

Comparative study on the gas-phase adsorption of hexane over zeolites by calorimetry and inverse gas chromatography

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Abstract

The scope of this work is to carry out a systematic comparison of inverse gas chromatography (IGC) and microcalorimetry as tools for the study of the gas-phase adsorption of organic vapours (using hexane as model compound) on zeolitic materials (using different Mn, Co and Fe-exchanged NaX and CaA zeolites). Adsorption isotherms were recorded using both techniques in the temperature range of 150–250 °C, being observed that the shape of the isotherms obtained with the dynamic (IGC) and static (microcalorimetry) techniques was surprisingly similar in the pressure range at which both techniques are applicable (low surface coverages). Concerning to the measurement of the strength of the adsorption, calorimetric data provide two parameters related to the adsorption enthalpy: the initial differential heat and the isosteric adsorption enthalpy. A great coincidence was found between the last one and the adsorption enthalpy determined by IGC (4–20% of difference, depending on the studied material). The behaviour of the initial differential heat depends strongly on the studied material, being in some cases closely related to the other two parameters and temperature-independent (in the case on Mn-exchanged zeolites), whereas for the Co-CaA and Fe-CaA zeolites, it is temperature-dependent, being not correlated with the other parameters in this case. The main conclusion of this work is that IGC is an attractive alternative to the static microcalorimetric data for obtaining information on the adsorption of organic compounds on microporous materials.

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1. Introduction

Adsorption phenomena are of high scientific interest and widely used in practical applications. Adsorption processes are used in the removal of volatile organic compounds (VOCs), whose molecules are retained by a solid adsorbent as a result of intermolecular forces. This process is used for effluents from vents and storage tanks, although it can also be used in connection with other emission sources. Furthermore, the nature of the interaction of molecules with the catalyst surfaces is important for the evaluation of the performance of potential catalyst for a given reaction.

Determination of the adsorption properties will certainly help to understand catalytic performance. The characteristics of zeolites are generally determined by adsorption of gases

and vapours, their adsorption isotherms being determined by static or dynamic methods. Whereas static techniques are usually carried out under vacuum and they are very time-consuming, dynamic methods are fast and they are carried out at conventional pressures and in a wide range of temperature. Adsorption microcalorimetry (static method) has been vastly employed for the determination of adsorption properties of hydrocarbons over zeolites [1–4], being considered as one of the most accurate methods and a reference method for comparing the results obtained by other alternative techniques.

On the other hand, gas–solid chromatography has been used for many years to study adsorption and catalytic reactions. When its goal is the characterization of the stationary phase, instead of the separation of solutes in the mobile phase, the technique is known as inverse gas chromatography (IGC). IGC has been widely utilized to study synthetic and biological polymers, copolymers, polymer blends, adsorbents [5], foods [6], carbon blacks [7] and fibers [8]. More recently, it has been also employed in the study of mesoporous catalysts [9,10] and

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zeolites [11–14]. However, the application of the IGC to microporous materials has been discouraged in the literature for microporous materials [15]. This is so because one of the hypotheses assumed for obtaining adsorption data from the IGC eluted peak is to consider instantaneous adsorption equilibrium. In the case of microporous data, transport of the solutes through the porous structure could delay the equilibrium, becoming more difficult to satisfy this hypothesis.

Zeolites, also called “molecular sieves” or “shape selective catalysts”, are widely used in catalytic and separation technologies. The specific properties of zeolites result mainly from their well-defined structure, including microporous channels and cavities as well as from their ability of formation catalytic or adsorption centers inside the micropores. Zeolites can be regarded as model adsorbents as, due to the rigid crystal lattice, the pore structure has constant dimensions and so the adsorption properties of the zeolites can be systematically changed. These changes are brought about by cation-exchange, decationization or dealumination.

In this way, zeolites are a suitable support for transition metals due to their open structure and ion-exchange capacities with many applications in heterogeneous catalysis [16]. Transition metal (Co^{2+} , Fe^{3+} , Cu^{2+} , Cu^+) exchanged zeolites ZSM-5 have been successfully tested for the oxydehydrogenation of ethane with oxygen [17], and the oxidation of propane has been carried out over Fe^{3+} , Co^{2+} and Mn^{2+} exchanged zeolite ZSM-5 [18]. SO_2 oxidation has been carried out with Mn^{2+} heterogenised on NaX zeolite [16]. Moreover, Fe^{3+} , Co^{2+} and Mn^{2+} have been found to be the most active metals in methane combustion [19,20]. Likewise, in our previous work, the deep oxidation of *n*-hexane over zeolites NaX and CaA with transition metals (Co^{2+} , Mn^{2+} and Fe^{3+}) incorporated into their structures was studied [21].

Our previous work [22], devoted to the determination of properties of adsorption of different gas pollutants hydrocarbons over transition metals (Co^{2+} , Mn^{2+} and Fe^{3+}) exchanged NaX and CaA zeolites by IGC, showed that, in general, the highest interactions took place over the exchanged zeolite CaA. Thus, in the present work, the adsorption properties of a representative hydrocarbon, *n*-hexane, over Co-CaA, Mn-CaA and Fe-CaA were determined by microcalorimetry and IGC, comparing the results obtained. Likewise, the zeolite Mn-NaX has been also studied in order to observe the influence of the zeolitic structure. Due to the microporosity of the zeolites and the above-mentioned effects, these materials are appropriate to check the suitability of the IGC for the measurement of adsorption properties for this kind of materials. So, if both techniques provide similar results for these materials, it can be inferred that IGC is a useful

Table 2

Characteristics of the samples studied (bulk composition by ICP elemental analysis, surface composition by XPS)

Zeolites	Weight (%)		Atomic ratio			
	Si/Al	Me	(Si/Al) _b	(Si/Al) _s	(Si/Me) _b	(Si/Me) _s
Co-CaA	1.13	8.0	1.09	1.88	5.19	1.11
Mn-CaA	1.14	16.7	1.10	1.46	2.26	14.28
Fe-CaA	1.27	18.0	1.22	3.59	2.12	2.04
Mn-NaX	1.24	8.0	1.19	3.12	5.20	11.11

technique for the assessment of the adsorption properties of the most of the microporous materials.

2. Experimental

2.1. Materials

The solute used, *n*-hexane, was supplied by Fluka, with a purity higher than 99.5%, and it was used without further purification.

Two different zeolitic materials, zeolites NaX and CaA (Alltech), available in the interval 40/60 mesh, have been studied and compared to various metal cation-exchanged zeolites. The ion-exchange with Co^{2+} , Mn^{2+} and Fe^{3+} solutions was carried out at 70 °C for 24 h, followed by a calcination at 500 °C for 4 h, as was reported elsewhere [22]. Their physicochemical characteristics are given in Table 1. The crystalline structure was determined by X-ray diffraction (XRD), the crystallinity of the protonated samples, was measured according to the procedure proposed by López-Fonseca et al. [23] (based on the determination of the intensities of the main diffraction peaks and assuming 100% of crystallinity for the starting material). The textural characteristics, surface area as well as mesopore and micropore volumes, of the zeolites were determined by N_2 adsorption at -196 °C (see more details in reference [22]).

The percentage of cation-exchanged of all the samples was determined by inductively coupled plasma (ICP) MS, being the metal loadings and Si/Al ratios expressed both in weight percent and as atomic ratio Si/Me (Table 2).

Likewise, the elemental ratio of metal in the XPS sampling region was evaluated at room temperature with an Escalab 200R (VG Scientific) spectrometer using a monochromatic and focused Al $\text{K}\alpha$ radiation (1486.6 eV) under a residual pressure of 5×10^{-8} Pa. The binding energy of Co $2p_{3/2}$ (780.51 eV) found could correspond to two different cobalt oxides (CoO and Co_3O_4), due to their similarity. In the case of manganese, it was found Mn^{4+} over both Mn-CaA and

Table 1
Crystallinity, Langmuir surface area, micropore volume and mesopore volume and percentage of exchange of the zeolites

Zeolites	Crystallinity (%)	S_{Langmuir} (m^2/g)	$V_{\text{mesopores}}$ (BJH) (cm^3/g)	$V_{\text{micropores}}$ (<i>t</i> -Lippens) (cm^3/g)	Na/Ca exchanged (%)
Co-CaA	16	422	0.138	0.093	39.1
Mn-CaA	82	553	0.071	0.167	92.3
Fe-CaA	≈0	301	0.333	0.004	98.1
Mn-NaX	61	720	0.135	0.220	46.5

Mn-NaX zeolites. Regarding the zeolite Fe-CaA (binding energy of Fe $2p_{3/2} = 711.30$ eV), the width of the peak could indicate that there is a mixture of Fe_2O_3 and Fe_3O_4 . Si/Co and Si/Fe atomic ratios derived from XPS were lower than the bulk ratio, especially in the case of Co-CaA zeolite since in the case of Fe-zeolite, iron seems to be homogeneously distributed between the surface and the bulk. On the other hand, in the case of Mn-zeolites, the metal exchange took place preferentially in the bulk of the material instead of in the surface, especially in the case of Mn-CaA although its total metal amount is double than that of Mn-NaX. As regards to the Si/Al ratio, it is noted a slight metal substitution for Al, more important in the surface, substitution that is clearer in the case of the Fe-CaA zeolite.

2.2. Inverse gas chromatography

A conventional gas chromatograph (Varian 3800) with a thermal conductivity detection (TCD) system was used for the adsorption measurements. A loading of 0.6 g of each zeolite was placed into a 27 cm length of Supelco Premium grade 304 stainless steel column, with passivated inner walls and an inside diameter of 5.3 mm (O.D. 1/4 in.). Each column was packed with mechanical vibration, and the two ends were plugged with silane-treated glass wool. The columns were stabilized in the GC system at 300 °C overnight under a helium flow-rate of 30 mL/min. In order to avoid detector contamination, the column outlet was not connected to the detector during this period.

Measurements were carried out in the temperature range of 200–270 °C. Helium was used as carrier gas, and flow-rates were measured using a calibrated soap bubble flowmeter. In order to meet the requirement of adsorption at infinite dilution, corresponding to zero coverage and GC linearity [24], the samples injected were in the range from 0.05 to 0.8 μ L. For each measurement, the sample was injected three times, obtaining reproducible results (0.5%). The specific retention volume, V_g , in cm^3/g , was calculated from the equation:

$$V_g = Fj \frac{(t_R - t_M)}{m} \left(\frac{p_0 - p_w}{p_0} \right) \left(\frac{T}{T_{meter}} \right) \quad (1)$$

where F is the carrier gas flow-rate, t_R is the retention time in min, t_M is the retention time of a non-adsorbing marker (air), p_0 is the outlet column pressure, p_w is the vapour pressure of water at the flowmeter temperature, T_{meter} is the ambient temperature in K, T is the column temperature, m is the mass of adsorbent and j is the James–Martin compressibility factor. According to the procedure outlined in a previous paper [9], adsorption isotherms were determined according to elution by characteristic point (ECP) method, using the Bechtold method for correcting the peak broadening caused by diffusion, non-equilibration and changes in velocity [25].

At low surface coverage, the heat of adsorption is obtained by plotting $\ln V_g$ against $1/T$, according to Eq. (2):

$$\Delta H_{ads} = -R \frac{\partial(\ln V_g)}{\partial(1/T)} \quad (2)$$

2.3. Microcalorimetry

The calorimetric experiments were carried out in a Tian-Calvet microcalorimeter (C80 from Setaram, France) linked to a volumetric line in order to study the gas–solid interactions. This type of microcalorimeter usually employs two cells, one containing the adsorbent and the other an empty reference cell. The adsorption takes place by repeatedly sending small doses of gas onto the initially outgassed solid while recording the heat flow signal and the concomitant pressure evolution. The equilibrium pressure was measured after each dose by a Barocel Capacitance Manometer (Datametrics, USA). The adsorption temperature is maintained at a constant value.

In this study, a 50 mg sample of the zeolite was outgassed under vacuum overnight at 400 °C prior to any measurement. The microcalorimetric studies of *n*-hexane were performed at 150, 200 and 250 °C. By measuring the adsorbed amounts at increasing pressures and the heat evolved from the adsorption of each one of the subsequent doses of adsorbate, the volumetric and differential calorimetric isotherms were simultaneously obtained. More details about the experimental procedures are given in reference [26].

3. Results and discussion

The differential heats of adsorption of the *n*-hexane for the studied zeolites are depicted in Fig. 1. Typically, the differential heat of adsorption, defined as the heat evolved during the adsorption of a small quantity of gas at a constant temperature, is determined as a function of the surface coverage [26]. In all the cases, it is observed a plateau, this plateau ending up with a marked decrease of Q_{diff} as the amount adsorbed increases. This plateau is relatively long (in terms of adsorbate concentration range) in the case of the zeolite Co-CaA and even longer for the zeolite Mn-NaX; however, the plateau is shorter, due to the appearance of a more or less pronounced increase of the adsorption heat before the final fall, for Fe-CaA and Mn-CaA at 250 °C. The plateau at these values of Q_{diff} corresponds to the progress of adsorption in the micropores so that the final decline of the adsorption heat defines the completion of micropore filling [3]. However, according to Table 1, although the micropore volume corresponding to Mn-NaX is the largest among the studied zeolites, in the case of the zeolite Co-CaA this volume is much lower, being the mesopore volume the most important. The rise of the adsorption heat before the final fall has been associated with interactions between adsorbate molecules [3]. The decreasing heats of adsorption observed in the other cases suggest that these materials contain sorption sites varying in strength, the strongest sites being initially covered [27]. The increasing sorption enthalpies, observed only at 250 °C, could indicate that this loss in heat of adsorption due to the sorption in weaker sites is compensated by adsorbate–adsorbate interactions, interactions that could be higher with the increase of temperature, effect explained by the increase of collisions among *n*-hexane molecules. Moreover, these calorimetric curves exhibit the known path of the enthalpy values of *n*-paraffins adsorbed in Mn-exchanged faujasites (Mn-NaX) [28].

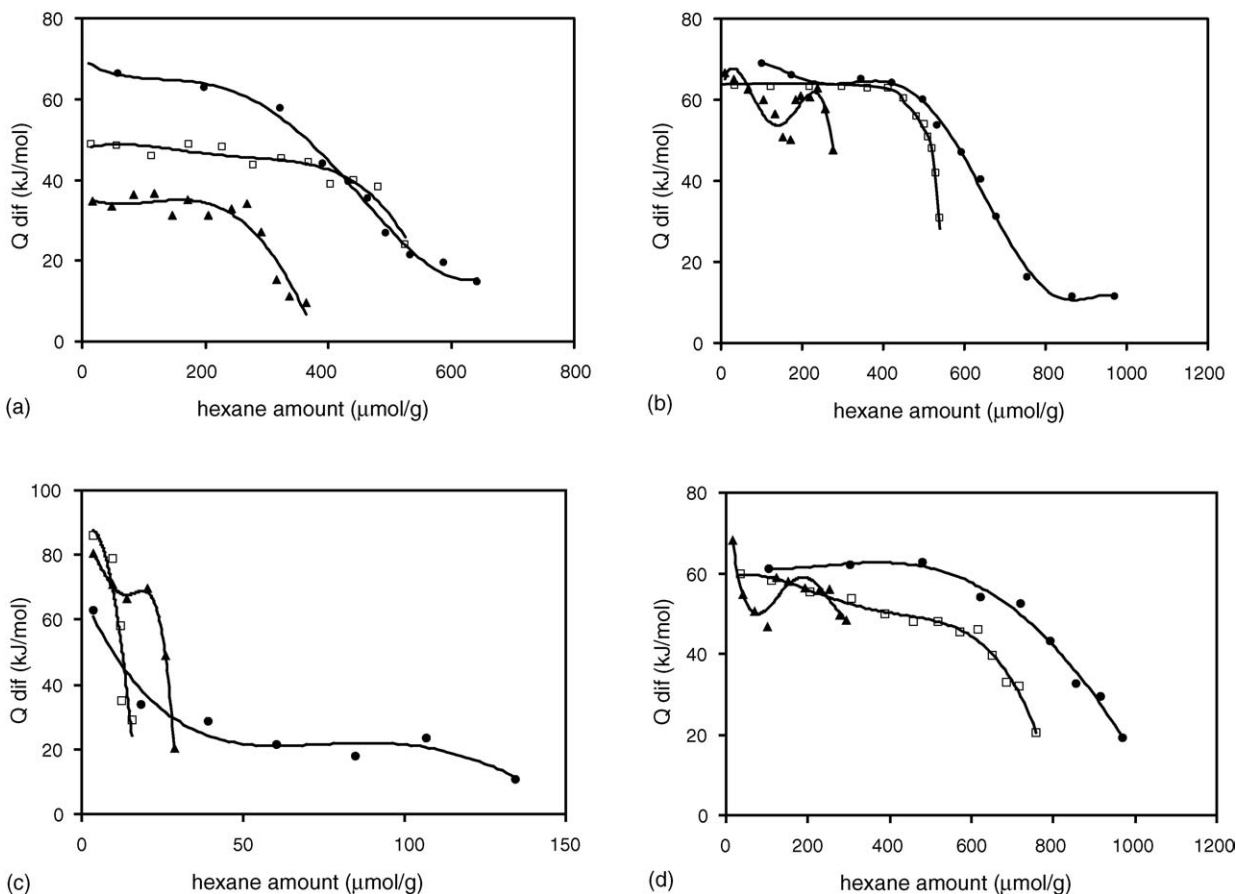


Fig. 1. Differential heats of *n*-hexane adsorption at 150 °C (●), 200 °C (□) and 250 °C (▲) over: (a) Co-CaA; (b) Mn-CaA; (c) Fe-CaA; and (d) Mn-NaX.

The existence of this increase in the interaction before the final fall is defined by the size of the microporous space and the specificity of the adsorbate bond to the surface [3]. Eder and Lercher [27] aimed that high aluminum content produces a continuous plateau without a heat maximum at high coverages. All the studied zeolites present a very low Si/Al ratio, and however, it is observed a maximum at the highest temperature in all the cases. The different behaviour between our results and those previously reported is caused by the higher temperature of our experiences, their experiments being carried out at 60 °C.

Volumetric adsorption isotherms of *n*-hexane at 250 °C over the zeolites studied, obtained both by calorimetry and IGC, are shown in Fig. 2. It was observed that both techniques provide surprisingly similar results at low partial pressures, when both techniques are applicable. So, the isotherms recorded for the adsorption of hexane over the tested materials are exactly the same for both techniques, except in the case of Mn-CaA and Fe-CaA. The slightly higher adsorption capacities predicted by IGC for Mn-CaA and Fe-CaA zeolites could be caused by either experimental error or surface modification during the pretreatment of the samples (He for IGC measurement and vacuum for calorimetric measurements).

As IGC is carried out at infinite dilution, the sample size must be small enough for ensure that the surface is covered with an adsorbate monolayer, and as result, the data fall into straight lines, representative of Henry law region. For this rea-

son, the adsorption pressure does not exceed the 10 mmHg for the zeolites Co-CaA, Mn-CaA and Mn-NaX and only achieves 30 mmHg in the case of Fe-CaA, who adsorbs a minor amount of *n*-hexane. Regarding the calorimetric curves, it must be pointed out that only physisorption, reversible adsorption, has occurred, as can be supposed working at these relatively high temperatures.

From the experimental isotherms obtained by calorimetry, it is possible to plot the corresponding isosteres (evolution of

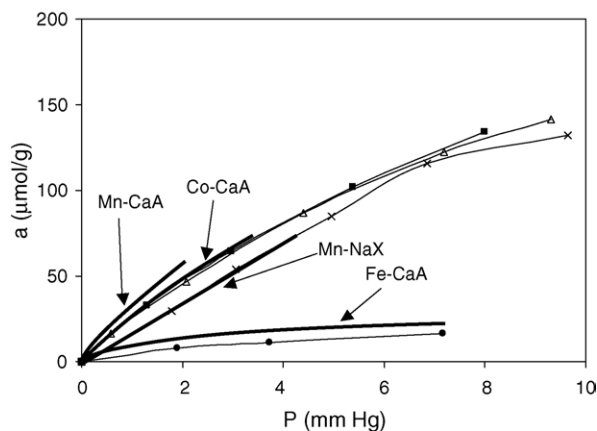


Fig. 2. *n*-Hexane adsorption isotherms obtained by calorimetry at 250 °C over Co-CaA (■); Mn-CaA (Δ); Fe-CaA (●); and Mn-NaX (×), and by IGC (bold lines).

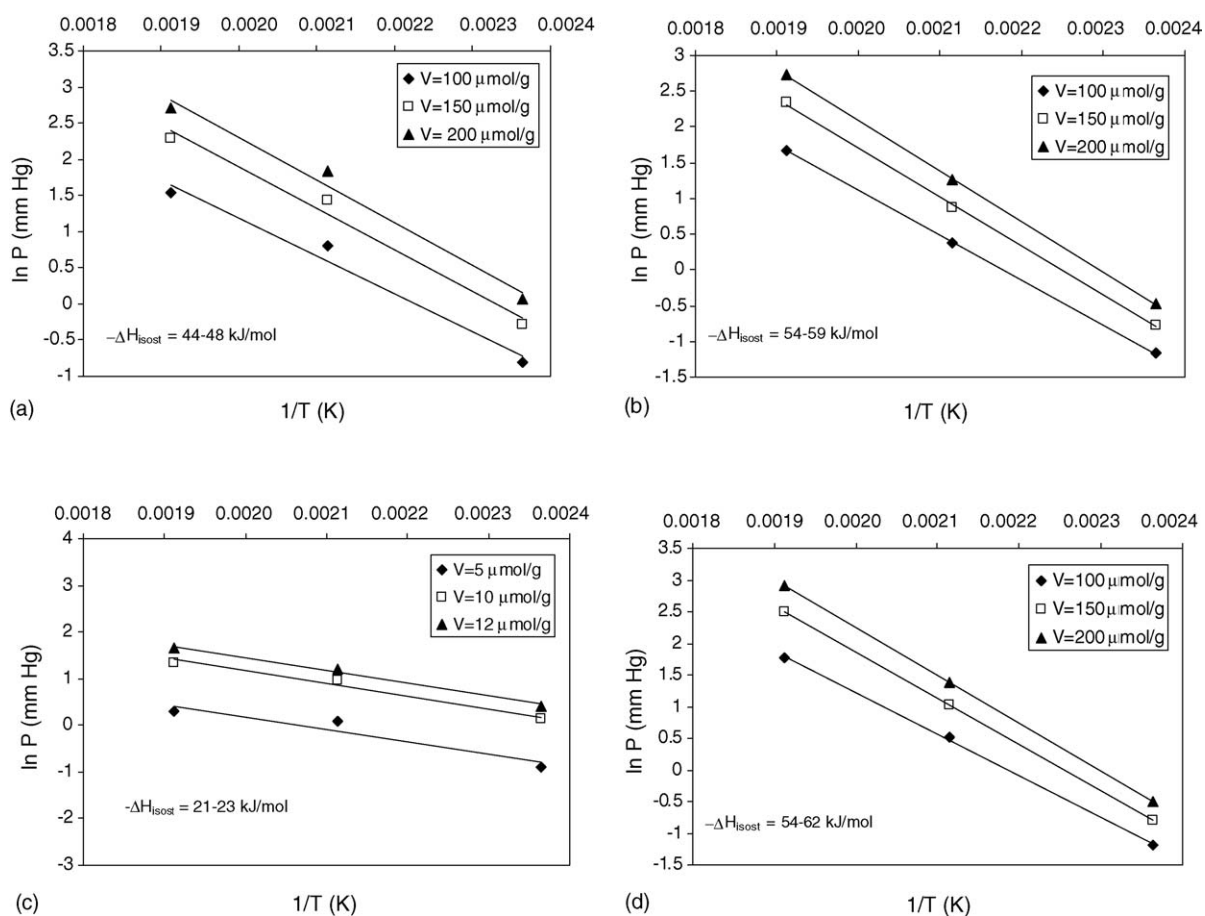


Fig. 3. Adsorption isotherms and isosteric heats for the studied samples obtained from calorimetric data: (a) Co-CaA; (b) Mn-CaA; (c) Fe-CaA; and (d) Mn-NaX.

the partial pressure with the temperature at a constant value of surface coverage, usually represented in linearised form as plots of $\ln P$ versus $1/T$, as depicted in Fig. 3. From the slopes of these lines, isosteric heats of adsorption can be calculated according to Clausius–Clapeyron equation [28,29]:

$$\Delta H_{\text{isot}} = -RZ \left(\frac{\partial \ln P}{\partial (1/T)} \right)_n \quad (3)$$

where P and T denote, respectively, the equilibrium pressure and absolute temperature, R is the universal gas constant, Z is the compressibility coefficient and n is the adsorbate coverage. The isosteric heats obtained from the three coverages for each zeolite show a deviation smaller than 14% in all cases, which suggests that mainly monolayer adsorption is taking place.

Table 3 shows the values of ΔH_{isot} obtained from the isotherms, the enthalpies of adsorption obtained from the IGC

Table 3
Enthalpy of adsorption obtained by IGC and isosteric and initial heat of adsorption obtained by calorimetry

Samples	$-Q_{\text{diff}}$ initial (kJ/mol) calorimetry		$-\Delta H_{\text{isot}}$ (kJ/mol) calorimetry	$-\Delta H_{\text{ads}}$ (kJ/mol) IGC
	T_{ads} (°C)	$-Q_{\text{diff}}$ initial		
Co-CaA	150	70	46	58
	200	49		
	250	37		
Mn-CaA	150	67	57	53
	200	63		
	250	70		
Fe-CaA	150	70	22	23
	200	86		
	250	84		
Mn-NaX	150	62	58	43
	200	63		
	250	56		

experiments from the slope of a plot of $R \ln V_g$ versus $1/T$, based on Eq. (2), and values of initial heats of adsorption. These initial values are obtained extrapolating the differential heat of adsorption for *n*-hexane to zero coverage, which is representative for the pure adsorbent–adsorbate interaction. With increasing pore-filling, however, the adsorbate–adsorbate interaction increases, which is most pronounced for the large pore FAU [2].

As it can be observed in Table 3, the values of ΔH_{isost} obtained from calorimetry are very similar to those of ΔH_{ads} obtained from IGC, being the largest discordance the case of the zeolite Mn-NaX, with a deviation of 26% between both values. Hence, quite similar values of initial heats and adsorption enthalpies are obtained in all the cases, except in the case of Fe-CaA, where surprisingly it was obtained the lowest value of initial heat of adsorption at 150 °C. The different behaviour of the iron-loaded zeolites could be explained considering both its different porous structure (the microporous structure is almost completely transformed into a mesoporous structure) and the high concentration of iron. The calorimetric results obtained for Fe-zeolite suggest different adsorption mechanism depending on temperature. So, at low temperature (150 °C), the shape of the curve suggests the adsorption of the hexane on the mesoporous structure. The importance of this adsorption sharply decreases as temperature increases, adsorption taking place in the remaining microporous structure. As the micropore volume of this zeolite is very low, the amounts adsorbed are also lower than the corresponding to the other studied materials. In any case, it is observed that, even considering the complexity of the adsorption, results obtained by IGC and calorimetry are comparable both on terms of adsorption isotherms and in the evaluation of the adsorption enthalpies.

It should also be noted (Table 3) the differences into the trends observed for Q_{diff} for Mn-zeolites if compared with Co- and Fe-zeolites. In the former case, the value of Q_{dif} is very similar at all the studied temperatures, whereas a strong variation on the temperature has been observed in the last cases. These differences could be explained if it is considered that in “ideal” adsorption (i.e. all the active centers are equivalent and there are no interactions between adsorbate molecules), adsorption enthalpy will be constant (not dependant neither on temperature nor in the adsorbed amount), the Q_{dif} values being closely related to this thermodynamic parameter. So, the proximity in the initial parts of the curves in the case of the Mn-exchanged zeolites suggests that the active sites for the adsorption are equivalent, whereas the calorimetric data obtained for Co- and Fe-zeolites suggest the presence of different adsorption sites.

The surface coverages in the range of physical adsorption in the isosteres used to obtain the isosteric heats were: 100, 150 and 200 $\mu\text{mol/g}$, for Co-CaA, Mn-CaA and Mn-NaX, and 5, 10 and 12 $\mu\text{mol/g}$ for Fe-CaA. So, after the first calorimeter dose, the reduced micropore volume of the Fe-CaA zeolite was filled, being the cause for the absence of plateau in this zeolite. The following doses filled the mesopore volume, which corresponds to the final drop of heat of adsorption [3].

Concerning to the ΔH_{ads} obtained from IGC, the decrease in the strength of interaction, although they were obtained at infi-

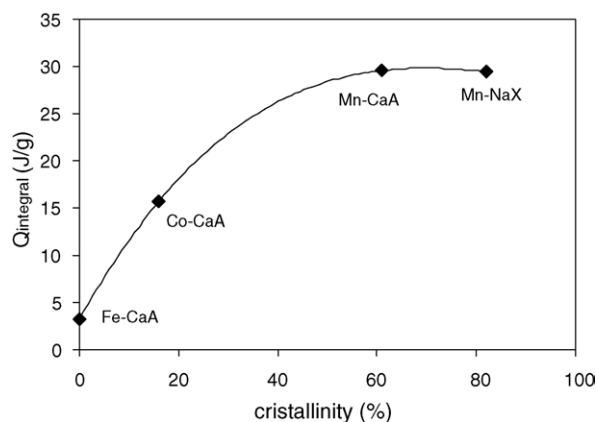


Fig. 4. Dependence of integral heats of *n*-hexane adsorption, obtained at 200 °C under an equilibrium pressure of 20 mmHg, on crystallinity.

nite dilution conditions, has been attributed to the lowest surface area and micropore volume of Fe-zeolites [22]. From Fig. 2, it is obvious that the manganese benefit the *n*-hexane adsorption. In fact, the Mn-CaA zeolite shows a high interaction, being slightly lower in the case of Mn-NaX. The amount of manganese in the Mn-CaA zeolite doubles the corresponding to the zeolite Mn-NaX. In both cases, the manganese is placed mainly in the bulk instead of on the surface, especially for Mn-CaA zeolite, so the superficial particles do not seem to be involved in the adsorption.

The variation of integral heats of *n*-hexane adsorption obtained under an equilibrium pressure of 20 mmHg as a function of crystalline is depicted in Fig. 4. This integral heat, Q_{int} , is defined as the total heat evolved associated to the adsorption of n_a moles of gas. The integral heat of adsorption increases as the crystallinity increases. If these integral heats are plotted as function of micropore volume (Fig. 5), the same trend is observed. This result suggests, in good agreement to literature findings for similar materials [30], that both parameters are closely related.

From these plots (Figs. 4 and 5), it is inferred that the better behaviour of Mn-zeolites is due mainly to the zeolitic structure. Keeping the morphological properties, such as the external surface area, micropore volume and degree of crystallinity after

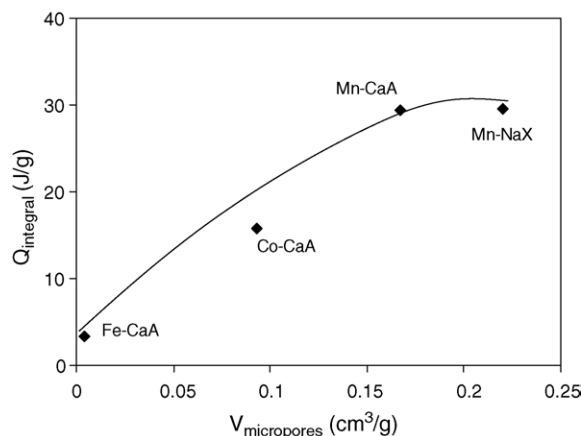


Fig. 5. Dependence of integral heats of *n*-hexane adsorption, obtained at 200 °C under an equilibrium pressure of 20 mmHg, on micropore volume.

the exchange allows obtaining the highest interaction. In fact, it is remarkable that the ion-exchange in manganese zeolites takes place mainly in the bulk, whereas in the case of cobalt, and especially iron, the exchange takes place mainly on the surface, blocking the pores and hindering the adsorption over the surface.

4. Conclusions

Different ion-exchanged zeolites (Co-CaA, Mn-CaA, Fe-CaA and Mn-NaX) have been studied by gas calorimetry and IGC. *n*-Hexane was used as adsorbate and isotherms of adsorption as well as the isosteric heats of adsorption and enthalpies of adsorption obtained, respectively, by the earlier mentioned methods were determined. Furthermore, the studied samples were characterized by XRD, ICP-MS and XPS.

The comparison between the volumetric adsorption isotherms of *n*-hexane at 250 °C obtained both by IGC and calorimetry reveals that, at low pressures (when both techniques are applicable), the results obtained by both techniques are very similar. Moreover, the strength of adsorption is also quantified by the heat of adsorption (IGC) and the isosteric heat (calorimetry), obtaining deviations among them in the range of 4–20%, depending on the material.

Thus, comparison between chromatographic and calorimetric data suggests that IGC (which is more widely available and more economical from the points of view of both apparatus costs and analysis time required) can supply enough accurate data for the characterization of zeolitic materials, and could be a useful technique for preliminary adsorption studies of these materials. If it is considered that, according to the literature, these microporous materials are among the materials for which the classical hypotheses of the IGC technique are most difficult to fulfill, it is concluded that IGC is a very powerful technique for the characterization of porous adsorbents and catalysts, even in the case of the microporous ones.

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References

- [1] H. Stach, K. Fiedler, J. Jänchen, *Pure Appl. Chem.* 65 (1993) 2193.
- [2] J. Jänchen, H. Stach, L. Uytterhoeven, W.J. Mortier, *J. Phys. Chem.* 100 (1996) 12489.
- [3] J.M. Guil, R. Guil-López, J.A. Perdigón-Melón, A. Corma, *Micropor. Mesopor. Mater.* 22 (1998) 269.
- [4] A. Corma, A. Chica, J.M. Guil, F.J. Llopis, G. Mabilon, J.A. Perdigón-Melón, S. Valencia, *J. Catal.* 189 (2000) 382.
- [5] M.P. Elizalde-González, R. Ruíz-Palma, *J. Chromatogr. A* 845 (1999) 373.
- [6] A. Boutboul, F. Lenfant, P. Giampaoli, A. Feigenbaum, V. Ducret, *J. Chromatogr. A* 969 (2002) 9.
- [7] E. Papirer, E. Brendle, F. Ozil, H. Balard, *Carbon* 37 (1999) 1265.
- [8] A. Vega, F.V. Díez, P. Hurtado, J. Coca, *J. Chromatogr. A* 962 (2002) 153.
- [9] E. Díaz, S. Ordóñez, A. Vega, J. Coca, *Micropor. Mesopor. Mater.* 70 (2004) 109.
- [10] E. Díaz, S. Ordóñez, A. Vega, J. Coca, *Micropor. Mesopor. Mater.* 77 (2005) 245.
- [11] J. Xie, M. Bousmina, G. Xu, S. Kaliaguine, *J. Mol. Catal.* 135 (1998) 187.
- [12] O. Inel, D. Topaloğlu, A. Aşkin, F. Tümsük, *Chem. Eng. J.* 88 (2002) 255.
- [13] F. Tümsük, O. Inel, *Chem. Eng. J.* 94 (2003) 57.
- [14] E. Díaz, S. Ordóñez, A. Vega, J. Coca, *J. Chromatogr. A* 1049 (2004) 139.
- [15] F. Thielman, *J. Chromatogr. A* 1037 (2004) 115.
- [16] J. García-Martínez, D. Cazorla-Amorós, A. Linares-Solano, *Appl. Catal. B* 47 (2004) 203.
- [17] Y.-F. Chang, G.A. Somorjai, H. Heinemann, *J. Catal.* 154 (1995) 24.
- [18] K. Nowinska, A. Waclaw, A. Izbinska, *Appl. Catal. A* 243 (2003) 225.
- [19] L. Lisi, G. Bagnasco, P. Ciambelli, S. De Rossi, P. Porta, G. Russo, M. Turco, *J. Solid State Chem.* 146 (1999) 176.
- [20] R. Spinicci, A. Tofanari, M. Faticanti, I. Pettiti, P. Porta, *J. Mol. Catal. A* 176 (2001) 247.
- [21] E. Díaz, S. Ordóñez, A. Vega, J. Coca, *Appl. Catal. B* 56 (2005) 313.
- [22] E. Díaz, S. Ordóñez, A. Vega, J. Coca, *J. Chromatogr. A* 1049 (2004) 161.
- [23] R. López-Fonseca, B. de Rivas, J.I. Gutiérrez-Ortiz, A. Aranzabal, J.R. González-Velasco, *Appl. Catal. B* 41 (2003) 31.
- [24] B. Charmas, R. Lebeda, *J. Chromatogr. A* 886 (2000) 133.
- [25] E. Bechtold, in: M. van Swaay (Ed.), *Gas Chromatography*, Butterworth, London, 1963, p. 49.
- [26] A. Auroux, *Top. Catal.* 4 (1997) 71.
- [27] F. Eder, J.A. Lercher, *J. Phys. Chem. B* 101 (1997) 1273.
- [28] H. Stach, U. Lohse, H. Thamm, W. Schirmer, *Zeolites* 6 (1986) 74.
- [29] D.M. Young, A.D. Crowell, *Physical Adsorption of Gases*, Butterworth, London, 1962.
- [30] M. Huang, A. Auroux, S. Kaliaguine, *Micropor. Mater.* 5 (1995) 17.