

Differential Heat of Adsorption and Isotherms of Carbon Dioxide on Synthetic Mordenite

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ABSTRACT

Differential heats of adsorption of carbon dioxide on synthetic mordenite were calorimetrically measured over 10^{-5} atm $< P < 1$ atm and $-77^{\circ}\text{C} < T < +120^{\circ}\text{C}$; adsorption isotherms were determined over 10^{-5} atm $< P < 50$ atm and $-77^{\circ}\text{C} < T < +160^{\circ}\text{C}$. Integral molar entropy, specific heat and density of adsorbed phase were calculated.

Introduction

Differential heats of adsorption of carbon dioxide on synthetic mordenite were calorimetrically measured. Thermal properties give information about adsorbent-adsorbate interactions. Owing to carbon dioxide characteristics, a large range of temperature and pressure can be explored. Consequently, adsorption isotherms were determined from 10^{-5} atm to 50 atm and thermal properties were measured up to 1 atm. Temperatures range from -77°C to $+160^{\circ}\text{C}$.

Experimental

Apparatus. Sorption and thermal measurements were made at the same time between 10^{-2} and 5 torr with a microcalorimeter connected with a classical volumetric system.

Pressure variations were measured, and knowing all different apparatus volumes, adsorbed amounts were calculated using the ideal gas law. We used a differential microcalorimeter devised by Barberi (1) and commercialized by Arion-Electronique.

Thermal effects were also measured up to 1 atm, using known adsorbed amounts which had been thermogravi-

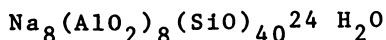
metrically determined. Between 1 and 760 torr, mass variations were measured with a McBain type balance.

A volumetric sorption system is perfected to measure adsorbed amounts from 1 atm up to 50 atm (2). Absolute adsorption was obtained from pressure variations and by measuring gas volumes at atmospheric pressure.

Experimental conditions and evaluations. Before each sorption run, the sample was evacuated by an oil diffusion pump to 10^{-5} torr at $+400^{\circ}\text{C}$ for ten hours. The sample weight was 0.1 g or 0.2 g. The accuracy in the amount adsorbed does not exceed 5% up to 1 atm and 10% above.

With calorimetry the heat quantity ΔQ is measured as a function of the number of moles adsorbed on. The ratio $\Delta Q/\Delta n$ will be closer to the differential of heat adsorption dQ/dn as Δn is smaller. This isothermal technique is such that it has a Δn value of about 10^{-4} mole per gram of anhydrous zeolite, and ΔQ of about 1 cal. The accuracy of these thermal effects measurements is about 10% (3).

Materials. The zeolite we study was synthetic mordenite with the formula:



for a unit cell. It was a powder produced by the CECA Society (4). Its crystal structure has been studied by Meier (5). The structure consists of infinite chains of (AlO_4) tetrahedra, so that a two dimensional channel system appears. The main channels parallel to the c-axis are linked by small channels parallel to the a-axis. These channels have an approximately elliptical opening with a major and minor diameter of 6.95 Å and 5.81 Å for the main channels 4.72 Å and 3.87 Å for the small ones. The volume of these channels is 0.156 cm^3 per gram of anhydrous zeolite. This number was calculated (6) and measured by adsorption of different gases (7).

Differential heats of adsorption

Differential heat curves were plotted against the number of moles adsorbed over the range $-77^{\circ} + 120^{\circ}\text{C}$. Separate curves are obtained for each temperature. They have the same shape with three main features (Figure 1):

- Differential heat has a high value for the initial adsorbed molecules and then decreases.
- it increases again and rises to a maximum.
- then it decreases continuously to a constant value.

Initial range. Interactions between carbon dioxide and the crystal has four components: dispersion and short-range repulsion energies Φ_D and Φ_R , polarization energy Φ_P , and quadrupole energy Φ_{FQ} . Interaction energy between pairs of carbon dioxide molecules may be omitted, because we shall be concerned only with the determination of initial heats (i.e., heats as the adsorbed amount approaches zero).

Barrer and Gibbons (8) have calculated these energies for CO_2 sorbed by ion-exchanged faujasite. Their results indicate that the most important part is played by quadrupole energy Φ_{FQ} . These interactions which seem to be associated more with the quadrupole moment of the CO_2 molecule than with zeolite, may be related to the very high initial values observed. This first range is characteristic of a strong adsorbent-adsorbate interaction. The internal electrostatic field is stronger near sodium ions ensuring crystal-electro-neutrality. Consequently these ions may be energetically active centers leading to a strongly localized adsorption.

Taking important relative variations of q_p into account, these curves exhibit a heterogeneous surface character for the initial adsorbed molecules and at the highest temperatures.

Maximum range. When the most energetic centers are occupied, interactions between adsorbed molecules increase, and so does q_p . Curves show very marked maxima. This may be the consequence of increasing interactions leading to a new kind of sorption with different energetic features. Such a pronounced maximum at high temperatures is unusual. However, Kington and MacLeod (9) have also noted it with carbon dioxide sorption by chabazite at 0°C . This range would be typical of strong adsorbate-adsorbate interactions with a new arrangement of adsorbed molecules leading to a new kind of sorption with different energetic features.

In the first range, centers have very different and high energies, whereas after the maximum, centers have lower energies, which are similar to each other. This change in the sorption energetic features can be seen from the important maximum noted on the curves.

Terminal range. In this terminal part of the curve, the differential heat has small variations with increasing amount adsorbed. At any temperature the solid shows a homogeneous surface in this range; q_p values have the magnitude of heats of liquefaction corresponding to the transition of molecules from the

gaseous to the liquid phase. For each temperature, the differential heat tends toward a constant value.

Temperature influence. The important point as evidenced in Figure 1 is that the curves are distinct for each temperature. Few studies gave us informations about temperature influence around the critical point. We can refer to Huang and Zwiebel about CO_2 and SO_2 with H-mordenite (10). For ammonia adsorption by NaA zeolite there are also different curves for each temperature (11). On the other hand indistinguishable curves are found for nitrogen adsorption by silica-gels. However, the temperature variation is small, and the temperature itself is near the adsorbate boiling point (12).

"Initial heat" is frequently obtained by extrapolation of the q_D vs. n curve to $n = 0$. In our case, differential heats show important variations for initial adsorbed molecules, and it is difficult to extrapolate such curves. Qualitatively it appears that the initial value is higher at higher temperatures. This shows that adsorption centers seem to have higher energies at high temperatures, and the surface appears more heterogeneous.

The maximum value of q_D increases as the temperature rises. This behavior is characteristic of strong interactions of the adsorbate-adsorbate type. Thus molecular motion becomes more intense as the temperature increases, limited by the degrees of freedom allowed by adsorption; so interactions are all the stronger.

Instead of plotting differential heats against n , it is possible to plot against degree of coverage $\Theta = n/n_0$. n_0 is the maximum number of adsorbed molecules at temperature T , experimentally determined from isotherms plotted up to 50 atm., where saturation vapor pressure is reached or where adsorption isotherms level out, above critical point.

These maxima are for lower Θ values as the temperature is raised. If we assumed that formation of a condensed phase occurs at the maximum, this would appear at a higher degree of filling at high temperature, i.e. contrary to observations. At the opposite, an energetic distribution of the sites involved by temperature, superposed upon a numerical distribution in relation to their respective energies can explain the initial shape of the curves of differential heats, and their positions in relation with one another.

At temperature T , for a monolayer on a heterogeneous surface the number of sites N_1 of energy E_1 may be

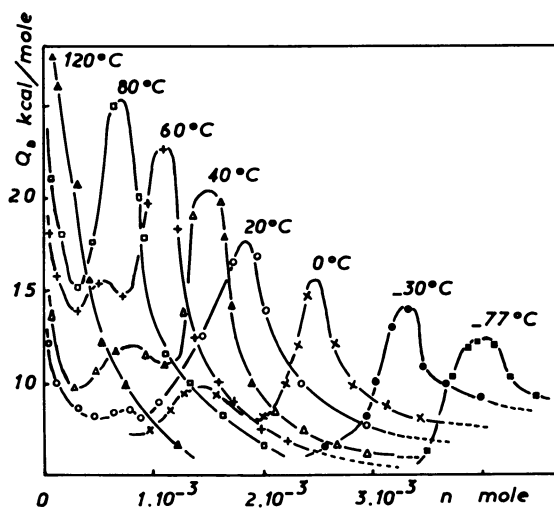


Figure 1. Differential heat of adsorption

an exponential function of this energy (C is a constant) (13):

$$N_i = C \cdot \exp \left(-\frac{E_i}{RT} \right) \quad (1)$$

A law of distribution where E_i would also be a function of temperature has not been formulated. In our case heat curves show that increasing temperatures lead to the formation of energy-rich sites. So, initial q_D values would be more important as temperature increases. As the energy of these sites increases, their number decreases according to exponential law of distribution (relation 1). And so, these sites are completely occupied for rather low degrees of filling ($\theta = 0,05$ at $+120^\circ\text{C}$, $\theta = 0,22$ at $+80^\circ\text{C}$) where the maximum appears.

At low temperature the energy of the sites is low and their number much higher. So, the initial values of q_D are lower and the maximum appears for higher values of θ ($\theta = 0,66$ at 0°C , $\theta = 0,83$ at -30°C)

This double distribution of sites allows us to explain the separate curves and their evolution with temperature.

Thermodynamic data for adsorbed phase

Molar integral entropy S_a of adsorbed phase can be calculated (8) from the following relationship:

$$S_a = \frac{1}{n} \int_0^n \bar{S}_a \, dn \quad (2)$$

n is the number of moles adsorbed, \bar{S}_a the molar differential entropy:

$$\bar{S}_a = S_g - \frac{q_{st}}{T} \quad (3)$$

S_g is the molar integral entropy of the gas. Working with a differential calorimetric system according to an isothermal process, isotheric heat q_{st} can be calculated from the experimental values of differential heat q_D :

$$q_{st} = q_D + RT \quad (4)$$

assuming the ideal behavior of the gas (14). Molar integral entropy of adsorbed phase is calculated by graphical integration of the area under \bar{S}_a vs. n curve. These calculations can be made from $+20$ to $+120^\circ\text{C}$ (Figure 2). For initial adsorbed molecules, molar integral entropy is very low in relation to the well-ordered state characteristic of strongly localized adsorption. Then S_a increases and reaches a maximum,

after which the curves approach an approximately constant value which is when the degree of filling becomes important. Barrer and Gibbons (8) have noted maximum and minimum values on integral entropy curves for CO₂ sorption by faujasite. According to them, such curves would be characteristic of heterogeneous surface.

For a given degree of filling θ , integral entropy decreased as temperature increased. This supports the assumption of the formation of very energy-rich sites at high temperatures in relation to a well-ordered state of adsorbed molecules.

Specific heat C_p of adsorbed phase can be calculated from the relationship:

$$C_p = T \frac{dS_a}{dT} \quad (5)$$

Using integral entropy curves plotted for several temperatures, ratios $\Delta S_a/\Delta T$ are calculated for each couple of similar temperatures and for several degrees of filling (Figure 3). Heat capacity of zeolites is negligible compared with that of the adsorbed phase (15). Specific heat goes through a maximum between + 40 and + 60°C rising to values much higher than can be attributed to the liquid phase.

Similar curves are found with methane adsorption by CaA (16) and with n-heptane by the same zeolite (11). In the first case, measurements are carried out with a drop calorimeter allowing a direct measurement of the specific heat of adsorbed phase.

Hill (17) suggested that transition between a localized and mobile sorption type could be seen by a maximum of specific heat C_p . He showed that this transition might appear at rather low temperatures (50°K), but was all the higher as the energetic barrier between the sites was large. As we showed that mordenite has a heterogeneous surface from intermediate temperatures (+ 40°C), the observed maximum near + 50°C on specific heat curves could exhibit a similar change in the adsorption. This remark would agree with the illustration of two adsorption ranges on differential heat and integral entropy curves: a first strongly localized type and a second with much less energy-rich sites.

On the other hand, the shape of the curves is the same as the one representing variations of specific heat during the second order Λ transformation. The main character of this transformation is that we never find two phases together; the phenomenon occurs in a single phase where the system goes through an order-disorder transformation.

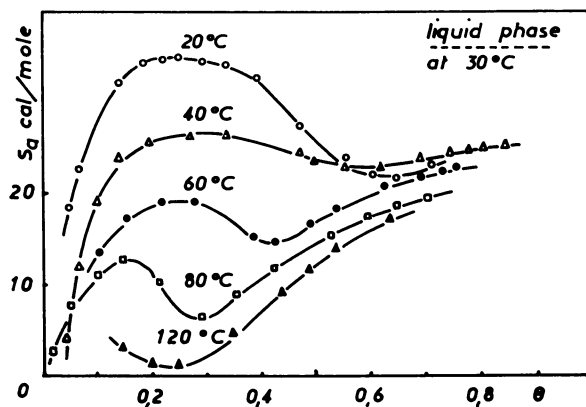


Figure 2. Molar integral entropy of adsorbed phase

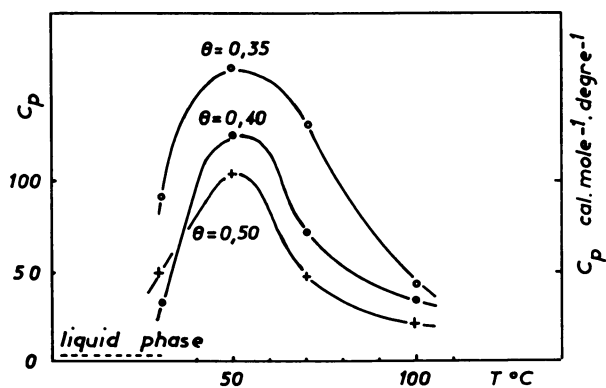


Figure 3. Specific heat of adsorbed phase

Adsorption isotherms

Adsorption isotherms were determined from 10^{-5} atm up to 50 atm and in the range -77 to $+160^{\circ}\text{C}$ with the three experimental techniques described before. The data are plotted in Figure 4. Adsorbed amounts are given in moles per gram of anhydrous zeolite.

Depending on the temperature, isotherms are like sigmoid curves or straight lines in these coordinates, which seems to be a general characteristic for microporous materials (18). However in the usual diagram, these isotherms are like type I of Brunauer *et al.* classification (19). Adsorption and desorption isotherms coincide perfectly.

Isotherms have the same shape on both sides of the critical point; differential heat curves have the same property; this leads us to think that no change appears in adsorption on either side of this temperature (20), (21).

When micropore filling is important, the adsorbed phase is like a condensed phase similar to a liquid from many points of view, even above the critical point (22). This is the reason why we can assume the idea of density in this filling range.

For isotherms plotted up to 50 atm, saturation vapor pressure is reached at $+15^{\circ}\text{C}$. At this pressure, adsorbed amount n_0 represents the whole micropore filling W_0 . Adsorbed phase density is ρ :

$$\rho = M \frac{n_0}{W_0} \quad (6)$$

W_0 was determined earlier (7); M is the molecular weight. Adsorbed amounts on external surfaces of crystallites are negligible compared with that adsorbed in the micropores (23).

Above the critical point, from $+40^{\circ}\text{C}$ to $+120^{\circ}\text{C}$, isotherms level out corresponding to saturation of micropores. The data of ρ vs. temperature are plotted in Figure 5 for No-Mordenite, H-Mordenite, and a 22% strontium exchanged form (24).

The following three remarks can be noted:

- no discontinuity appears in the plot of adsorbed phase density through the critical point.
- above the critical temperature, the adsorbed phase density has the same magnitude as the liquid phase density. However, at the same temperature, the adsorbed phase always appears more dense than the liquid phase. This has often been observed (22), (25).

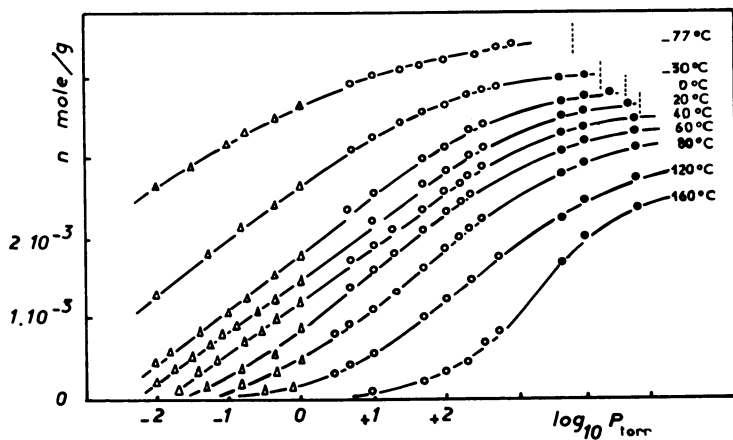


Figure 4. Adsorption isotherms. Data from different experimental techniques. (Δ), volumetry-calorimetry; (\circ), thermogravimetry; (\circ), high pressure volumetry.

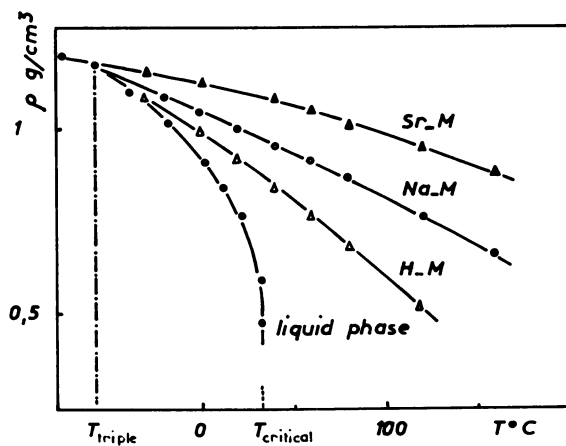


Figure 5. Density variations of adsorbed phases against temperature

- separate curves are obtained for each adsorbent, and each curve is different from the liquid phase curve. This has also been observed previously (26), (27), (28).

Conclusion

Calorimetrically measured thermal properties have given important information about the nature of interactions between carbon dioxide and synthetic mordenite; they are not as simple as theoreticians would like. The data show two adsorption ranges:

- the first relating to a strongly localized adsorption and a heterogeneous surface, which changes with temperature
- a second characterized by sites of identical and low energies.

The temperature dependence of the maxima and of the curves themselves lead to the conclusion that there is a double distribution of sites:

- one, as a function of temperature: its increasing leads to formation of very energy-rich sites.
- the other, as a function of the respective energy of these sites: the most energetic are fewer in number.

Both the shape of the experimental curves of integral entropy and of the specific heat of adsorbed phase, support these assumptions. Adsorption isotherms plotted up to 50 atm allow the adsorbed phase density to be determined experimentally and its condensed nature to be specified.

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