

## Thermochemistry of *n*-alkylamines interaction with ETS-10 titaniunsilicate

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### Abstract

According to the data from calorimetric adsorption of methylamine, under the best experimental conditions, 10 mg ETS-10 was saturated with 20  $\mu\text{l}$  portions of an aqueous solution of methylamine at 0.05 mol dm<sup>-3</sup> concentration corresponding to 0.490 mmol of methylamine per gram of solid. From calorimetric titration data, the thermodynamic values of  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  were calculated, showing favourable *n*-alkylamine–ETS-10 interactions, from which the most favourable occurs for *n*-butylamine. The adsorption of these bases did not affect the structure of the titaniunsilicate as the XRD profile of ETS-10 is not altered. The FTIR spectra showed that with the increase in the amine mass the bands corresponding to the symmetric and asymmetric deformations at 1390 and 1467 cm<sup>-1</sup> increase in intensity along with the NH<sub>2</sub> deformation at 1530 cm<sup>-1</sup> as expected. The thermogravimetry shows two mass losses for ETS-10 that correspond to physisorbed water and water in smaller channels and cavities. After methylamine adsorption, the same behaviour was observed, however for butyl- and pentylamine three other mass losses were observed corresponding to decomposition and/or release of *n*-alkylamines.

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### 1. Introduction

Zeolites are aluminosilicates with silicon and aluminium atoms in tetrahedral geometry bound to each other through oxygen atoms in a crystalline structure. Isomorphous substitutions turned possible the synthesis of different compositional variants, among which the titaniunsilicates, TS-1, for example, that proved to be efficient catalysts for redox reactions [1].

Titanium in TS-1 occupies a site of silicon thus the solid has a neutral framework [2] ETS-4 and -10, Engelhardt titaniunsilicate structures [3,4], are new potentially important materials because besides the titanium redox characteristics it may also show acidic features.

The crystalline structure of ETS-10 was proposed previously [5] as made of silicon tetrahedra and titanium octahedra connected through oxygen ions. The octahedral Ti ion bears a -2 charge that is counterbalanced by extraframework cations such as sodium or hydrogen [2,5–10]. The porous

structure is tridimensional and disordered, composed of 12, 7, 5 and 3 membered-rings [8].

The charge on the titanium ions in ETS-10 makes this structure unique among molecular sieves; highly hydrophilic with a high adsorption capacity for polar molecules and an ion exchange capacity similar to that for the NaY zeolite [2,6,11]. The unit cell formula for ETS-10 is  $M_{2/m}TiSi_5O_{13}^{m+}$ , where M is a *m*+ cation.

The understanding of the energetics of the adsorption sites is paramount to the thorough use of these solids in catalysis and adsorption. Several molecular sieves and zeolites were studied through the calorimetry of adsorption of molecules such as alcohols [12–14], amines [15,16], CO, N<sub>2</sub> [17], etc.

In the present investigation, the calorimetry was used to determine the average enthalpy of amines adsorption on active ETS-10 sites. The experimental conditions thus determined were applied to batch experiments in order to prepare a larger mass of solid for structure examination.

### 2. Experimental part

ETS-10 was prepared by the procedure described in the literature [8]. Briefly, 20 g of sodium silicate solution

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(8% Na<sub>2</sub>O, 27% SiO<sub>2</sub>, BDH) was dissolved into 15.4 g of distilled water, 2.47 g sodium hydroxide (Merck), 2.33 g sodium chloride (Merck) and 3.63 g potassium chloride (Merck). This mixture was vigorously stirred until complete dissolution of all components. After that, 10.7 g of an acid aqueous solution of titanium trichloride (1.9 in 2 mol dm<sup>-3</sup> HCl, Aldrich) was added under stirring, until a homogeneous gel was formed. The hydrothermal crystallization was performed for 24 h at 503 K. The product was filtered, washed twice with 500 cm<sup>3</sup> of distilled water and dried during the night at 383 K. The gel had the following composition: 4.7Na<sub>2</sub>O:1.5K<sub>2</sub>O:TiO<sub>2</sub>:5.5SiO<sub>2</sub>:122H<sub>2</sub>O.

The thermal effects due to amine interaction in the titaniunsilicate ETS-10 were followed by using an isothermal microcalorimetric LKB 2277 system at a controlled temperature of 298.15 ± 0.02 K. In this system the aqueous suspension of the solid was calorimetrically titrated with the amine also in aqueous solution until support saturation. From the obtained thermal effect the corresponding value for amine dilution and the solvation of the host were subtracted. From the net result the enthalpic contribution can be calculated as before [18]. Three titrations were performed to obtain the complete thermodynamical cycle: (i) solvation of the matrix in water ( $Q_s$ ); (ii) dilution of the amines solution in water ( $Q_{dil}$ ); (iii) interaction of amines with the matrix in water ( $Q_r$ ).

The thermal effect is given by  $\sum Q_{int} = \sum Q_r - \sum Q_{dil} - \sum Q_s$ . As the thermal effect of matrix hydration is nil, the equation is simplified to  $\sum Q_{int} = \sum Q_r - \sum Q_{dil}$ . The interaction processes were fitted to the modified Langmuir equation. The molar enthalpy for the interaction processes was calculated by  $\Delta H = \Delta h_{int}/N_f$ , where  $\Delta h_{int}$  is the specific enthalpy for the interactive process and  $N_f$  is the number of moles of amines adsorbed. The Gibbs free energy and the entropy were calculated by  $\Delta G = -RT \ln K$  and  $\Delta G = \Delta H - T\Delta S$  [19], respectively.

The initial adsorption conditions were determined with 5, 10 and 20  $\mu$ l of methylamine solutions at 0.05, 0.10 and 0.50 mol dm<sup>-3</sup>, respectively. These solutions were added to a suspension of 10 mg of ETS-10 in 2 cm<sup>3</sup> of water, under intensive stirring. The batch adsorption experiments were performed following the same calorimetry conditions, maintaining the identical proportion but with larger amount of material.

The number of moles of amines adsorbed ( $N_f$ ) was determined by the expression  $N_f = (N_i - N_s) m^{-1}$ , where  $N_i$  and  $N_s$  are the initial and final number of moles of amines in solution.

X-ray diffraction was measured with a Shimadzu XRD 6000 equipped with graphite monochromator with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) generated by a 40 kV tension, 30 mA current, at room temperature, the scanning rate was 2° 2 $\theta$  min<sup>-1</sup>. FTIR spectra were obtained in the transmission mode in a Bomem Michelson MB-102, between 4000 and 400 cm<sup>-1</sup>, 4 cm<sup>-1</sup> resolution and 16 scans. Samples were mixed with KBr at 0.25 wt.%. Thermogravimetry was

made in a TA5100, TA Instruments thermal balance, with a module TGA2050, from 300 to 1273 K at a heating rate of 10 K min<sup>-1</sup> and under a 30 cm<sup>3</sup> min<sup>-1</sup> flow of argon on samples of 10 mg in average.

Elemental analysis was performed by X-ray fluorescence in a Shimadzu EDX700. The sample has a Si/Ti molar ratio of 3.7 and approximately half of the ion exchange sites occupied by potassium and the other half by protons.

### 3. Results and discussion

The choice of the best conditions for the calorimetric analysis was made from the results obtained for the adsorption thermal effects versus amount of methylamine added [20], as displayed in Fig. 1.

For 10 mg of titaniunsilicate sample and an amine concentration of 0.05 mol dm<sup>-3</sup>, Fig. 1a shows that the volume of titrant that allows for the best evaluation of the thermal effects is 20  $\mu$ l. The same is true if the amine concentration is increased to 0.10 mol dm<sup>-3</sup>, as in Fig. 1b. Fig. 1c summarizes showing that for 20  $\mu$ l portions the best concentration of methylamine solution is still 0.05 mol dm<sup>-3</sup>. Therefore, for 10 mg mass of sample, the best conditions for calorimetric measurements are addition of 20  $\mu$ l increments of a 0.05 mol dm<sup>-3</sup> aqueous solution of amine. These conditions were employed for the remaining alkylamines ethyl-, propyl-, butyl- and pentylamines, giving the corresponding values for  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  displayed in Table 1.

The thermodynamic data (Table 1) showed as expected that the interaction of ETS-10 with *n*-alkylamines is of an exothermic nature. The behaviour of adsorption indicates a general increase in  $\Delta H$  values as the chain length increase, except for the inversion between methyl and ethylamine. The energetically favourable interaction is further confirmed by the negative values of the Gibbs free energy and positive values of entropy at the solid/liquid interface. From the variation of the values, it is possible to conclude that the adsorption of alkylamines on ETS-10 is driven by enthalpy.

The negative values of enthalpy variation are perfectly justified by the acid–base interaction between the amines and acid sites on ETS-10. The trend on entropy variation points to an increasingly more organized situation as the chain length of the adsorbed amine increases. As the number of molecules increase in the cavities and channels, a higher organization might be necessary in order to allow the simultaneous presence of such number of entities.

These propositions are further confirmed by the results of batch adsorption in Fig. 2. In this set of curves one observes that the amount of amine adsorbed increases at low volumes of titrant added until a plateau is reached. This point is well-defined for methyl and ethylamines and poorly or not defined at all for the other longer molecules. The maximum adsorption values are 0.490, 0.363, 0.336, 0.226 and 0.190 mmol g<sup>-1</sup> for methyl-, ethyl-, propyl-, butyl- and pentylamine, respectively, that is decreased values for

Table 1

Thermochemical data for the *n*-alkylamines CH<sub>3</sub>–(CH<sub>2</sub>)<sub>*n*</sub>–NH<sub>2</sub> (*n* = 0–4) ETS-10 interaction in aqueous solution at 298.15 ± 0.02 K

<i>n</i> -Alkylamines	$-\Delta h_{\text{int}}$ (J g <sup>-1</sup> )	$-\Delta H$ (kJ mol <sup>-1</sup> )	$\ln K$	$-\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (JK <sup>-1</sup> mol <sup>-1</sup> )
CH <sub>3</sub> –NH <sub>2</sub>	9.86	20.11 ± 0.56	16.11	39.9 ± 0.1	67 ± 1
CH <sub>3</sub> –CH <sub>2</sub> –NH <sub>2</sub>	6.35	17.49 ± 0.27	13.59	33.5 ± 0.2	54 ± 1
CH <sub>3</sub> –(CH <sub>2</sub> ) <sub>2</sub> –NH <sub>2</sub>	8.16	24.29 ± 0.39	13.28	32.9 ± 0.1	29 ± 1
CH <sub>3</sub> –(CH <sub>2</sub> ) <sub>3</sub> –NH <sub>2</sub>	7.33	32.42 ± 0.99	17.26	42.8 ± 0.1	35 ± 1
CH <sub>3</sub> –(CH <sub>2</sub> ) <sub>4</sub> –NH <sub>2</sub>	6.65	34.99 ± 0.43	14.63	36.3 ± 0.3	4 ± 1

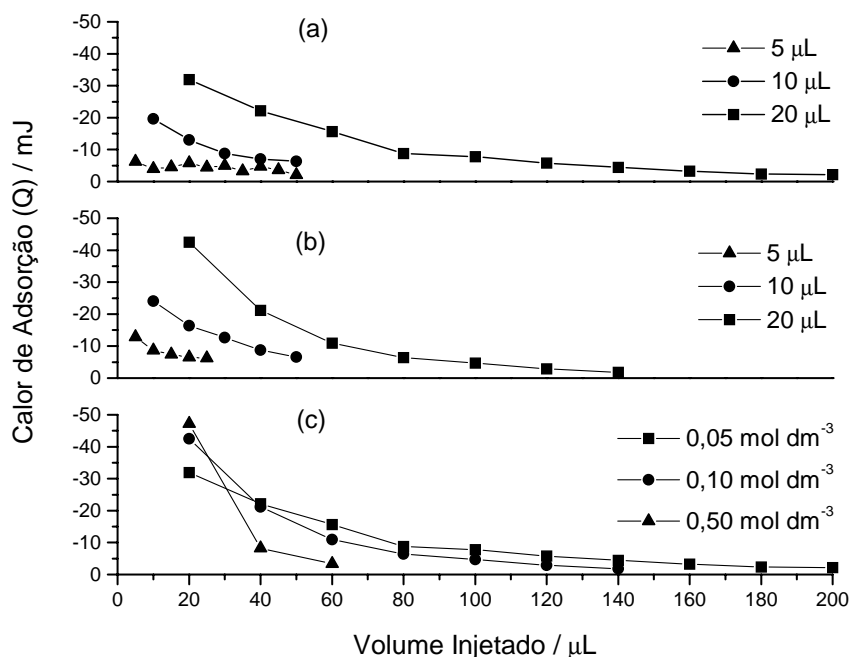


Fig. 1. Thermal effects of adsorption ( $\sum Q$ ) as a function of added methylamine ( $\blacktriangle$ ) 5  $\mu\text{L}$ , ( $\bullet$ ) 10  $\mu\text{L}$ , ( $\blacksquare$ ) 20  $\mu\text{L}$  at concentration of (a) 0.05 mol dm<sup>-3</sup>, (b) 0.10 mol dm<sup>-3</sup> and varying concentrations of ( $\blacksquare$ ) 0.05 mol dm<sup>-3</sup>, ( $\bullet$ ) 0.10 mol dm<sup>-3</sup>, ( $\blacktriangle$ ) 0.50 mol dm<sup>-3</sup>, with volume of addition of (c) 20  $\mu\text{L}$ .

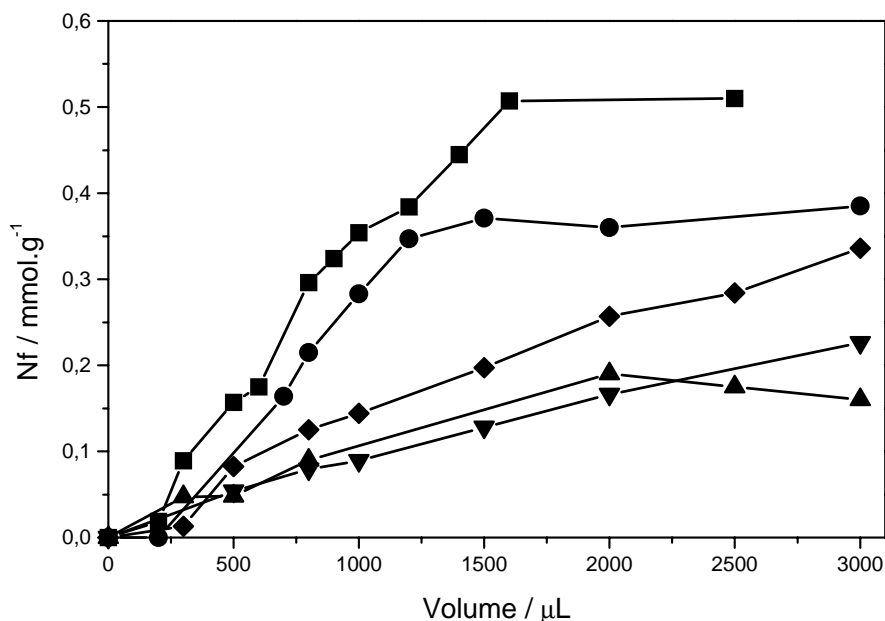


Fig. 2. Adsorption isotherms of *n*-alkylamines on ETS-10 for ( $\blacksquare$ ) methylamine, ( $\bullet$ ) ethylamine, ( $\blacklozenge$ ) propylamine, ( $\blacktriangle$ ) butylamine and ( $\blacktriangledown$ ) pentylamine.

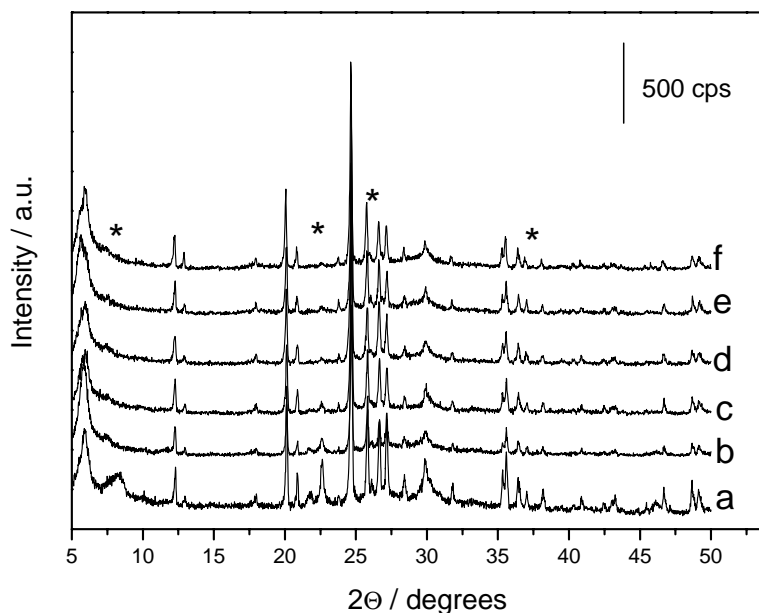


Fig. 3. X-ray diffractograms of (a) ETS-10 and ETS-10 with (b) methylamine, (c) ethylamine, (d) propylamine, (e) butylamine and (f) pentylamine. The asterisk shows the peak corresponding to ETS-4, another crystalline phase.

amines with increasing chain length. This fact, as well as the plateau definition, might be related with the adsorption on the ETS-10 12-MR channels, with approximately  $4.9 \text{ \AA} \times 7.6 \text{ \AA}$ , limiting the total dimension of the adsorbed molecules as well as the number of smaller molecules adsorbed.

The X-ray diffractogram of ETS-10 is shown in Fig. 3a. The characteristic peaks of as-synthesized ETS-10 appear at 15.2, 7.2, 4.4, 3.6, 3.5, 3.3, 2.5 and 1.9 Å. There is also a small contribution of ETS-4 at 10.45, 3.9, 3.3 and 2.9 Å. It is possible to observe that the basic features of the ETS-10

structure are fully preserved after adsorption of each amine (Fig. 3b–f).

The FTIR spectra are displayed in Fig. 4 and show that the short distance order is also preserved upon adsorption. The structure region between  $1300$  and  $400 \text{ cm}^{-1}$  is essentially not disturbed upon adsorption of alkylamines. On the other hand, it is observed that bands corresponding to asymmetric stretching of  $-\text{CH}_3$  ( $2970$ – $2955 \text{ cm}^{-1}$ ) and of  $-\text{CH}_2-$  ( $2870$ – $2800 \text{ cm}^{-1}$ ) increase as expected as the chain length of the adsorbed amine increases. From propylamine up to pentylamine bands corresponding to

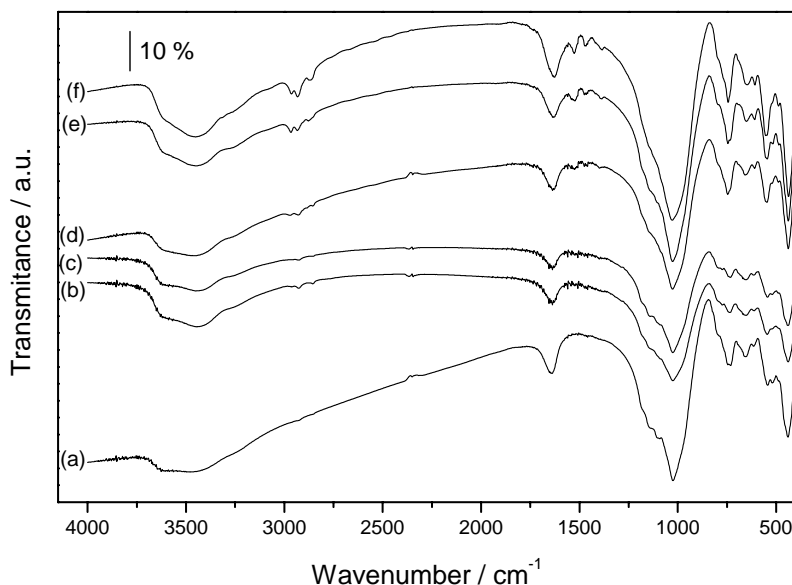


Fig. 4. FTIR spectra of (a) ETS-10 and ETS-10 with (b) methylamine, (c) ethylamine, (d) propylamine, (e) butylamine and (f) pentylamine.

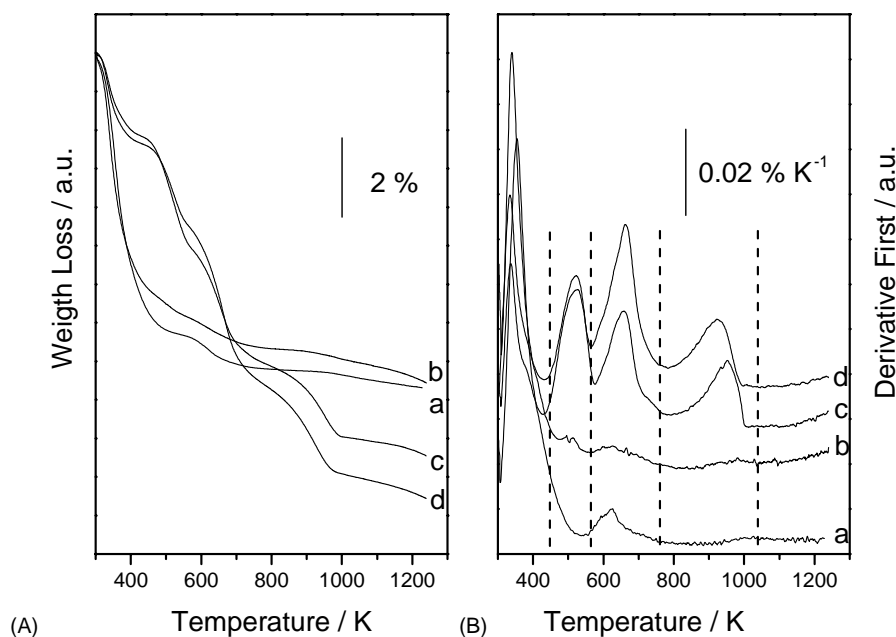


Fig. 5. Thermogravimetry (A) and derivative thermogravimetry (B) of (a) ETS-10 and ETS-10 with (b) methylamine, (c) butylamine and (d) pentylamine.

symmetric and asymmetric deformation of amines at  $1390$  and  $1467\text{ cm}^{-1}$  ( $-\text{NCH}_2-$ ) and  $1530\text{ cm}^{-1}$  due to  $\text{NH}_2$  deformations in aqueous solutions also increase in intensity.

Confirming the FTIR data, Fig. 5A and B show that the larger the amine chain length, the larger the mass loss in thermogravimetry (Fig. 5A, curves c and d). The derivative thermogravimetry also shows a better definition of mass losses for the larger amines (Fig. 5B, curves c and d). For butyl- and pentylamines, four mass losses are clearly observed at  $303$ – $530\text{ K}$  for water,  $433$ – $578$ ,  $578$ – $783$  and  $783$ – $1033\text{ K}$  regions for *n*-alkylamines decompositions. For the methylamine–ETS-10 system, most of the mass loss occurs as for ETS-10, in the beginning of the temperature range and corresponds to water release as shown in Fig. 5A, curves a and b. The total amount of water is diminished in the sample where methylamine was absorbed because the amine displaces water molecules.

#### 4. Conclusions

The adsorption of alkylamines on ETS-10 is driven by enthalpy. It was observed that as the alkyl chain length increases, the amount of alkylamines adsorbed decreases.

Thermochemical data demonstrated that the alkylamines/ETS-10 interactions are strongly favoured. The increase in the amine chain length forces the molecules to better organize into the cavities in order to access the acid centres

inside the cages, which caused a proportional decrease in entropic values.

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