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ACID PROPERTIES OF THE HZSM-12 ZEOLITE WITH DIFFERENT Si/Al RATIO BY THERMO-PROGRAMMED DESORPTION

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Abstract

In this work was studied the acid properties of a series of HZSM-12 zeolites with different Si/Al molar ratio. The samples of ZSM-12 were synthesized by the hydrothermal method starting from a gel with the following molar composition: 20MTEA:10Na_2O:$x$$Al_2O_3$:100$SiO_2$:200$H_2O$, where: x=2, 1, 0.67 and 0.50, respectively. After the synthesis, the samples of ZSM-12 were ion-exchanged NH_4Cl solution to obtain zeolite in the acid form (HZSM-12). The acid properties were evaluated by *n*-butylamine thermodesorption in a TG equipment at three different heating rates. The model-free kinetic model was applied in the TG integral curves to estimate the apparent activation energy (E_a) of the *n*-butylamine desorption process. The results obtained showed that the HZSM-12 zeolite presents two kinds main of acid sites: one with E_a in the range of 115–125 kJ mol^{-1} classified as weak and other kind with E_a varying of 230–250 kJ mol^{-1} classified as strong.

Keywords: acidity properties, HZSM-12 zeolite*,* *n*-butylamine adsorption

Introduction

Solid acid catalysts such as aluminas, silica-alumina and zeolites are widely used in various petrochemical processes [1–3]. The main properties of the catalysts, the activity and the selectivity are intimately related to both the number and the strength of acid sites distributed over the surface of the materials [4–7], therefore the selection of catalysts to certain reactions depends on an accurate understanding of their acidic properties.

The characterization of acidity of a solid catalyst is normally obtained by adsorption of basic substances with molecular sizes smaller than the pore size of the materials, such as ammonia, *n*-butylamine and pyridine [8–10]. The removal of ad-

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sorbed substances in the acid sites is usually performed employed the technique of temperature-programmed desorption (TPD) [11–15]. In the TPD classical method, desorption rate of a pre-adsorbed base is continuously measured by heating linearly the catalyst in an inert gas stream (such as helium or nitrogen). Due to desorption of base, it occurs variations in the composition of inert gas flowing through catalytic reactor, which are monitored by a thermal conductivity detector. Compared to many others analytical techniques of acidity characterization, TPD provide information, which is closely related to the catalytic properties in reaction conditions. With the choice adequate of probe molecule, it is possible to relate TPD curves to activity and selectivity of a particular catalyst and determine the probable comportment of the catalyst under reaction conditions [16, 17]. Another great advantage of the method of TPD to acidity characterization is the possibility to determine the overall values of apparent activation energy (E_a) for desorption of probe molecules through the execution of a number reduced of experiments [11, 12, 18–20].

In this work was employed the *n*-butylamine adsorption to characterization of the acidic properties of several HZSM-12 zeolites synthesized with different Si/Al molar ratio. The amounts of *n*-butylamine adsorbed on the acid sites of the materials were determined by TPD method using a thermobalance to monitor the mass variation due to desorption of base. The data of mass loss *vs.* temperature obtained of the TPD-TG experiments were analyzed employed a model of non-isothermal kinetics proposed by Vyazovkin [21]. This model allows estimate the apparent activation energy of *n*-butylamine desorption process, using dynamic integral TG curves obtained in several heating rates. The E_a is important quantitative parameters to characterize the relative strength of the acid sites of a catalyst.

Experimental

The ZSM-12 zeolite has been synthesized according to the method proposed by Robson [22], which was adapted to obtained samples with Si/Al molar ratio in gel of 25, 50, 75 and 100, respectively. The materials 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:

$$20\mathrm{MTEA}:10\mathrm{Na_2O}:x\mathrm{Al_2O_3}:100\mathrm{SiO_2}:2000\mathrm{H_2O},$$

with x=2, 1, 0.67, and 0.50, respectively [23]. After preparation of the gel, it was transferred into PTFE lined stainless-steel autoclaves and heated at 140°C, in static conditions for 6 days. After synthesis, the materials were calcined to removal of template, submitted to three successive ion exchange procedures with a 0.6 M NH_4Cl solution in the temperature of 80°C for 2 h. After this process, they were calcined to 500°C for 3 h to generate the samples in acidic form (HZSM-12).

The identification of the crystalline phases formed after crystallization process were performed by X ray diffraction in an equipment Shimadzu (XRD 6000) using

Ni-filtered CuK$_\alpha$ radiation, with diffraction angle (2θ) at range of 3–50°. The degree of crystallinity of the samples were determined through X ray diffraction (XRD) by the measure of the areas of the peaks at 2θ=7.36, 8.80, 20.88, 22.88 and 23.20 degrees and comparison with the areas of a sample considered as 100% crystalline. The morphology and size of the crystals were determined by scanning electron microscopy, using a Philips ESEM microscope. The Si/Al molar ratio of the materials was determined by atomic absorption in equipment Varian AA-100.

The experiments of *n*-butylamine adsorption 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 for 95°C and the nitrogen flow was deviated to bubbler flask containing liquid *n*-butylamine. The nitrogen stream saturated with the *n*-butylamine vapors flowed through reactor containing HZSM-12, for 40 min. After this, the sample was submitted to pure nitrogen flow by 40 additional minutes to remove the *n*-butylamine physically adsorbed. The determination of the amounts of amine adsorbed on the acid sites of the HZSM-12 samples was performed by thermodesorption in Mettler TG/SDTA 851 equipment employed the following experimental conditions:

- All the runs were carried out in alumina crucibles of 70 μL containing ca. 10 mg of HZSM-12 pre-adsorbed with *n*-butylamine.
- The carrier gas was high purity nitrogen with flow of 25 mL min^{-1}.
- Before the experiments the samples were slowly heating (5°C min^{-1}) from room temperature to 100°C and kept in the temperature for 1 h.
- After the pre-treatment of catalyst, this was heating from 100 to 800°C with three different heating rates (5, 10 and 20°C min^{-1}).

The TPD-TG data of the experiments of *n*-butylamine thermodesorption obtained in three different heating rates were applied in the Vyazovkin kinetic model [21] to determine the apparent activation energy associated to *n*-butylamine desorption process of the acid sites of the catalysts.

Results and discussion

The X-ray diffractograms of the uncalcined samples in form are shown in Fig. 1. All the materials presented a diffractogram characteristic of a ZSM-12 zeolite with high crystallinity [19], except sample Z25 that present a small amount of contaminant phase, as indicated for asterisks in Fig. 1a, this contaminant phase is probably the ZSM-5 zeolite.

In Table 1 are indicated the aluminum concentration per gram of zeolite, the Si/Al molar ratios of gel of synthesis and of the solids obtained after the crystallization process, as well as the crystallinity degree of ZSM-12 samples calculate of the XRD analysis. The composition data indicated that Si/Al ratio of the solid obtained after crystallization were lower than in gel employed to synthesis. Gopal *et al.* [24] found similar results in study of the synthesis of ZSM-12 zeolite with tetraethylammonium as template; it attributed this phenomenon to inefficiency in the crystalli-

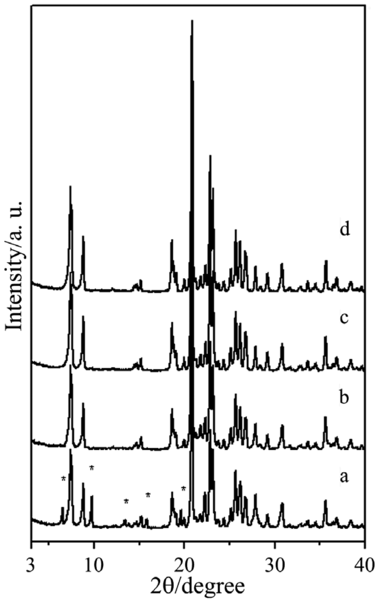


Fig. 1 X-ray powder diffraction pattern of the ZSM-12 zeolite samples, where a – Z25, b – Z50, c – Z150 and d – Z100

zation process. The crystallinity degree of the materials increases as the Si/Al ratio is raised indicated 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 present crystallites with prismatic shapes very well defined. The average diameter of these crystallites decreases, as the Si/Al molar ratio of the materials increases.

The thermogravimetric curves obtained during the *n*-butylamine thermodesorption of the samples of HZSM-12 zeolites are shown in Figs 3 and 4. This curves were denominated of temperature-programmed desorption by thermogravimetric analysis

Table 1 Properties related to chemical composition and crystallinity degree of the solid obtained after crystallization

Sample[a]	Si/Al molar ratio		Al concentration/ mmol (gzeolite)$^{-1}$	Crystallinity degree/%
	gel	solid		
Z25	25	24	0.67	82
Z50	50	43	0.38	88
Z75	75	65	0.25	99
Z100	100	88	0.19	100

[a] The sample name adopted: ZN, where ‘N’ represents the Si/Al molar ratio in the gel of synthesis.

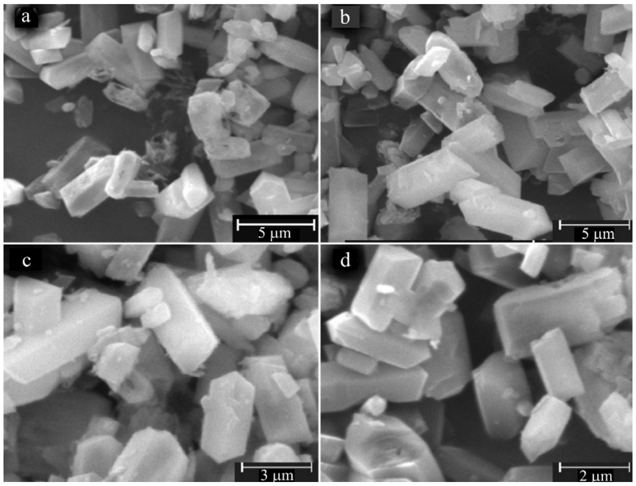


Fig. 2 Micrographs of the samples of ZSM-12 zeolite in the as-synthesized form, where a – Z25, b – Z50, c – Z150 and d –Z100

(TPD-TG). On the basis of the derivative of the TPD-TG curves were identified two main events of mass loss, as indicated by (I) and (II) in Fig. 3.

The analysis of the gases collected during the experiments of *n*-butylamine thermodesorption was carried out employed a gas chromatograph equipped with mass detector (CG-MS) to identify the products desorbed. These experiments showed that the first step of mass loss in the temperature range of 100–300°C was formed by the desorption of *n*-butylamines molecules. The second step of mass loss between 300 and 550°C was identified as has been formed mainly of butene together with ammonia and small amounts of propene and methylamine resultant of the *n*-butylamine decomposi-

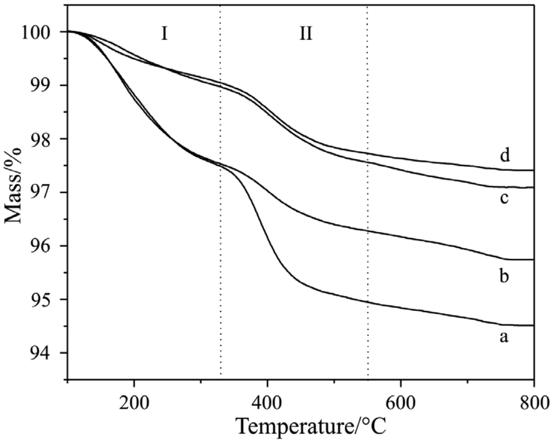
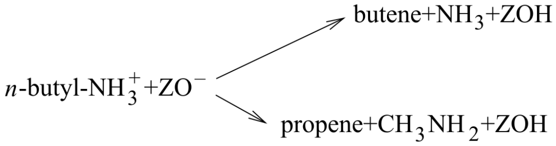


Fig. 3 TPD-TG curves obtained with heating rate of 5°C min^{-1}, showing two main events mass loss related to the thermodesorption of *n*-butylamine of the acid sites: weak (I) and strong (II); a – HZ25, b – HZ50, c – HZ75 and d – HZ100

tion over strong acid sites of the zeolites. It appears that the decomposition occurs through a reaction mechanism similar to the Hoffman elimination reaction, as shown in Eqs (1) and (2). These results are similar to found by Takahashi *et al.* in TPD studies of *n*-butylamine on acid sites of silica-alumina [9].

$$n\text{-butyl–NH}_2\text{+ZOH}\leftrightarrow n\text{-butyl–NH}_3^+\text{+ZO}^- \quad (1)$$



$$n\text{-butyl-NH}_3^+\text{+ZO}^- \begin{array}{l} \nearrow \text{butene+NH}_3\text{+ZOH} \\ \searrow \text{propene+CH}_3\text{NH}_2\text{+ZOH} \end{array} \quad (2)$$

The second peak of the DTG curve shows a shoulder around 480°C (Fig. 4), which is probably related to desorption of ammonia and methylamine originated from the *n*-butylamine decomposition over the strong acid sites of the HZSM-12 zeolite.

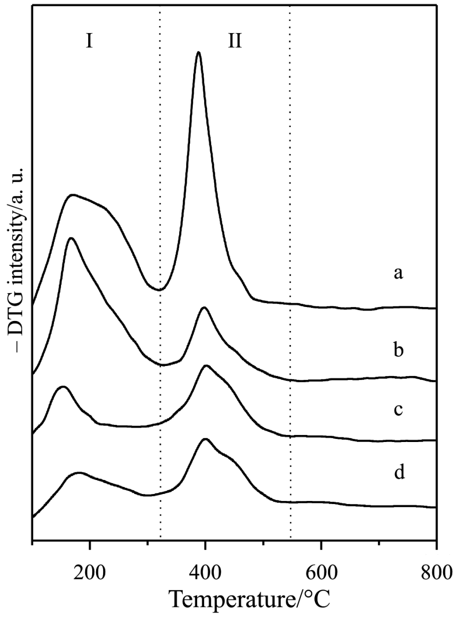


Fig. 4 DTG curves obtained with heating rate of 5°C min^{-1}, showing two main peaks related to the thermodesorption of *n*-butylamine of the acid sites: weak (I) and strong (II); a – HZ25, b – HZ50, c – HZ75 and d – HZ100

The identification of the products desorbed indicated that there are two kinds of *n*-butylamine adsorption sites on the zeolite surface; the first is related to the acid sites where occurs physical adsorption and weak chemisorption and were denominated of weak acid sites; the second is related to acid sites capable of decomposition of the *n*-butylamine molecules and were denominated of strong acid sites. Kofke *et al.* [25] studied the desorption of amine complexes on acid zeolites and concluded that the desorption of isopropylamine over ZSM-12 zeolite occurred with a 1:1 relation of adsorption complex of amine to framework aluminum only at high temperatures and that at low temperatures the amine should not necessarily be assigned to Si–OH–Al groups due to the presence of differences in the acid strength of OH groups. In this work a pretreatment of the samples at 100°C in dynamic flow of nitrogen was performed in order to eliminate the physisorbed *n*-butylamine of the very weak acid sites that do not contribute effectively to chemisorption phenomena at low temperatures [26]. The amounts of *n*-butylamine desorbed of both kinds of acid sites are indicated in Table 2, as well as the total acidity that is defined as sum of the amounts of *n*-butylamine desorbed by the two kinds of acid sites present in the materials.

Table 2 Main events of mass loss associated the thermodesorption of *n*-butylamine of the HZSM-12 zeolite samples

Sample[a]	Weak acid sites		Strong acid sites		Total acidity/ mmol g^{-1}
	ΔT/°C	Acidity/mmol g^{-1}	ΔT/°C	Acidity/mmol g^{-1}	
HZ25	100–330	0.34	330–547	0.38	0.72
HZ50	100–335	0.28	335–544	0.15	0.43
HZ75	100–325	0.13	325–546	0.17	0.30
HZ100	100–336	0.12	336–545	0.15	0.27

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

The comparison of the data of total acidity with Al concentration present in the zeolites indicated that there is approximately one *n*-butylamine molecule adsorbed to each aluminum atom. The small excess of *n*-butylamine adsorbed (ca. 0.05 mmol g^{-1}) is probably related to physically adsorbed molecules that were not completely removed during the pre-treatment carried out after adsorption process. Therefore to reach a coverage degree of one *n*-butylamine molecule per aluminum atom is necessary to increase the temperature and/or the time of pre-treatment to remove all physically adsorbed molecules. The use of *n*-butylamine as probe molecule for determination of acid properties in several molecular sieves has been previously reported [26, 27].

From the TPD-TG curves obtained at three different heating rates was applied an isoconversional kinetics model proposed by Vyazovkin [10] to determine the E_a in function of *n*-butylamine desorption degree of the weak and strong acid sites, as shown in Fig. 5. The values of E_a associated to thermodesorption of *n*-butylamine of the weak and strong acid sites of the HZSM-12 zeolite samples are given in Table 3.

The obtained data indicate that the E_a values related to the strong acid sites had been approximately the double of those observed for the weak acid sites. However the E_a values to the same kinds of acid sites were almost identical for samples with different aluminum concentrations, indicated that the Al concentration influence only in the amount of acid sites and not in its relative strength.

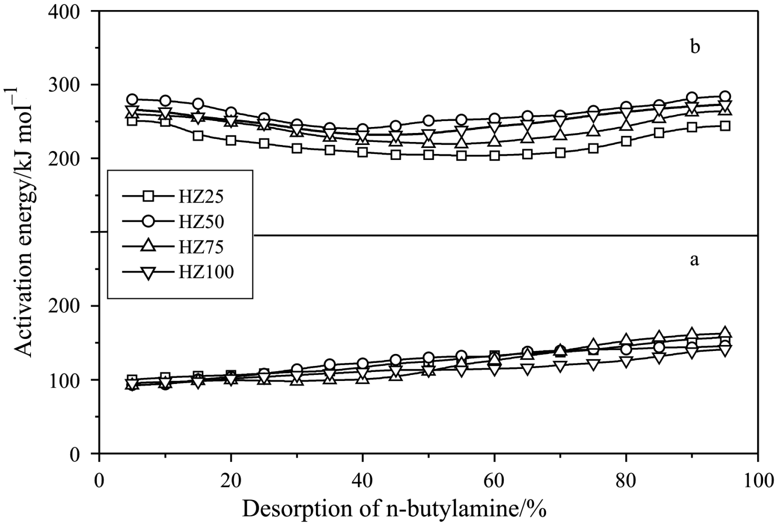


Fig. 5 DTG curves showing two main peaks related to the thermodesorption of *n*-butylamine of the weak and strong acid sites obtained with heating rate of 5°C min^{-1}; a – HZ25, b – HZ50, c – HZ75 and d – HZ100

Table 3 Average apparent activation energy to the thermodesorption of *n*-butylamine of the HZSM-12 zeolite samples

Sample	Apparent activation energy/kJ mol^{-1}	
	Weak acid sites	Strong acid sites
HZ25	125±18	230±18
HZ50	124±17	260±14
HZ75	121±19	240±16
HZ100	115±14	250±14

Conclusions

The *n*-butylamine adsorption followed by temperature programmed desorption and thermogravimetric analysis for characterization of the superficial acidity of a series of HZSM-12 zeolites samples with different Si/Al molar ratio revealed that: from the DTG curves were identified two main events of mass loss, in the temperature range from 100 to 330°C related to *n*-butylamine desorption of the weak acid sites, and from 330 to 550°C associated to decomposition of the *n*-butylamine molecules over strong acid sites. The identification of the products formed by CG-MS indicated that the *n*-butylamine suffered a Hoffman elimination reaction producing mainly butenes and ammonia. The total acidity indicated that there is approximately one *n*-butylamine molecule adsorbed to each aluminum atom in the zeolite. The E_a values related to the strong acid sites were approximately the double of those observed for the weak acid sites. However the E_a values to the same kinds of acid sites were practically identical for samples with different Si/Al molar ratio indicating that the Al concentration influence only in the amount of acid sites.

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