

Study of Fourier transform infrared-temperature-programmed desorption of benzene, toluene and ethylbenzene from H-ZSM-5 and H-Beta zeolites

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Abstract

In the present study, an infrared (IR) high temperature cell was used, in combination with a Fourier transform infrared (FTIR) spectrometer for the development of an alternative temperature-programmed desorption (TPD) procedure. Three different adsorbates, i.e., benzene, toluene and ethylbenzene were non-isothermally desorbed from two zeolites H-ZSM-5 and H-Beta. The FTIR-TPD profiles were fitted with the help of the complementary error function. The fitting process was carried out with the help of a computer program which allows us to calculate two parameters, the temperature, T_0 (K) and the temperature range ΔT (K), which, in conjunction with the complementary error function, characterizes the FTIR-TPD profile. Was found that the parameter T_0 is linked with the adsorption energy of the adsorbate in the zeolite and the parameter ΔT was correlated with the transport process of the desorbed molecules inside the zeolites during the desorption process and with the presence of more than one type of adsorption sites. In conclusion, was confirmed that the FTIR-TPD methodology is appropriate for in situ observation of adsorbed molecules on zeolites, and that this technique makes available information concerning the adsorbed state of guest molecules in non-isothermal desorption.

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1. Introduction

Zeolites are microporous crystalline solids of great interest in pollution abatement and industry [1–13] as catalysts [1–4], adsorbents [5–7], ion-exchangers [8–10] and cationic conductors [11–13]. The study of diffusion, adsorption and desorption of hydrocarbons in highly siliceous acid zeolites is of special interest not only from a fundamental point of view, but also

because several petrochemical processes involves the transformation of organic molecules within the pores of these materials [1,2]. Besides, the migration of sorbed molecules through the pores and cages within the zeolite crystals could be used to further characterize these materials [14–20]. In addition, the study of the interaction of molecules with zeolites yield important information about some properties important in catalytic reactions, such as adsorption rates, capacities and energies, as well as rates and activation energies of desorption and diffusion coefficients [2,5–7,14–20]. In this sense, temperature-programmed desorption (TPD) [21–27] and adsorption calorimetry [7,28,29] are well

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established experimental methods that yield important information on zeolites.

In the present study, we report and discuss the results of Fourier Transform Infrared-Temperature-Programmed Desorption (FTIR)-TPD experiments with three different adsorbates, i.e., benzene, toluene and ethylbenzene which were, non-isothermally, desorbed from H-ZSM-5 and H-Beta zeolites. The studied guest molecules (benzene, toluene and ethylbenzene) were chosen in such a way that all enter through 10- and 12-ring pores of H-ZSM-5 and H-Beta zeolites, since, σ_m , the kinetic diameter of the studied guest molecules [16] is approximately 5.8 Å [15–17] and σ_w the maximum free channel diameter [16] of the studied zeolites are 5, 8 Å for ZSM-5 and 7.0 Å for Beta [15–17]. The framework of H-ZSM-5 exhibit a 10MR two-dimensional channel systems with apertures of 5.3 Å × 5.6 Å and 5.1 Å × 5.5 Å, respectively, and H-Beta zeolite which show a 12MR three-dimensional channel system with apertures of 7.6 Å × 6.4 Å and 5.5 Å × 5.5 Å, respectively [30]. An additional important characteristic of the studied zeolites is the micropore volume, W , which is 0.13 cm³ g for ZSM-5 zeolite and 0.28 cm³ g for Beta zeolite [31]. Moreover, the studied adsorbates show increasing relative basicity [32,33] and dipole moment [34] in the order benzene < toluene < ethylbenzene, due to the addition of methyl- and ethyl-functional groups.

The aim of the present paper is to illustrate the suitability of an IR high temperature cell to be utilized, in combination with an FTIR spectrometer for the development of an alternative TPD methodology.

2. Experimental

2.1. Materials

The original ZSM-5 zeolite was prepared template free according to a recipe given in literature [35], it has bulk Si/Al = 27 and coffin shaped crystals with average dimensions 1.35 μm × 0.6 μm × 2.7 μm [17]. The original Beta zeolite was prepared with bulk Si/Al = 18 following a method reported in the literature [36,37] and it showed fairly mono-disperse crystallites with an average diameter of 0.9 μm [17]. The chemical composition of the zeolite samples was determined by chemical analysis using atomic

absorption (Varian SpectrAA 10 Plus) and the morphology was studied by SEM (JEOL-ISM 6300) [17]. The small size of the crystals used in the present study was beneficial, because the FTIR-TPD profiles are less influenced by diffusional restrictions than would be the case with larger crystals.

The acid form of the ZSM-5 zeolite (H-ZSM-5) and Beta zeolite (H-Beta) were prepared by ion exchange with 2M, NH₄Cl solution, followed by calcination at 550 °C [17,18]. The Al content and the quantity of strong acid sites of the samples studied here, i.e., H-ZSM-5 and H-Beta are reported in Table 1 [18]. The H-ZSM-5 zeolite has 0.61 mmol/g strong acid sites which represents one acid site per Al, moreover, the amount of benzene adsorbed in this sample at $P = 30$ Pa and $T = 298$ K was 0.83 mmol/g which represent slightly more than one adsorbed molecule per strong acid site (see Table 1) [18]. The H-Beta zeolite has 0.54 mmol/g strong acid sites which represents 0.6 strong acid site per Al. The amount of benzene adsorbed in this sample at $P = 30$ Pa and $T = 298$ K was 1.47 mmol/g which represent approximately three molecules per strong acid site. The higher adsorption in the case of H-Beta is probably related to the bigger micropore volume of this zeolite in comparison to H-ZSM-5, although both amounts are well below the pore volume capacity. It is also necessary to state at this point that the adsorption data above reported for benzene is used throughout the paper, also, for the approximate description of the adsorption behavior of toluene and ethylbenzene. This is possible, because benzene is an essential probe to describe aromatic/adsorbent interactions at the molecular level [38].

The IR spectrum of H-ZSM-5 zeolite shows at least three kinds of OH groups, silanol-bands at 3742 cm⁻¹, strong Brønsted sites at 3601 cm⁻¹ and one weak

Table 1

Al content, quantity of strong acid sites and amount of benzene adsorbed at $P = 30$ Pa and $T = 298$ K for the samples of H-ZSM-5 and H-Beta zeolites studied here [18]

Zeolites	Al ^a (mmol/g)	Strong acid sites ^b (mmol/g)	Amount of benzene adsorbed (mmol/g)
H-ZSM-5	0.62	0.61	0.83
H-Beta	0.93	0.36	1.47

^a From bulk chemical composition.

^b Measured by NH₃-TPD.

and broad band at 3656 cm^{-1} . The IR spectrum of H-Beta zeolite exhibit at least two kinds of OH groups; silanol-bands at 3733 cm^{-1} and strong Brønsted sites at around 3610 cm^{-1} [17,18].

The adsorbates used were benzene, Normasolv, purissima. Toluene, Merck, p.a. 99.5%, and ethylbenzene, Fluka, >99%. Nitrogen grade 6N was used as carrier gas. This gas had less than 0.5 ppm humidity which was found mandatory in order to avoid accumulation of water in the zeolites during the experiments.

2.2. Methods

FTIR-TPD experiments were performed in an IR high temperature cell from AABSPEC (model 2000), made of 316 stainless steel, in which the sample under test can be treated in situ up to 973 K, at pressures up to 13 MPa. The temperature of the sample holder was electronically controlled within $\pm 1\text{ K}$. The optical path length of the cell is 42 mm and the dead volume 70 cm^3 . The cell is water cooled and equipped with CaF_2 windows. This cell was mounted in the sample section of a BIO RAD FTS 40 A FTIR spectrophotometer. The same experimental set up was previously used for the study of diffusion in acid zeolites [17,18,39,40] applying the FTIR methodology of Karge and Niessen [19,20].

Adsorption and desorption measurements were carried out as follows: the organic compound to be adsorbed was filled in a stainless steel saturator, which was held thermostatically at $25\text{ }^\circ\text{C}$. A flow of N_2 was divided in two and each of these streams were passed through a flow controller. One stream (1–22 ml/min) went through a tube with a sinterplate in the base into the saturator where the N_2 bubbles in the liquid adsorbate and it is anticipated that the stream through the saturator became saturated with the organic substance. This gas flow was mixed with the bypass stream of pure N_2 (340 ml/min) at the outlet of the saturator and the unified stream, with a partial pressure of around 15–30 Pa of adsorbate, was then passed through the IR-cell.

H-ZSM-5 and H-Beta zeolite powders were pressed to self sustaining wafers ($6\text{--}9\text{ mg/cm}^2$, dry weight) under a pressure of 400 MPa for 3–4 s. The wafers were loaded into the IR cell and dehydrated at 673 K for an interval of 2–3 h in a flow of pure nitrogen (340–400 ml/min). After this activation, the samples

were cooled to the required temperature and kept at this temperature with the help of a thermostat and a background spectrum of the pure degassed zeolite was always collected as a reference before any experiment started. Adsorption of benzene toluene and ethylbenzene on the three zeolites at 298 K for partial pressures ranging from about $P/P_0 = 0.01$ to $P/P_0 = 0.8$ were first performed [18,19] and it appears that all the systems approach saturation at $P/P_0 = 0.1\text{--}0.2$. Therefore, we decided to carry out the adsorption of the adsorbate molecules at partial pressures of 15–30 Pa. The uptake process was followed by purging for 7 min and subsequently the TPD was carried out.

The results were obtained by monitoring the decrease, during desorption, of the absorbance, A , measured in arbitrary units (a.u.), of a typical IR band of the adsorbate molecules, where A is proportional to N ($A = K \times N$), where N is the amount of adsorbate in the zeolite and K a proportionality constant [18–20]. For benzene, the region between 1450 and 1550 cm^{-1} was integrated to obtain a measure of the intensity of the band around 1482 cm^{-1} . For toluene and ethylbenzene, the segment between 1477 and 1517 cm^{-1} was integrated to obtain an intensity measure for the band around 1497 cm^{-1} [17,18].

For the generation of the FTIR-TPD profiles (A versus T), the decrease in the intensity (absorbance) of one of the selected bands was monitored, during heating at a constant rate ($\beta = dT/dt = 8.5\text{ K/min}$ from 298 to 500 K), with the BIORAD FTS 40 A FTIR spectrometer with a resolution of 8 cm^{-1} . The area of the selected band for one spectrum was calculated each 8.5 K, i.e., one spectrum per minute with the spectrometer employing the following conditions: one scan per spectrum, 0.85 s per scan without delay between scans.

3. Results and discussion

The FTIR-TPD profiles (A versus T) for the desorption of benzene, toluene and ethylbenzene from H-ZSM-5 and H-Beta are reported in Figs. 1 and 2. These results were fitted with the complementary error function, i.e.: $\text{erfc}(z) = [1 - \text{erf}(z)]$, where $\text{erf}(z)$ is the error function [41,42]. The concrete equation used for the fitting process was

$$A(T) = \left(\frac{a}{2}\right) [1 - \text{erf}(z)] \quad (1)$$

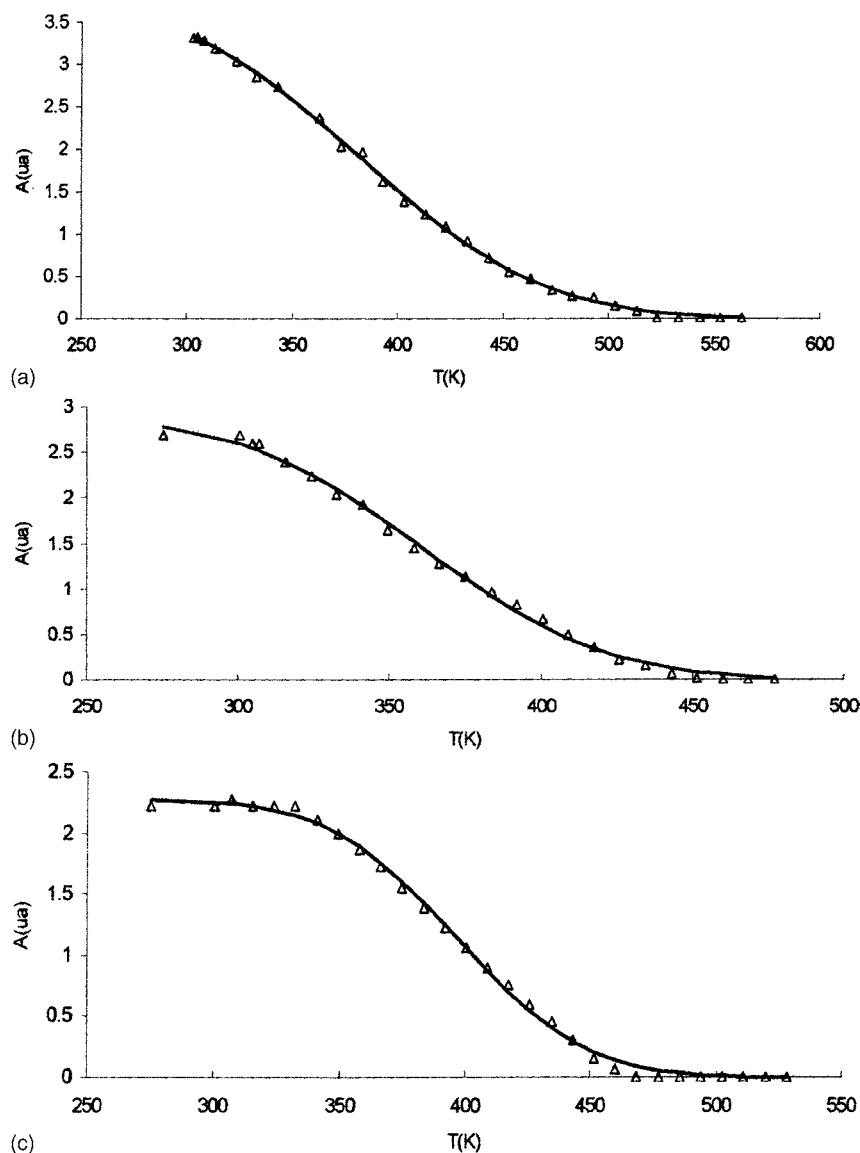


Fig. 1. FTIR-TPD profile (A (a.u.) versus T) of (a) benzene, (b) toluene and (c) ethylbenzene in H-ZSM-5 zeolite.

where $a = A(298\text{ K})$, is the initial value of $A(T)$, $z = [(T - T_0)/2^{1/2}\Delta T]$, T (K) is the absolute temperature and the temperature T_0 (K) and the temperature range ΔT (K) are the parameters which characterize the FTIR-TPD profile. The fitting process was carried out with a program based on a least square procedure [43] which allows us to calculate the best fitting parameters of Eq. (1), specifically, a , T_0 and ΔT , the

regression coefficient and the standard errors. The calculated regression coefficients fluctuated between 0.98 and 0.99. The values calculated for the parameters T_0 and ΔT and the standard errors of the parameters are reported in Table 2. The values obtained for the parameter, $a = A(298\text{ K})$, are not reported in Table 2, since absolute adsorption magnitudes are not directly measured by the FTIR methodology [17–20],

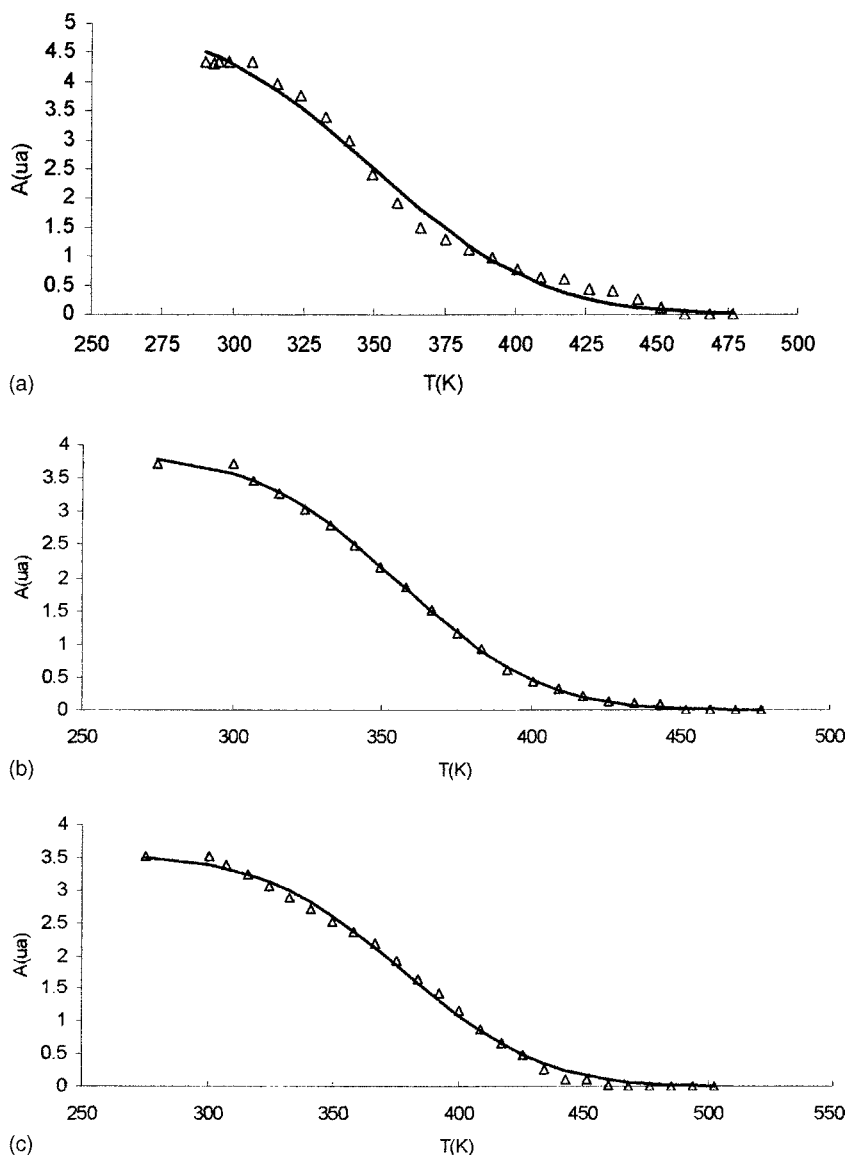


Fig. 2. FTIR-TPD profile (A (a.u.) versus T) of (a) benzene, (b) toluene and (c) ethylbenzene in H-Beta zeolite.

therefore, the parameter a is not a useful information for our purpose in the present paper.

The proposed FTIR-TPD methodology has some advantages and disadvantages. The benefit of using the band area (absorbance) measurement in an IR-cell in contrast with other TPD methodologies are the simplicity of performance, the fact that the cell permits an excellent temperature control and the

reduction of inter-crystalline diffusion retention and re-adsorption due to the small thickness of the wafer and a high purging rate [18]. One of the limitations, as was commented above, is related to the fact that absolute adsorption magnitudes are not directly obtained. An additional weakness is the feature that we simply monitored the reduction, during desorption, of the absorbance of a characteristic IR band of the guest

Table 2
FTIR-TPD parameters

Zeolite	Hydrocarbon	T_0 (K)	ΔT (K)
H-ZSM-5	Benzene	382 ± 2	68 ± 1
H-ZSM-5	Toluene	361 ± 2	48 ± 2
H-ZSM-5	Ethylbenzene	397 ± 1	40 ± 2
H-Beta	Benzene	349 ± 4	47 ± 4
H-Beta	Toluene	356 ± 1	38 ± 1
H-Beta	Ethylbenzene	378 ± 2	44 ± 2

molecules, thus, we are not reporting desorption rates (dN/dt) as is customary in TPD practice [22]. However, by using the complementary error function this circumstance is partially surmounted. In this sense, it is evident that

$$\frac{dN}{dt} = K \frac{dA}{dT} \quad (2)$$

where $N = KA$ as was above stated.

Now it is easy to show that the desorption rate

$$\frac{dN}{dt} = K \left(\frac{dA}{dT} \right) \left(\frac{dT}{dt} \right) = K\beta \frac{dA}{dT} \quad (3)$$

is proportional to the temperature derivative of the absorbance. In addition, with the help of Eq. (1), the temperature derivative of the absorbance becomes

$$\frac{dA}{dT} = F(T) = -b \exp[-(z)^2] \quad (4)$$

a negative Gaussian Function, where b is a constant in arbitrary units. Therefore,

$$\frac{dN}{dt} = K\beta F(T) \quad (5)$$

Subsequently, the parameters T_0 and ΔT give an approximate description of the desorption rate. However, for the future development of the methodology, it would be necessary to improve the hardware and the software of the data acquisition system in order to report directly the desorption rate with better resolution.

For the discussion of the meaning of the obtained FTIR-TPD data (T_0 and ΔT , Table 2), it is necessary to consider the energy of interaction of the zeolite framework with the adsorbate molecules and the transport properties of these guest molecules in the zeolite channels.

When a molecule circulate within a zeolite, it is subjected to diverse energy fields distinguished by

distinct potentials [2,5–7]. These include dispersion, repulsion, polarization, field dipole energy, field gradient quadrupole energy, adsorbate–adsorbate interaction energy [5–7] and acid–base interactions [2] if the zeolite, as in the present case, contains hydroxyl bridge sites. The dispersion, repulsion, polarization, field dipole, field gradient and adsorbate–adsorbate interactions increases in the following order benzene < toluene < ethylbenzene, because of the addition of methyl and ethyl groups [44,45]. This fact is evident in the case of the field dipole interaction, since the dipole moment increase in the sequence benzene < toluene < ethylbenzene [34]. Furthermore, the relative basicity for benzene, toluene and ethylbenzene are 0.61, 0.92 and 1.06, respectively [32,33], and consequently, as the three adsorbates in consideration experience an interaction with the Brønsted sites of the acid zeolites considered, then the acid–base interaction will increase, also in the following order: benzene < toluene < ethylbenzene. Based on the ideas previously discussed the meaning of T_0 can be now explained.

For the H-Beta zeolite, the increase of the parameter T_0 follows the order of increase of the adsorption interactions, i.e., dispersion, repulsion, polarization, field dipole energy, field gradient quadrupole energy, adsorbate–adsorbate and acid–base interactions [2,5–7,44,45] as was explained above.

The H-ZSM-5 zeolite shows a relatively different behavior in relation with the increase of the parameter T_0 , because it follows the order of increase of the adsorption interactions, for toluene and ethylbenzene but not for benzene; nevertheless, this anomalous behavior for benzene could be explained with the large value of ΔT measured for the desorption of benzene from H-ZSM-5. Additionally, in the case of H-ZSM-5 zeolite, the values obtained for T_0 are higher than those obtained for H-Beta. This fact is a consequence of two effects, first, the higher interaction of the zeolite framework with the adsorbate molecules in 10MR zeolites in comparison with 12MR zeolites [46], because of the nearer distance between the adsorbed molecule and the zeolite framework, and secondly the larger interaction of the molecules adsorbed in H-ZSM-5 with the acid sites in relation with H-Beta; since, in the first case there is one adsorbed molecule per strong acid site and in the case of H-Beta zeolite there are three adsorbed molecules per strong acid site. As a result,

all the molecules adsorbed in H-ZSM-5 are in close contact with the acid sites and the interaction is larger. As a consequence, it could be concluded that the parameter T_0 is linked with the adsorption energy of the adsorbate in the zeolite.

Another source for the augment of T_0 in the case of H-ZSM-5, in relation with H-Beta is the higher Si/Al ratio of the studied ZSM-5 sample (Si/Al = 27) relative with the Si/Al ratio of the Beta sample (Si/Al = 18). Since, as is very well known [2], the acid strength of zeolites increases with the increment in the Si/Al ratio, as a result, the three adsorbates in study suffer an acid–base interaction with the Brønsted acid sites of the zeolites considered, which increase in the following order H-ZSM-5 > H-Beta. Besides, the existence of large amounts of silanols groups in the H-Beta zeolite, which do not contribute to the acidity of this acid zeolite, also point in the direction of a lower acid–base interaction between H-Beta zeolite and the three examined adsorbates in comparison with the H-ZSM-5 zeolite [2].

The parameter ΔT is linked essentially with two effects. Firstly with the transport process of the desorbed molecules within the zeolites during the desorption process; given that ΔT is connected with time, through the constant heating rate (8.5 K/min). Therefore, a lower desorption rate, implies bigger ΔT . Secondly, zeolites are heterogeneous adsorbents, i.e., the heat evolved during adsorption is dependant on the zeolite volume coverage [7,28,47], so, during the desorption process, the overlap of desorption from different adsorption sites must also contribute to ΔT , because different adsorption sites requires distinct desorption temperatures.

It is evident (see Table 2) that ΔT is bigger for the desorption of benzene and toluene from H-ZSM-5 in comparison to the ΔT values for H-Beta, whereas in the case of ethylbenzene there is no a significant difference. The transport of guest molecules through zeolite cavities and channels is clearly influenced by geometrical factors [15,16]. In the desorption experiment, evidently the rate of desorption must be slower for the H-ZSM-5 zeolite than for H-Beta, because the framework of the H-ZSM-5 zeolite, having a 10MR, two-dimensional channel systems with maximum free channel diameter of $\sigma_w = 5.8 \text{ \AA}$ and the H-Beta zeolite has a 12MR, three-dimensional channel system with a maximum free channel diameter of

$\sigma_w = 7.0 \text{ \AA}$ [15–17,30]. Since the minimum kinetic diameter, σ_m , of benzene, toluene and ethylbenzene is 5.8 \AA the molecular transport of benzene, toluene and ethylbenzene is more expedite within the framework of H-Beta zeolite. Therefore, with the assistance of the ideas previously discussed about ΔT it is evident that this parameter must be larger for H-ZSM-5, because H-Beta has a bigger maximum free channel diameter and a three-dimensional channel system and as a result the diffusion is faster in H-Beta zeolite.

With respect to the second effect affecting the broadening of the FTIR-TPD profile, i.e., the heterogeneity of the adsorption process in the zeolite, it is possible to affirm that the adsorption process in zeolites could be considered a physisorption process, because even the interaction with hydroxyl groups in zeolites can be taken into account as a Van der Waals-type interaction [48]. The interactions of the guest molecule with the zeolite framework depends on the relative position of the guest molecule in the zeolite channels and/or cavities in relation with the framework atoms and the charge compensating cations of the zeolite. An exact evaluation of all these contributions is out of the scope of the present paper, however, it can be stated that in the case of H-ZSM-5, because of the fact that there is approximately one adsorbed molecule per strong acid site [18], it appears that each adsorbate molecule interacts with one acid site. For H-Beta, there are around three adsorbed molecules per strong acid site [18], consequently not all the adsorbed molecules are directly interacting with the acid sites, i.e., some adsorbed molecules are related with the acid sites and the rest should be located in other sites, such as the center of the two different 12MR windows, present in the Beta framework [49–52]. The interaction of the adsorbate with the OH groups is a direct interaction [53] and it is possible to make some inferences with the help of the IR spectra. In this sense, the IR spectrum of H-ZSM-5 zeolite shows, at least, three kinds of OH groups, silanol-bands, strong Brønsted sites and one weak and broad band at 3656 cm^{-1} , and the IR spectrum of H-Beta zeolite exhibit, at least, two kinds of OH groups; silanol and strong Brønsted sites. Therefore, the heterogeneity of OH groups [54] also contributes to the broadening of the desorption profiles for H-ZSM-5 and H-Beta zeolites. However, the OH groups corresponding to the weak and broad band at 3656 cm^{-1} which is present in the H-ZSM-5

sample and is not present in H-Beta, contribute to a larger broadening in H-ZSM-5, since the other two OH group are very similar for both zeolites. On the other hand, the presence of the 12MR windows sites in the Beta framework [49–52] contribute also to a bigger broadening of the FTIR-TPD profile in H-Beta, since in H-ZSM-5 all the adsorbed molecules are interacting directly with the acid sites. Therefore, notwithstanding the fact that the adsorption heterogeneity evidently is a factor affecting the broadening of the FTIR-TPD profile, it is difficult within the frame of the present discussion, to elucidate which of the effects contributing to the adsorption heterogeneity broadening will play a major role.

4. Conclusions

FTIR-TPD profiles of: benzene, toluene and ethylbenzene from H-ZSM-5 and H-Beta have been fitted with the complementary error function. to calculate two parameters, the temperature, T_0 (K) and the temperature range ΔT (K), which, in combination with the complementary error function, typifies the FTIR-TPD profile. It was shown that the parameter T_0 is associated with the adsorption energy of the adsorbate in the zeolite. In addition, the parameter ΔT was linked with the transport of molecules inside the zeolites channels during the non-isothermal desorption process as well with the heterogeneous character of adsorption in zeolites.

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