Selective adsorption of formaldehyde and water vapors in NaY and NaX zeolites
Jean Pierre Bellat, Weber Guy, Igor Bezverkhyy, Jean-Francois Lamonier

To cite this version:

HAL Id: hal-03023843
https://hal.science/hal-03023843
Submitted on 25 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Selective adsorption of formaldehyde and water vapors in NaY and NaX zeolites

Jean-Pierre Bellat*a, Guy Webera, Igor Bezverkhyya and Jean-François Lamonierb

a Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS, Université de Bourgogne Franche-Comté, 9 avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France

b Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, 59000 Lille, France

* Corresponding author

Abstract

Coadsorption of formaldehyde and water vapors on NaX and NaY zeolites is studied at 298 K in the pressure range 0 – 2 hPa by manometry coupled with gas phase chromatography and calorimetry. Coadsorption isotherms, adsorption selectivities and coadsorption heats are measured. Results show that the coadsorption process is selective for water at low filling and for formaldehyde at high filling. The adsorption selectivity for formaldehyde over water is however too low to consider the possibility of using such adsorbents for the development of air handling units. On the other hand, a preliminary study carried out on the adsorption of formaldehyde and water in pure gas phase on a hydrophobic FAU zeolite reveals that high silica zeolites could be promising adsorbents for the capture of formaldehyde in the presence of water.

Keywords: coadsorption, formaldehyde, water, zeolite, selectivity
Introduction

Formaldehyde is a VOC (Volatile Organic Compound), which is ubiquitously present in the atmosphere, because it is produced by various natural sources and anthropogenic activities. In the environment, formaldehyde is released through biomass decomposition and combustion (forest fires) or through volcanic eruptions for instance. Anthropogenic sources include the combustion of fuels, tobacco and wood, the incineration of industrial and household wastes and all the on-site emissions in automobile, and also chemical and wood industries. The cooking of food can even produce formaldehyde. It is particularly found in air at high concentration in the manufactures of plywood and chipboard, which use formaldehyde-based compounds as binder agent. Formaldehyde is also extensively used in the medical sector for its biocide and disinfectant properties. Due to its high volatility, formaldehyde is easily released in indoor air from various materials containing formaldehyde by-products as for example the furniture that is present in almost every classroom, office, house and building. Since 2015, formaldehyde is recognized as carcinogenic for human [1]. Therefore, its utilization is restricted to professionals and strictly regulated. Nowadays, in France and in many other European countries, the maximal concentration of formaldehyde in indoor air should not exceed 30 µg.m⁻³. The objective is to reduce this level to 10 µg.m⁻³ in 2023 [2]. As a consequence, there is an urgent need to develop, on the one hand, gas sensors of high sensitivity to detect traces of formaldehyde and, on the other hand, air treatment facilities able to capture this very toxic VOC in order to improve indoor air quality.

Physisorption on microporous solids appears as a promising way to detect and capture formaldehyde [3]. As the physical adsorption-desorption phenomenon is reversible, it is possible to design gas sensors and air treatment facilities based on an adsorbent easily
regenerable by simple heating or depressurization at moderate temperature and pressure, thus allowing a continuous detection and purification. This cannot be implemented if formaldehyde is chemically bound on the adsorbent. In that case, once saturated, the adsorbent must be changed or at least regenerated at high temperature under vacuum or inert gas flow. This is the reason why numerous studies on the capture of formaldehyde by physical adsorption on various adsorbents, in particular activated carbon, have been performed in the last decade [4-31].

In a previous study, devoted to a screening of nanoporous materials able to capture formaldehyde by physisorption in the gas phase, we have shown that the NaX and NaY FAU zeolites were very efficient adsorbents [32]. They exhibit high adsorption capacity and strong adsorption affinity making them suitable for trapping formaldehyde at very low concentration in the gas phase. These adsorption properties are attributed to the presence of Na\(^+\) charge compensating cations in the zeolitic structure, which constitute strong specific adsorption sites for polar molecules such as formaldehyde. However, since these materials are strongly hydrophilic, it is to be expected that competitive adsorption between formaldehyde and water could occur. In our view it is therefore particularly relevant to study the coadsorption of these two molecules in order to understand how the presence of water can interfere with the capture of formaldehyde by physisorption in this type of microporous materials.

The present paper is thus devoted to the study of the coadsorption of water (H\(_2\)O) and formaldehyde (H\(_2\)CO) in gas phase on NaX and NaY FAU zeolites by using an original technique combining manometry, calorimetry and gas phase chromatography. For the first time, coadsorption and partial adsorption isotherms, adsorption selectivities and coadsorption heats of water and formaldehyde have been measured. Experimental results are compared with those predicted from single adsorption equilibria in DaY, a non-cationic FAU-type
zeolite, by using the IAS theory; the feasibility of using such zeolites for air purification is also discussed.

**Experimental**

The NaX and NaY FAU zeolites were supplied free of binder by Union Carbide. The powdered dealuminated Wesssalith DaY faujasite was purchased from Degussa. The pure gaseous formaldehyde was generated by thermal decomposition of paraformaldehyde as explained in reference [32]. Some physico-chemical characteristics of the adsorbents and the adsorptives are given in Table 1.

Adsorption isotherms of single components were measured with a home-made McBain thermobalance equipped with a quartz spring, using the ultra-high vacuum technology. A CCD camera allowed the measurement of the spring elongation, which is proportional to the sample weight variation. Pressure of gas inside the balance was measured with Baratron pressure sensors. More details about the experimental procedure can be found in reference [32]. The weight of the sample was around 15 mg. The adsorption temperature was maintained at 298 K and the pressure was varied from $10^{-4}$ to 2 hPa. Prior to adsorption, the sample was outgassed at 673 K under dynamic vacuum ($10^{-4}$ hPa) for 12 h. The accuracies of temperature, pressure and weight measurements were ± 1 K, ± 0.001 hPa and ± 0.01 mg.

Coadsorption of H$_2$O and H$_2$CO was studied by using an original setup constructed in the laboratory. This apparatus is composed of a manometry unit made of pyrex coupled with a differential calorimeter (SETARAM C80) and a gas phase chromatograph (GPC-HP 4890) equipped with a TCD detector (Figure 1). The manometric device was connected to the chromatograph by means of a six-way gas injection valve (GIV) equipped with a sample loop, thus allowing injection of a small amount of gas mixture in the GPC. Coadsorption
experiments were performed at 298 K over the total pressure range $10^{-2} - 2$ hPa with an equimolar mixture of formaldehyde and water and a sample weight of around 100 mg. As for thermogravimetric measurements, the sample was degassed at 673 K for 12 h before coadsorption measurements. The accuracy on temperature and pressure were the same as for thermogravimetry. The relative errors on measurements were around 5 % for the adsorbed amount, 10 % for the mole fractions and not less than 15 % for the selectivity. The total and partial adsorbed amounts ($N^a$) were expressed in molecules of gas adsorbed per unit cell of activated zeolite (molec.uc$^{-1}$).

Coadsorption isotherms were determined by applying the following procedure. First, a gas mixture was prepared in the reservoir of volume $V_R$ (Table 1). The initial (i) gas composition defined by the mole fractions of water ($y_{H_2O,i}$) and formaldehyde ($y_{H_2CO,i}$) was fixed by controlling the partial pressure of each component with the Baratron pressure sensor (BPS). Then, a first small dose of gas mixture was introduced in the flask of volume $V_F$ under the initial pressure $P_i$. This dose of gas mixture was put in contact with the adsorbent present in the calorimetric cells of volume $V_C$. Once the equilibrium was reached, the total pressure $P$ was measured with the pressure sensor BPS and the gas composition (defined by the mole fractions $y_{H_2O}$ and $y_{H_2CO}$) was analyzed by GPC. Afterwards the calorimetric cells were isolated and a new dose of gas mixture was introduced in the flask in order to perform a second adsorption experiment and so on. Let us consider the gas as ideal, the total amount of gas mixture adsorbed at the equilibrium after the j-th injection was calculated using equation [1]:

$$N_{total,j}^a = \frac{V_F}{RT_F}(P_{i,j} - P_j) + \frac{V_C}{RT_C}(P_{j-1} - P_j) + n_{j-1}^a$$

where $T_F$ and $T_C$ are the temperatures of the volumes $V_F$ and $V_C$, respectively, $R$ is the ideal gas constant, $n_{j-1}^a$ is the amount adsorbed at the equilibrium after the (j-1)-th gas mixture
injection, $P_j$ and $P_{j-1}$ are the equilibrium pressures after the j-th and (j-1)-th injections, respectively, and $P_{ij}$ is the initial pressure in the volume $V_F$ before the j-th injection of gas mixture in the cells $V_C$.

The partial amount of formaldehyde adsorbed was calculated using equation [2]:

$$N^a_{H_2CO,j} = \frac{V_F}{RT_F} (y_{H_2CO,i,j}P_{i,j} - y_{H_2CO,j}P_j) + \frac{V_C}{RT_C} (y_{H_2CO,i-1,j}P_{i-1,j} - y_{H_2CO,j}P_j) + n^a_{H_2CO,j-1}$$

[2]

and that one of water with equation [3]:

$$N^a_{H_2O,j} = N^a_{total,j} - N^a_{H_2CO,j}$$

[3]

Then the mole fractions of each component in the adsorbed phase were calculated by using the following two relations:

$$x_{H_2CO,j} = \frac{N^a_{H_2CO,j}}{N^a_{total,j}}$$

[4]

$$x_{H_2O,j} = 1 - x_{H_2CO,j}$$

[5]

Finally, the thermodynamic adsorption selectivity for formaldehyde over water was calculated as a function of the total filling, using equation [6]:

$$a_{H_2CO,H_2O,j} = \frac{x_{H_2CO,j} y_{H_2O,j}}{x_{H_2O,j} y_{H_2CO,j}}$$

[6]

In addition, the integration of the heat flux recorded by the calorimeter during the j-th gas mixture adsorption measurement allowed to determine the molar coadsorption heat $Q_j^a$. This technique is described in more detail in references [33, 34].

Results and discussion

**Adsorption of single components**
Adsorption isotherms of single formaldehyde and water vapor on the NaX and NaY zeolites are displayed in Figure 2. As expected for microporous solids the isotherms show a type-I behavior according to the IUPAC classification.

Henry’s constants ($K_H$) of H$_2$CO and H$_2$O in the FAU zeolites, which are determined from the slope of the adsorption isotherms at the limit of zero pressure, are given in Table 2. Furthermore $K_H$ is related to the adsorption free enthalpy according to equation [7]:

$$G^a = -RT\ln\left(\frac{P^o}{N_s^a K_H}\right)$$

[7]

with $P^o$ the stander pressure ($P^o = 1000$ hPa) and $N_s^a$ the maximal amount adsorbed at saturation.

For a given zeolite, the values of $K_H$ are higher for water than for formaldehyde indicating that at low filling the NaX and NaY zeolites exhibit a stronger adsorption affinity for water. This result suggests that in the case of a gas mixture containing H$_2$CO and H$_2$O, the NaX and NaY zeolites would preferentially adsorb water. However, the fact that the adsorption affinity is stronger for water than for formaldehyde is in contradiction to what we could expect on the basis of the value of the permanent dipole moments of water and formaldehyde (Table 1). Indeed, formaldehyde, which has a higher permanent dipole moment, should be more strongly adsorbed than water. However, the values of dipole moment reported in Table 1 are given for isolated molecules in the ground state. Due to the strong electrical field present in zeolite cages, the polarization of the molecules can be largely modified by Stark effect when molecules are located in the cages. With the presence of $\pi$ electrons, H$_2$CO is particularly sensitive to this effect. Values of polarizability given in Table 1 show indeed that H$_2$CO is much more polarizable than H$_2$O [35]. So, when adsorbed, formaldehyde may be in an excited state with a dipole moment lower than the dipole moment of water in the ground state [36-38]. On the other hand, the confinement of water molecules in a narrow pore may induce a significant increase of
their dipole moment [39, 40]. It is worthy to note that for \( \text{H}_2\text{CO} \) adsorption the Henry’s constants are similar for the NaX and NaY zeolites while for water adsorption the Henry’s constant is far higher for NaX (Table 2). This is attributed to the fact that NaX possesses more extra-framework sodium cations, which makes this zeolite more hydrophilic.

Concerning the adsorption capacities of NaX and NaY zeolites, the volumes occupied by the adsorbed phase \((V^a)\) at the plateau of the adsorption isotherm \((P = 2 \text{ hPa})\) are given in Table 2. They are calculated assuming the adsorbate as a liquid with a density of 1 g.cm\(^{-3}\) for water and 1.09 g.cm\(^{-3}\) for formaldehyde at 298 K. The values of \(V^a\) are very similar to those of crystallographic microporous volumes of NaX and NaY zeolites (Table 1), indicating that the filling of cationic FAU zeolite cages is almost complete in these conditions. As water, formaldehyde can be adsorbed not only in the supercages but also in the small sodalite cages of FAU zeolites owing to its small molecular size and high polarity.

*Prediction of adsorption selectivity by IAS theory*

The adsorption selectivity for formaldehyde over water has been predicted from the single adsorption isotherms by the well-known Ideal Adsorbed Solution theory (IAST) [41]. Predictions have been performed for NaY at two values of total pressure: 0.25 and 1 hPa. Figure 3 shows the x-y diagram representing the mole fraction of formaldehyde in the adsorbed phase as a function of the mole fraction of formaldehyde in the gas phase. The gas phase is always richer in formaldehyde than the adsorbed phase indicating that the adsorption process is in favor of water, whatever the pressure is. The value of the adsorption selectivity \(\alpha_{\text{H}_2\text{CO}/\text{H}_2\text{O}}\) is around 0.82 and 0.65 under 0.25 and 1 hPa, respectively. Similar results are obtained for NaX.

*Adsorption of binary mixtures*
Total and partial adsorption isotherms of equimolar mixture of water and formaldehyde on NaX and NaY zeolites are given in Figure 4. For NaY, the partial amounts of water and formaldehyde adsorbed are similar in the whole range of pressure investigated. This is not the case for NaX. Above 0.5 hPa, the amount of H$_2$CO adsorbed becomes higher than that of water, suggesting that the adsorption process becomes slightly selective for formaldehyde.

The adsorption selectivity for formaldehyde over water, which is the most relevant parameter to assess the coadsorption process, is given as a function of filling in Figure 5. The selectivity curves for NaY and NaX show the same trend. Below 150 molec.uc$^{-1}$ for NaX and 125 molec.uc$^{-1}$ for NaY, the adsorption selectivity is constant and less than one, meaning that the zeolites adsorb preferentially water. As expected, the selectivity is lower on NaX than on NaY because NaX has the strongest hydrophilic character due to the presence of more sodium cations in its structure. Above these fillings, a sharp increase of the selectivity is observed and the adsorption process becomes in favor of formaldehyde. The separation however remains poor with a value of the adsorption selectivity which does not exceed 1.8. This value is too low to envisage the development of an efficient removal process of formaldehyde using such adsorbents. This increase in selectivity at high filling is not unusual in FAU zeolites. It has been already observed during the coadsorption of aromatic compounds, paraffins and mercaptans. It is attributed to configurational entropic effects consecutive to steric hindrance, which appears on approaching the complete filling of zeolite cages [33, 34].

For NaY, the mole fractions of formaldehyde measured in the gas and adsorbed phases at pressures of 0.25 and 1 hPa are reported in the x-y selectivity diagram (Figure 3). Under 0.25 hPa, which corresponds to a filling of around 150 molec.uc$^{-1}$, we observe a good agreement between IAS prediction and experiment. At this filling the selectivity is in favor of water. The cages are far from being completely filled. The molecular interactions in the adsorbed mixture are not so different from those in the pure water or formaldehyde adsorbed
phases. Therefore, the adsorbed mixture behaves as a quasi-ideal solution. On the contrary, under 1 hPa, IAS prediction and experiment are not in agreement. Under this pressure, the total amount adsorbed is around 211 molec.uc\(^{-1}\). The filling of cages is almost complete and the zeolite preferentially adsorbs formaldehyde. The steric hindrance is important in the cages. Entropic effects appear and the intermolecular interactions in the adsorbed mixture become different from those existing when single components are adsorbed, leading thus to deviation from ideality.

Figure 6 displays the coadsorption heats of water and formaldehyde in the NaX and NaY zeolites as a function of total filling. Both coadsorption heat curves show the same trend. Up to a filling of around 50-80 molec.uc\(^{-1}\), corresponding approximately to the adsorption of one molecule per sodium cation, the coadsorption heats are constant with a value of about 90 and 80 kJ.mol\(^{-1}\) on NaX and NaY, respectively. These high values of coadsorption heat account for strong adsorbate-adsorbent interactions. In this filling range, the highly polar formaldehyde and water molecules interact with sodium cations, which are initially located on sites I’ in sodalite cages and on sites II and III (for NaX) in supercages (Table 1) [42]. The adsorption selectivity is constant and in favor of water. Then, with increasing filling, the coadsorption heats continuously decrease down to the liquefaction enthalpy of gas mixture (≈ 34 kJ.mol\(^{-1}\)). Besides, the adsorption selectivity sharply increases to become in favor of formaldehyde. This decrease in the coadsorption heat is, at first, attributed to the adsorption on less energetic sites where molecules do not directly interact with charge compensating cations (adsorption in the center of supercages for example). It results also from endothermic effects arising from the displacement of one adsorbed molecule by another one and from the breaking of hydrogen bonds due to molecular rearrangements created by entropic effects.

*Adsorption on hydrophobic FAU zeolite*
Because of the competitive adsorption of formaldehyde and water, the cationic NaX and NaY faujasites cannot be used as adsorbent in air treatment unit, unless a first step of dehydration with another adsorbent (such as a 3A zeolite) having a weaker adsorption affinity for formaldehyde is included in the process. Another alternative could be to use a hydrophobic adsorbent. However, because of the high degree of similarity in the physical-chemical properties of formaldehyde and water, it is unlikely that the coadsorption process will be more selective than on cationic zeolites. Nevertheless, we have studied the adsorption of single water and formaldehyde on the dealuminated DaY zeolite. This material, which has the same FAU structure as the NaX and NaY zeolites, contains very few sodium cations and, therefore, is hydrophobic. Single adsorption isotherms of formaldehyde and water on DaY are shown in Figure 7. At very low pressure (below 0.02 hPa), the adsorption affinity is also stronger for water than for formaldehyde (see the Henry’s constants in Table 2) because it remains few Na\(^+\) cations in the structure, which are very strong adsorption sites for water. But surprisingly, as the pressure is increased, the amount of adsorbed formaldehyde becomes higher than that of water. This is certainly due to the fact that the non-specific interactions are stronger with formaldehyde because of the presence of the carbon atom. This suggests that this material could adsorb more favorably formaldehyde. The adsorption selectivity of this DaY zeolite has been predicted with the IAS theory. Results are shown on the x-y diagram in Figure 3. Under the total pressure of 1 hPa the coadsorption process should be in favor of formaldehyde with a selectivity of around 2.5, which is higher than the value obtained with NaX or NaY (1.7 and 0.9 respectively). The adsorption capacities are however low (Table 2) in comparison with those of cationic faujasites and coadsorption measurements must be done to confirm this result.
Conclusion

For the first time, adsorption equilibria of formaldehyde and water binary mixtures on sodium faujasite zeolites have been experimentally determined. Results show that the selective adsorption process is in favor of water at low filling due to strong interaction between water and sodium cations. At high filling, the adsorption selectivity is reversed because of entropic effects and the NaX and NaY zeolites become selective for formaldehyde. The adsorption selectivity for formaldehyde over water is however very low (~1.8). Though the NaX and NaY zeolites are very efficient adsorbents for trapping pure formaldehyde vapor, they become unable to capture selectively formaldehyde in the presence of water. Therefore, these microporous materials cannot then be used as adsorbent to develop an air treatment unit unless a first step of dehydration is added in the process. A possible alternative is to use hydrophobic zeolites, which could adsorb more formaldehyde than water, as shown in the first preliminary study performed with the dealuminated DaY faujasite. In this case, however, the adsorption capacity is low. Nevertheless, one could expect to improve the adsorption capacity and selectivity in favor of formaldehyde by using other zeolitic structures with smaller pore size and different pore geometry in order to reinforce non-specific adsorbate-adsorbent interactions which are stronger for formaldehyde than for water. Indeed, it is possible now to elaborate pure silica zeolitic materials, so-called zeosils, having different structures (MFI, BEA, CHA, LTA, ITQ…), which are very hydrophobic adsorbents. As outlined by Joël Patarin, who is a pioneer in this field, these zeosils could be very efficient for the capture of VOCs as formaldehyde in the presence of water [43, 44]. Works on the capture of various VOCs on such hydrophobic materials are in progress.
Acknowledgment

The authors are grateful to the ADEME (French Environment and Energy Management Agency) for its financial support (project CAT CORTEA # 1181C0158).
References


[36] D.W. Davies, R. Elvin, Ground and excited state dipole moments and energies for n-π transitions in carbonyl compounds: INDO configuration interaction calculations, Journal of


Tables
Table 1. Some physical-chemical characteristics of adsorbents and adsorptives. The micropore volume ($V_{\text{micro}}$) of adsorbents is calculated from crystallographic considerations as explained in reference [32].

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>Type</th>
<th>Scheme of porous structure</th>
<th>Chemical formula of unit cell</th>
<th>$V_{\text{micro}}$ (cm$^3$.g$^{-1}$)</th>
<th>Cationic distribution (anhydrous state)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaX</td>
<td></td>
<td></td>
<td>Na$<em>{86}$[Al$</em>{86}$Si$<em>{106}$O$</em>{384}$]</td>
<td>0.335</td>
<td>32S$<em>{\text{II}}$+24S$</em>{\text{III}}$+30S$_{\text{I}'}$</td>
</tr>
<tr>
<td>NaY</td>
<td></td>
<td></td>
<td>Na$<em>{52}$[Al$</em>{52}$Si$<em>{140}$O$</em>{384}$]</td>
<td>0.339</td>
<td>32S$<em>{\text{II}}$+10S$</em>{\text{I}}$+10S$_{\text{I}'}$</td>
</tr>
<tr>
<td>DaY</td>
<td></td>
<td></td>
<td>Na$<em>2$[Al$<em>2$Si$</em>{190}$O$</em>{384}$]</td>
<td>0.355</td>
<td>2S$_{\text{II}}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ADSORPTIVE</th>
<th>Chemical formula</th>
<th>Molecular structure</th>
<th>Kinetic diameter (nm)</th>
<th>Dipolar moment (ground state of gas) (D)</th>
<th>Polarizability (C$^2$.m$^2$.J)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$CO</td>
<td></td>
<td>0.243</td>
<td>2.33</td>
<td>27.25 $10^{-41}$</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td></td>
<td>0.265</td>
<td>1.86</td>
<td>16.58 $10^{-41}$</td>
</tr>
</tbody>
</table>
Table 2. Henry’s constants ($K_H$) of adsorption and volumes adsorbed ($V_a$) at the plateau of the adsorption isotherms under a water or formaldehyde vapor pressure of 2 hPa at 298 K.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>$K_H$ / (molec.uc⁻¹,hPa⁻¹)</th>
<th>$V_a$ / (cm³.g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2CO$</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>NaX</td>
<td>7689</td>
<td>23963</td>
</tr>
<tr>
<td>NaY</td>
<td>6028</td>
<td>15740</td>
</tr>
<tr>
<td>DaY</td>
<td>181</td>
<td>642</td>
</tr>
</tbody>
</table>
Figure 1. Scheme of the coadsorption experimental set-up combining manometry ($V_R$: volume of the reservoir; $V_F$: volume of the flask), gas phase chromatography (GPC) and differential calorimetry ($GIV$: six-way gas injection valve; $BPS$: Baratron Pressure Sensor; $V_C$: volume of the calorimetric cells).
Figure 2. Adsorption isotherms of $\text{H}_2\text{CO}$ and $\text{H}_2\text{O}$ in pure gas phase on NaX and NaY zeolites at 298 K.
Figure 3. x-y selectivity diagram predicted by IAS theory under constant pressure for NaY (0.25 and 1 hPa) and DaY (1 hPa) zeolites. Open circles correspond to experimental measurements performed on NaY.
Figure 4. Coadsorption isotherms and partial adsorption isotherms of an equimolar binary gas mixture of $\text{H}_2\text{CO}$ and $\text{H}_2\text{O}$ on NaX and NaY zeolites at 298 K.
Figure 5. Dependence of the adsorption selectivity of NaX and NaY zeolites for an equimolar binary gas mixture of H$_2$CO and H$_2$O on filling at 298 K.
**Figure 6.** Coadsorption heats of an equimolar binary gas mixture of H₂CO and H₂O on NaX and NaY versus filling at 298 K.
Figure 7. Adsorption isotherms of H$_2$CO and H$_2$O in pure gas phase on a hydrophobic DaY zeolite at 298 K.