

STIRRING EFFECT ON ZEOLITES SYNTHESIS WITH DIFFERENT Si/Al MOLAR RATIOS USING 1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE AS STRUCTURE-DIRECT AGENT

Efeito da agitação na síntese de zeólitas com diferentes razões molares Si/Al utilizando cloreto de 1-butil-3-metilimidazólio como direcionador de estrutura

Marcelo L. Mignoni¹; Victor de Aguiar Pedott¹; Catia S. Z. Battiston²; Carolina E. Demaman Oro¹, Michele O. de Souza³; Sibeles B.C. Pergher⁴; Rogério Marcos Dallago¹; Roberto F. de Souza^{3#}; Katia Bernardo-Gusmão³

¹Departamento de Química, Universidade Regional Integrada do Alto Uruguai e das Missões, Erechim, RS. *E-mail* address: mignoni@uricer.edu.br

²Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul – Campus Erechim, RS.

³Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS.

⁴LABPEMOL, Instituto de Química, Universidade Federal do Rio Grande do Norte, Natal.

In memoriam

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Resumo: Diferentes tipos de zeólitas podem ser sintetizadas alterando variáveis no processo de síntese. O presente trabalho estuda o efeito de agitação na síntese de zeólitas com diferentes proporções molares de Si/Al (1, 8, 20, 50 e 120), usando o líquido iônico cloreto de 1-butil-3-metilimidazólio (BMI. Cl) como agente direcionador da estrutura. Os resultados obtidos mostraram a alta eficiência do líquido iônico BMI. Cl como agente direcionador, para a cristalização de zeólitas tipo A, ZSM-5, Beta e ZSM-35. O efeito de agitação nos parâmetros morfológicos e composicionais aparentam ser significativos. Sendo assim, diagramas ternários de composição foram plotados para as condições estáticas e de agitação, evidenciando a influência da agitação na composição e morfologia dos materiais gerados. Nos diagramas ternários foi possível verificar as condições de obtenção das zeólitas ZSM-5 e ZSM-35 puras, bem como as diferentes morfologias encontradas para as mesmas

regiões, quando as zeólitas foram sintetizados em condições estáticas e de agitação. Observa-se, também, que as zeólitas ZSM-35 e Beta mostram uma quantidade maior de Al_2O_3 (4% em mol e 1,6% em mol) apenas quando a reação é realizada sob condições de agitação.

Palavras-chave: Materiais microporosos. Síntese. Morfologia. Zeólita.

Abstract: Different types of zeolites could be synthesized changing the variables in the synthesis process. This paper studies the stirring effect on zeolites synthesis at different Si/Al molar ratios (1, 8, 20, 50 and 120) using the ionic liquid 1-butyl-3-methylimidazolium chloride (BMI.Cl) as structure-direct agent. The results suggest that the ionic liquid BMI.Cl would be a highly effective directing agent for the crystallization of zeolites type A, ZSM-5, Beta and ZSM-35. The stirring effect on compositional and morphological parameters seems to be significant. Therefore, ternary composition diagrams were plotted for the static and stirring conditions, showing the influence of stirring on the composition and morphology of the generated materials. It was possible to verify, in the ternary diagrams, the conditions for obtaining the pure ZSM-5 and ZSM-35 zeolites, as well as the different morphologies found for the same regions, when the zeolites were synthesized under static and stirring conditions. It is also observed that the zeolites ZSM-35 and Beta show a greater amount of Al_2O_3 (4 mol% and 1.6 mol%) only when the reaction is carried out under stirring conditions.

Keywords: Microporous materials. Synthesis. Morphology. Zeolite.

Introduction

Zeolites are microporous materials with framework characterized by TO4 (T = Si, Al) tetrahedral three-dimensional structure with interconnected cavities and channels, which leads to high specific surface areas (MOLINER; MARTÍNEZ; CORMA, 2015). The amount of Al within the framework can vary over a wide range of Si/Al relations, which could lead to different zeolites frameworks (INGLEZAKIS; ZORPAS, 2012).

Zeolites are usually synthesized under hydrothermal conditions, where the reaction variables including time, temperature,

gel composition, stirring and reactant source influence the framework formation (CORMA; MOLINER; ROMA, 2019). Another factor that could influence on framework is the use of Structure Directing Agents (SDA's), composed by organic and inorganic cations, causing a competition between zeolitic phases (DI RENZO, 1998; HAMILTON et al., 1993; HINCAPIE et al., 2004; LIMA, 2014; MINTOVA et al., 2007; VALTCHEV et al., 1995). Therefore, the gel formation is a crucial parameter in the nucleation process, where a large number of cores are produced, due to high degree of supersaturation caused by the ionic species, which affects the crystal size and morphology of zeolite phases (KUZIELOVÁ et al., 2020; MINTOVA et al., 2016).

Many studies show that the composition of the starting gel used in the synthesis have a great influence on crystal size and morphology (DI RENZO, 1998; HINCAPIE et al., 2004; VALTCHEV et al., 1995; ZHUANG et al., 2018). Stirring conditions on the starting gel has been shown as a very important parameter, whose effects have been explained as consequences of changes in local concentrations, transport properties and in the "structure" of the gel (KIM; CHUNG, 2003).

Zeolite frameworks as Beta and TON-type, synthesized under hydrothermal conditions, require stirring during synthesis, where with these conditions, the gel properties as TEAOH/SiO₂ molar ratio, crystallization kinetics, particle size and particle size distribution, lead to structure formation, as described in literature (DING et al., 2006).

Ionic liquids could act as SDA and solvent in zeolite synthesis, assigning great potential for its application due to its properties as green-chemistry, low vapor pressure and the possibility of imidazolium-based cations lead to many different geometries in synthesis of zeolite structures (MORRIS, 2009; VINACHES; BERNARDO-GUSMÃO; PERGHER, 2017). The association between the use of the supramolecular arrangements, well-known in the ionic liquids, induce specific crystallization of zeolitic structures (LOPES et al., 2015; SACHSE et al., 2015).

Many works involving ionic liquids acting as SDA's have been published along the years, obtaining different zeolites frameworks as, H-ZSM-5, MER-type zeolites, 10-MR zeolites and NaP zeolites and also for a wide range of materials (HAOUAS et al., 2014; HUANG; CHEN, 2013; LI et al., 2019, 2020; SOLL; ANTONIETTI; YUAN, 2014; ZARE et al., 2020; ZHAO et al., 2009).

Zeolites have many important industrial applications, they practically dominate the

heterogeneous catalysis and are also used as adsorbents for the removal of ions, gases and etc. (QUEROL et al., 1997; SINGH; KOLAY, 2002). Mostly used as acid catalyst in petrochemical industry, zeolites have several desirable catalytic properties due to limitations from pore size, which brings a shape selectivity regarding the products. They are also used as supports for transition metals, creating unique catalytic sites, with defined and ordered structure (CORMA, 2003; SONG et al., 2004).

Therefore, for a better understanding of stirring influence on zeolite framework formation, this paper will be presented to study the effect of stirring on the synthesis of zeolites with different molar ratios Si/Al (1, 8, 20, 50 and 120) using the ionic liquid 1-butyl-3-methylimidazolium chloride as structure-direct agent.

Experimental

Zeolites were synthesized under static and stirring conditions using 1-butyl-3-methylimidazolium chloride (BMI.Cl) as structure-direct agent. The ionic liquid was synthesized according to published procedure (DUPONT et al., 2002). The reactants used in this study were sodium aluminate (Na₂Al₂O₄, Riedel-de-Haen) as the aluminum source, SiO₂ (aerosil 200, Degussa) as the silica source, the ionic liquid 1-butyl-3-methylimidazolium chloride (BMI.Cl) as SDA, NaOH pellets (Sigma-Aldrich 97%) and deionized water.

In order to study the crystallization of zeolites, five syntheses were performed with different molar compositions. Table I shows the percentage molar ratios used in each synthesis.

The zeolite synthesis occurred as follows: *i*) in a beaker, the SiO₂ was dissolved in

deionized water (60 mL), under 15 minutes of agitation, and then the BMI.Cl was added, obtaining solution A. *ii*) initially the NaOH was solubilized in deionized water (60 mL) and then the $\text{Na}_2\text{Al}_2\text{O}_4$ was added, obtaining solution B. This solution was stirred for 15 minutes. *iii*) Finally, the solution B was added in solution A to originate the synthesis gel (solution C) which was left under agitation for further 15 minutes to total homogenization of the reactants.

Table 1 - Percentage molar and molar ratios used in each synthesis

Synthesis	Si/Al	mol% SiO_2	mol% Al_2O_3	mol% Na_2O
1	1	44.5	19.2	36.3
2	8	74.0	4.0	22.0
3	20	76.8	1.6	21.6
4	50	89.0	1.0	10.0
5	120	81.3	0.3	18.4

Then, three equal volumes of the solution C gel were poured into 60-mL capacity Teflon-lined stainless-steel autoclaves and maintained in an oven at 180 °C for 3, 7 and 14 days, where the samples were submitted to static or stirring conditions. After the reaction time, the solids were filtered and washed with 50 mL of deionized water and 50 mL of acetone, and then dried for 5 h at 105 °C.

The zeolitic phase of samples was characterized by X-ray diffraction (XRD) on a Siemens D500 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). For X-ray data collection, after calcination (600 °C), a sample was placed in a glass measurement cell that was quickly closed to avoid contact with moisture, then degassed at 300 °C under vacuum prior to measurements. The morphology and particle size of the products were investigated using a SSZ 550 (Shimadzu)

scanning electron microscope (SEM). The specific surface areas were determined from nitrogen adsorption on Micrometrics Gemini VacPrep 061 using the BET method.

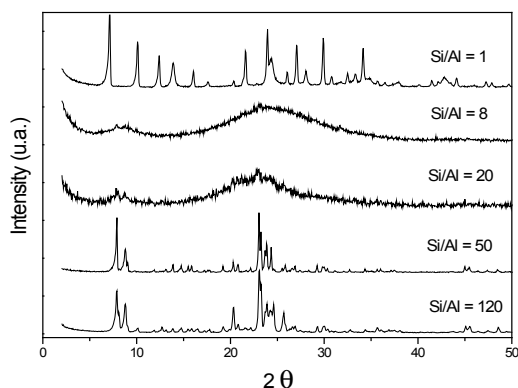
Results and discussion

Different compositions of the synthesis gel were originated by mixing SiO_2 , $\text{Na}_2\text{Al}_2\text{O}_4$, NaOH, and BMI.Cl in water, leading to different zeolitic structures, which were also influenced by the reaction parameters like composition, agitation and temperature

Synthesis under static condition

Figure 1 shows the XRD patterns of the materials obtained with different silicon/aluminum molar ratios under static conditions

Figure 1 - X-ray diffractograms of materials obtained in 3 days of synthesis using BMI.Cl as template at different ratios under static conditions



The synthesis of zeolites, under static conditions, were conducted at three different times, where the results obtained from 3, 7 and 14 days of synthesis are the same, showing that the reaction time have no influence in the structure formation for the tested Si/Al molar relations. The diffractogram for Si/Al = 1 show very characteristic 2θ lines

of zeolite A at 7.13°, 10.22°, 12.51°, 16.19°, 21.68°, 23.94°, 27.17°, 30.02°, 34.08° and 42.77° (TREACY; HIGGINS, 2001). However, we also observe the appearance of peaks in 14.04° and 24.29°, characteristic of sodalite zeolite. In molar ratios of 8 and 20 no structure are formed, the obtained material presents an amorphous morphology.

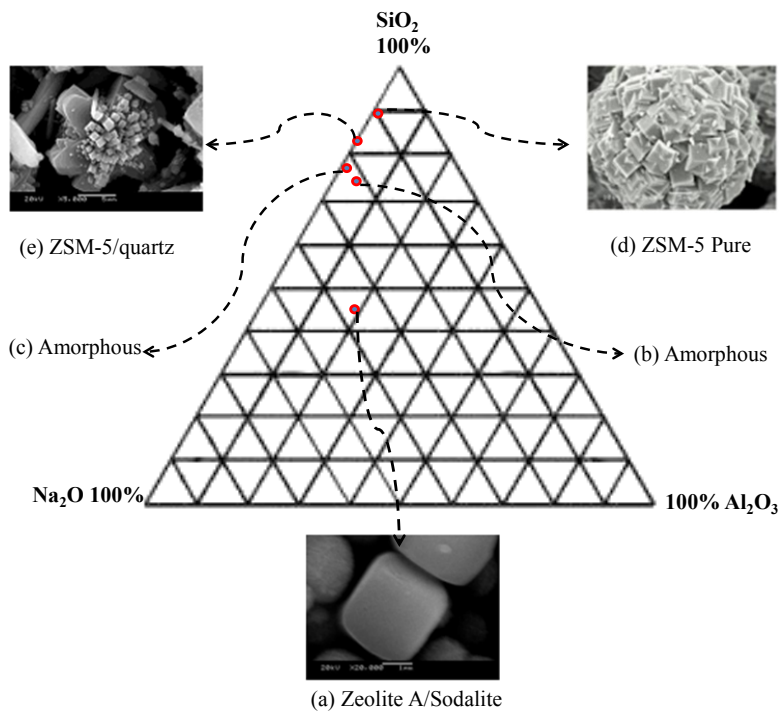
From a molar ratio Si/Al = 50 and Si/Al = 120 is possible to verify the presence of peaks indicating the obtainment of a crystalline material showing very characteristic lines of a ZSM-5 framework at 7.97°, 8.82°, 23.10°, 23.35°, 23.86°, and 24.35° (VALTCHEV et al., 1995). However, the Si/Al = 120 ration have a mixture of phases like demonstrated by the peaks in 20.3° and 26.0° characteristic of quartz phase.

In order to clearly demonstrate the effect of individual component on the crystalliza-

tion of zeolites and the interaction between components, under static conditions, a ternary compositional diagram for SiO₂, Al₂O₃ and Na₂O was drawn in Figure 2 at constant BMI.Cl, NaOH and H₂O contents.

As can be seen in Figure 2, there are two compositional zones in which zeolite ZSM-5 are formed, pure or in a mixture of phases. It is interesting to notice that the pure ZSM-5 zeolite is more likely formed with a less Al₂O₃ content, approximately 2 mol%. However, for greater contents of Al₂O₃, there is the presence of quartz as an impurity phase as demonstrated in Figure 1. A closer look at microspheres in Figure 2 (d), for pure zeolite ZSM-5, shows agglomerates of hexagonal prisms with dimensions of approximately 30 μm forming these spheres. Therefore, it is concluded that pure zeolite ZSM-5 is likely formed in the compositional zone of 89 mol%

Figure 2 - Ternary diagram of the gel composition of the synthesis of zeolite without agitation, with different molar ratios Si/Al: (a) 1, (b) 8, (c) 20, (d) 50 and (e) 120



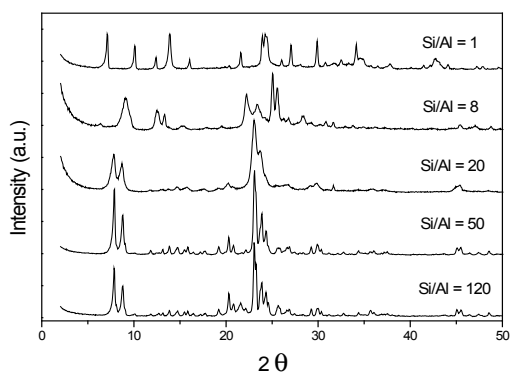
SiO_2 , 1mol% Al_2O_3 and 10.0 mol% Na_2O .

For samples (b) and (c) with molar Si/Al ratios of 8 and 20, respectively, an amorphous morphology was shown, as verified by XRD (Fig. 1), however, for the (a) sample, it is possible to notice the formation of two phase zeolite A/sodalite, characteristic of small molar Si/Al ratio (JANOS B.NAGY, PIERRE BODART, I. HANNUS, 1998).

Synthesis under stirring conditions

The XRD diffractograms of the materials synthesized with different molar ratios under stirring conditions are shown in Figure 3.

Figure 3. X-ray diffractograms of materials obtained in 3 days of synthesis using BMI.Cl as directing agent at different ratios with stirring



The X-ray diffractograms obtained for stirring conditions shows similar results for relation Si/Al = 1, to those obtained under static conditions, where it causes the appearance of peaks characteristic of zeolite A, along with peaks in 14.04° and 24.29° of zeolite sodalite which appears with greater intensity when synthesized in static conditions. For relation Si/Al = 8 is possible to observe the influence of stirring in the synthesis process. In these case, we observe the formation of peaks characteristic of ZSM-35 framework

at 2θ values of 9.23°, 12.68°, 13.38°, 22.21°, 23.45°, 25.04°, 25.52° and 28.31°, showing that stirring has a positive influence on the formation of ZSM-35 structures (GUO et al., 2017).

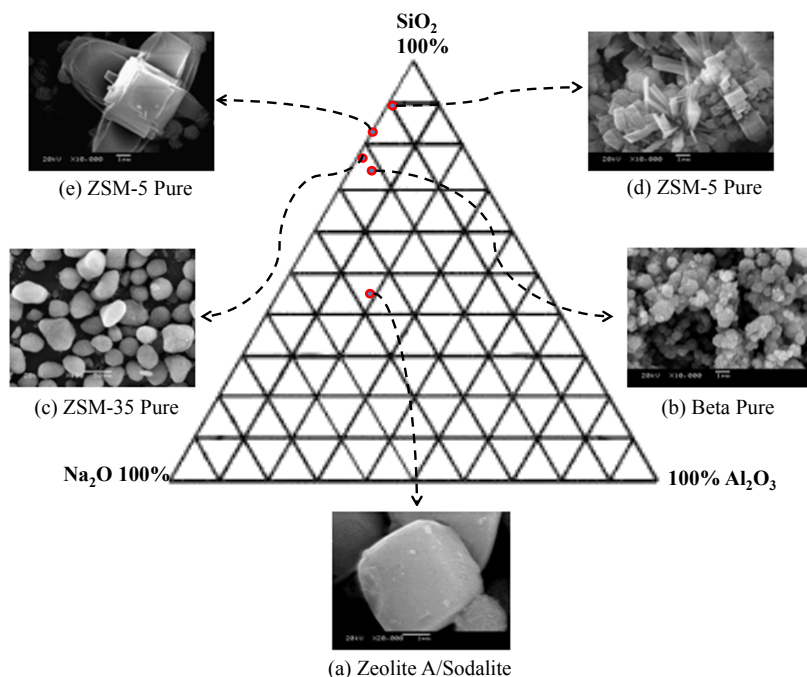
Analyzing the molar relationship Si/Al = 20, it is possible to observe the formation of a crystalline phase, with peaks at 7.7°, 8.8° and 23.0°, characteristic of β -zeolites (GUO et al., 2017), where in the synthesis process under static conditions, for the same relation, no structure was obtained. When the Si/Al ratio increased to 50, well-defined peaks are observed, indicating the presence of a crystalline phase, characteristic 2θ lines of a ZSM-5 framework at 7.97°, 8.82°, 23.10°, 23.35°, 23.86°, and 24.35° (GUO et al., 2017) where this result can also be observed in the synthesis without agitation showing little influence of stirring for these relations. Results of synthesis with molar ratios Si/Al of 20 and 50 were previously reported by our research group (MIGNONI et al., 2010).

When the molar ratio increases to Si/Al = 120 in the reaction under stirring conditions, the pure phase zeolite ZSM-5 is formed. This result was not observed in the synthesis without agitation, where there was the formation of ZSM-5 phase with impurities of quartz, concluding that stirring disfavors the formation of quartz.

For a better visualization of the obtained results under stirring conditions, a ternary compositional diagram for SiO_2 , Al_2O_3 and Na_2O is shown in Fig. 4 at constant BMI.Cl, NaOH and H_2O contents.

Under stirring conditions a molar composition of 74.0 mol% SiO_2 , 4.00 mol% Al_2O_3 and 22.0 mol% Na_2O , leads to the obtaining of pure beta zeolite, a fact not observed in the synthesis under static conditions. In addition, the utilization of 76.8 mol% SiO_2 , 1.6 mol% Al_2O_3 and 21.6 mol% Na_2O under stirring conditions directs to obtaining of pure zeolite

Figure 4 - Ternary diagram of the gel composition of the synthesis of zeolite with stirring, with different molar ratios Si/Al: (a) 1, (b) 8, (c) 20, (d) 50 and (e) 120



ZSM-35 phase.

Comparing the ternary compositional diagrams, it is possible to notice the influence of static or stirring conditions, under stirring conditions ZSM-35, beta, Zeolite A/Sodalite and ZSM-5 structures were obtained and under static conditions only zeolite A/sodalite, pure ZSM-5 and ZSM-5/quartz zeolites structures were obtained, showing the positive influence of stirring for the investigated Si/Al relations. In addition, it is clearly seen that the obtaining of pure ZSM-5 structures is a compositional zone with molar ratio between Si/Al = 50 and 120 under stirring or static conditions.

The morphology of the obtained materials depends on the synthesis system used. Under static or stirring conditions, the main influence on shape of crystals seems to be given by density of the synthesis gel (BODART et

al., 1984). When the gel is denser over the elongated shape, the formation of hexagonal prisms is favored, where static conditions favors the appearance of hexagonal prisms due to higher densities of the synthesis gel.

Surface properties

For materials that showed crystallinities, specific areas of the synthesized materials were obtained by textural analysis of N_2 adsorption/desorption, these results are shown in Table II.

Observing the Table II it is possible to verify that the crystalline materials obtained under static conditions, the highest surface area was obtained for the zeolite with a Si/Al ratio 50. For the zeolite obtained with Si/Al = 1 a very low area are obtained, explained by the no accessibility of the molecule N_2 to the interior of the zeolite due to small

Table II - Specific areas of the synthesized materials were obtained by textural analysis of N₂ adsorption and desorption

	Ratios Si/Al	Surface area BET (m ² .g ⁻¹)	Microporous volume (cm ³ .g ⁻¹)	Mesoporous volume (cm ³ .g ⁻¹)
Without stirring	1	4	-	-
	8	-	-	-
	20	-	-	-
	50	384	0.10	-
	120	253	0.18	-
With stirring	1	3	-	-
	8	285	0.11	-
	20	342	0.13	0.70
	50	312	0.13	-
	120	248	0.15	-

values of openings rings cavities. This fact is a consequence of the presence of Na⁺ cations, causing small opening of the ring cavities, smaller than the size of N₂ molecule, thus, it was not possible to determine the pore size (RIGO et al., 2009; XU et al., 2007).

Under stirring conditions, it is observed that all obtained materials are crystalline and showed high surface areas, except for the Si/Al = 1, fact also observed in the synthesis without stirring. As can be seen in table 2, at Si/Al = 20 relations, under stirring conditions, occurs the appearance of mesopores leading to high values of surface area for these material.

Conclusions

Several conclusions have been drawn through this study. The results suggest that ionic liquid BMI.Cl would be highly effective directing agent for the crystallization of zeolites type A, ZSM-5, Beta and ZSM-35. The effect of stirring on the composition and morphology seems to be significant. The ternary compositional diagram shows that the

compositional zone for pure zeolite ZSM-5 under static and stirring conditions has been shifted to lower Al₂O₃ content of less than 2.0 mol%, but it is possible to observe the difference between the morphology when zeolites synthesized in static or stirring conditions. Also observed, the zeolite ZSM-35 and Beta, showing a higher amount of Al₂O₃ (4 mol% and 1.6 mol%), are obtained only when the reaction is carried out under agitation.

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