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CHEMISORPTION AND PHYSISORPTION OF CO_2 ON CATION EXCHANGED ZEOLITES *A*, *X* AND MOR

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Calorimetric measurements of the heat of adsorption of CO_2 on zeolites with variable content of mono- and divalent cations lead to common conclusions. High initial heats (up to 120 $kJ\cdot mol^{-1}$ for NaA), generally associated with a slow and activated rate of adsorption, are found for high contents of Na^+, Li^+ or Ca^{2+}. They are attributed to a limited number of chemisorption sites (0.3 per α cage in NaA).

Physisorption results in lower heats (25–50 $kJ\cdot mol^{-1}$). The lowest values are obtained with partially or totally decationized zeolites. Transition metal cations induce frequently weaker interactions than IA or IIA. Finally the stronger the energy of adsorption is, the larger the adsorbed amount is.

Keywords: chemisorption, physisorption, zeolites

Introduction

Cations in zeolites are known to bring out strong interactions with polar or easily polarizable adsorbates. This is the main reason why zeolites with high cation content, i.e. low Si/Al ratio, are frequently used in gas separation processes. According to the Loewenstein rule (Si/Al $\geq$1) and to the criterion, the best adsorbent is zeolite type *A* (Si/Al $\approx$1), but *X* type (Si/Al $\approx$1.25) and mordenites (Si/Al$\approx$5) are also commonly used.

Carbon dioxide is present in many gas mixtures. Its linear molecule has an important quadrupole moment, which interacts strongly with the gradient of the electric field induced by the cations, as revealed by infrared studies in zeolites A [1], *X* and *Y* [2–7], and confirmed by theoretical evaluations of the energies of adsorption in zeolite *A* [8] and mordenite [9]. The physisorbed state of CO_2 is commonly described by a linear complex [7]:

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$$(\text{cation})...O = C = O$$

Chemisorption of CO_2 was also detected by infrared studies, else as a carboxylate form, in NaA [1d, 10], NaX and some Ca-poor NaCaX [2, 3, 11], else as a carbonate form, in Ca-rich zeolites NaCaA [1d, 10] and NaCaX [3]. The latter form generally occurs at high temperature, and is more stable [3, 10] than the former. Carbonate formation involves pulling out of oxygen from the zeolitic framework [12, 13].

The aim of this paper is to measure the heat of adsorption of CO_2 on common zeolites *A*, *X* and MOR, as a function of the cation content, for a variety of cations, and to relate it to physisorption and chemisorption, in relation with the polarizing power of the cations. Calorimetry is a direct mean for investigating the adsorbate-adsorbent interaction. Concerning CO_2, it was mainly used for zeolites containing IA and IIA cations, or decationized (zeolites *A*: [14–21]; *X*, *Y*: [14, 15, 17, 22–24]; MOR: [14–17, 23, 25–27].

Experimental

We used an isothermal calorimeter [28] (main time constant: 80 s, sensitivity: around 75 $mV \cdot W^{-1}$, slightly dependent on the cell temperature). Owing to its differential design, the integrated thermal effect is proportional to $|\Delta H|$ for the adsorbed amount [30, 31]. Doses of adsorbate were sequentially introduced. The adsorbed amounts were obtained by the manometric technique from an *in situ* material balance [29–31]. To insure optimal accuracy, the isotherm of adsorption was determined only in regions for which more than one third of the doses introduced was adsorbed at equilibrium. Accuracy on molar ΔH is ±5%. The time to establish thermal and pressure equilibrium ranged from 15 min to one hour. Long equilibration times were generally attached to high molar energies and ascribed to chemisorption.

We also used a more sensitive apparatus (Micromeritics 2100) to determine some adsorption isotherms (adsorbed amount *vs.* pressure) in a large range of equilibrium pressure [29–31].

The starting zeolitic materials for ion exchange were in a powder form: NaA, NaX and NaCaX from Linde, hydrogen mordenite (H-MOR) from Société Chimique de la Grande Paroisse (Si/Al = 5.6), or Zeocat (Si/Al = 5.5). The exchange for cation *M* was obtained conventionally, using MCl or MCl_2 (zeolites *X*: [30], *A*: [31–33] or LiOH and NaOH in the special case of H-MOR. Samples were flushed by dry nitrogen in a fixed bed column at 673 K prior to be transferred in the calorimeter, and finally outgassed under vacuum at 473 K for 10 hours.

Results and discussion

Zeolite A

As indicated in Fig. 1, some NaA samples exhibit an initial heat of adsorption as high as 110–120 kJ·mol^{-1}, in agreement with Masuda *et al.* (128 kJ·mol^{-1}, [10]. Some runs give lower values (80–90 kJ·mol^{-1}). Nevertheless, the region of high adsorption energy always abruptly finishes at ca. 0.3 CO_2 pert α cage. It is followed by a plateau at ca. 40 kJ·mol^{-1}, up to 3–4 CO_2 per α cage. The same plateau is observed at ca. 30–40 kJ·mol^{-1} in all the cation exchanged NaMA samples. On the contrary, the initial region gets narrower and narrower when sodium is exchanged for transition metal cations (Ni^{2+}, Cu^{2+}: Fig. 1 and [33]; Co^{2+} and Zn^{2+} [32]. It vanishes when the exchange level reaches ca. 20%. Li^{2+} causes a less pronounced narrowing (only by 50% up to the exchange level 64%).

According to Masuda [10], who combined calorimetry and IR spectroscopy, the plateau corresponds to physisorption only, a statement corroborated in our case by:

i) the moderate value of $|\Delta H|$, compared to the latent heat of sublimation: 25.1 kJ·mol^{-1} at the triple point;

ii) the rapidity of the adsorption. The height of the plateau is not obviously related to the cationic population (Fig. 1, [32, 33].

The initial high value of $|\Delta H|$ in NaA at ambient temperature is ascribed to the formation of a carboxylate [10] on a site which is eliminated by divalent cation exchange. Masuda identifies this site with Na_{III}, the more labile Na^+, present on only one site per α cage in NaA. Takaishi [13] ascribes the chemisorption site to cationic pairs, mainly Na_I-Na_{III}. In fact, we find only 0.3 high energy site per α cage using different NaA samples:

i) a sample with 10.9 Na^+ per α cage, instead of 12 in the ideal structure (Fig. 1);

ii) the same, recationized up to 11.4 Na^+ per α cage (Fig. 1);

iii) another one with 12.1 Na^+ and 12.6 Al per 12 Si [29] (Fig. 2). In the latter case, the proof is given by the transitional plateau at 0.3 CO_2 per α cage on the adsorption isotherms between 110° and 195°C in a log-log plot; on the opposite, isotherms for zeolite 5A, i.e. NaCaA, follow the Henry law up to about

1 CO_2 per α cage. As a conclusion, no final assignment of the chemisorption center to a definite crystallographic site may be made.

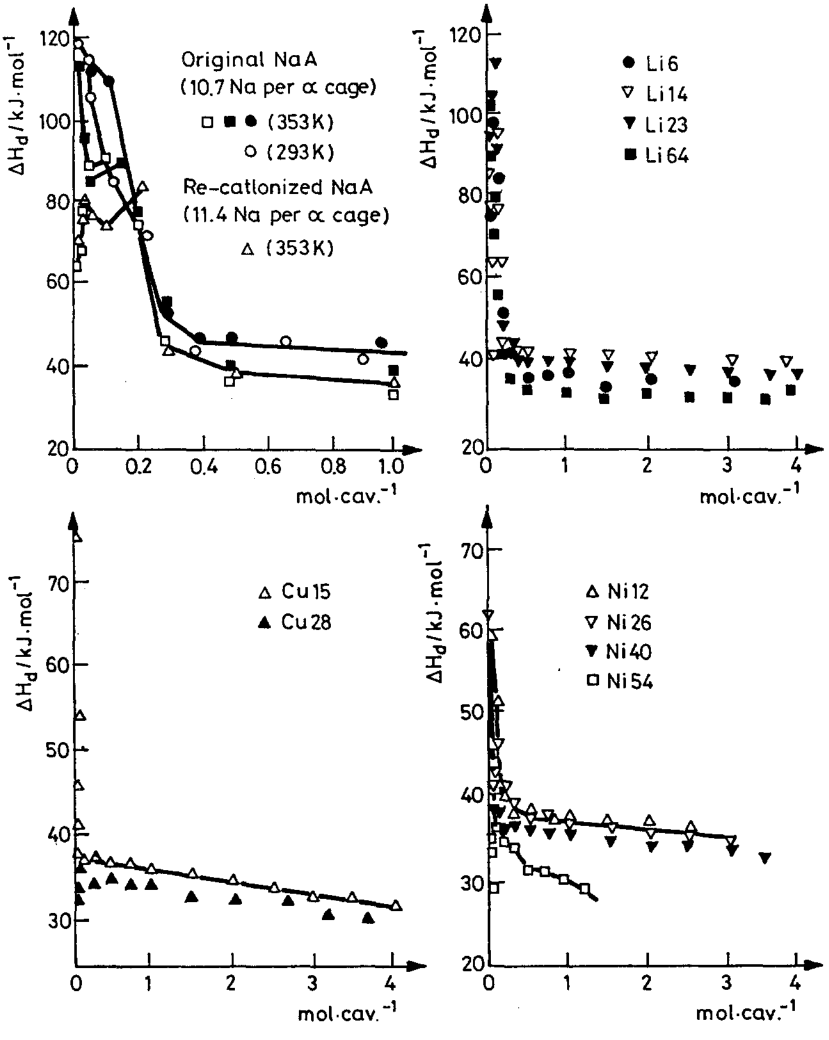

Fig. 1 Heat of adsorption of CO_2 at 353 K zeolites NaMA, *vs.* the adsorbed amount. M = Li, Co, Ni, Zn. Samples are referred to as: Mx (x = percent of Na exchanged for M)

Zeolites X

At low adsorbed amounts on NaX, high energies of adsorption and low adsorption rates could be observed, but only if the temperature was high enough

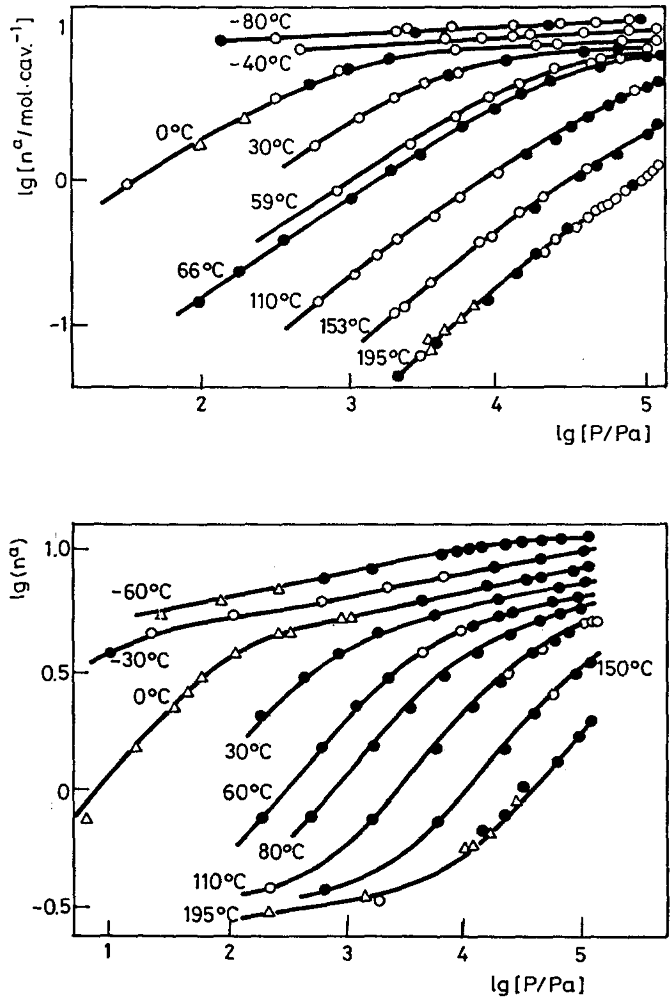

Fig. 2 Isotherms of adsorption of CO_2 on zeolite 5A (left) and 4A (right). Solid lines correspond to a theoretical model [29]

(Fig. 3). At low temperature the slow adsorption process was hidden by the quicker low-energy process. By IR spectroscopy, Jacobs [5] evidenced the formation of carboxylate from the ambient to 200°C, involving $3CO_2$ chemisorbed by u.c. Carboxylate disappears when Na^+ is exchanged at a sufficient level; for Ca^{2+} or a monovalent cation [5]. IR also evidenced two kinds at least of linear (physisorbed) CO_2 in NaX [5, 6], one of them being similar to free CO_2. We may tentatively ascribe the higher adsorption energies found here (say, more than 60 $kJ \cdot mol^{-1}$) to chemisorption, and the lower energies (less than

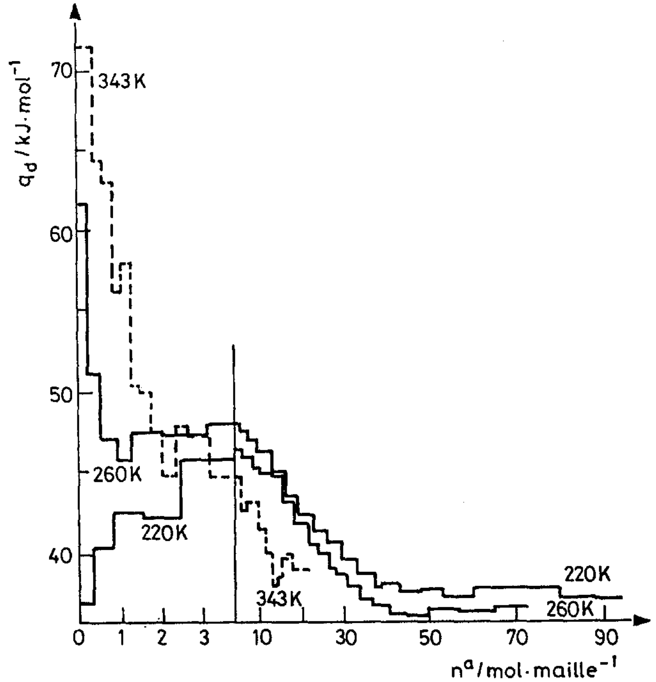

Fig. 3 Heat of adsorption of CO_2 on zeolite NaX *vs.* the adsorbed amount and the temperature

50 kJ·mol^{-1}) to physisorption. As experiments were reproducible after an overnight outgassing at 200°C, the chemisorbed species is probably carboxylate.

In Fig. 4 the following characteristics appear:

i) high energies vanish when Na^+ is replaced by K^+, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or when NaX is decationized *via* heating of $NaNH_4X$. On the contrary, quite a total exchange for Li^+ makes the high energy domain stronger and broader. So, only Na^+ and Li^+ appear to be involved in chemisorption sites.

ii) in the low energy region, no peak is found, contrarily to [14–15]. Well defined plateaus are less frequently encountered than for *A* zeolites. Physisorption appears to be more heterogeneous. As many cations in *X* zeolites are hidden in sites I and I', less cations are accessible to CO_2, including energetic heterogeneity in the adsorbed phase.

iii) decationization of NaX reduces the electric field in the micropores and consequently $|\Delta H|$ at the plateau: the lowest values (30–35 kJ·mol^{-1}) are obtained for a sample decationized at 47%. Replacement of Na^+ for Co^+ also decreases the physisorption heat, according to the exchange level. A smaller decrease is observed when Ca^{2+} replaces Na^+. For comparable exchange levels, Cu^{2+} reduces more than Ni^{2+}. As transition metals in the zeolitic water form hydrocations only partly destroyed by outgassing [34], these cations have a less polarizing effect than cations IA and IIA. Cu^{2+} is specially known to make

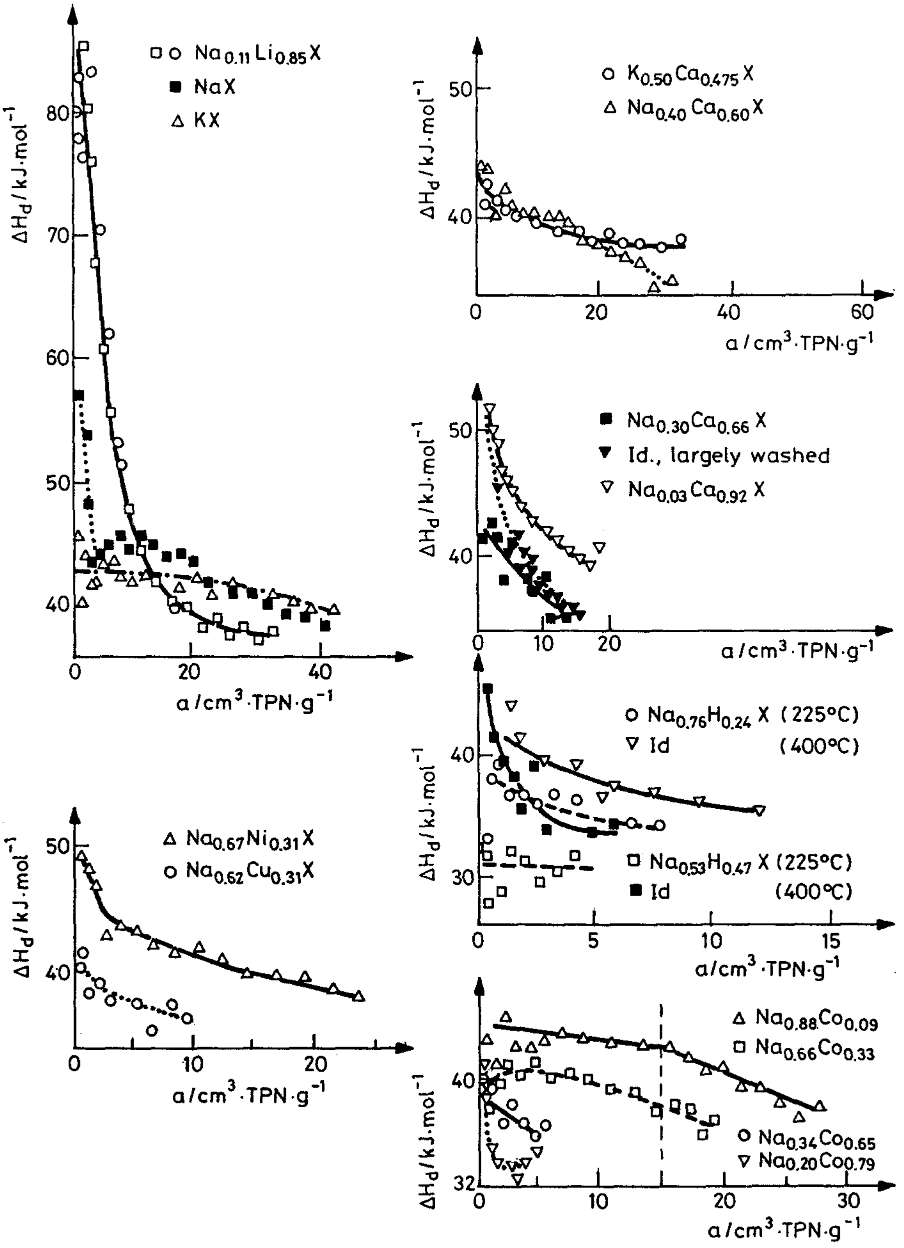

Fig. 4 Heat of adsorption of CO_2 at 343 K on zeolites NaMX, *vs.* the adsorbed amount. M = H, Li, K, Ca, Ni, Cu

Cu–O–Cu bridges upon dehydration [34], losing most of its polarizing power. Finally, a general trend is: the more polarizing the cation is, the stronger the heat of adsorption is.

Mordenites

Chemisorbed forms of CO_2 have not been reported for mordenites, and somewhat lower experimental temperatures were used (Figs 5–7). $|\Delta H|$ again continuously decreases with the adsorbed amount (Figs 5, 6), and displays no peak,

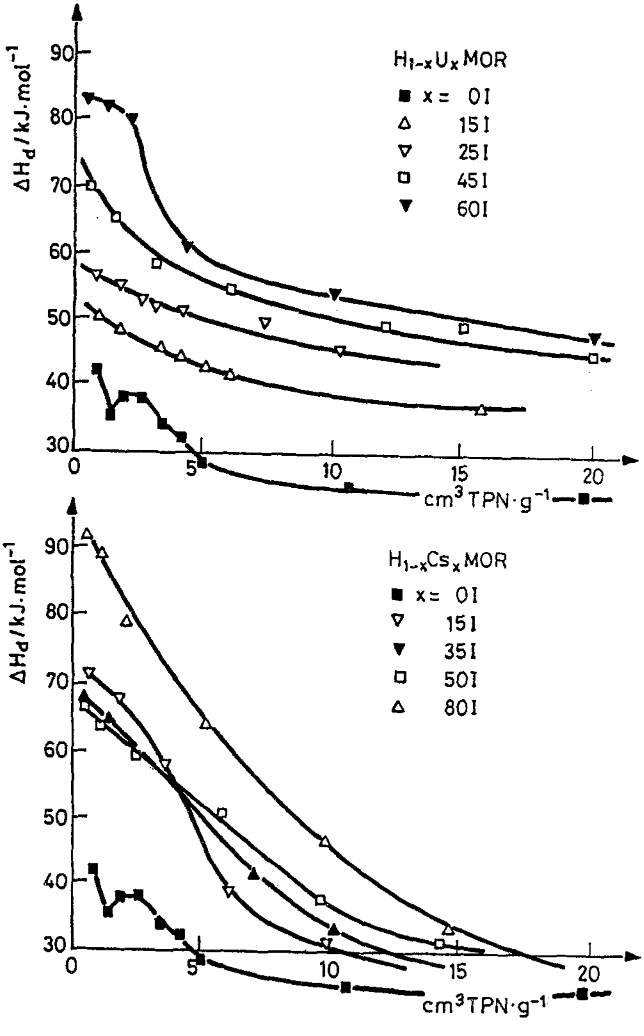

Fig. 5a,b Heat of adsorption of CO_2 at 303 K on Li, Na, Ca cation-exchanged mordenites, *vs.* the adsorbed amount contrarily to [14, 16, 27], in agreement with [23, 25, 26]. For the totally decationized samples, $|\Delta H|$ is at a very low value: 25–40 kJ·mol^{-1} (Si/Al = 5.5, Fig. 5), or 30–35 kJ·mol^{-1} (Si/Al = 5.6, Fig. 6). When H-MOR is exchanged for Li$^+$, Na$^+$ or Ca^{2+}, the curves get steeper and steeper. For a given adsorbed amount, the adsorption energy monotonely increases with the exchange level (except in the low adsorbed amount domain for Ca^{2+}) (Fig. 5). Although no slow

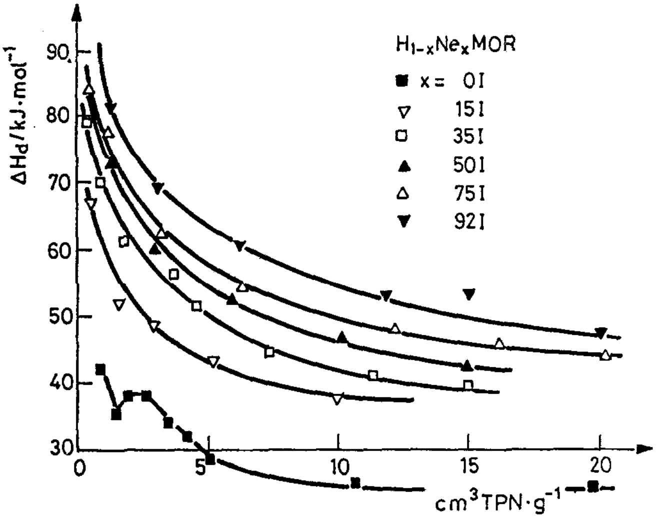

Fig. 5c Heat of adsorption of CO_2 at 303 K on Li, Na, Ca cation-exchanged mordenites, *vs.* the adsorbed amount

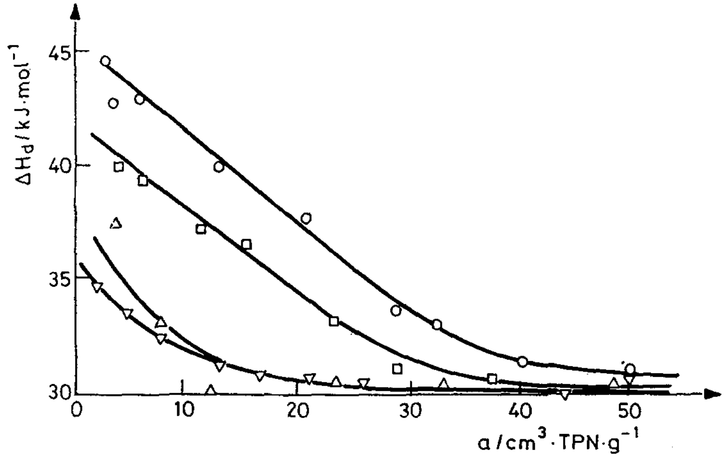

Fig. 6 Heat of adsorption of CO_2 at 303 K on mordenites *vs.* the adsorbed amount ∇: 100% H mordenite Δ:2%Ni □:17% Cu; o:19% Co

process was detected, values as high as 80–90 kJ·mol^{-1} were observed for the more exchanged samples. Exchange for Cu^{2+} or Co^{2+} also enhances the heat of adsorption and makes the curves steeper (Fig. 6); for a similar exchange level, Cu^{2+} is less effective than Co^{2+}.

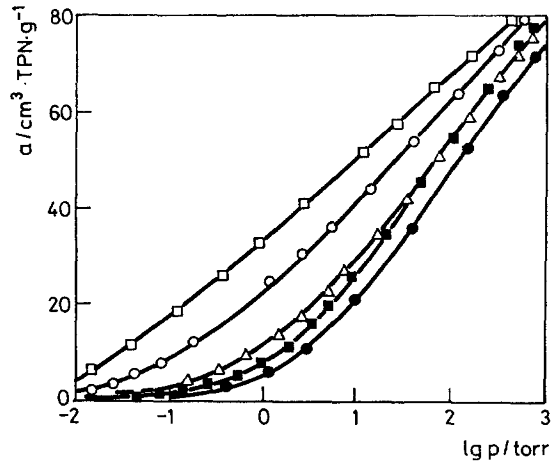

Fig. 7 Isotherms of adsorption of CO_2 at 273 K on $H_{1-x}Na_x$ mordenites *vs*. the exchange level. x = • 4%; ■ 9%; Δ 18%; o 43%; □ 63%

All the cations in mordenite are accessible to CO_2, even when located in sites I (six oxygen rings), the most stable site for cations [35]. Two conclusions arise:

i) the higher heats of adsorption concern strongly polarizing cations, probably in the most accessible sites.

ii) the relation between the cation features and the heat of adsorption appears even clearer than for zeolite *X*, as no cationic site is hidden.

Finally, Fig. 7 presents the evolution of the isotherm of adsorption on HNa-MOR *vs*. the Na^+ content: at a given temperature and pressure, the higher the Na^+ content, the higher $|\Delta H|$ (Fig. 6), the higher the adsorbed amount. This is a rather general trend and was observed on a number of samples [30, 31]. As a practical consequence, calorimetry may be used for selecting adsorbents.

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Zusammenfassung — Kalorimetrische Messungen der Adsorptionswärme von CO_2 an Zeolithen mit einem unterschiedlichen Gehalt an ein- und zweiwertigen Kationen führen zu allgemeinen Schlußfolgerungen. Für einen hohen Gehalt an Na^+, Li^+ oder Ca^{2+} werden hohe Initiierungswärmen (bis zu 120 $kJ\cdot mol^{-1}$ für NaA) gefunden, die immer in Verbindung mit langsamen und aktivierten Adsorptionsgeschwindigkeiten auftreten. Dies wird einer begrenzten Anzahl an Stellen für die Chemisorption zugeschrieben (0.3 pro -Cage in NaA). Physisorption verursacht niedrigere Wärmen (25-50 $kJ\cdot mol^{-1}$). Die niedrigsten Werte erhält man mit teilweise oder total entkationisierten Zeolithen. Kationen von Übergangs-metallen verursachen häufig schwächere Wechselwirkungen als IA- oder IIA-Kationen. Je höher die Adsorptionsenergie, um so größer ist die adsorbierte Menge.