Journal of Thermal Analysis, Vol. 37 (1991)2507-2523

HEAT OF ADSORPTION OF CARBON DIOXYDE AND ETHENE ON ZEOLITES A EXCHANGED WITH Li^+, Ni^{2+} AND Cu^{2+}

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LABORATOIRE SCIENCE DES SURFACES ET MATÉRIAUX CARBONÉS U.R.A. C.N.R.S.
N° 413 E.N.S. D'ÉLECTROCHIMIE ET D'ÉLECTROMÉTALLURGIE DE GRENOBLE,
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(Received May 31, 1991)

Various contents of Li^+, Ni^{2+} or Cu^{2+} were introduced in zeolite NaA by conventional cation exchange. Crystal damages are observed on samples having suffered the lower *pH*.

The heat of adsorption of CO_2 and C_2H_4 was determined by isothermal calorimetry. Very high initial heats (100–120 kJ mol^{-1}) are found in NaA as well as in Li^+ exchanged samples, perhaps due to chemisorption on alkaline cations; they vanish when Ni^{2+} or Cu^{2+} replaces more than 20% of Na^+, in like manner with Co^{2+} or Zn^{2+}. For the adsorption of C_2H_4, high initial heats are absent in the case of NaA, but gradually appear when divalent cations are introduced.

Apart from these strong initial values, the heats of adsorption present a plateau *vs.* the adsorbed amount. Abnormal low values at the plateau are indicative of crystal damages.

Introduction

In a previous paper [1], we have measured the heat of adsorption of CO_2 and C_2H_4 on a series of partly exchanged zeolites NaMA, where $M = Co^{2+}$ or Zn^{2+}. We evidenced the outstanding influence of the cation nature and of the exchange level: CO_2 is strongly adsorbed on a little number of peculiar sites of NaA (less than 0.3 per α cage), that are removed by cation exchange. On the contrary, the exchange of Na^+ for a divalent induces the formation of high energy sites for the adsorption of C_2H_4. Each type of site was tentatively ascribed to definite cations in some peculiar crystallographic positions.

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The aim of the present paper is to complete that work, determining enthalpies of adsorption of the same adsorbates (CO_2, C_2H_4) in NaA zeolites exchanged:

(i) with other cations of the first series of the transition metals: Ni^{2+} and Cu^{2+};

(ii) with the monovalent cation Li^+. Divalent cations with electronic configuration $3d^7$ to $3d^{10}$ (Co^{2+} to Zn^{2+}) are the most easily introduced in zeolites from all the transition metals, and may lead to interesting catalytical properties, whereas Li^+ is the only monovalent cation except Na^+ allowing adsorption in the α cage.

Experimental part

The original zeolite NaA differs slightly from the ideal formula [2] and appears decationized – or protonized – since 1.1 ±0.5 Na^+ per 12 Si, i.e. per α cage, are replaced by protons [1].

The cation exchange was performed with aqueous solutions of cation chloride as earlier described; the original zeolite was also partly recationized up to 11.4 ±0.5 Na^+ per α cage using a NaCl solution [1]. Each sample will be named Mx after the exchanging metal M and the percentage x of Na^+ exchanged (Li64, Ni6, Cu13...).

Table 1 reports the main features of the exchanging operations. As for Co^{2+} and Zn^{2+}, this operation induces a deprotonation (or a recationization) of the zeolite. The cation content may even exceed the theoretical value of 12 elementary charges per α cage, whereas the exchanging cation concentration in the solution remains below the solubility limit. The equilibrium concentration of the divalent cation is almost zero up to an exchange level of 19% (for Ni^{2+}) or 46% (for Cu^{2+}), a result which confirms the high selectivity of zeolite A towards divalent cations [3]. At higher exchange levels, the selectivity remains favourable for copper, but reverses for nickel, since the Ni^{2+}/Na^+ ratio becomes higher in the aqueous phase than in the zeolite. As expected [4], the Li^+-Na^+ equilibrium is always favourable to Na^+. In the latter cases, several exchange operations are needed for reaching high exchange levels.

After the cation exchange, the equilibrium *pH* is always basic for Li^+ introduction, basic or slightly acid for Ni^{2+}-Na^+ exchange, and reaches the most acid value (*pH* 4.6) for Cu72. For NaA in pure water, the measured *pH* is 10.7. The samples which suffered *pH*'s lower than 6.5 underwent some loss of crystallinity [5]: many X-rays reflections have disappeared for Ni54, and sample Cu72 exhibits a smooth diffraction pattern; the microporous volume measured by O_2 adsorption at 77 K markedly diminishes for Ni40 and Ni54 and collapses for Cu46, Cu72; the particle outer surface area increases with the Ni^{2+} content, and the alteration of the structure is revealed by SEM for the higher nickel or copper contents. On the contrary the most exchanged LiNaA sample (Li64) appears undamaged, although it adsorbs only slowly oxygen at 77 K. This slow diffusion is rather due to the shrinking of the unit cell (lattice parameter, NaA : 1.233 nm; Li64 : 1.203 nm [5]), or to the presence of some Li^+ in the 8 oxygen ring.

Table 1 Cation exchange data. (1): u.c. for the Pm3m space group. Numbers in parentheses are estimated standard deviations on the last digit. (*): unmeasurable concentration. (.): after several exchange operations

	Init. conc. M $mol \cdot m^{-3}$	Equil. conc. M $mol \cdot m^{-3}$	Equil. conc. Na^+ $mol \cdot m^{-3}$	Equil. pH	Na^+/u.c. (1)	M/u.c. (1)	$Na^+ + M^+$ or $Na^+ + 2M^{2+}$ per u.c.
Li6	12.8	4.2	10.3	11.5	10.1 (6)	0.507 (3)	10.5
Li7	16.0	5.5	11.6	11.4	10.0 (6)	0.623 (3)	10.6
Li8	21.3	9.4	14.6	11.4	9.8 (5)	0.71 (1)	10.5
Li9	32.0	12.3	16.4	10.6	9.7 (5)	0.88 (2)	10.6
Li14	64.0	32.2	26.9	10.3	9.1 (5)	1.88 (2)	11.0
Li23	128.0	60.5	42.4	10.1	8.2 (5)	3.99 (6)	12.2
Li27	222.2	151.3	49.1	9.6	7.8 (4)	4.2 (6)	12.0
Li64(.)	224.6	203.2	13.5	9.4	3.8 (2)	9.2 (2)	13.0
Ni6	6.7	0*	10.3	7.7	10.1 (6)	0.394 (1)	10.9
Ni12	13.1	0*	21.7	7.7	9.4 (5)	0.774 (1)	11.0
Ni19	21.6	0.2	35.4	6.9	8.6 (5)	1.26 (2)	11.1
Ni23	65.4	33.0	41.9	6.5	8.2 (5)	1.91 (3)	12.0
Ni24	130.8	93.7	38.7	6.5	8.1 (5)	2.19 (3)	12.5
Ni26	163.5	122.7	47.2	6.1	7.9 (4)	2.41 (5)	12.7
Ni40	196.8	141.0	73.9	5.9	6.3 (3)	3.30 (6)	12.9
Ni54(.)	196.8	181.6	22.6	5.9	5.0 (3)	4.20 (8)	13.4
Cu13	13.1	0*	24.4	8.2	9.2 (4)	0.775 (1)	10.8
Cu15	16.3	0*	27.9	7.6	9.0 (5)	0.966 (1)	10.9
Cu28	32.6	0*	51.6	6.9	7.6 (5)	1.932 (1)	11.5
Cu46	52.4	0.02	83.2	6.2	5.8 (4)	3.099 (6)	12.0
Cu72	90.5	9.4	130.2	4.6	3.0 (2)	4.80 (2)	12.6

The heats of adsorption were measured with an isothermal differential calorimeter (sensitivity : 74 mV·W^{-1} at 353 K, main time constant : 80 s). Zeolite samples were flushed by dry nitrogen in a fixed bed column at 673 K, quickly transferred to the calorimeter and subsequently outgassed at 473 K, 10^{-2} Pa, during about ten hours prior to be brought to the working temperature. The relative accuracy about molar heats of adsorption, either from theoretical evaluation or from reproducibility runs, is better than ±5% for adsorbed amounts ranging from 0.05 to 4 molecules adsorbed per α cage ('molecule·cav^{-1}' hereafter), and is worse out of this range.

Adsorption of CO_2

As previously found [1], the molar heats of adsorption *vs.* the adsorbed amount exhibits an abruptly falling part, followed by a plateau stretching from less than 0.4 to more than 4 molecule·cav^{-1} (Figs 1–4). The measurements were made at 293 K and 353 K. The results depend only slightly on the temperature (Fig. 1): for instance at 293 K the molar heats at 1 molecule·cav^{-1} are on average only 2.2 kJ·mol^{-1} higher than at 353 K (standard deviation: 1.7 kJ·mol^{-1} over 19 samples), and the adsorbed

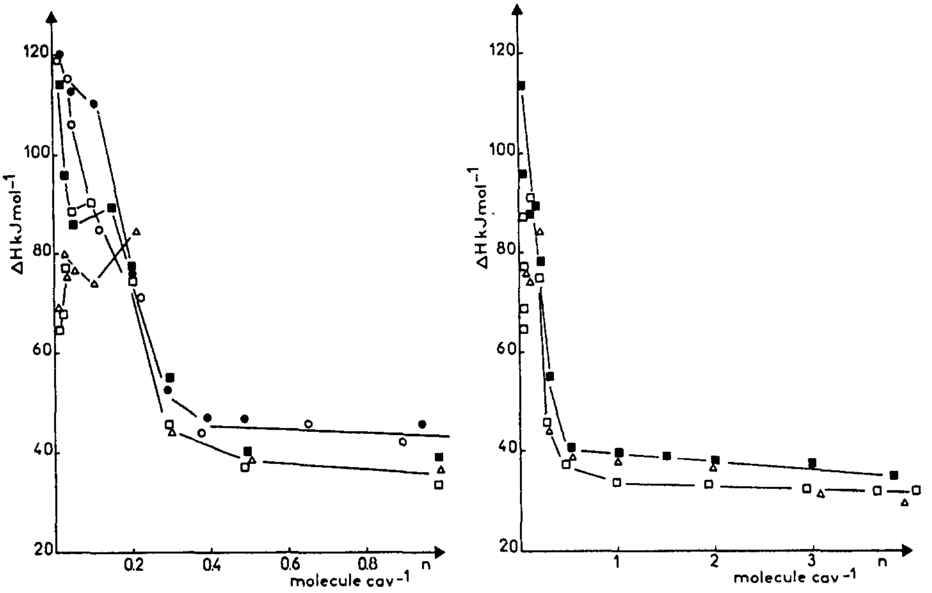

Fig. 1 Heat of adsorption of CO_2 on NaA *vs.* the adsorbed amount. (□■ ●): pristine NaA zeolite at 353 K; (o): the same at 293 K; (Δ): NaA partly recationised by Na^+ at 353 K

amounts corresponding to a molar heat of 60 kJ·mol^{-1} are 0.010 molecule·cav^{-1} lower (standard deviation: 0.024 molecule·cav^{-1}). Results at 293 K were therefore omitted on Figs 2–6. On the other hand, previous results [1] concerning Co^{2+} and Zn^{2+} are presented again in Fig. 5 (adsorbed amounts corresponding to 60 kJ·mol^{-1}, i.e. the end of the more energetic region) and Fig. 6 (heat of adsorption at the plateau, evaluated at 1 CO_2 adsorbed per α cage).

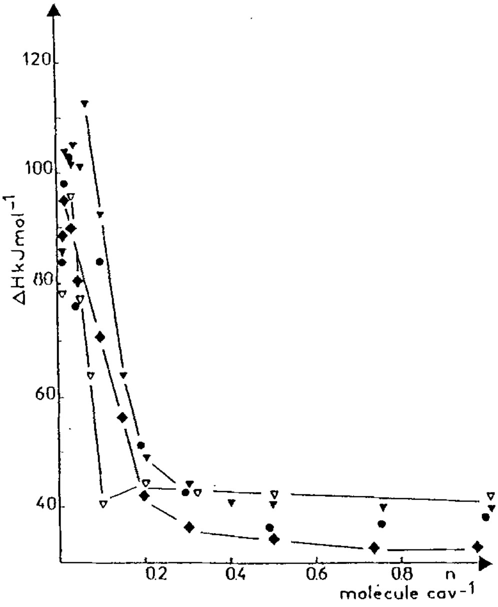

Fig. 2 Heat of adsorption of CO_2 on LiNaA zeolites at 353 K. (●): Li6; (▽): Li14; (▼): Li23; (◆): Li64

For the case of the original or recationized NaA, and LiNaA (Figs 1–2), the initial heats are high (120 to 80 kJ·mol^{-1} for NaA, more than 100 kJ ·mol^{-1} for most of the LiNaA samples), and the plateau is significantly lower (33 to 45 kJ·mol^{-1}). For LiNaA-CO_2 systems, Vasil'eva and Khvoshchev [6] do not report initial heats greter than 52 kJ·mol^{-1} for exchange levels less than 80%. The plateau in their results is somewhat higher (48 to 51 kJ·mol^{-1} at 1 molecule·cav^{-1} for 0%, 12% and 62% exchanged samples). This problem will be discussed later.

According to Masuda *et al.* [7], the high initial heats of adsorption on NaA may be ascribed to chemisorption of CO_2 in a carboxylate form linked to a Na$^+$ cation. Unlike these authors, we have suggested this peculiar Na$^+$ is in site I (axis of the six-oxygen ring) [1]. Li$^+$ is known to replace Na$^+$

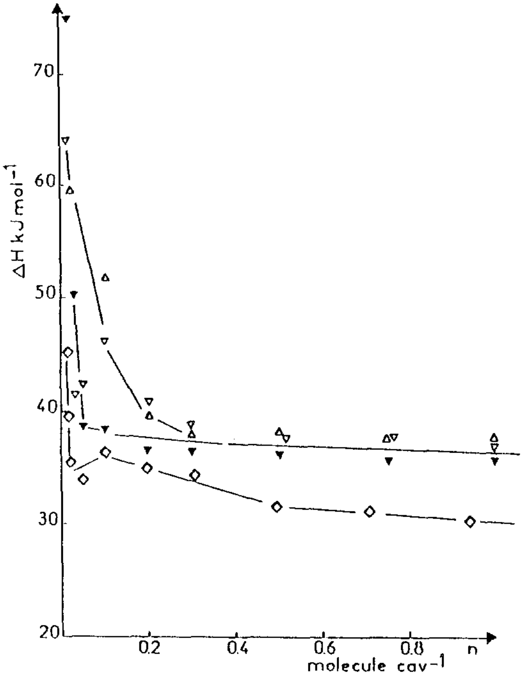

Fig. 3 Heat of adsorption of CO2 on NiNaA zeolites at 353 K. (Δ): Ni12; (∇): Ni26; (▼): Ni40; (◇): Ni54

preferentially in sites I [8–10]; as high initial heats are maintained after the introduction of Li^+, our hypothesis seems to be no longer valid. In fact, the number of adsorption sites corresponding to an adsorption heat larger than 60 kJ·mol^{-1} drastically decreases from 0.3 to 0.07 molecule·cav^{-1} (Fig. 2, Fig. 5) for low exchange levels, a result which supports our hypothesis, and then rises again and stabilizes around 0.15 molecule·cav^{-1} (Fig. 5 at 353 K; the same values are found at 293 K [1]). Thus we may view that about one half of the Na I chemisorption sites is ultimately replaced by Li I chemisorption sites. The strong polarizing power of Li^+ supports this assumption although the screening effect of the O atoms may be more effective for a little cation [6]. As a matter of fact, powder diffraction reveals that Li I and three coordinating O are displaced towards the β cage, and the three other O of the six O ring towards the α cage, when Li^+ replaces Na^+ in NaA [9]. Unfortunately no anisotropic temperature factor was evaluated, so a splitting of the Li I sites may not be discarded. On another hand, it was yet observed that the total exchange of Na^+ for Li^+ in a zeolite X increases at the same time the initial heat of adsorption (from 60 to 85 kJ per mole of CO_2) and the number of the corresponding strong adsorption sites [11], or creates such sites in a zeolite A [6]. Finally the variation in number of these sites may be due in each case to a proportion of site I cations displaced towards the α cage, which differs between the NaA (resp. NaX) and LiA (resp. LiX) zeolite: Li^+ induces a considerable contraction of the unit cell [2, 5, 9, 12, 13], which reveals significant ionic displacements in the crystal. Similarly the variation of the plateau height (Fig. 6) may probably be attributed to the same displacement and distortion effect.

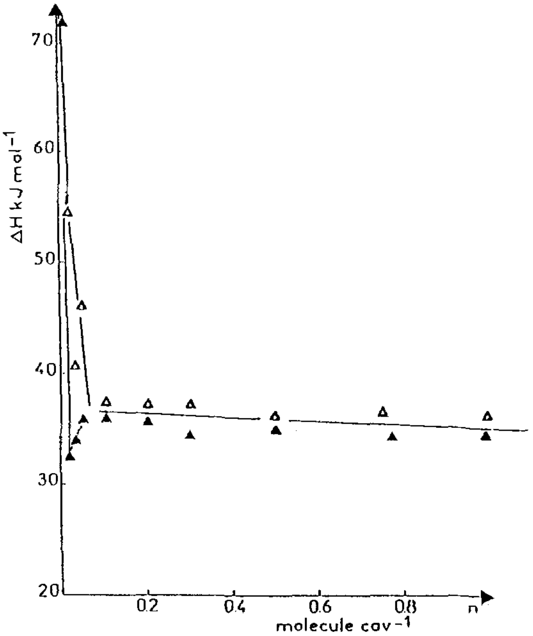

Fig. 4 Heat of adsorption of CO_2 on CuNaA zeolites at 353 K. (Δ): Cu15; (▲): Cu28

On another hand, let us examine the role of the decationisation: in NaA the number of high energy sites is essentially the same (about 0.3 per u.c in the Pm3m space group) for our two samples containing 0.6 or 1.1 proton per u.c. (Fig. 1), and for another sample with 12.1 Na^+ and 12.6 Al per u.c [14]. On the contrary such sites were not found by Khvoshchev [6] with 12.24 $Na^+$and 12.0 Al per u.c. Furthermore, the recationization markedly diminishes the initial heat of adsorption (Fig. 1). We may conclude the proton content is not directly connected to this number of sites, and that other differences in crystal may be involved.

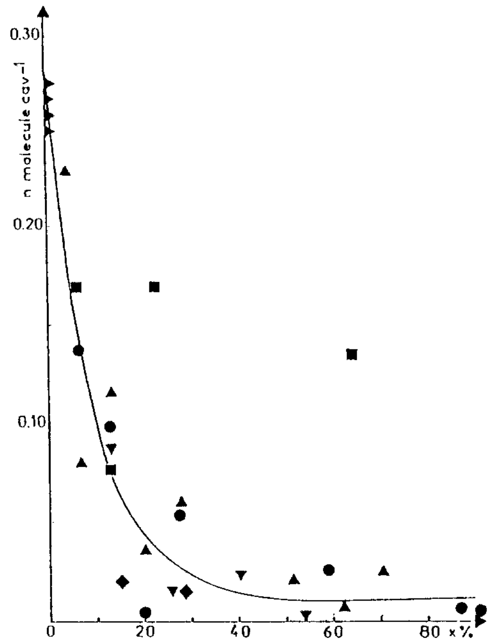

Fig. 5 Amount of adsorbed CO2 corresponding to $|\Delta H|$ = 60 kJ·mol^{-1}, at 353 K, *vs*. the ion exchange level. (►): NaA; (■): LiNaA; (▲): CoNaA; (▼): NiNaA; (♦): CuNaA; (●): ZnNaA

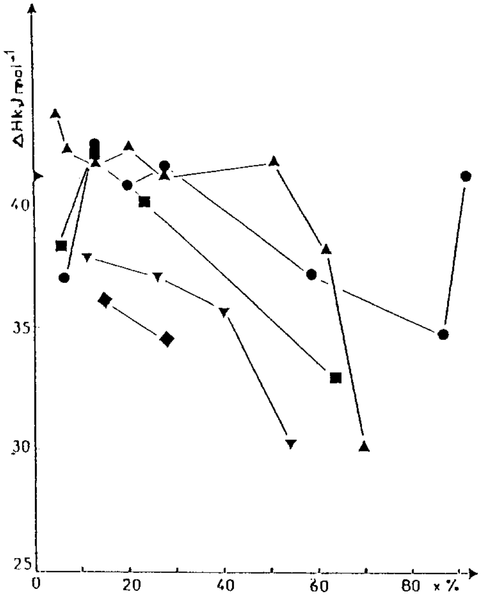

Fig. 6 Heat of adsorption of CO2 at 353 K for three CO2 adsorbed per α cage. Same symbols as in Fig. 5

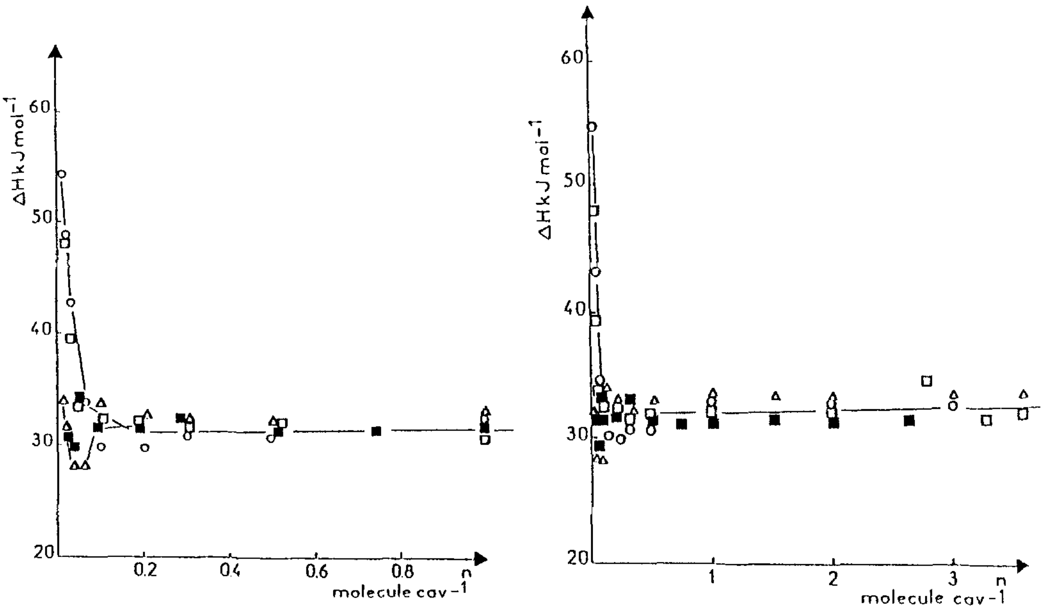

Fig. 7 Heat of adsorption of C_2H_4 on NaA *vs.* the adsorbed amount.(□ ■): pristine NaA zeolite at 353 K; (o): the same at 293 K; (Δ): NaA partly recationised by Na^+ at 353 K

For the case of NiNaA and CuNaA, there is also a sharp decrease of the heat of adsorption *vs.* the adsorbed amount, and a plateau at about 35 $kJ \cdot mol^{-1}$, except for Ni54 which presents a continuous decrease down to 30 $kJ \cdot mol^{-1}$ (Figs 3, 4). The adsorbed amounts on these samples are generally lower than on NaA and LiNaA, and could not be measured at the usual level precision farther than 1.2 $molecule \cdot cav^{-1}$ [1, 5]. As the replacement of Na^+ for Ni^{2+} or Cu^{2+} goes along, high energy sites decrease in number (Fig. 5) and practically vanish. The same was found with Co^{2+} and Zn^{2+} [1]. We therefore confirm the chemisorption sites involve the first Na^+ cations exchanged, as previously suggested in the literature [7, 11, 15, 16]. If we admit the cationic site occupation diagram proposed by Takaishi *et al.* [17] is the same for all the Na^+-divalent cation systems, the first exchanged Na^+ would be Na I and Na III. We have recently discussed the problem [1]: we discarded Na III as a chemisorption site because the site III is essentially occupied by protons; we also discarded the cationic pairs proposed by Takaishi and Endoh [18], and only retained Na I. The same conclusion was obtained by Curtenelle [10] when using the adsorption of nitrogen between 213 K and 273 K on NaA containing chemisorbed CO_2, or empty.

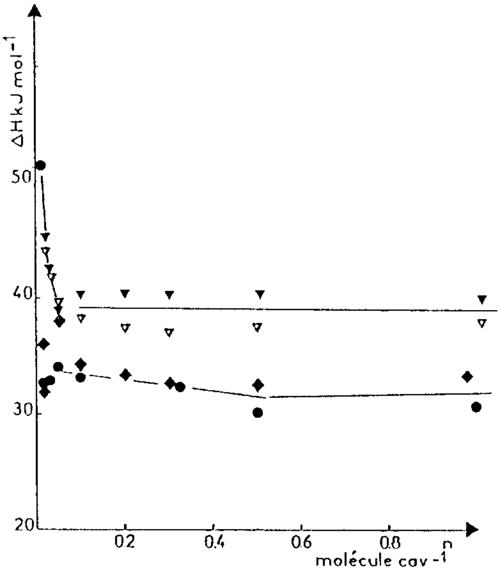

Fig. 8 Heat of adsorption of C_2H_4 on LiNaA zeolites at 353 K. (●): Li6; (▽): Li14; (▼): Li23; (◆): Li64

Despite the limited accuracy of the measurements (±2 kJ·mol^{-1}), Fig. 6 – where are gathered the results for all the cations – reveals that the plateau height generally decreases as the exchange level increases, much faster for Cu^{2+} and Ni^{2+} than for the other cations; even for the latter, the largest exchange level generally results in a drop of the plateau height. From the textural and structural study of these zeolites by X-ray diffraction, SEM and gas – O_2, N_2 – adsorption at 77 K [5, 19], it appears that at more than 40% of Na^{+} exchanged for Ni^{2+}, or 28% for Cu^{2+}, the microporous volume accessible to the adsorbate drastically decreases, and the area of the outer surface of the particles increases. This phenomenon is probably due to a crystalline damaging, or even to crystal collapse, we formerly related to the ion-exchange *pH*: the introduction of Cu^{2+} does not distort its zeolitic environment [20–23], the damaging is mainly due to the ionization of H_2O in the cages and subsequent formation of $CuOH^{-}$ [24]. Inconsistent results are found in the literature for Ni^{2+}: insensitivity [25], or more often, damaging of the crystals [4, 26] were observed. Our result (insensitivity up to 40% exhanged) is partly in agreement with the work by Coughlan [27]. A hydrolysis phenomenon is generally invoked to explain the crystal damage [27, 28]. The case of Li64 – an undamaged sample – is no doubt different, and was formerly examinated. So, for a given zeolite, the less energetic the adsorption in the plateau region is, the more damaged the crystal is.

The lower value obtained on the plateau – 30 kJ·mol^{-1} for Co62 and Ni54 – was yet found with a cation-free undamaged *H* mordenite [33], or a largely decationized, partly damaged NaHX zeolite [11]. So, this value appears the lower limit of the heat of adsorption of CO_2 when no polarizing cation is accessible on the surface of a negative framework.

Adsorption of C_2H_4

Results

As formerly found [1] for NaCoA and NaZnA zeolites, the molar heat of adsorption *vs.* adsorbed amount plots generally presents high values at low coverage, followed by a plateau beginning at less than 1 C_2H_4 adsorbed per *α* cage (Figs 7–10). The influence of the temperature may be neglected, as in the case of CO_2 (Fig. 7).

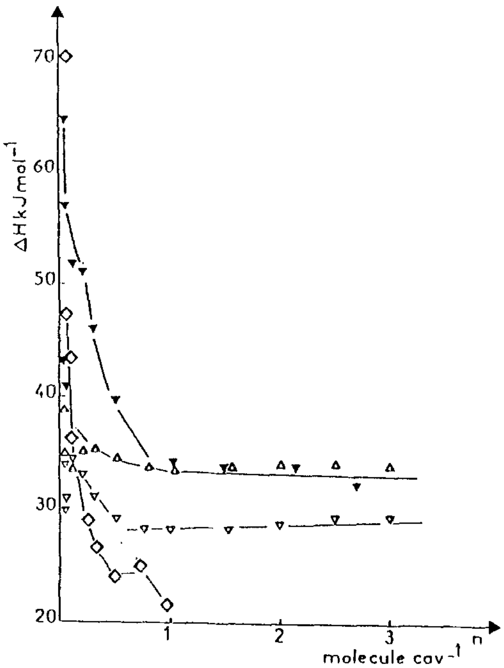

Fig. 9 Heat of adsorption of C_2H_4 on NiNaA zeolites at 353 K. (Δ): Ni12; (∇): Ni26; (▼): Ni40; (◇): Ni54

Except for Ni40, strong initial heats are found only in narrow domains (less than 0.05 molecule·cav^{-1}), where the reproducibility is not good (Fig. 7), or are absent. For Ni40, this domain is near 0.25 molecule·cav^{-1}. Initial values exceeding 70 kJ·mol^{-1}, found for NaCoA and NaZnA [1], cannot be met here.

Sample Ni54 does not present the characteristic plateau: the heat of adsorption continuously decreases down till 21 kJ·mol^{-1}, a value significantly lower than for other samples (28 to 40 kJ·mol^{-1}). The adsorbed amount at a given pressure was also lower than generally, and the experiment rather quickly stopped because the usual accuracy criterion was no longer fulfilled (Fig. 8). All these features are consistent with the formerly announced damage of the sample.

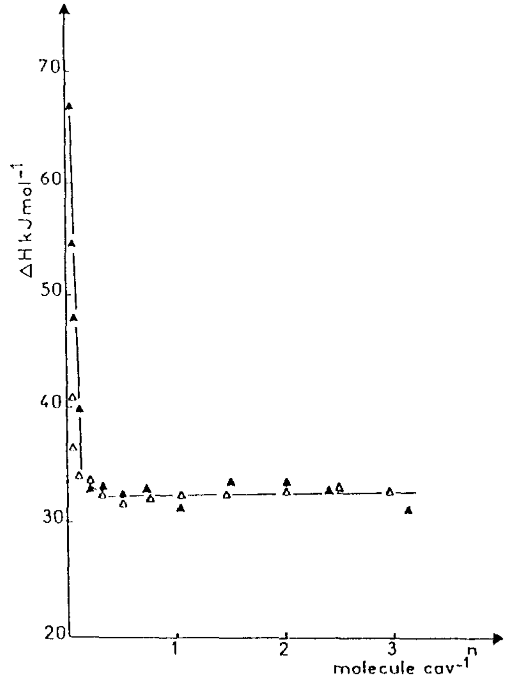

Fig. 10 Heat of adsorption of C_2H_4 on CuNaA zeolites at 353 K. (Δ): Cu15; (▲): Cu28

For other samples, the plateau experimentally extends to 3 and more molecules adsorbed per α cage. In fact, previous works evidence the saturation of zeolites NaA [14] or NiNaA [10] occurs for exactly 5 C_2H_4 per α cage. The height of the plateau at one C_2H_4 adsorbed per α cage is quite the same for NaA, Cu15, Cu28, Li6 and Li64 (about 31–33 kJ·mol^{-1}), hardly different for Ni12, Ni28, Ni40 (29–34 kJ·mol^{-1}), and really different only for Li14 and Li23 (38–40 kJ·mol^{-1}). The classification is unchanged at two C_2H_4 per *α* cage (Fig. 12), except for Li64.

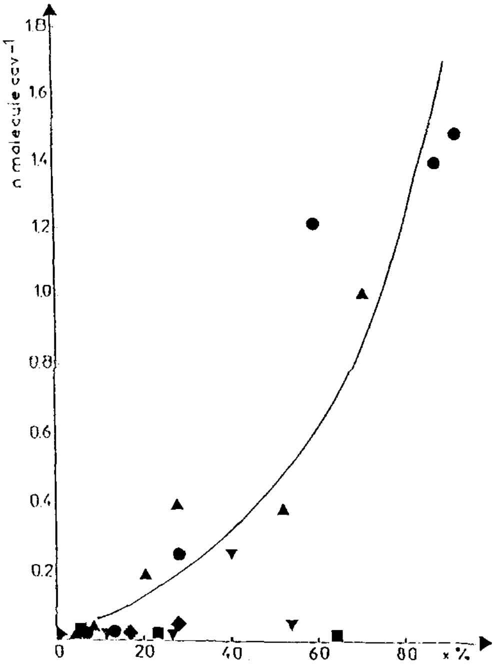

Fig. 11 Amount of adsorbed C_2H_4 corresponding to $|\Delta H|$ = 48 kJ·mol^{-1}, at 353 K, *vs.* the ion exchange level. (►): NaA; (■): LiNaA; (▲): CoNaA; (▼): NiNaA; (♦): CuNaA; (●): ZnNaA

The result for NaA at the plateau strongly departs from the isosteric heat (43–45 kJ·mol^{-1}: [14]; 42–43 kJ·mol^{-1}: [30]), a difference we cannot explain. No data are available in the literature for zeolite *A* exchanged with Li^+, Ni^{2+} or Cu^{2+}, whereas a value of 37 kJ·mol^{-1} is given in [31] for the adsorption in a zeolite *X* exchanged at 62% for Li^+. Otherwise no data exist for the initial heat of adsorption, even for NaA.

Discussion

Ethene as well as carbon dioxyde interacts strongly with the electrostatic field near cations in an undamaged zeolitic environment. The main difference is the way the adsorbate approaches the cation: CO_2, owing to its quadrupole moment, is adsorbed by an extremity, i.e. an oxygen. This was verified in NaA [14]. On the contrary, C_2H_4 is likely to be fixed flat on the cation by the middle of its double bond, as in NiNaA [32], CoNaA [33], AgA [34], CuNaA [23, 35], various cationic forms of zeolite X [36], or like C_3H_6 in NaX [34].

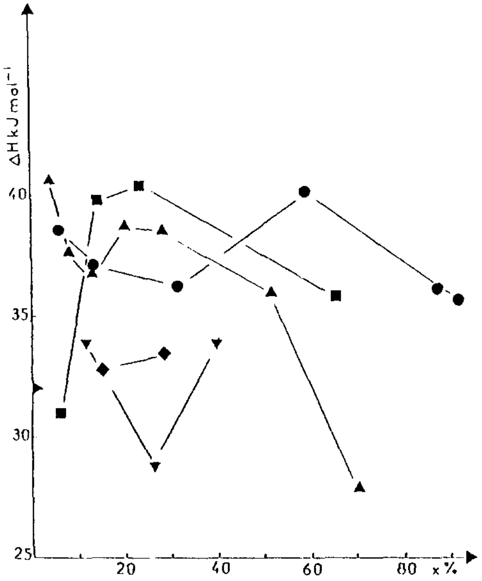

Fig. 12 Heat of adsorption of C_2H_4 at 353 K for two C_2H_4 adsorbed per α cage. Same symbols as in Fig. 11.

At first, as for the case of CO_2, the unusually low heats of adsorption of C_2H_4 are correlated to damages of the crystal structure. The damages are confirmed to appear at all the more low exchange levels since one passes from Zn^{2+}, Co^{2+} or Li^{+} to Ni^{2+} and finally to Cu^{2+}, an effect which is related to the difference in hydration and hydrolysis properties of the cations: Li^{+} does not form aquocomplex cation, contrarily to the transition metals, and Cu^{2+} is known as the most acidic cation of the first transition metal series.

Figure 11 collects the widths of the domains with heat of adsorption of C_2H_4 greater than 48 kJ·mol^{-1} for all the cations we have studied. Literature data indicate the heat values found are not indicative of chemisorption [1]. The result for Ni40 is consistent with the mean curve drawn for Co or Zn exchanged samples [1]. On the contrary, for the too undamaged Ni26 and Cu28 samples, the high energy domain is significantly narrower than for samples equally exchanged by Zn^{2+} or Co^{2+}. These differences have to be explained: a strong interaction involves the adsorbate can approach a highly polarizing zeolitic cation. Cu^{2+} is the less easily dehydrated of the cations we studied: it makes complexes with water, hydroxyles, zeolitic oxygens, and even forms Cu–O–Cu chains on outgassing the zeolite [24]. A zeolitic copper therefore carries a lesser electrical charge than a fully dehydrated cation, and is difficultly approached. From our results, the dehydration obviously becomes easier with Ni^{2+} and moreover Co^{2+} and Zn^{2+}.

Li^+ does not give rise to a strong interaction with C_2H_4 (Fig. 11), although it may be entirely dehydrated in the zeolite. As formerly suggested, some of the lithium cations are likely unaccessible to C_2H_4 as well as to CO_2, because they are displaced from the six-oxygen ring (site I) to the β cage. The remaining cations, due to their small size, are placed in the six-oxygen ring without protruding into in the α cage. From powder diffraction three O of the six oxygen ring are shifted towards the α cage by about 0.04 nm from the mean plane determined by the three other oxygens and LiI [9]. Thus Li^+ is accessible to an extremity of CO_2, but cannot come into close contact with the C_2H_4 molecule because of the three O barrier. Such a barrier effect does not come into play for the larger transition metal cations, because the six-oxygen ring is not as much distorded.

For the plateau height now, it may be observed (Fig. 12) that all the Li (except Li6), Co (except Co62), and Zn samples correspond to more than 35 $kJ \cdot mol^{-1}$, whereas Cu and Ni samples are near the value for NaA, a grading which is as a whole consistent whith the former considerations.

In two previous works a simple model was proposed for the adsorption of C_2H_4 in NaA between 273 K and 353 K [14], or in NiNaA samples exchanged up to 32% at 273 K [10], involving localized adsorption on five identical sites per α cage, with a small attractive lateral interaction (i.e. attraction between neighbouring adsorbed molecules). These features suffice to quantitatively describe the adsorption isotherms and the flat part of the heat of adsorption *vs.* adsorbed amount plot. The only problem was the identification of the five adsorption sites, which could not be finalized; here again, no conclusive argument allows one to choose between sites I and sites II.

As a conclusion, Ni^{2+} and especially Cu^{2+} behave rather differently from Co^{2+} and Zn^{2+}. Although they displace the peculiar Na^+ cations responsible for the CO_2 chemisorption as well as the latter do, their introduction difficultly gives rise to high energy adsorption centers for C_2H_4, unlike Co^{2+} and Zn^{2+}. Li^+ in some sites I, owing to its small size, is a high energy adsorption center accessible to CO_2, not to C_2H_4. finally, we evidenced the adsorption calorimetry is relevant to detect crystal damages, which is related to oddly low heats of adsorption.

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Zusammenfassung — In einen Zeolith NaA wurden durch herkömmlichen Kationenaustausch ein verschiedener Gehalt an Li^+, Ni^{2+} oder Cu^{2+} eingebracht. Kristallschäden wurden an Proben beobachtet, die einem niedrigerem pH ausgesetzt waren.

Mittels isothermer Kalorimetrie wurde die Adsorptionswärme von CO_2 und C_2H_4 bestimmt. Sowohl bei NaA als auch bei Li^+substituierten Proben wurden sehr hohe Initialwärmen (100-120 kJ/mol) gefunden, was vielleicht mit der Chemisorption an Alkalikationen zu tun hat; diese verschwinden, wenn mehr als 20 % Na^+ durch Ni^{2+} oder Cu^{2+}, in ähnlicher Weise

durch Co^{2+} oder Zn^{2+} ersetzt werden. Für die Adsorption von C_2H_4 fehlen im Falle von NaA hohe Initialwärmen, treten aber nach und nach auf, wenn bivalente Kationen eingeführt werden.

Weitab von diesen hohen Anfangswerten zeigen die Adsorptionswärmen keine Abhängigkeit von der adsorbierten Menge. Abnormal niedrige Werte auf diesem Plateau sind ein Indikator für Kristallschäden.