

SYNTHESIS OF ZSM-23: INFLUENCE OF CRYSTALLIZATION TIME, SILICON AND ALUMINUM SOURCES

SÍNTESE DA ZSM-23: INFLUENCIA DO TEMPO DE CRISTALIZAÇÃO, FONTES DE SILÍCIO E ALUMÍNIO

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RESUMO: A zeólita ZSM-23 foi sintetizada, utilizando diferentes fontes de silício e alumínio e diferentes tempos de cristalização (30 a 60 horas). Nitrato de alumínio, hidróxido de alumínio, aluminato de sódio e sulfato de alumínio foram utilizados como fonte de alumínio, sílica aerosil, e as sílicas coloidais ludox HS-30, LS-30 e AS-30 como fontes de silício. Os materiais obtidos foram caracterizados por análise textural de adsorção de nitrogênio, difração de raios-X (DRX), análise termogravimétrica e microscopia eletrônica de varredura. Por meio dos resultados obtidos, conclui-se que a zeólita ZSM-23 pode ser sintetizada com diferentes fontes de alumínio e silício e em diferentes tempos de cristalização, onde os materiais mais cristalinos foram obtidos entre 40 e 48 horas de síntese, utilizando sílica Ludox LS-30 e hidróxido de alumínio.

Palavras-chave: Zeólita. ZSM-23. Síntese. Fontes de alumínio. Fontes de silício.

ABSTRACT: ZSM-23 zeolite was synthesized using different sources of silicon and aluminum and different crystallization times (30 to 60 hours). Aluminum nitrate, aluminum hydroxide, sodium aluminate and aluminum sulfate were used as aluminum source, aerosil silica, and Ludox HS-30 as colloidal silica, LS-30 and AS-30 as a silicon source. The materials obtained were characterized by Textural analysis, nitrogen adsorption, X-Ray Diffraction (XRD), thermogravimetric analysis and Scanning Electron Microscopy. Through the results it is concluded that the zeolite ZSM-23 can be synthesized

with different aluminum and silicon sources and at different crystallization times, where the most crystalline materials were obtained between 40 and 48 hours synthesis using Ludox LS-30 silica and aluminum hydroxide.

Keywords: Zeolite. ZSM-23. Synthesis. Aluminum source. Silicon source.

Introduction

Zeolite was first synthesized by Plank et al. from Mobil Oil Corporation with a MTT topology structure, which is a medium pore high silica. The framework topology of this zeolite is composed of 5-, 6-, and 10-rings without intersecting channels, and that 10-ring linear channels have a pore diameter of 0,45 nm x 0,52 nm (ROHRMAN, 1985; WANG, 2004).

Zeolites are crystalline aluminosilicates which have a structure that encloses cavities occupied by large ions and water molecules (GUEVARA, 2000), with strongly acidic Brønsted sites dispersed within a network of pores with molecular dimension (TEKETEL, 2012). They have a highly regular and open microporous structure formed by a three-dimensional network of SiO_4 and AlO_4 tetrahedral (ALFARO, 2007). The dimensions of the pores allow the adsorption of certain molecules, rejecting the larger ones. Because of this property, these materials are known as molecular sieves (BRAGA, 2007). This type of zeolite microporous structure gives a very large internal surface, compared to its external surface (RIGO, 2009). Due to their special structures with a large surface area and uniform pore size, which provides the unique selectivity, zeolites have been exploited by petrochemical and fine chemical industries to perform many shape-selective hydrocarbon reactions (DA LUZ, 1995; MASCARENHAS, 2001; SCHERZER, 1996).

Process for catalytic conversion of n-alkanes on long-chain bifunctional zeolites with pore system formed by rings of 10

members (10 - MR) has been applied in several stages related to petroleum refining production of diesel, kerosene and lubricants (Jacobs, 1991). Zeolites with monodimensional pore system with 10 - MR, as the topology structure TON, MTT and AEL, limit cracking during the isomerization of long chain n-alkanes. Investigations of ramification of the structure of n-alkanes on bifunctional 10-MR zeolite have produced several explanations for the unique properties of these zeolites, including the transition state selectively (ERNST, 1989; NGHIEM, 2000) and diffuse selectivity (WEBB, 1998; MAESEN, 1999). According to them, the reaction of adsorbed hydrocarbon molecule is partially inside the pore, and partially on the external surface of zeolite crystal. Distinction between the entry pore and key-lock catalysis is based on the penetration of the molecule in a pore or two entries, respectively (MARTENS, 1995). Short-chain alkanes, such as octane, are converted mainly by catalysis at the entrance of the pores (NARASIMHAN, 2003). Long-chain molecules may work as a foundation between the adjacent opening of micropore and react through the key-lock mechanism to open the way with acid sites on the outer surface, and pore entry for catalysis (NARASIMHAN, 2004). Lateral chains are generated in the hydrocarbon chain located outside of the first 10 - MR along the pore. A kinetic model based on the key has been developed and successfully implemented to describe the hydroconversion of n-alkanes using the catalyst Pt/H-ZSM-22 (HUYBRECHTS, 2006; MÖLLER, 2011). In bifunctional, hydrocarbons are converted to an intermediate ion alkylcarbenio on the

protonation of alkenes formed by dehydrogenation of the noble metal.

Medium-pore zeolites are often of great interest due to their specific molecular sieving effects. Thus, 10-membered-ring zeolite structures such as MTT (ZSM-23) are important catalysts for isomerization reactions of small alkenes. For instance, MTT showed good characteristics in catalytic cracking of small alkenes to ethylene and propylene and in selective conversion of n-butene to isobutene, as well as a high isomerization activity for para-xylene. An important aspect that distinguishes MTT from other one-dimensional medium-pore zeolites is the unusual teardrop channel geometry in contrast to a circular or oval pore structure. The continuous interest in the MTT structure is illustrated in numerous recent patents regarding its applications in hydrocracking, isomerization or metathesis reactions of light olefins (<http://www.iza-online.org/synthesis/default.htm>, accessed in June 2014). The ZSM-23 zeolite can be used in a wide variety of conversion reactions of organic compounds and is used particularly for polymerization, aromatization, esterification, reforming and cracking (DALUZ, 1995; MOLLER, 2011; GIANETTO, 1990; YE, 2009).

Due to the growing importance of ZSM-23 zeolite as catalyst, the following study was conducted with the primary purpose of studying the synthesis of ZSM-23 zeolite using different crystallization times of 30, 40, 48 and 60 hours, different sources of silicon, such as silica aerosil, Ludox AS-30, LS-30 and HS-30, and different sources of aluminum, such as aluminum sulfate, aluminum hydroxide, sodium aluminate and aluminum nitrate.

Experimental

The synthesis of ZSM-23 was adapted from the procedure IZA ([http://www.iza-](http://www.iza-online.org/synthesis/default.htm)

[-online.org/synthesis/default.htm](http://www.iza-online.org/synthesis/default.htm), accessed in June 2014). (“International Zeolite Association”) varying the time of synthesis and sources of aluminum and silicon.

The gel was prepared as it follows:

In one beaker (1) 97.9 g of distilled water and 2.2 g of sodium hydroxide and homogenized were added. After that it was added 8.25 g of silica aerosil, was added mixing for 5 min under mechanical stirring.

In another beaker (2) it was added 12.2 g of distilled water, 4.4 g of pyrrolidine and 0.895 g of aluminum sulphate and homogenized were added.

Afterwards the solution of beaker (2) was poured into solution of beaker (1) under mechanical stirring. Then was added 1.14 mL of sulfuric acid (99%). The synthesis of the final gel had pH of 12.6.

Subsequently, the synthesis gel was transferred to four stainless steel autoclaves with internal deep Teflon (60 mL of capacity) and maintained at 180°C for different times (30, 40, 48 and 60 h) with stirring. The solid material obtained was filtered and washed with distilled water to provide pH = 9. Afterwards the solid was dried for 16h at 100°C and calcined at 550°C.

For the synthesis with different silicon sources, silica aerosol was replaced by colloidal silica Ludox AS-30, HS-30 and LS-30 (30% SiO₂). To perform the synthesis with different aluminum sources, the aluminum sulfate was replaced by aluminum hydroxide [Al(OH)₃], sodium aluminate (56% Al₂O₃) and aluminum nitrate [Al(NO₃)₃].

The materials were characterized by complementary techniques. The crystallinity was detected by X-ray Diffraction (XRD) on a Siemens D500 Diffractometer (IF-UFRGS) using nickel filter with Cu K α radiation ($\lambda = 1.54056\text{\AA}$). Thermogravimetric analyses were performed on a TA Instruments TGA Q50 V6.4 Build 193 where the samples were

heated at 10°C/min from 20 to 800°C, under nitrogen flow. The morphology and particle size of the products were investigated using a JEOL/EO JSM 6060 Scanning Electron Microscope (SEM) at CME-UFRGS, with 20 Kv and magnification of 2.000, 5.000 and 10.000. The specific surfaces areas of the samples, pre-treated for 3h at 300°C, were determined from Nitrogen Adsorption/Desorption on Micrometrics TriStar II 3020 using the BET method.

Calculations of relative crystallinity of the synthesized materials were carried out using XRD analysis and calculated by the equation (1).

$$\% \text{ Crystallinity} = \frac{\sum \text{ peak area of the sample}}{\sum \text{ peak area of the pattern}} \times 100 \quad (1)$$

To calculate the crystallinity, it was selected a range of diffraction angle 2θ of 19.2 to 27.2° was selected.

Results and Discussion

Figures 1 and 2 show the XRD patterns of X-ray standard IZA sample and the sample synthesized using silica aerosil and aluminum sulfate at 40 h, respectively. The peak position and intensity of the materials obtained were compared with standards found in the literature and it was observed that it is, effectively, the ZSM-23 zeolite (84.3% of crystallinity).

Figure 1 - XRD of sample pattern IZA.

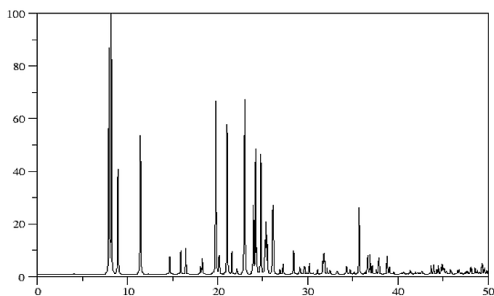
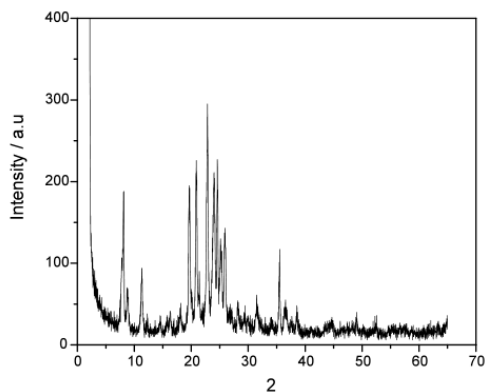


Figure 2 - XRD of the sample synthesized.



The ZSM-23 zeolite synthesized was submitted to a calcination process at 550°C to remove structure directing agent (Figure 3). There was an increase in crystallinity after calcination procedure (87.3%) compared to the sample not calcined (84.3%). The better definition of the peaks in X-ray diffractogram of the calcination process is related to the increase in size of the crystallites.

Figure 3 - XRD of sample calcined.

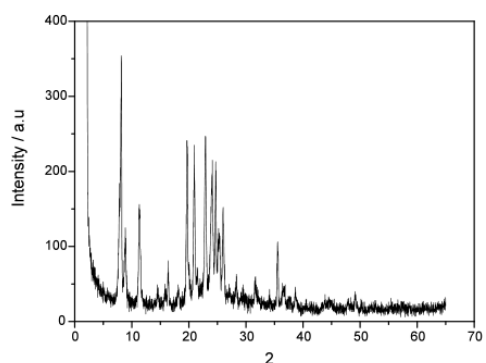
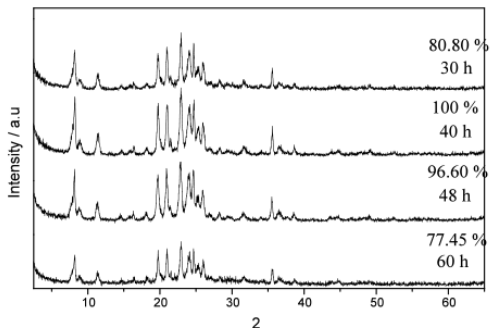


Figure 4 shows XRD results for the synthesis of ZSM-23 zeolite at different times (30, 40, 48 and 60 h). The phase ZSM-23 appears at all times employed with relative crystallinity ranging from 77.45% to 100%. The time required for the synthesis of zeolites is related to the proper time for crystalliza-

tion. In the case of the synthesis of ZSM-23 zeolite, it is between 40 and 48h.

Figure 4 - XRD of sample synthesized at different times.



Values of BET area and of crystallinity are shown in Figure 5. It is observed that higher crystallinity and higher areas occur between 40 and 48 h of synthesis and subsequent to time it is decreased due to dissolution of the material in the basic reaction medium. These results are consistent with those presented in the XRD analysis. Similar results were obtained by Wen-Quing Xu 1994 (Xu, 1994), in which time from 40 to 100 hours synthesis it is observed a decrease of specific area (BET) of 278 to 198 m²/g.

Figure 5 - Comparison of the crystallinity (▲) and surface area (■) of the synthesized materials.

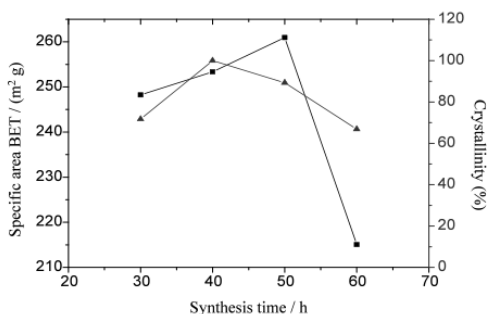


Figure 6 shows the micrograph of ZSM-23 zeolite in natural form (A) and calcined (B). It was observed that crystals have the ellipsoidal shape with sizes ranging from 0.5

to 5 μm confirming a morphology typical of ZSM-23(Mériaudeau, 1998).

Figure 6 - Micrographs of the natural ZSM-23 zeolite (A) and calcined (B).

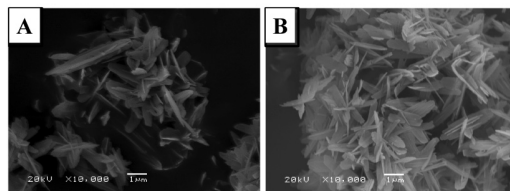
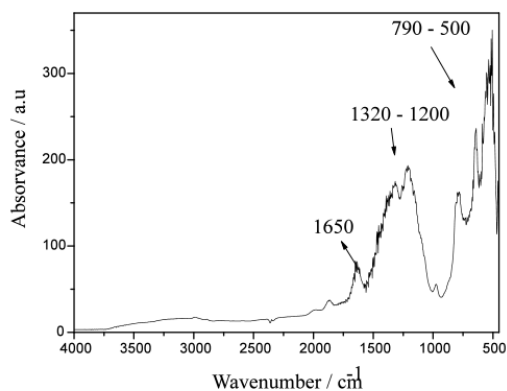


Figure 7 shows the IR analysis of the ZSM-23 zeolite. We can see at a wavelength of 1650 cm⁻¹, the interaction of the OH with O of the zeolite structure, between 1320 and 1200 cm⁻¹ asymmetrical vibrations occur and 790-510 cm⁻¹ have symmetric vibration, confirming that it is a zeolitic material.

Figure 7 - Infrared of the sample ZSM-23.



After the calcination of ZSM-23 sample, it was observed, through the sample color (gray), that the material still presented a certain percentage of organic matter showing that the calcination process was not adequately effective. For this reason, a thermogravimetric analysis was performed to determine the most suitable temperature for calcination of the material and removal of the structure directing agent (pyrrolidine). Table I shows these results, in which three major regions of

weight loss can be observed. The first is from 5 to 180°C due to loss of water. The other regions are between 180-350°C and 420-550°C due to loss of water of hydration of the cations and pyrrolidine, respectively. In view of these results, samples were calcined at a temperature of above 550°C.

Table I - Results of thermogravimetric analysis of ZSM-23 zeolite.

Temperature (°C)	Mass loss (%)	Assignment of the bands
5 a 180	0.53	Water loss
180 a 350	1.27	Water of hydration and the directing agent loss
420 a 550	2.87	Water of hydration and the directing agent loss

We studied the effect of different sources of aluminum in the synthesis of ZSM-23 zeolite. Aluminum nitrate ($\text{Al}(\text{NO}_3)_3$), aluminum hydroxide ($\text{Al}(\text{OH})_3$) and sodium aluminate (AlO_2Na) were used as different sources of aluminum, and compared to aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), which is the standard synthesis reagent.

Figure 8 also shows the standard synthesis using $\text{Al}_2(\text{SO}_4)_3$, and it can be observed that it is more crystalline and pure than the others materials. Other materials prepared with other sources of aluminum than $\text{Al}_2(\text{SO}_4)_3$ have a cristobalite phase at $2\theta \sim 22^\circ$ as impurity.

Different sources of siliceous constituted another variable studied in this work for the synthesis of ZSM-23 zeolite. The silica Ludox HS-30%, LS-30% and AS-30% were silicon sources used and the results were compared to those obtained using the silica aerosil, which is the standard synthesis reagent. The difratograms are shown in Figure 9. It is observed that, in all syntheses obtained, the phase ZSM-23 zeolite with high crystallinity, but in the synthesis with silice in gel

promotes the cristobalite phase as impurity at $2\theta \sim 22^\circ$.

Figure 8 - XRD of samples of the samples with a range of sources of aluminum.

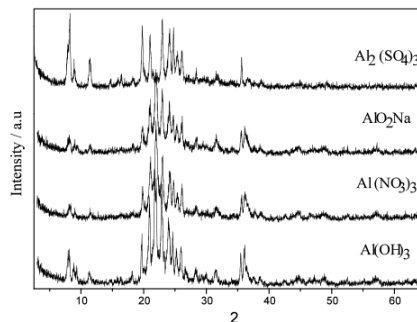
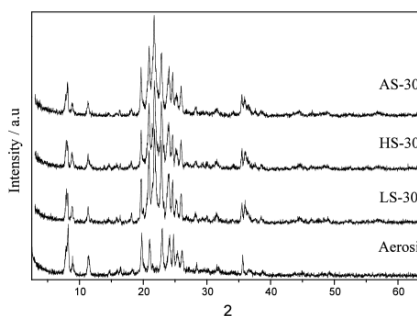


Figure 9 - XRD of the samples with a range of sources of silicon.



Conclusion

We performed the synthesis of ZSM-23 zeolitic material varying the crystallization time, sources of aluminum and silicon sources. It was noticed that the proposed synthesis method is effective to obtain the crystalline phase ZSM-23. The crystallization time was used between 30 and 60 h, strongly influencing the crystallinity. Between 40 and 48h, crystalline material was obtained at further and more specific area.

Different aluminum sources were used: sodium aluminate, aluminum hydroxide, aluminum sulphate and aluminum nitrate. Aluminum sulphate showed better crystallinity. Different silicon sources were used:

aerosil silicas, Ludox HS-30% LS-30% and AS-30%, and, in all cases, crystalline ZSM-23 was obtained. The best results obtained were the ones using silica aerosol. It was observed cristobalite phase as impurity.

The different parameters studied in this work, like the crystallization time, aluminum and silicon sources had a strong influence on the kinetics of the crystallization process in the synthesis of ZSM-23 zeolite.

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REFERENCES

- ALFARO S., RODRÍGUEZ C., VALENZUELA M. A., BOSCH P., Aging time effect on the synthesis of small crystal LTA zeolites in the absence of organic template. **Mat. Lett.**, v. 61, n. 23-24, p. 4655-4658, 2007.
- BRAGA A. A. C, MORGON N. H, Descriptions of crystalline structures of zeolites. **Quím. Nova**, v. 30, n.1, p. 178-188, 2007.
- DA LUZ, A. B. **Zeólitas: propriedades e usos industriais**. CETEM/CNPq: Rio de Janeiro, 1995.
- ERNST S, WEITKAMP J, MARTENS J. A, JACOBS P. A, Synthesis and shape-selective properties of ZSM-22. **Appl. Catal.**, v. 48, n. 1, p. 137-148, 1989.
- GIANETTO, G.; MONTES, A.; RODRIGUEZ, G. **Zeólitas: características, propiedades y aplicaciones industriales**. Venezuela, 1990.
- GUEVARA H. A, OREA C. A, VIGIL O, VILLAVICENCIO H, SINENCIO S. F, Thermal and optical characterization of $Zn_xCd_{1-x}S$ embedded in a zeolite host. **Mat. Lett.**, v. 44, n. 6, p. 330–335, 2000.
- <<http://www.iza-online.org/synthesis/default.htm>>. Acesso em: 14 Jun. 2014.
- HUYBRECHTS W, THYBAUT J. W, DE WAELE B. R, VANBUTSELE G, HOUTHOOFD K. J, BERTINCHAMPS F, DENAYER J. F. M, GAIGNEAUX E. M, MARIN G. B, BARON G. V, JACOBS P. A, MARTENS J. A, Bifunctional catalytic isomerization of decane over MTT-type aluminosilicate zeolite crystals with siliceous rim. **J. Catal.**, v. 239, n. 2, p. 451-459, 2006.
- JACOBS, P. A.; FLANIGEN, E. M.; JANSEN, J. C.; BEKKUM, H. V. **Introduction to Zeolite Science and Practice**. Amsterdam, 1991.
- MAESEN T. L. M, SCHENK M, VLUGT T. J. H, LONGE J. P, SMIT B, The Shape Selectivity of Paraffin Hydroconversion on TON-, MTT-, and AEL-Type Sieves. **J. Catal.**, v. 188, n. 2, p. 403-412, 1999.
- MARTENS J. A, SOUVERIJNS W, VERRELST W, PARTON R, FROMENT G. F, JACOBS P. A. Selective Isomerization of Hydrocarbon Chains on External Surfaces of Zeolite Crystals. **Angew. Chem. Int. Ed**, v. 34, n. 22, p. 2528-2530, 1995.

- MASCARENHAS A. J, OLIVEIRA E. C, PASTORE H. O, Peneiras Moleculares: Selecionando as Moléculas por seu Tamanho. **Quím. Nova na Escola, Cadernos temáticos**, edição especial, p. 25-35, 2001.
- MÉRIAUDEAU P, TUAN V. A, Characterization of isomorphously substituted ZSM-23 and catalytic properties in n-butene isomerization. **J. Chem. Soc., Faraday Trans.**, v. 94, n. 3, p. 467-471, 1998.
- MÖLLER K, BEIN T, Crystallization and porosity of ZSM-23. **Micropor. Mesopor. Mat.**, v. 143, n. 2-3, p. 253-262, 2011.
- NARASIMHAN C. S. L, THYBAUT J. W, MARIN G. B, JACOBS P. A, MARTENS J. A, DENAYER J. F, BARON G. V, Kinetic modeling of pore mouth catalysis in the hydroconversion of n-octane on Pt-H-ZSM-22. **J. Catal.**, v. 220, n. 2, p. 399-413, 2003.
- NARASIMHAN C. S. L, THYBAUT J. W, MARIN G. B, DENAYER J. F, BARON G. V, MARTENS J. A, JACOBS P. A, Relumped single-event microkinetic model for alkane hydrocracking on shape-selective catalysts: catalysis on ZSM-22 pore mouths, bridge acid sites and micropores. **Chem. Eng. Sci.**, v. 59, n. 22-23, p. 4765-4772, 2004.
- NGHIEM V. T, SAPALY G, MÉRIAUDEAU P, NACCACHE C, Monodimensional tubular medium pore molecular sieves for selective hydroisomerisation of long chain alkanes: n-octane reaction on ZSM and SAPO type catalysts. **Top. Catal.**, v. 14, n. 1, p. 131-138, 2000.
- RIGO R. T, PERGHER S. B. C, A new procedure for a zeolite synthesis from natural clays. **Quim. Nova**, v. 32, n. 1, p. 21-25, 2009.
- ROHRMAN JR. A. C, LAPIERRE R. B, SCHLENKER J. L, WOOD J. D, VALYOCSEK E. W, RUBIN M. K, HIGGINS J. B, ROHRBAUGH W. J, The framework topology of ZSM-23: A high silica zeolite. **Zeolites**, v. 5, n. 6, p. 352-354, 1985.
- SCHERZER, J.; GRUIA, A. J. **Hydrocracking Science and Technology**. Marcel Dekker, Inc., New York. 1996.
- TEKETEL S, SKISTAD W, BENARD S, OLSBYE U, LILLERUD K. P, BEATO P, SVELLE S, Shape Selectivity in the Conversion of Methanol to Hydrocarbons: The Catalytic Performance of One-Dimensional 10-Ring Zeolites: ZSM-22, ZSM-23, ZSM-48, and EU-1. **ACS Catal.**, v. 2, n. 1, p. 26-37, 2012.
- WANG B, GAO Q, GAO J, JI D, WANG X, SUO J, Synthesis, characterization and catalytic C4 alkene cracking properties of zeolite ZSM-23. **Appl. Catal. A-Gen.**, v. 274, p. 167-172, 2004.
- WEBB E. B, GREEST G. S, Influence of intracrystalline diffusion in shape selective catalytic test reactions. **Catal. Lett.**, v. 56, n. 2-3, p. 15-23, 1998.
- XU W. Q, YIN Y. G, SUIB S. L, YOUNG C. L, Selective Conversion of n-Butene to Isobutylene at Extremely High Space Velocities on ZSM-23 Zeolites. **J. Catal.**, v. 150, n. 1, p. 34-45, 1994.
- YE L, ZHENDONG W, YUN L, XIANBO L, YUEMING L, PENG W, Synthesis of ZSM-23 Zeolite Using Isopropylamine as Template. **Chinese Journal of Catalysis**, v. 30, n. 6, p. 525-530, 2009.