic Liquid Template. *Chem. Eur. J.* **2013**, *19*, 2122–2130. [CrossRef] [PubMed]
49. Jo, D.; Park, G.T.; Shin, J.; Hong, S.B. A Zeolite Family Nonjointly Built from the 1,3-Stellated Cubic Building Unit. *Angew. Chem.* **2018**, *130*, 2221–2225. [CrossRef]
50. Simancas, R.; Dari, D.; Velamazán, N.; Navarro, M.T.; Cantín, A.; Jordá, J.L.; Sastre, G.; Corma, A.; Rey, F. Modular Organic Structure-Directing Agents for the Synthesis of Zeolites. *Science* **2010**, *330*, 1219–1222. [CrossRef] [PubMed]
51. Simancas, R.; Jordá, J.L.; Rey, F.; Corma, A.; Cantín, A.; Peral, I.; Popescu, C. A New Microporous Zeolitic Silicoborate (ITQ-52) with Interconnected Small and Medium Pores. *J. Am. Chem. Soc.* **2014**, *136*, 3342–3345. [CrossRef]
52. Simancas, J.; Simancas, R.; Bereciartua, P.J.; Jorda, J.L.; Rey, F.; Corma, A.; Nicolopoulos, S.; Pratim Das, P.; Gemmi, M.; Mugnaioli, E. Ultrafast Electron Diffraction Tomography for Structure Determination of the New Zeolite ITQ-58. *J. Am. Chem. Soc.* **2016**, *138*, 10116–10119. [CrossRef]
53. Sáez-Ferre, S.; Lopes, C.W.; Simancas, J.; Vidal-Moya, A.; Blasco, T.; Agostini, G.; Espallargas, G.M.; Jordá, J.L.; Rey, F.; Oña-Burgos, P. Use of alkylarsonium directing agents for the synthesis and study of zeolites. *Chem. Eur. J.* **2019**. [CrossRef]
54. Vinaches, P.; Bernardo-Gusmão, K.; Pergher, S.B.C. An Introduction to Zeolite Synthesis Using Imidazolium-Based Cations as Organic Structure-Directing Agents. *Molecules* **2017**, *22*, 1307. [CrossRef]
55. Mignoni, M.L.; de Souza, M.O.; Pergher, S.B.C.; de Souza, R.F.; Bernardo-Gusmão, K. Nickel oligomerization catalysts heterogenized on zeolites obtained using ionic liquids as templates. *Appl. Catal. A Gen.* **2010**, *374*, 26–30. [CrossRef]
56. Maldonado, M.; Oleksiak, M.D.; Chinta, S.; Rimer, J.D. Controlling Crystal Polymorphism in Organic-Free Synthesis of Na-Zeolites. *J. Am. Chem. Soc.* **2013**, *135*, 2641–2652. [CrossRef]
57. Dempsey, E.; Kuehl, G.H.; Olson, D.H. Variation of the lattice parameter with aluminum content in synthetic sodium faujasites. Evidence for ordering of the framework ions. *J. Phys. Chem.* **1969**, *73*, 387–390. [CrossRef]
58. Macrae, C.F.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, M.; van de Streek, J. Mercury: Visualization and analysis of crystal structures. *J. Appl. Crystallogr.* **2006**, *39*, 453–457. [CrossRef]

59. Lopes, C.W.; Finger, P.H.; Mignoni, M.L.; Emmerich, D.J.; Mendes, F.M.T.; Amorim, S.; Pergher, S.B.C. $TiO_2$-TON zeolite synthesis using an ionic liquid as a structure-directing agent. *Microporous Mesoporous Mater.* **2015**, *213*, 78–84. [CrossRef]
60. Lopes, C.W.; Gómez-Hortigüela, L.; Rojas, A.; Pergher, S.B.C. Fluoride-mediated synthesis of TON and MFI zeolites using 1-butyl-3-methylimidazolium as structure-directing agent. *Microporous Mesoporous Mater.* **2017**, *252*, 29–36. [CrossRef]
61. Camblor, M.A.; Villaescusa, L.A.; Díaz-Cabañas, M.J. Synthesis of all-silica and high-silica molecular sieves in fluoride media. *Top. Catal.* **1999**, *9*, 59–76. [CrossRef]
62. Variani, Y.M.; Rojas, A.; Pergher, S.B.C. Synthesis and characterization of Ti-STF zeolite using 1,2,3-triethyl-4-methylimidazolium as structure-directing agent. *Microporous Mesoporous Mater.* **2018**, *262*, 106–111. [CrossRef]
63. Vinaches, P.; Gonçalves, E.C.; Variani, Y.; Rojas, A.; Rodríguez-Castellón, E.; Pergher, S.B.C. Aluminium introduction on the STF zeolite synthesized with the organic structure-directing agent 123TE4MI. *Catal. Today* **2019**. [CrossRef]
64. Vinaches, P.; Pergher, S.B.C. Organic Structure-Directing Agents in SAPO Synthesis: The Case of 2-Ethyl-1,3,4-trimethylimidazolium. *Eur. J. Inorg. Chem.* **2018**, *2018*, 123–130. [CrossRef]