

New structure directing agent in the synthesis of ZSM-5 zeolite

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Resumo/Abstract (Helvética, tam. 12)

RESUMO - O presente trabalho descreve a utilização de um novo agente direcionador de estrutura para a preparação de um material zeolítico de topologia MFI puro. Para a obtenção do referido material zeolítico, utilizou-se o líquido iônico cloreto de 1-(4-fenilbenzil)-3-metilimidazólio [PhBzMIm.Cl]. O método descrito no presente estudo envolve a utilização de SiO₂ (fonte de sílica), NaOH como agente mineralizante, Na₂Al₂O₄ como fonte de alumínio, e H₂O como o solvente da reação. O método descrito é vantajoso por utilizar temperatura branda (150 °C) e utilizar o agente direcionador de estrutura fácil de ser sintetizado e que é classificado dentro da química verde. O método trata-se da obtenção dos materiais zeolíticos com relação Si/Al = 50 com topologia MFI puro e cristalino o que torna esse processo tecnicamente e comercialmente atrativo.

Palavras-chave: Líquido iônico, Agentes direcionadores de estrutura, Zeólitas, ZSM-5, Síntese.

ABSTRACT - This work describes the use of a novel structure-directing agent for the preparation of a pure MFI zeolitic material. The ionic liquid 1-(4-phenylbenzyl)-3-methylimidazolium chloride [PhBzMIm.Cl] was used to obtain this zeolitic material. The method described in this study involves the use of SiO₂ (silica source), NaOH as a mineralizing agent, Na₂Al₂O₄ as an aluminum source, and H₂O as the reaction solvent. The described method is advantageous because it uses a mild temperature (150 °C) and uses a structure-directing agent that is easy to synthesize and is classified within green chemistry. The method aims to obtain zeolitic materials with a Si/Al ratio = 50 and a pure and crystalline MFI topology, which makes this process technically and commercially attractive.

Keywords: Ionic liquid, Structure-directing agents, Zeolites, ZSM-5, Synthesis.

Introduction

Zeolite synthesis plays a fundamental role in industry and scientific research, due to its importance in various applications. The synthesis of these materials allows to control their physical and chemical properties, making them highly versatile in areas such as catalysis, gas separation, water purification and environmental remediation. The ability to synthesize zeolites tailored for specific applications is crucial to developing more efficient and sustainable technologies [1].

The choice of the appropriate SDA depends on the desired zeolite structure and synthesis conditions. The use of SDA allows obtaining zeolites with specific properties such as pore size, pore distribution and acidity. This is particularly important in industrial applications such as heterogeneous catalysis, selective adsorption, gas separation and chemical purification[2-4]. In summary, the use of ionic liquids as directing agents in zeolite synthesis is a promising

approach that offers significant advantages such as structural versatility, recyclability, and mild synthesis conditions.

This approach has the potential to drive advances in the area of zeolitic materials and open up new possibilities for more efficient and sustainable industrial applications.

Experimental

Synthesis of the ionic liquids 1-(4-phenylbenzyl)-3-methylimidazolium chloride [PhBzMIm.Cl]

For the synthesis of ionic liquid 1-(4-phenylbenzyl)-3-methylimidazolium chloride [PhBzMIm.Cl], initially 1.01 g (0.012 mol) of methylimidazole was added to a beaker. In another beaker, 2.5 g (0.012 mol) of 4-phenylbenzyl chloride were added. Subsequently, the reagents were added to a Schlenk flask, along with 10 mL of acetonitrile and left to reflux at 80 °C for 48h. At the end of the reaction, the final product was dried under vacuum until constant weight.

Application of synthesized ionic liquid in the synthesis of zeolites

The zeolite synthesis was performed by mixing SiO_2 (18.5 g of aerosil 200, Degussa), NaOH (2.44g, Aldrich), $\text{Na}_2\text{Al}_2\text{O}_4$ (0.58 g, Riedel-de-Haen), $[\text{PhBzMIIm.Cl}]$ (0.9 g) or $[\text{PhBzEt}_3\text{N.Cl}]$ (2.7g) and H_2O (130g). These compositions corresponds to molar ratios $\text{Si}/\text{OH} = 5$, $\text{H}_2\text{O}/\text{Si} = 53$, $\text{Si}/\text{Na} = 5$ and $\text{Si}/\text{Al} = 50$. The hydrothermal synthesis of zeolitic material followed the classic literature route [5]. After mixing the reagents and the ionic liquid, a gel was formed and transferred to stainless steel autoclaves lined internally with Teflon. These autoclaves were then subjected to static heating at 150°C for a period of 1, 7 and 14 days of synthesis.

Results and discussion

Hydrothermal synthesis using $[\text{PhBzMIIm.Cl}]$ as SDA, for 3 to 14 days, produced solid materials, and these, when analyzed by XRD, presented the diffractograms shown in Figure 1.

The diffractograms presented in Figure 1 show that after 3 days a material with lines characteristic of a zeolitic structure with ZSM-5 morphology is formed. This zeolitic phase is confirmed by the presence of peaks (2θ) equal to: 7.94, 8.83, 20.78, 23.09, 26.65, 36.60, 39.48, 42.42, 45.61, 50.10, 54.99, 59.83 and 68.18 which are peaks reported in the literature for the ZSM-5 zeolitic phase[6].

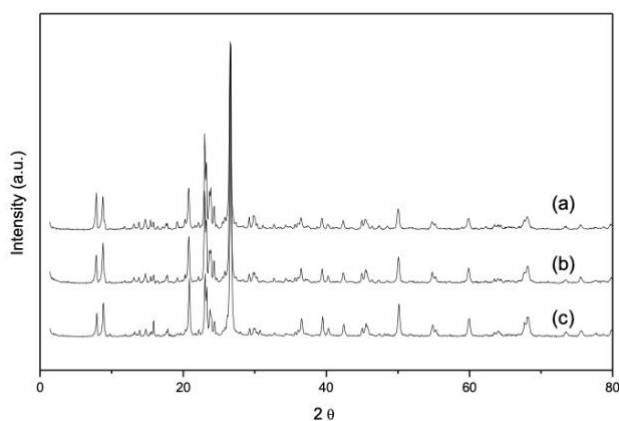


Figure 1. X-ray diffractograms of the zeolite ZSM-5 obtained in the presence of $[\text{PhBzMIIm.Cl}]$ with reaction times of (a) 3 days, (b) 7 days and (c) 14 days at 150°C and Si/Al ratio of 50.

The N_2 adsorption analysis show this is a type I isotherm, characteristic of microporous solids[7]. The calculation of the specific area gives $304 \text{ m}^2\cdot\text{g}^{-1}$ and the pore volume is $0.17 \text{ cm}^3\cdot\text{g}^{-1}$, in the usual range for ZSM-5 zeolites.

The zeolite ZSM-5 obtained in 3 days of synthesis was analyzed by SEM. The results are presented in Figure 2.

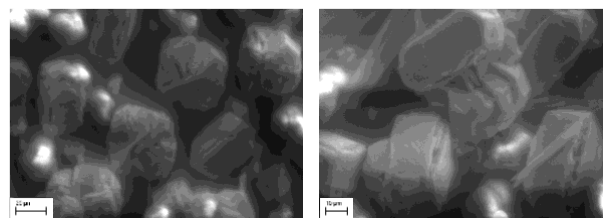


Figure 2. Representative SEM micrographs of ZSM-5 zeolite synthesized at 150°C at a Si/Al ratio of 50 with a reaction time of 3 days.

In Figure 2(a), it is observed that the morphology of the crystalline material is ellipsoidal with diameters of 20-30 μm . Analyzing Figure 2(b) it is possible to verify that most of these crystals presented the hexagonal morphology typical of MFI (ZSM-5).

Conclusion

This work synthesized a new structure-directing agent (SDA) and utilized it in the synthesis of a zeolite with an MFI topology. Obtaining the pure, crystalline ZSM-5 zeolite structure confirms the successful synthesis of the new SDA, thus creating a new synthesis route for this type of material.

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