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# Crystallization of ZSM-12 Zeolite with Different Si/Al Ratio

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**Abstract.** In this work the acid properties of a series of HZSM-12 zeolites with different Si/Al ratio were studied. The ZSM-12 crystals were synthesized by the hydrothermal method starting from a gel with the following molar composition: 20MTEA:10$Na_2O$:x $Al_2O_3$:100$SiO_2$:2000$H_2O$, with $x = 0.50$, 0.67, 1, 1.25 and 2, respectively. The gels were crystallized at 140°C for 6 days, then washed, dried and calcined to remove the MTEA template. The samples were ion-exchanged with an ammonium chloride solution and calcined again to obtain the zeolites in the acid form. The materials thus obtained were characterized by XRD, SEM, BET, TG and *n*-butylamine adsorption. The Si/Al ratio in the reaction mixture affects the amount of zeolite produced and the size of the particles. The XRD analysis indicated that the ZSM-12 zeolite crystallizes in a pure form only with Si/Al ratio above 33. The SEM analysis showed the presence of crystallites with very well defined prismatic shapes. The removal of the MTEA of the pores of the ZSM-12 by TG indicated that there are two kinds of internal sites occupied by MTEA inside the structure. The BET area of the ZSM-12 decreases proportionally with the crystallinity of materials. The desorption of n-butylamine showed that the acid site density is proportional to aluminum content, but the Si/Al ratio shows little influence on the relative strengths of these sites.

**Keywords:** ZSM-12 zeolite synthesis, hydrothermal crystallization, different Si/Al ratio, aluminum concentration, *n*-butylamine adsorption

## Introduction

ZSM-12, a high-silica zeolite, was synthesized for the first time by Rosinski and Rubin (1974) in the laboratories of Mobil Oil Co. ZSM-12 has an one-dimensional pore system with elliptic opening formed by 12 tetrahedra $TO_4$ ($T$ = Al or Si), with diameter of $5.6 \times 6.2$ Å (Fyfe et al., 1990; Meier et al., 1996). Its crystalline structure is denominated in standard form as MTW. The acid form of ZSM-12 can be used as catalyst for various reactions of refining of petroleum, such as cracking, hydrocracking, alkylation, isomerization, etc. (Zhang and Smirniotis, 1999; Yoo et al., 2001; Jones et al., 1999).

Several tetraalkylammonium cations can be used as a templating agent in the synthesis of ZSM-12, the most common being: tetraethylammonium ($TEA^+$), methyltriethylammonium ($MTEA^+$) and benzyltrimethylammonium ($BTMA^+$), which are added during the synthesis in the form of hydroxides, chlorides and bromides (Rosinski and Rubin, 1974; Chu and Kuehl, 1984; Rubin, 1986). Reviewing the literature data on the synthesis of ZSM-12, Jacobs and Martens (1987) identified that the lowest Si/Al ratio in which ZSM-12 can be crystallized, as a pure phase, is approximately 40 when monomeric molecules of quaternary ammonium cations are used as templating additive. However a recent work of Gopal et al. (2001), using TEAOH as the template, crystallized a pure ZSM-12 phase with Si/Al ratio of 31.

There is great interest not only in the zeolites synthesis with new crystalline structures (Shantz et al., 1999; Zones et al., 1998; Yoshikawa et al., 1998) but also in

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the development of synthesis techniques to adjust the catalytic and adsorption properties of existing materials (Zhang et al., 2000; Armor, 1998; Smirniotis and Zhang, 1996). Basically there are two guest ways of altering the physicochemical properties of a zeolite:

1. Through post-synthesis modifications by processes such as ion exchange, treatment with dilute solutions of inorganic acids or calcination in the presence of steam (dealuminization methods) and addition of other elements through impregnation of solutions, deposition from the gas phase and impregnations in the solid state (mechanical mixture), followed by calcination for decomposition of the precursor of element. These methods alter properties such as acidity, selective adsorption and can introduce bifuncionalities inside of the zeolite.
2. The other way is through modifications during the synthesis. In this case there are changes in key variables such as composition of the reaction mixture; precursor materials; addition of others elements besides Si, Al and Na; the kind of organic template; temperature and time of crystallization.

In the case of modifications during the synthesis, the most important parameter in the definition of the physical and chemical properties of a zeolite is the composition of the reaction mixture. This parameter controls the Si/Al ratio of the final material and consequently the catalytic properties of the zeolite, because the aluminum atoms are responsible for the properties of ion exchange and acidity (Kapustin et al., 1988; Jacobs and Von Ballmons, 1982; Kentgens et al., 1983).

This study had the objective to crystallize and characterize samples of ZSM-12 zeolite with different Si/Al molars ratios, therefore, with different acid properties, through modifications in the composition of the reaction mixture. Starting from these synthesis data it should be possible to crystallize ZSM-12 with a specific Si/Al ratio, in order to adjust the acid properties for a particular hydrocarbon conversion reaction or a particular adsorption separation process.

## Experimental

### *Synthesis of the Samples*

ZSM-12 zeolite has been synthesized according to the method proposed by Robson (2001), which was adapted to obtain samples with different Si/Al ratio. The samples were synthesized using the following chemicals as starting materials: silica gel (Merck), sodium hydroxide (Merck), pseudoboehmite (Catapal B-Vista) and methyltriethylammonium chloride (MTEACl-Sigma) as organic template. These reactants were combined to obtain a gel with the following stoichiometric proportion: 20MTEA: $10Na_2O$: $xAl_2O_3$: $100SiO_2$: $2000H_2O$, with $x = 0.50$, 0.67, 1, 1.25 and 2, respectively. The $x$ values were chosen to obtain reaction mixtures with Si/Al molar ratio equals to 100, 75, 50, 40 and 25, respectively. Starting from the chemical composition of the synthesis gel, the samples of ZSM-12 synthesized in this study were denominated ZN, being N the Si/Al molar ratio. The procedure for preparation of the gel involved the followings steps:

1. Dissolution of NaOH in half of the water necessary for the synthesis.
2. Addition of the pseudoboehmite, followed by heating to 70°C, under agitation for 1 hour (solution A).
3. Dissolution of MTEACl in the remaining of the water (solution B).
4. Mixing of the solutions A and B, with the system under strong agitation for 20 min.
5. Addition of the silica gel to the suspension obtained in the item 4, followed by agitation for 2 hours.

The gel was then transferred into PTFE lined stainless-steel autoclaves and heated at 140°C under autogenous pressure in static conditions for 6 days. After the crystallization, the autoclave was removed from the oven, cooled to room temperature, the contents were homogenized by agitation and the pH was measured. The resultant solid was separated from the liquid phase by filtration, washed thoroughly with distilled water and dried to 100°C for 12 hours.

The synthesized materials were calcined to remove the template by a two step procedure: (i) heating to 550°C under $N_2$ flow of 100 mL $min^{-1}$ for one hour; (ii) The $N_2$ stream was substituted by dry air at the same flow rate and calcination was continued for additional 4 hours. This calcination method has the objective of removing the organic template in a milder way to avoid high temperatures and possible structural damage caused when the sample is exposed to oxygen.

The calcined samples were submitted to three successive ion exchange procedures with 0.6 M $NH_4Cl$ solution in the temperature of 80°C for 2 hours. After this process, they were calcined again at a temperature

of 500°C for 3 hours to generate the samples in the acidic form (HZSM-12).

*Characterization*

The Si/Al ratio of the materials in the calcined form was determined by atomic absorption in equipment Varian SpectrAA-100. The average diameter of the particles of zeolite obtained after the crystallization was measured in a Cilas particles size analyzer, model 1064L. These analyses were carried out with previously calcined samples of ZSM-12. Each analysis was done with a sample of mass between 10 and 30 mg, disperse in distilled water through an ultrasonic bath.

The identification of the crystalline phases formed after the crystallization process was carried out by X-ray diffraction (XRD) in a Shimadzu XRD 6000 using Ni-filtered CuK$\alpha$ radiation, with diffraction angle ($2\theta$) at range of 3–40°. The degree of crystallinity of the samples was determined through X-ray diffraction by the measurement of the areas of the peaks at $2\theta = 7.36$, 8.80, 20.88, 22.88 and 23.20 degree and comparison with the areas of the same peaks of a standard sample considered as 100% crystalline. The morphology and size of the crystals were determined by scanning electron microscopy, using a Philips ESEM microscope.

The specific surface area of the zeolites was determined through the adsorption of $N_2$ to 77 K using the BET method in a Quantachrome model NOVA-2000 equipment. Prior to each analysis approximately 0.1 g of sample in the acid form was pretreated at 200°C under vacuum for 3 hours to remove the humidity from the surface of the solid. $N_2$ adsorption isotherms were obtained at P/Po in the range from 0.02 to 0.95.

Template removal studies were performed by thermogravimetric analysis in a Mettler TGA/SDTA 851 thermobalance, at a heating rate of 10°C min$^{-1}$, in the temperature range from room temperature to 900°C using nitrogen flow of 25 mL min$^{-1}$. The experiments were performed in alumina crucibles of 70 $\mu$L containing ca. 10 mg of sample in the as-synthesized form.

*Acidity Measurements*

The *n*-butylamine adsorption experiments on the HZSM-12 samples were performed in a reactor containing ca. 0.1 g of catalyst, which was activated initially at 400°C, under nitrogen flow of 100 mL min$^{-1}$ for two hours. After this activation, the temperature was reduced to 95°C and nitrogen was passed through a bubbler flask containing liquid *n*-butylamine. The nitrogen stream saturated with the *n*-butylamine vapors flowed through a reactor containing HZSM-12 for 40 min. The sample was then submitted to pure nitrogen flow for 40 additional minutes in order to remove any physically adsorbed *n*-butylamine. The determination of the amounts of amine adsorbed on the acid sites of the HZSM-12 samples was performed by thermodesorption in a thermobalance Mettler TGA/SDTA 851. The runs were carried out in alumina crucibles of 70 $\mu$L containing ca. 10 mg of HZSM-12 pre-adsorbed with *n*-butylamine. Prior to the experiments the samples were heated slowly (5°C min$^{-1}$) up to 100°C and kept at this temperature for one hour. Finally, the samples were heated up at 10°C min$^{-1}$ from 100 to 800°C in a high purity $N_2$ flow of 25 mL min$^{-1}$ in order to desorb the chemisorbed base.

## Results and Discussion

The main parameters related to the synthesis of ZSM-12 zeolite are given in Table 1. The pH values before and after the crystallization process were very similar.This small variation in pH during the synthesis is

*Table 1.* Main parameters related to synthesis and recovery of solid phase after crystallization of ZSM-12 zeolite with different Si/Al molar ratio.

| | pH | | | |
|---|---|---|---|---|
| Sample[a] | Initial | Final | Yield (*g* of zeolite/100 g of gel) | Average diameter of the particles ($\mu$m) |
| Z25 | 11.92 | 11.75 | 12.0 | 14.5 |
| Z40 | 12.08 | 11.87 | 11.8 | 16.7 |
| Z50 | 12.04 | 11.90 | 10.9 | 14.0 |
| Z75 | 12.25 | 11.82 | 10.3 | 11.3 |
| Z100 | 12.33 | 11.86 | 9.8 | 7.0 |

[a]The "H" prefix indicate that the samples are in the acid form.

explained by the large quantities of NaOH added to the reaction mixture in order to improve the solubility of the silica. After crystallization, most of the sodium hydroxide remained in the system. The yield in solids decreased as the Si/Al ratio was raised, but the average diameter of the particles showed the opposite behavior (Table 1). Clearly the increase of the Si/Al ratio of the gel caused a decrease in the size of the particles of ZSM-12 hindering its complete recovery by filtration and consequently there was a reduction in the yield in solids.

The X-ray diffractograms of the samples in as-synthesized form are shown in Fig. 1. All the materials showed diffractograms characteristic of a ZSM-12 zeolite with high crystallinity (Treacy et al., 1996), except the sample Z25 which showed a small amount of an unidentified contaminant phase, as indicated by asterisks in Fig. 1(a).

In Table 2 the Si/Al molar ratios of the synthesis gels and of the solids obtained after crystallization and subsequent calcinations are indicated as well as the degree of crystallinity of the ZSM-12 samples calculated from

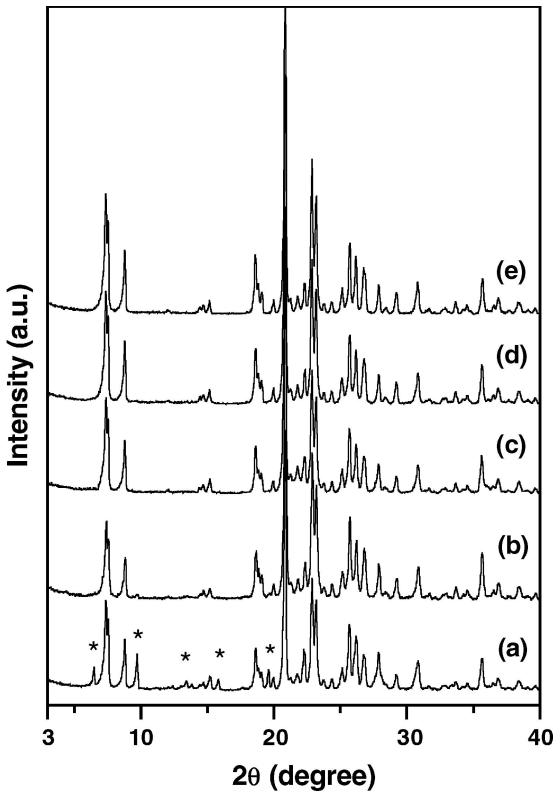


*Figure 1.* X-ray powder diffraction pattern of the ZSM-12 zeolite samples; (a) Z25, (b) Z40, (c) Z50, (d) Z75 and (e) Z100.

*Table 2.* Properties related to chemical composition and crystallinity degree of the solid phase obtained after crystallization of ZSM-12 zeolite with Si/Al molar ratio.

| | Si/Al molar ratio | | |
|---|---|---|---|
| Sample | Gel | Solid | Degree of crystallinity (%) |
| Z25 | 25 | 24 | 82 |
| Z40 | 40 | 33 | 90 |
| Z50 | 50 | 43 | 88 |
| Z75 | 75 | 65 | 99 |
| Z100 | 100 | 88 | 100 |

the XRD analysis. The composition data indicate that the Si/Al ratio of the solid obtained after crystallization is lower than that in the synthesis gel. Gopal et al. (2001) found similar results in the synthesis of ZSM-12 zeolite with tetraethylammonium as template. He attributed this phenomenon to inefficiency in the crystallization process. The degree of crystallinity of the materials increases as the aluminum concentration in the reaction mixture is reduced (increase of Si/Al ratio). These data indicate that the ZSM-12 zeolite crystallizes preferentially with low aluminum concentration.

The micrographs of the samples of ZSM-12 zeolite are shown in Fig. 2. It is possible to visualize that all the materials yield crystallites with very well defined prismatic shapes. The average size of these crystallites decreases slightly as the Si/Al ratio of the materials increase.

The thermogravimetric derivative curves (DTG) obtained under nitrogen atmosphere are shown in Fig. 3, in which three mass loss steps are observed at temperature range below 550°C. Theses steps were attributed to:

(I) Desorption of intracrystalline water;
(II) Decomposition of MTEA-OH molecules entrapped into the porous of the ZSM-12 zeolite;
(III) Decomposition of the MTEA cations strongly bonded to the surface.

Gopal et al. (2001) studied the thermal decomposition of a series of ZSM-12 samples synthesized using TEA as template. They had attributed the mass loss in the temperature range from 430 to 550°C to decomposition of charge compensating TEA cations. In a similar way, we attribute step III of mass loss, in the ZSM-12 samples synthesized in presence of MTEA, to pyrolysis of the template molecules occupying positions

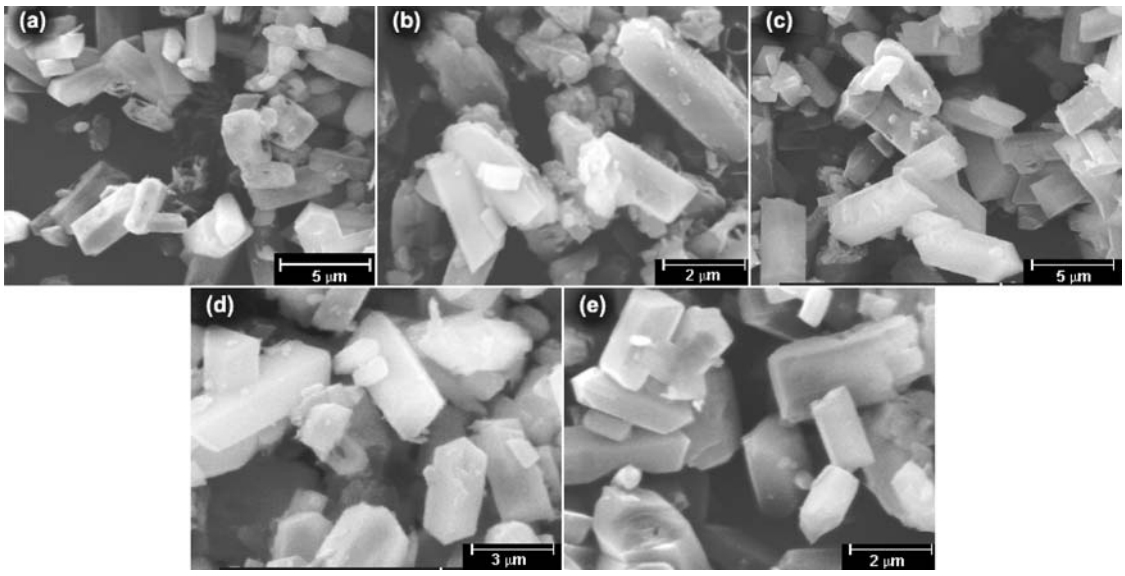


*Figure 2*. Micrographs of the samples of ZSM-12 zeolite in the as-synthesized form; (a) Z25, (b) Z40 (c) Z50, (d) Z150 and (e) Z100.

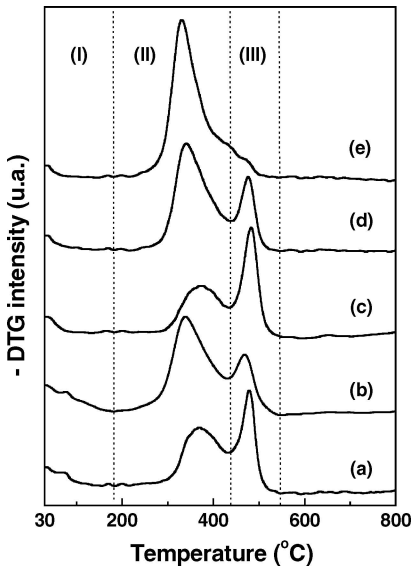


*Figure 3*. DTG curves obtained with heating rate of $10^{\circ}C\,min^{-1}$, showing three main peaks related to removal of water (step I) and of organic template MTEA (steps II and III); (a) Z25, (b) Z40, (c) Z50, (d) Z75 and (e) Z100.

close to the aluminum atoms of the framework acting as counter-ions. The decrease in the mass loss values of step III (Table 3), as the Si/Al ratios of ZSM-12 samples are raised, suggests that this assignment is correct.

Another important conclusion obtained from Table 3 is that the total amount of MTEA (steps II + III) occluded in the pores of ZSM-12 is practically independent of framework Si/Al. Therefore the methyltriethylammonium molecules act mainly as a pore-filling agent.

The specific surface areas of the ZSM-12 samples in acid form are indicated in Table 4. These areas (280–323 $m^2\,g^{-1}$) are very close to values previously reported (Gopal et al., 2001; Ernst et al., 1987) for pure ZSM-12 phase. It is important to note that the surface area of the samples decreases proportionally to the degree of crystallinity of the samples. Thus the surface area can be used as an indicative parameter of the degree of crystalline purity of a zeolite sample.

The amounts of *n*-butylamine desorbed from the surface of the ZSM-12 samples during the thermodesorption experiments are indicated in Table 4. The temperature range for removal of *n*-butylamine from all samples was practically identical, indicating that the aluminum concentration causes little influence on the relative strength of the zeolite samples acid sites. However the number of acid sites present in these materials is proportional to the aluminum content, confirming that the Al atoms are mainly responsible for the acid properties of ZSM-12.

## Conclusions

The synthesis of ZSM-12 zeolite in the presence of methyltriethylammonium with different Si/Al ratios revealed that the aluminum concentration in the reaction

*Table 3*. Mass loss steps associated to removal of water (step I) and MTEA (steps II and III) molecules of the pores of ZSM-12 zeolites.

| | ΔT step (°C) | | | Mass loss step (%) | | | |
|---|---|---|---|---|---|---|---|
| Sample | (I) | (II) | (III) | (I) | (II) | (III) | (II) + (III) |
| Z25 | 30–180 | 180–432 | 432–548 | 1.46 | 4.12 | 2.84 | 6.96 |
| Z40 | 30–187 | 187–431 | 431–545 | 2.23 | 5.53 | 2.46 | 7.99 |
| Z50 | 30–179 | 179–436 | 436–551 | 1.05 | 3.91 | 3.10 | 7.01 |
| Z75 | 30–178 | 178–442 | 442–553 | 0.64 | 5.80 | 2.11 | 7.91 |
| Z100 | 30–178 | 178–440 | 440–549 | 0.56 | 7.61 | 0.78 | 8.39 |

*Table 4*. Main events of mass loss associated the thermodesorption of *n*-butylamine of the HZSM-12 zeolite samples.

| | | Total acidity | | |
|---|---|---|---|---|
| Sample[a] | Al concentration (mmol/$g_{zeolite}$) | $\Delta T$ (°C) | Acidity (mmol $g^{-1}$) | BET surface area ($m^2$ $g^{-1}$) |
| HZ25 | 0.67 | 100-547 | 0.72 | 280 |
| HZ40 | 0.49 | 100-551 | 0.53 | 293 |
| HZ50 | 0.38 | 100-544 | 0.43 | 287 |
| HZ75 | 0.25 | 100-546 | 0.30 | 314 |
| HZ100 | 0.19 | 100-545 | 0.27 | 323 |

[a]The "H" prefix indicate that the samples are in the acid form.

mixture affects the amount of zeolite produced per gram of gel (yield in solids) and the size of the crystals obtained. The X-ray diffraction analysis showed that the ZSM-12 zeolite crystallizes in a pure form only at Si/Al ratios above 33, confirming the siliceous character of this material. Analysis of the micrographs of the ZSM-12 samples showed the presence of crystallites with very well defined prismatic shapes. The size of these crystallites decreases slightly with the Si/Al ratio. Removal of the methyltriethylammonium molecules from the ZSM-12 pores by thermogravimetry indicated that there are two types of internal sites occupied by MTEA inside the structure: (i) in which the molecules are only filling out the pores, and (ii) in which the molecules act as compensation cations for the framework electronic balance. The surface areas of the ZSM-12 samples decrease proportionally to the degree of crystallinity of the samples showing that these measurements could be employed to verify the purity of a zeolitic sample. The desorption of *n*-butylamine from the ZSM-12 surface showed that the acid site density is proportional to aluminum content, but the Si/Al ratio causes little influence on the relative strength of these sites.

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