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Study of adsorption sites heterogeneity in zeolites by means of coupled microcalorimetry with volumetry

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Abstract Adsorption of CO_2 as probe molecule on alkali-metal zeolites of MFI structure was investigated by joint volumetry–calorimetry. Consideration was given to the interpretation of the heat evolved when a probe molecule is adsorbed on the surface. In particular, the number and the strength of adsorption sites are discussed as functions of zeolite structure, concentration, and nature of extra-framework cation. The adsorption heats (q_{iso}) of CO_2 interaction with alkali-metal cations decrease for MFI zeolite with high Si/Al in the sequence $\mathrm{Li}^+ > \mathrm{Na}^+ > \mathrm{K}^+$ from 54 kJ/mol to 49 and 43 kJ/mol, respectively. In addition, the adsorption heats are influenced by concentration of Al in the framework. This phenomenon is attributed to formation of bridged CO_2 adsorption complexes formed between two cations. On the base of quantitative analysis of adsorption processes, presence of geminal adsorption complexes was suggested for adsorption at higher equilibrium pressures.

Keywords Adsorption · Heat · Carbon dioxide · CCS · Zeolite · MFI · Calorimetry

Introduction

Separation and purification of gas mixtures and wastes by pressure or thermal swing adsorption process is well established operation procedure in the chemical industry. Future progress in the adsorption technology depends on the level of understanding of the adsorbate–adsorbent interaction at the atomic scale level and elucidating of the factors which determine selective adsorption of a particular gas from the gas mixture. The equilibrium adsorption is characterized by the adsorption isotherm and heat of adsorption. The heat evolved during the interaction of the gas molecule with solid surface is called the heat of adsorption. It is related to the energy of the bonds formed during the adsorption process and thus represents a measure of the strength of these interactions. Therefore, adsorption heats bring information about heterogeneity of the adsorption sites on the surface of the adsorbent. In addition, knowledge of the adsorption heat is very important for the calculation energy balance in the packed columns. The adsorption heat determines the temperature profile inside the column and the energy required for the regeneration of the columns, which is the major cost for thermal swing adsorption process. The accurate measurements of the heat evolved and the amounts adsorbed are difficult. In order to detect energetic heterogeneity of the surface, which is of primary interest in adsorption and catalysis, small doses of probe gas (typically <10 μmol/g of solid) have to be admitted successively on the solid, in order to saturate the active sites progressively. Corresponding heats range from 0.1 up to 1 J per one dose and require up to a few hours for being evolved.

Experimental data are usually reported as a set of adsorption isotherms and so-called isosteric heat is calculated from the isosteres on the base of Clausius–Clapeyron equation:

$$q_{\mathrm{iso}} = -R\left(\frac{\partial \ln f}{\partial\left(\frac{1}{T}\right)}\right)_n - h^{\mathrm{R}}$$

where q_{iso} is isosteric heat of adsorption, R is gas constant, f is fugacity of the gas, which is adsorbed, h^{R} is residual

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enthalpy (for ideal gas is equal to zero), and n is adsorbed amount. Limiting slope of the adsorption isotherms is called Henry's constant, H, and it is defined by the equations:

$$H = \lim_{P \to 0} \left(\frac{n}{P} \right) = \lim_{P \to 0} \left(\frac{\mathrm{d}n}{\mathrm{d}P} \right)$$

The temperature dependence of the Henry's constant value yields the isosteric heat at the limit of zero-coverage (q^0_{iso}).

$$q^0_{\mathrm{iso}} = R \left[\frac{\mathrm{d} \ln H}{\mathrm{d}\left(\frac{1}{T}\right)} \right]$$

Both of these techniques suffer from the inaccuracy associated with differentiation, especially in the case of Henry's constants extrapolation. The method of isosteric plot construction requires the precise measurement of the isotherms, especially in the range of low pressures. Any error in pressures can lead to important mistakes in the determination of the adsorption heat. In addition, measurement of the adsorption isotherms is time consuming process and obtaining of the set of isotherms at least three different temperatures demands a couple of days or weeks for measurements.

Direct calorimetric measurements of the adsorption heats can be more convenient and accurate. Heat-flow microcalorimeters of the Tian–Calvet type are most commonly used for this purpose. These high sensitive calorimeters need to be connected to a sensitive volumetric system in order to determine accurately the adsorbed amounts. The principles of calorimetry in the adsorption have been established by Hill [1], who defined various types of adsorption heats corresponding to different experimental procedures and design of calorimeter. If both dosing system and sample cell are inside the calorimeter, so-called differential heat of adsorption (q_{d}) is registered. Such arrangement is conceptually very simple but difficult to construct. Most experimental instruments are open systems, with the dosing system outside the calorimeter. If the gas enters calorimeter at the temperature of the sample and if the same amount of adsorptive enters the sample cell and a reference cell, which is wired in reverse polarity, the calorimeter measures the heat which is equal to the isosteric heat. The differential and isosteric heats of adsorption are related by equation

$$q_{\mathrm{iso}} = q_{\mathrm{d}} + zRT$$

where z is the compressibility factor in the bulk gas phase, q_{iso} is the isosteric heat, and q_{d} is the differential adsorption heat.

In this contribution we report the study of CO_2 adsorption heats on the alkali-metal exchanged MFI zeolites with various Si/Al ratios. Adsorption is common industrial separation process, but its application to CO_2 capture is relatively new and very attractive topic at present time because the importance of the carbon dioxide capture and storage (CCS) for the protection of environment is now widely accepted. The purpose of CO_2 capture is to produce a concentrated stream of CO_2 at high pressure that can be transported to a storage site. Depending on the system, the CO_2 must be separated either at higher or at lower temperature and at different concentration of CO_2. It is therefore desirable to find materials for which the strength of interaction with CO_2 can be tuned in order to CO_2 capture at particular temperature and at the same time CO_2 can be released without much energy consumption [2]. Metal-exchanged zeolites seem to be a good candidate for developing of such systems due to their low price, easy regeneration and possibility to fine tune of properties by changing type of extraframework cation, Si/Al ratio and/or zeolite structure type. Several studies of CO_2 adsorption on zeolites appeared [3–11]. The experimental conditions and surface coverage, at which the adsorption heats are experimentally determined, strongly differ from study to study, making difficult a rigorous comparison between the different systems or data from different methods and laboratories. Therefore, to gain detailed information about the interaction of carbon dioxide molecules with cationic sites in zeolites, series of cation-exchanged MFI zeolites ($M = Li^+$, Na^+, K^+) with varying Si/Al ratios were investigated in this work.

Experimental

The original NH_4-MFI zeolites with Si/Al = 11.5 and 30 used in this study were supplied by Research Institute of Inorganic Chemistry, Ústí nad Labem. Samples of Li-, Na-, K-MFI with Si/Al = 30 and K-MFI with Si/Al 11.5 were prepared from parent zeolite by conventional ion exchange in 1 M chloride aqueous solution of alkaline metal at 323 K for 5 days. Powder X-ray diffraction of the exchanged samples showed good crystallinity and all diffraction lines appearing in the XRD patterns corresponded to the MFI structure type [12] (not shown for the sake of brevity). Complete ion exchange was checked by the absence of IR absorption bands corresponding to the (Brønsted acid) Si(OH)Al group (at 3610 cm^{-1}), which would be generated during thermal activation of the zeolite wafer for IR spectroscopy (see Fig. 1). The spectra were collected with a resolution of 2 cm^{-1} on a Nicolet 6700 FTIR spectrometer equipped with an MCT/A cryodetector. Cation-free pure silica MFI material (silicalite) was purchased from Zeolyst.

Prior to each adsorption experiment, the sample of the weight 400 mg was outgassed by slowly increasing

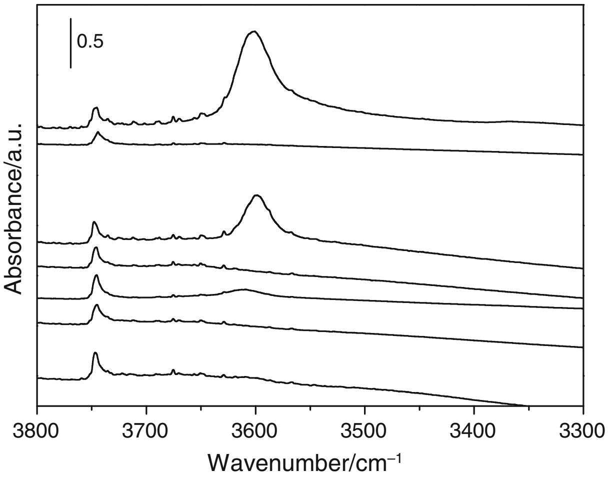

Fig. 1 FTIR spectra of thin self-supporting wafers of investigated samples and their parent zeolites in the region of OH group vibration after dehydration in the dynamic vacuum at 700 K. From *top to bottom*: H-MFI Si/Al 11.5, K-MFI Si/Al 11.5, H-MFI Si/Al 30, Li-MFI Si/Al 30, Na-MFI Si/Al 30, K-MFI Si/Al 30, MFI Si/Al 800 (silicalite)

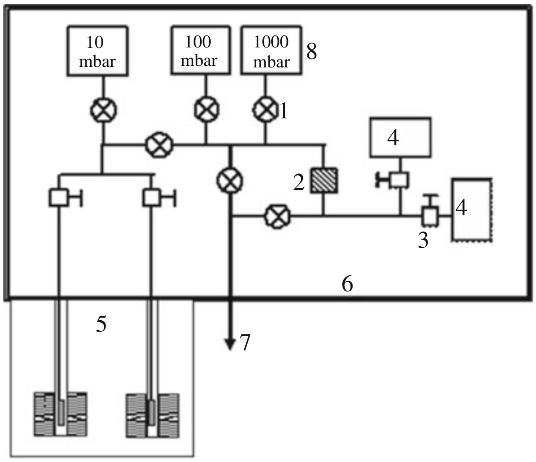

Fig. 2 Scheme of the experimental set-up. *1* Electrically operated vacuum valve, *2* dosing valve controlled by PC, *3* manual vacuum valve, *4* cartridge with adsorptive, *5* calorimetric block with sample and referent cell, *6* tempered box with controlled temperature, *7* connection to turbomolecular pump, *8* capacitance pressure gauges covering the 10, 100, and 1000 mbar ranges

temperature of sample with simultaneous careful evacuation up to residual pressure 10^{-4} Pa at 700 K. The heating profile was following: from 298 K temperature raised with 1 K/min to 380 K, isotherm was keep for 30 min, and then the temperature of sample was increased with heating rate 3 K/min to final temperature of 700 K. The adsorption-microcalorimetry experiments were carried out using an isothermal Tian–Calvet type microcalorimeter (BT 2.15 from SETARAM) combined with homemade volumetric–manometric device (a schematic representation of the whole assembly is shown in Fig. 2). Temperature of sample in the cell inside microcalorimeter was kept at 307 K, volumetric–manometric device was tempered at the same temperature. Experimental set-up represents open isothermal system allowing determination of so-called isosteric heat (in regard of Hill's definition). The free volume of the apparatus was determined by set of expansion experiments with helium as an inert/nonadsorbing gas at different pressure ranges. The adsorption isotherms and heats of adsorption were measured via step-by-step introduction of adsorptive into the cell. The CO_2 (purity of 99.997% supplied by Linde gas Corp.) was introduced via a system of electrically operated vacuum valves controlled by PC with software developed at our laboratory. Once pressure in the dosing volume was stabilized, the valve separating dosing volume from sample cell was opened to allow the adsorptive to reach the sample. Each dose was accompanied by exothermic effect detected by microcalorimeter until the equilibrium is attained. The integral of the peak in heat flow–time plot provided integral adsorption heat evolved at the dose. The equilibrium pressure, adsorbed amount, and integral adsorption heat were determined for each step of the experiment. The system was equilibrated at each dose for 50 min. All experiments consist of minimally 40 dosing cycles.

Results and discussion

FTIR spectra of investigated samples dehydrated at 700 K are shown in Fig. 1. It is clearly seen that intense band at 3610 cm^{-1} in the spectra of parent zeolites, corresponding to Brønsted acid OH groups generated by thermal decomposition of NH_4 cations compensating negative charge of zeolite framework, is completely missing in the spectra of zeolites ion exchanged by alkali-metal cation. This is evidence for quantitative ion exchange of NH_4 cation in the zeolite by alkali-metal cations. A small signal at 3745 cm^{-1} visible in IR spectra of all investigated samples is vibrational band of terminal Si–OH silanol groups.

CO_2 adsorption isotherms recorded on MFI zeolites under study at 307 K are presented in Fig. 3. For alkali-metal exchanged MFI having Si/Al = 30, the isotherms exhibit steep nonlinear concave shape, which is typical for interaction between carbon dioxide molecule and extra-framework cation of zeolites. Since concentration of cations in the MFI zeolite with Si/Al = 30 is 0.44 mmol per gram of zeolite (see Table 1), the amount of adsorbed CO_2 molecules is considerably higher. It implies that so-called geminal adsorption species ($M^+(CO_2)_2$) are formed in these zeolites, where some cations bind two molecules of the adsorptive. In contrast to alkali-metal MFI zeolites,

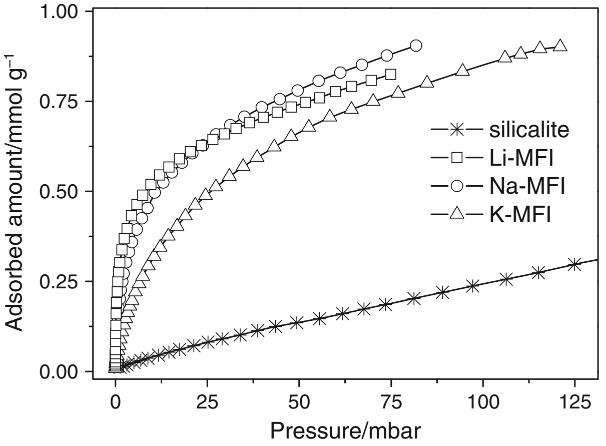

Fig. 3 Isotherms of carbon dioxide adsorption of MFI zeolite with Si/Al = 30 after ion exchanged modification and silicalite at 307 K

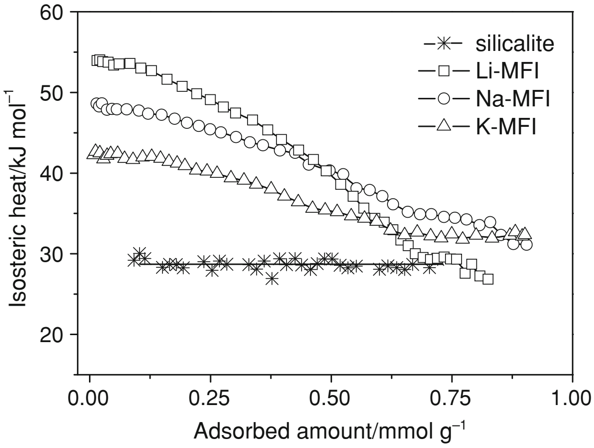

Fig. 4 Adsorption heats of carbon dioxide on alkali-metal exchanged MFI zeolites and silicalite as a function of CO_2 adsorbed amount at 307 K

Table 1 Chemical composition of the samples under study

Sample	Si/Al[a]	Unit cell composition[b]	$c(M^+)$/mmol g^{-1}[c]
Li-MFI	30	$Li_{3.1}Al_{3.1}Si_{92.9}O_{192}$	0.44
Na-MFI	30	$Na_{3.1}Al_{3.1}Si_{92.9}O_{192}$	0.42
K-MFI	30	$K_{3.1}Al_{3.1}Si_{92.9}O_{192}$	0.44
K-MFI	11.5	$K_{7.68}Al_{7.68}Si_{92.9}O_{192}$	1.05
Silicalite	∞	$Si_{96}O_{192}$	–

[a] Given by supplier

[b] Theoretical composition of unit cell on the base of given Si/Al ratio

[c] Alkali-metal cation content determined by ICP-OES after zeolite dissolution

adsorption isotherm of silicalite exhibits nearly linear behavior (so-called Henry's type of isotherm) typical for weakly interacting molecules.

Adsorption heats were measured simultaneously using the coupled volumetric apparatus with microcalorimeter. The calorimetric data (adsorption heats vs. adsorbed amount) for Li-, Na-, and K-MFI zeolites with Si/Al = 30 are reported in Fig. 4. Depending on type of the extra-framework cation, the zero-coverage limit of adsorption heats range from 54 to 43 kJ/mol (54, 49, and 43 kJ/mol for Li-, Na-, and K-MFI zeolite, respectively). Generally, the CO_2 molecule undergoes a small distortion upon adsorption on cation. The bond adjacent to the cation slightly lengthens, whereas the other bond becomes shorter. This can be understood, in simple terms, assuming that the positive electric charge of the cation stabilizes the canonical form of CO_2 molecule having separated charges, $^{\delta-}OCO^{\delta+}$, in which one bond has an order less than 2 and accordingly elongates, whereas second C=O bond has order slightly higher than 2 and its length shortens [7]. Energy of such polarization interaction is given by the charge and the radius of cation. For monovalent alkali-metal cations, the intensity of cation electric field increases in sequence $K^+ < Na^+ < Li^+$ and the adsorption heat increases in the same order. The similar range of initial adsorption heats of carbon dioxide adsorbed on the alkali-metal cations (determined mainly by means of isosteres) was found for ZSM-5 zeolites [4, 7, 13, 14], faujasites of X type [4, 15], and FER zeolites [16–18]. On the other hand, alkali-metal exchanged Y zeolites, MCM-22, and Al-SBA-15 materials exhibit significantly lower initial adsorption heats ranging from 38 to 31 kJ/mol [6, 19–22]. It is caused by differences in the structure of individual zeolitic frameworks which possess different sites to coordination of cations to the framework of zeolite. In addition, particular zeolite framework possesses a few different cation-exchanged sites given by sitting of aluminum atoms in the framework. This creates heterogeneity of zeolites from point of view adsorption behavior. This is also reason, why the adsorption heats monotonically decrease from initial value with adsorbed amount of CO_2 to heats about 30 kJ/mol (as a result of step-by-step occupation of less energetic sites and/or formation of geminal species, see Fig. 4). The shape of individual curves is reflecting different population of adsorption sites. Two main groups of cation sites exist in the MFI structure: (i) sites at intersection of zeolitic channels and (ii) sites on the channel wall. The nature of alkali-metal cation (diameter and charge) influences the cation occupation site preference as was found by quantum chemical calculations [23] or by IR study of intrazeolitic carbonyls formed during adsorption of CO in these zeolites [24–26]. Silicalite sample exhibits markedly different adsorption behavior—its CO_2 adsorption isotherms is nearly linear and adsorption heat is therefore almost constant regardless of adsorbed amount. This adsorption heat (29 kJ/mol) is very similar to heat reported by Dunne et al.

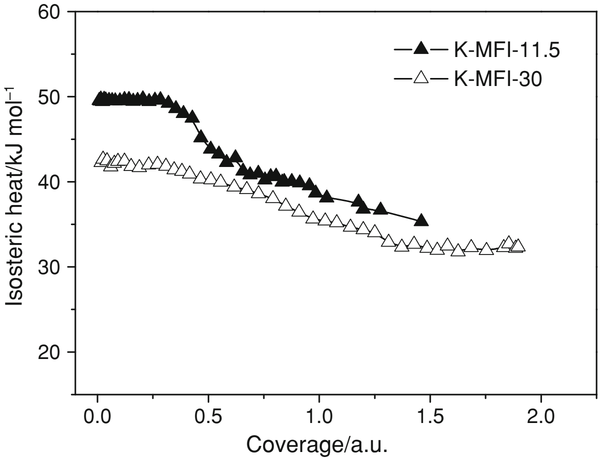

Fig. 5 Adsorption heats of carbon dioxide on K-MFI zeolites with different Si/Al ratio as a function of coverage at 307 K

[27] and can be attributed to non-specific so-called "dispersive" forces, what comprises the interaction of CO_2 molecule with Si–O skeleton of channel walls of silicalite. Nowadays, the more accurately DFT/CC calculations taking into account the dispersion interaction between CO_2 and zeolite framework in alkali-metal exchanged ferrierites are reported [16, 18].

The heats of adsorption of CO_2 on K-MFI zeolites with different Si/Al ratio are reported in Fig. 5. Evidently, adsorption heats of CO_2 on K-MFI with lower Si/Al ratio (and therefore higher concentration of cations in the inner space of zeolitic channels, 0.44 vs. 1.05 mmol of K^+ per gram of zeolite, cf. data in Table 1) are higher than on K-MFI with Si/Al 30 in whole range of coverage. The distinct differences in the initial (zero-coverage) adsorption heats for samples differing in Si/Al ratio can be accounted for a varying population of individual cationic positions and formation of different types of adsorption complexes. There is a lack of information about adsorption heat of CO_2 and its coverage dependence on alkali-metal exchanged zeolites (except Na-faujasites [4, 6, 15, 28, 29] or Na-ZSM-5 zeolites [4, 7, 30]) and mainly, attention was not focused on the effect of Si/Al ratio on the adsorption behavior of zeolites. To the best of our knowledge, the effect of Si/Al ratio is described only for Na-faujasites [15] and, very recently, differences in adsorption behavior of alkali-metal FER [16, 18] zeolites were published. In the case of faujasites, different adsorption enthalpies of Na–X and Na–Y zeolite were assigned to existence two (SIII$'$ and SII) and one (SII) preferential adsorption sites, respectively. For FER zeolites [16, 18], reported differences in isosteric heats of carbon dioxide adsorption are ascribed to the existence of bridged complexes, where CO_2 molecule interacts with two cations. This conclusion was supported by theoretical calculations on DFT level of theory. The calculations showed that complexes on dual sites are about 5–10 kJ/mol more stable than complexes on isolated sites. Our experimental data show that the zero-coverage limit adsorption heats of K-MFI zeolites differ about 7 kJ/mol in good agreement with theoretical prediction made for similar K-FER zeolitic system. In parallel with our previous investigation of CO adsorption on the same alkali-metal exchanged MFI zeolites [24], where dual adsorption sites were detected by IR spectroscopy, we believed that differences in the adsorption heats of CO_2 on the investigated samples are caused by existence of bridged $M^+\cdots O{=}C{=}O\cdots M^+$ complexes on dual cationic sites, which are more populated in the zeolites with higher concentration of extraframework cations, thus with lower Si/Al ratio.

Adsorption heats of both K-MFI zeolites become near with increasing coverage, but it differ even at the highest measured coverage of about 3 kJ/mol in despite of the same (less energetic) sites or geminal complexes are populated at higher coverage. This increase in adsorption heat on zeolite with higher concentration is probably caused by interaction of adsorbed CO_2 molecule with another adsorbed CO_2 molecule (so-called adsorbate–adsorbate interaction). Contribution of this interaction increases with spatial concentration of adsorbed molecules within zeolite channel (and therefore decreasing of distance between two CO_2 molecules).

Conclusions

Adsorption of CO_2 on alkali-metal exchanged MFI zeolites was studied by combination of volumetry–calorimetry method. The above discussed data allow us to draw the following conclusions:

1. The zero-coverage adsorption heats of CO_2 interaction with alkali-metal cations decrease for MFI zeolite with $Si/Al = 30$ in the sequence $Li^+ > Na^+ > K^+$ from 54 kJ/mol to 49 and 43 kJ/mol, respectively, reflecting differences in electrostatic field intensity of particular cations.
2. Dependence of adsorption heats on adsorbed amount clearly reflects heterogeneity of adsorption sites in all cation-exchanged zeolites caused by different localization and coordination of individual cations in the zeolite matrix.
3. K-MFI zeolite with low Si/Al ratio ($Si/Al = 11.5$) exhibits high population of so-called dual cationic sites, where CO_2 molecule interacts with two alkali-metal cations and forms bridged adsorption complex. Such complexes exhibit large stability; the differences in the adsorption heats of the zero-coverage limit for high and low Si/Al ratios are 7 kJ/mol.

4. High concentration of CO_2 molecules in the channel system of MFI zeolite (zeolite with lower Si/Al ratio) led to interaction of adsorbed molecules (adsorbate–adsorbate interaction), which is evidenced (for zeolite with lower Si/Al ratio) by increasing of adsorption heat at higher coverage about 3 kJ/mol.

Finally, the high-silica zeolites, such as MFI zeolite, are usually considered as potentially ideal systems in the thermodynamic sense constituting an ensemble of isolated and noninteracting adsorption sites in the fundamental studies of adsorption. Our results show that this conception, in contrast to "dilution" of adsorption sites on the inner surface of zeolite, can be invalid. The existence of dual cationic sites and bridged complexes formed on these sites teaches us that spatial complexity of the zeolite surface must be taken into account and it cannot be substituted by ideas derived from flat surface models.

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References

1. Hill TL. Statistical mechanics of adsorption. V. Thermodynamics and heat of adsorption. J Chem Phys. 1949;17(6):520–35.
2. Song CS. Global challenges and strategies for control, conversion and utilization of CO_2 for sustainable development involving energy, catalysis, adsorption and chemical processing. Catal Today. 2006;115(1–4):2–32.
3. Harlick PJE, Tezel FH. Adsorption of carbon dioxide, methane and nitrogen: pure and binary mixture adsorption for ZSM-5 with SiO_2/Al_2O_3 ratio of 280. Sep Purif Technol. 2003;33(2):199–210.
4. Dunne JA, Rao M, Sircar S, Gorte RJ, Myers AL. Calorimetric heats of adsorption and adsorption isotherms. 2. O_2, N_2, Ar, CO_2, CH_4, C_2H_6, and SF_6 on NaX, H-ZSM-5, and Na-ZSM-5 zeolites. Langmuir. 1996;12(24):5896–904.
5. Sircar S. Basic research needs for design of adsorptive gas separation processes. Ind Eng Chem Res. 2006;45(16):5435–48.
6. Ghoufi A, Gaberova L, Rouquerol J, Vincent D, Llewellyn PL, Maurin G. Adsorption of CO_2, CH_4 and their binary mixture in faujasite NaY: a combination of molecular simulations with gravimetry–manometry and microcalorimetry measurements. Microporous Mesoporous Mater. 2009;119(1–3):117–28.
7. Bonelli B, Civalleri B, Fubini B, Ugliengo P, Arean CO, Garrone E. Experimental and quantum chemical studies on the adsorption of carbon dioxide on alkali-metal-exchanged ZSM-5 zeolites. J Phys Chem B. 2000;104(47):10978–88.
8. Siriwardane RV, Shen MS, Fisher EP. Adsorption of CO_2 on zeolites at moderate temperatures. Energy Fuels. 2005;19(3): 1153–9.
9. Harlick PJE, Tezel FH. An experimental adsorbent screening study for CO_2 removal from N_2. Microporous Mesoporous Mater. 2004;76(1–3):71–9.
10. Bourrelly S, Maurin G, Llewellyn PL. Adsorption microcalorimetry of methane and carbon dioxide on various zeolites. In: Cejka J, Zilkova N, Nachtigall P, editors. Molecular sieves: from basic research to industrial applications, pts A and B. Studies in surface science and catalysis; 2005. p. 1121–8.
11. Erten Y, Gunes-Yerkesikli A, Cetin AE, Cakicioglu-Ozkan F. CO_2 adsorption and dehydration behavior of LiNaX, KNaX, CaNaX and CeNaX zeolites. J Therm Anal Calorim. 2008; 94(3):715–8.
12. Treacy MMJ, Higgins JB. Collection of simulated XRD powder patterns for zeolites. Amsterdam: Elsevier; 2001.
13. Yamazaki T, Katoh M, Ozawa S, Ogino Y. Adsorption of CO_2 over univalent cation-exchanged ZSM-5 zeolites. Mol Phys. 1993;80(2):313–24.
14. Barrer RM, Gibbons RM. Zeolitic carbon dioxide: energetics and equilibria in relation to exchangeable cations in faujasite. Trans Faraday Soc. 1965;61:948–61.
15. Plant DF, Maurin G, Deroche I, Llewellyn PL. Investigation of CO_2 adsorption in faujasite systems: grand canonical monte carlo and molecule dynamics simulations based on a new derived Na^+–CO_2. Microporous Mesoporous Mater. 2007;99(1–2):70–8.
16. Pulido A, Nachtigall P, Zukal A, Dominguez I, Cejka J. Adsorption of CO_2 on sodium-exchanged ferrierites: the bridged CO_2 complexes formed between two extraframework cations. J Phys Chem C. 2009;113(7):2928–35.
17. Bulanek R, Frolich K, Frýdová E, Cicmanec P. Microcalorimetric and FTIR study of the adsorption of carbon dioxide on alkali-metal exchanged FER zeolites. Topics in Catalysis. doi: 10.1007/s11244-010-9593-6
18. Zukal A, Pulido A, Gil B, Nachtigall P, Bludsky O, Rubes M, et al. Experimental and theoretical determination of adsorption heats of CO_2 over alkali metal exchanged ferrierites with different Si/Al ratio. Phys Chem Chem Phys. 2010;12(24):6413–22.
19. Zukal A, Mayerova J, Cejka J. Alkali metal cation doped Al-SBA-15 for carbon dioxide adsorption. Phys Chem Chem Phys. 2010;12:5240–7.
20. Plant DF, Maurin G, Deroche I, Gaberova L, Llewellyn PL. CO_2 adsorption in alkali cation exchanged Y faujasites: a quantum chemical study compared to experiments. Chem Phys Lett. 2006;426(4–6):387–92.
21. Zukal A, Pawlesa J, Cejka J. Isosteric heats of adsorption of carbon dioxide on zeolite MCM-22 modified by alkali metal cations. Adsorption. 2009;15(3):264–70.
22. Maurin G, Belmabkhout Y, Pirngruber G, Gaberova L, Llewellyn P. CO_2 adsorption in LiY and NaY at high temperature: molecular simulations compared to experiments. Adsorption. 2007; 13(5–6):453–60.
23. Kucera J, Nachtigall P. Coordination of alkali metal ions in ZSM-5: a combined quantum mechanics/interatomic potential function study. Phys Chem Chem Phys. 2003;5(15):3311–7.
24. Arean CO, Delgado MR, Frolich K, Bulanek R, Pulido A, Bibiloni GF, et al. Computational and Fourier transform infrared spectroscopic studies on carbon monoxide adsorption on the zeolites Na-ZSM-5 and K-ZSM-5: evidence of dual-cation sites. J Phys Chem C. 2008;112(12):4658–66.
25. Bonelli B, Fubini B, Onida B, Palomino GT, Delgado MR, Arean CO, et al. Room temperature interaction of co with alkali-metal cations in M-ZSM-5 zeolites as studied by joint FT-IR spectroscopy and microcalorimetry. Oxide based materials: new sources, novel phases, new applications. Studies in surface science and catalysis; 2005. p. 95–102.
26. Arean CO, Manoilova OV, Delgado MR, Tsyganenko AA, Garrone E. Formation of several types of coordination complexes upon CO adsorption on the zeolite Li-ZSM-5. Phys Chem Chem Phys. 2001;3(19):4187–8.
27. Dunne JA, Mariwala R, Rao M, Sircar S, Gorte RJ, Myers AL. Calorimetric heats of adsorption and adsorption isotherms. 1. O_2, N_2, Ar, CO_2, CH_4, C_2H_6, and SF_6 on silicalite. Langmuir. 1996; 12(24):5888–95.

28. Maurin G, Bell RG, Llewellyn PL. CO_2 adsorption in faujasite systems: microcalorimetry and molecular simulation. In: Cejka J, Zilkova N, Nachtigall P, editors. Molecular sieves: from basic research to industrial applications, pts A and B. Studies in surface science and catalysis; 2005. p. 955–62.
29. Bourrelly S, Maurin G, Llewellyn PL. Adsorption microcalorimetry of methane and carbon dioxide on various zeolites. Stud Surf Sci Catal. 2005;158:1121–8.
30. Bonelli B, Onida B, Fubini B, Arean CO, Garrone E. Vibrational and thermodynamic study of the adsorption of carbon dioxide on the zeolite Na-ZSM-5. Langmuir. 2000;16(11):4976–83.