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Isosteric heats of adsorption of carbon dioxide on zeolite MCM-22 modified by alkali metal cations

Arnošt Zukal · Justyna Pawlesa · Jiří Čejka

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Abstract Adsorption isotherms of carbon dioxide were measured on cation-exchanged (Li^+, Na^+, K^+, Cs^+) MCM-22 zeolite with the molar ratio of Si/Al = 15 and series of Na-MCM-22 of Si/Al molar ratios varying in the range from 15 to 40 at 273, 293, 313 and 333 K. Based on the known temperature dependence of CO_2 adsorption, isosteric heats of adsorption were calculated. The obtained dependences of isosteric heats related to the amount of CO_2 adsorbed have provided detailed insight into the interaction of carbon dioxide molecule with alkali metal cations.

Keywords MCM-22 zeolite · Alkali metal cation exchange · CO_2 adsorption · Isosteric heat of adsorption

Abbreviations

S_{BET}	BET surface area, m^2/g
$S_{external}$	external surface area, m^2/g
V_{total}	total pore volume, cm^3/g
V_{micro}	micropore volume, cm^3/g
q_{st}	isosteric heat of adsorption, kJ/mol
R	gas constant, kJ/mol·deg

1 Introduction

One of the major technological and environmental problems that our society faces today is economically favorable separation and storage of carbon dioxide. Very promising candidates for applications in adsorption and separation of carbon dioxide include nanoporous materials, namely metal organic frameworks, activated carbons, hydrotalcite-like compounds, metal oxide adsorbents and particularly zeolites (Yong et al. 2002). Numerous papers concerning CO_2 adsorption on zeolites A (Delaval and De Lara 1981; Amari et al. 1991), faujasites X and Y (Barrer and Gibbons 1965; Khelifa et al. 1999; Hasegawa et al. 2001; Walton et al. 2006; Plant et al. 2006), mordenites (Amari et al. 1992), ZSM-5 (Yamazaki et al. 1993; Dunne et al. 1996; Katoh et al. 2000), and chabazites (Zhang et al. 2008) can be found in the literature investigating CO_2 adsorption to determine the effect of the structure and cation type on the adsorption equilibrium and energetics of the adsorption process. Much research effort has been focused on the CO_2 adsorption on NaX and NaY at ambient temperature (Maurin et al. 2005; Plant et al. 2006, 2007) and more recently in NaY and LiY at high temperatures (Maurin et al. 2007) using a combination of Grand Canonical Monte Carlo simulations and microcalorimetry/gravimetry measurements. It has been clearly established that the extra-framework cations compensating the negative charge of the faujasite framework, play a decisive role in adsorption on these materials. The calculated enthapies $-\Delta H^o$ of interaction of CO_2 molecule with bare alkali metal cations are generally much larger than the experimental ones due to the absence of the zeolite framework (Garrone et al. 2002). Moreover, calculated enthalpies decrease quickly in the sequence $Li^+ > Na^+ > K^+ > Cs^+$ from 83.63 kJ/mol to 53.17, 32.40 and 20.50 kJ/mol, respectively. This clearly evidences that enthalpy of interactions decreases with increasing size of the alkali metal cation. For comparison, calculated enthalpies $-\Delta H$ of CO_2 adsorption on Y faujasite at 300 K extrapolated to zero coverage decrease in the same

A. Zukal · J. Pawlesa · J. Čejka (✉)
J. Heyrovský Institute of Physical Chemistry, v.v.i.,
Academy of Sciences of the Czech Republic, Dolejškova 3,
182 23 Prague 8, Czech Republic
e-mail: jiri.cejka@jh-inst.cas.cz

sequence from 33.20 kJ/mol to 17.17 kJ/mol (Plant et al. 2006). The values of $-\Delta H$ correlate well with M^+–O_{CO_2} distance which increases in the sequence LiY < NaY < KY < CsY (M^+ stands for the alkali metal cation). Therefore, the closer the oxygen of carbon dioxide approaches the extra-framework cation, the stronger interaction becomes. This trend is consistent with those previously reported from experimental and theoretical results for the adsorption of CO_2 on NaX (Barrer and Gibbons 1965) or other gases in various zeolite systems (Bezus et al. 1971; Dzhigit et al. 1971, 1979; Amelitcheva et al. 1978).

Although extensive experimental and theoretical works on the adsorption of CO_2 on different zeolites were published, to our knowledge there is only one report concerning the isothermal study of CO_2 adsorption on MCM-22 zeolite (Pawlesa et al. 2007). This zeolite (IZA code MWW) crystallizes as thin sheets or plates and has unique and unusual structure (Rubin and Chu 1990; Lawton et al. 1998). The thin crystals exhibit hexagonal morphology, with the unit cell *c*-axis perpendicular to the plate surface. The framework topology is comprised of two independent pore systems. One of these pore systems is defined by two-dimensional sinusoidal channels, which maintain an effective 10-ring diameter throughout the structure. The other is comprised of large supercages whose inner free diameter, 7.1 Å, is defined by 12-rings and whose inner height is 18.2 Å (Leonowicz et al. 1994; Dorset et al. 2005). The free diameters of the pore systems are 4.0 × 5.9 Å for the sinusoidal channels and 4.0 × 5.4 Å for the entrances to the supercages. Many studies describing particularly the catalytic behavior can be found in the literature focused on using of MCM-22 zeolite in catalytic cracking, olefin isomerization or the alkylation of paraffins and aromates with light olefins (Huss et al. 1991; Del Rossi and Huss 1992; Čejka et al. 2002).

In our previous paper we report on the influence of alkali metal cations on the carbon dioxide adsorption properties at 273 K using ion-exchanged MCM-22 zeolites (Pawlesa et al. 2007). We evidenced the decisive influence of the nature and the concentration of the charge-compensating cations on the CO_2 adsorption capacity of MCM-22 zeolite. The highest adsorption capacity was obtained on the K^+ form of MCM-22 zeolite with the molar ratio Si/Al = 15.

Useful approach to gain detailed information about the interaction of carbon dioxide molecule with various cationic forms of MCM-22 zeolite is to study the temperature dependence of the adsorption. For this reason, the attempt has been made to examine the influence of the nature of exchanged cations on the isosteric heat of CO_2 adsorption, which can be derived from adsorption isotherms recorded at different temperatures. Na-MCM-22 samples with three different Si/Al molar ratios and MCM-22 zeolite with Si/Al = 15 modified with alkali metal cation (Li^+, Na^+, K^+ and Cs^+) exchange were chosen for this investigation.

2 Experimental

2.1 Synthesis

Na-MCM-22 zeolites with Si/Al ratios in the range from 15 to 40 have been synthesized with sodium aluminate (50–56% Al_2O_3, 40–45% Na_2O, Riedel-de Haën) and Cab-O-Sil M5 (Cabot GmbH) as a source of aluminum and silicon, respectively. In all experiments, hexamethyleneimine (HMI, Aldrich) was employed as a structure directing agent. The MCM-22 sample with initial molar ratio of Si/Al = 15 was obtained starting with the following molar composition of the synthesis mixture: $Na_2O : Al_2O_3 : SiO_2 : HMI : H_2O = 0.081 : 0.033 : 1 : 0.56 : 45.4$. Crystallization of the reaction gel was done in a Teflon-lined stainless steel autoclave under agitation for 5 days at 423 K. The removal of the template was performed by calcination in air for 6 h at 813 K (ramping rate of 1 K/min).

Na-MCM-22 zeolites with different Si/Al ratios were used as starting materials for cation exchange. Calcined zeolites were subsequently converted into alkali forms by treatment with 1.0 M MNO_3 water solutions (M = Na^+, K^+, Cs^+) or LiCl in the case of Li^+ form (100 mL/1 g of zeolite). For this purpose 100 mL of the solution was used per 1 g of the sample. The procedure was repeated two times and each step took 8 h at 333 K. During ion exchange the pH values of the ion exchange suspensions were adjusted to the value of 9 with a 0.5 M MOH or LiOH solutions.

2.2 XRD characterization, chemical analysis

All calcined and ion-exchanged samples were checked for their crystallinity and phase purity by X-ray powder diffraction on a Bruker D8 X-ray powder diffractometer equipped with a graphite monochromator and position sensitive detector (Våntec-1) using CuKα radiation (at 40 kV and 30 mA) in Bragg-Brentano geometry. To estimate the chemical composition of synthesized zeolites and their ion-exchange forms the X-ray fluorescence spectroscopy (Philips PW 1404) was employed.

2.3 Adsorption experiments

Adsorption isotherms of nitrogen at 77 K and carbon dioxide in the temperature range from 273 to 333 K were determined using an ASAP 2020 (Micromeritics) static volumetric apparatus. In order to attain a sufficient accuracy in the accumulation of the adsorption data, the ASAP 2020 was equipped with pressure transducers covering the 1 torr, 10 torr and 1000 torr ranges. Before adsorption experiments the sample was outgassed under turbomolecular pump vacuum using a special heating program allowing for a slow removal of most preadsorbed water at low temperatures. This

Table 1 Characterization of MCM-22 zeolites

Sample code	Unit cell composition	BET surface area [m^2/g]	V_{micro} [cm^3/g]	Number of CO_2 mol. per unit cell at 273 K		Number of CO_2 mol. per cation at 273 K		Number of CO_2 mmol per gram at 273 K		Number of CO_2 mmol per m^2 at 273 K	
				10 torr	800 torr	10 torr	800 torr	10 torr	800 torr	10 torr	800 torr
Na-MCM-22/15	$Na_{4.7}$ $Al_{4.7}$ $Si_{66.5}$ O_{144}	542	0.17	2.02	13.22	0.43	2.81	0.45	3.00	0.0008	0.005
Na-MCM-22/20	$Na_{3.3}$ $Al_{3.3}$ $Si_{66.5}$ O_{144}	506	0.18	1.21	12.74	0.43	3.86	0.28	2.94	0.0006	0.006
Na-MCM-22/40	$Na_{1.7}$ $Al_{1.7}Si_{66.5}$ O_{144}	329	0.12	0.73	10.18	0.43	5.99	0.17	2.39	0.0005	0.007
LiNa-MCM-22/15	$Li_{2.3}$ $Na_{2.3}$ $Al_{4.7}$ $Si_{66.5}$ O_{144}	466	0.16	3.59	12.70	0.78	2.76	0.82	2.91	0.002	0.006
K-MCM-22/15	$K_{4.7}$ $Al_{4.7}$ $Si_{66.5}$ O_{144}	479	0.17	4.65	14.01	0.99	2.98	1.03	3.13	0.002	0.006
Cs-MCM-22/15	$Cs_{4.7}$ $Al_{4.7}$ $Si_{66.5}$ O_{144}	423	0.14	3.67	12.93	0.78	2.77	0.74	2.65	0.002	0.006

The number beyond fraction bar stands for Si/Al ratio

was done to avoid potential structural damage of the sample due to surface tension effects and hydrothermal alternation. Starting at ambient temperature the sample was outgassed at 383 K (temperature ramp of 0.5 K/min) until the residual pressure of 0.01 torr was obtained. After further heating at 383 K for 1 h the temperature was increased (temperature ramp of 1 K/min) until the temperature of 623 K was achieved. This temperature was maintained for 8 h. The check procedure performed after this time period indicated that the sample has been rid of contaminants.

The home-made thermostat maintaining temperature of the sample with accuracy of ±0.01 K was used for the measurement of carbon dioxide adsorption at 273, 293, 313 and 333 K. (The exact temperature of each measurement was determined using platinum resistance thermometer.) The carbon dioxide isotherms at given temperatures were measured immediately on the same sample, which was used for the nitrogen isotherm measurement. Before each measurement of carbon dioxide isotherm the sample was outgassed at 423 K for 12 h under turbomolecular pump vacuum.

3 Results and discussion

The sample codes and unit cell composition are listed in Table 1. Except for lithium, the degree of exchange of potassium and cesium cations attains almost 100%. The exchange of Li^+ for Na^+ cations is not favored due to the large diameter of hydrated lithium cation (Polato et al. 2004) and the degree of exchange reaches 50% only.

X-ray powder diffraction patterns of the Na-MCM-22 zeolites with Si/Al molar ratio 15, 20 and 40 (Fig. 1) evidence their high crystallinity. Within this Si/Al ratio range no changes in the intensities and line widths are observed. Diffraction patterns of samples LiNa-MCM-22/15, K-MCM-22/15 and Cs-MCM-22/15 (not shown) revealed that the crystallinity of the K-MCM-22/15 and Cs-MCM-22/15 remained unchanged after ion-exchange treatment. On the other hand, the lower intensity of the main diffraction lines in the X-ray diffraction pattern of the sample LiNa-MCM-22 indicates a certain decrease in the crystallinity.

Textural properties of the MCM-22 zeolites used for CO_2 adsorption were determined from the nitrogen adsorption data published in the foregoing paper (Pawlesa et al. 2007). The main texture parameters, i.e. BET surface area and micropore pore volume, are listed in Table 1; their values correspond well with the literature data (Rodriguez et al. 2000; Corma et al. 2001; Laforge et al. 2005). In general, the synthesized MCM-22 zeolites crystallize as very thin plates with large external surface area. Due to changes in the crystal morphology, the surface area of Na-MCM-22 zeolites decreases with the increasing Si/Al ratio. The surface area and micropore volume of the K-MCM-22/15 and Cs-MCM-22/15 are lower than those of Na-MCM-22 owing to the increasing weight of alkali metal cations. The relatively small surface area of LiNa-MCM-22/15 could be caused by a decrease in the crystallinity indicated by XRD pattern (Pawlesa et al. 2007).

CO_2 isotherms recorded on MCM-22 zeolites under study at temperatures 273, 293, 313 and 333 K are presented in Figs. 2 and 3. The amounts adsorbed expressed as the number of CO_2 molecules per unit cell at 10 torr and 800 torr and 273 K are listed in Table 1. The amounts of CO_2 expressed in milimols per gram and per m^2 of the sample given in Table 1 represent basic information on the adsorption capacities of studied samples. The data for samples Na-MCM-22/15, Na-MCM-22/20 and Na-MCM-22/40 clearly demonstrate that adsorption capacity at low equilibrium pressure decreases with decreasing content of sodium cations; less pronounced decrease of the adsorption capacity occurs at high equilibrium pressure as well. On the other hand, the maximum adsorption capacity is observed with sample K-MCM-22/15 containing potassium cations.

The amount adsorbed expressed as number of CO_2 molecules per one cation at 10 torr and 273 K equals to 0.43 independently on the number of sodium cations in Na-MCM-

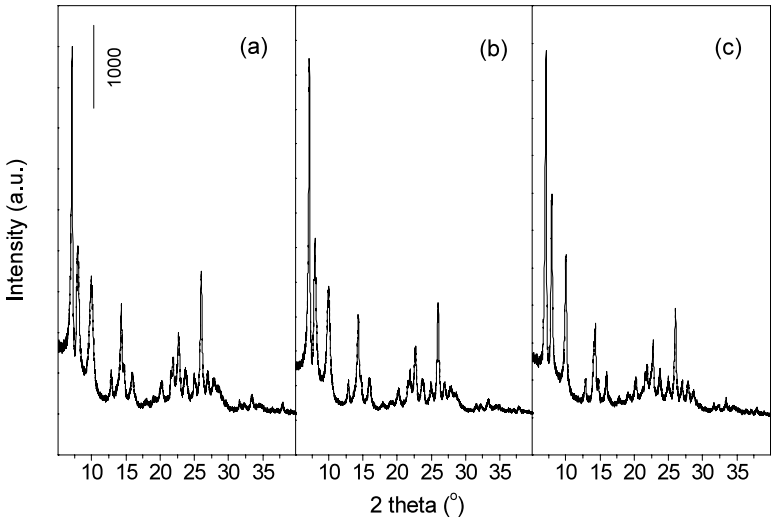

Fig. 1 X-ray diffraction patterns of calcined Na-MCM-22 zeolite with different initial ratio of Si/Al: (**a**) 15, (**b**) 20, (**c**) 40

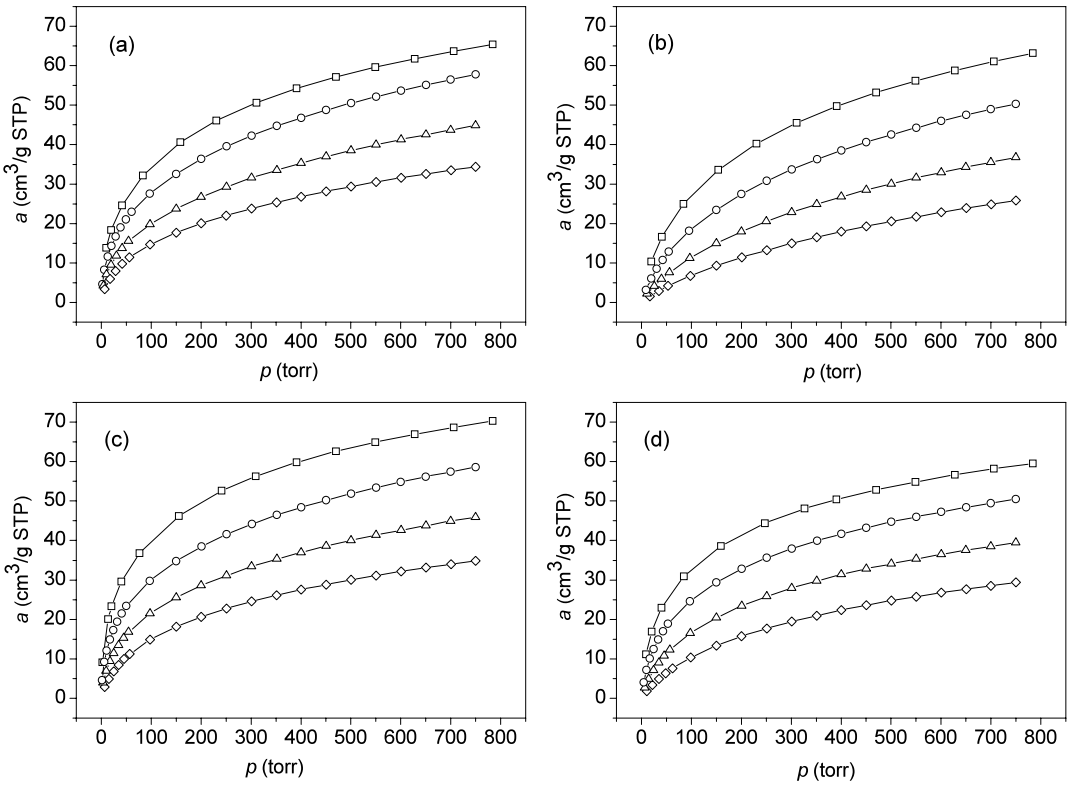

Fig. 2 Isotherms of carbon dioxide adsorption of MCM-22 zeolite with Si/Al = 15 after ion exchange modification with (**a**) Li^+, (**b**) Na^+, (**c**) K^+, (**d**) Cs^+; □ 273 K, ○ 293 K, △ 313 K, ◇ 333 K

22 zeolites (Table 1). It seems that at low pressures CO_2 molecules interact with the most accessible cations regardless of total amount of cations. A striking feature of thus expressed amount adsorbed is observed at 800 torr. The amount of CO_2 molecules per one cation decreases with increasing content of cations in the unit cell; thus, it appears that with increasing content of sodium cations their accessibility for CO_2 molecule gradually decreases. A comparison of MCM-22/15 zeolites containing different cations reveals that the number of CO_2 molecules per one cation at 10 torr reaches the maximum of 0.99 for potassium K-MCM-22/15. The number of CO_2 molecules per one cation at 800 torr practically does not depend on the cation nature.

Based on the determined temperature dependence of adsorption isotherm, adsorption isosteres were calculated. To this end, the isotherms were plotted in co-ordinates log p

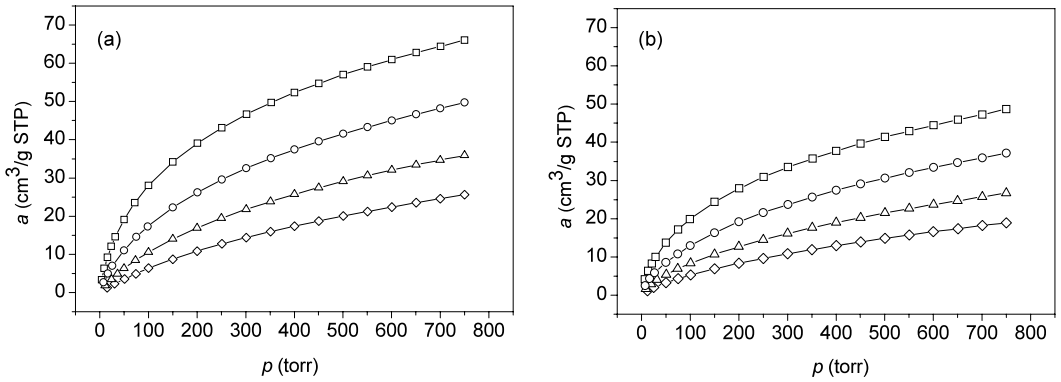

Fig. 3 Isotherms of carbon dioxide adsorption of MCM-22 zeolite with different Si/Al ratio (**a**) 20, (**b**) 40; □ 273 K, ○ 293 K, △ 313 K, ◇ 333 K

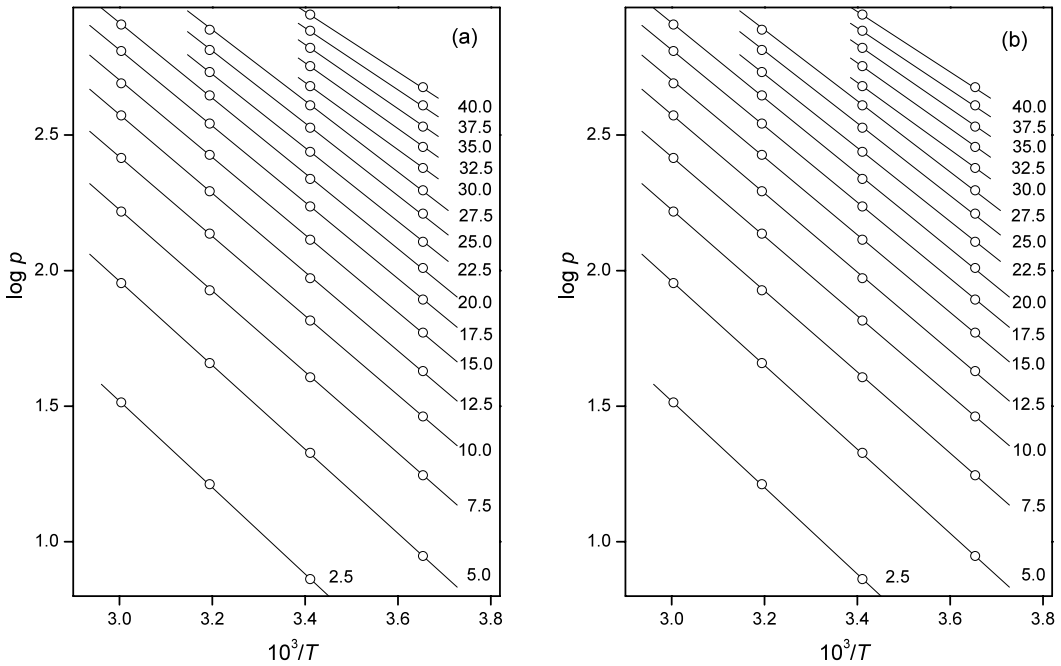

Fig. 4 Adsorption isosteres of CO_2 in temperature range from 273 to 333 K on (**a**) Na-MCM-22/40 and (**b**) K-MCM-22/15 Points were calculated by numerical interpolation, lines represent linear fit. All the isosteres are marked with corresponding amount adsorbed in cm^3/g STP

vs. a. Values of log p corresponding to a series of adsorbed amounts $a = 2.5, 5.0, 7.5, 10.0, \ldots, 50.0$ cm^3/g STP were calculated using a polynomial interpolation procedure. Isosteric adsorption heats q_{st} were calculated from the slope of adsorption isosteres using equation

$$\mathrm{d}(\log p)/\mathrm{d}(1/T) = -q_{st}/2.303 \cdot R, \quad (1)$$

where p is equilibrium pressure (torr), T temperature (K) and R gas constant.

Typical sets of adsorption isosteres in co-ordinates log p vs. $10^3/T$ for samples K-MCM-22/15 and Na-MCM-22/40, which display the highest and lowest isostere slope, respectively, are presented in Fig. 4. The linear fit shows that the isosteric adsorption heat does not depend on the temperature in the temperature interval investigated and it depends only on the amount adsorbed. Similarly to the presented samples K-MCM-22/15 and Na-MCM-22/40, the isosteric adsorption heats for other MCM-22 zeolites are independent on temperature.

In the case of MCM-22 the precise positions of alkali metal cations and their coordination to framework oxygen are not yet known. Therefore, the theoretical assessment of isosteric heats of CO_2 adsorption is not possible; these data must be gained experimentally. The dependences of isosteric heats of adsorption on the amount ad-

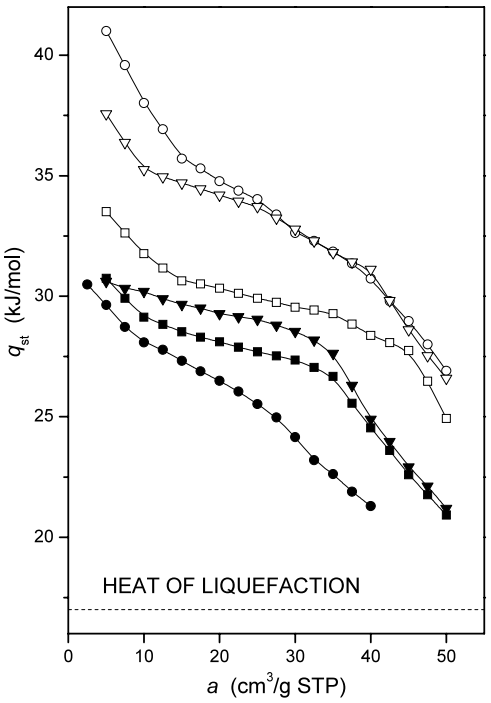

Fig. 5 Isosteric heat of adsorption of carbon dioxide on MCM-22 zeolite: ○ K-MCM-22/15, ▽ Cs-MCM-22/15, □ LiNa-MCM-22/15, ▼ Na-MCM-22/15, ■ Na-MCM-22/20, ● Na-MCM-22/40

sorbed for LiNa-MCM-22/15, Na-MCM-22/15, K-MCM-22/15 and Cs-MCM-22/15 samples are shown in Fig. 5. Isosteric heat of adsorption attains 41 kJ/mol for K-MCM-22/15 zeolite; in the region of the amount of CO_2 adsorbed lower than 10 cm^3/g STP it decreases in the sequence $K^+ > Cs^+ > Li^+Na^+ > Na^+$. The amount adsorbed, especially at low equilibrium pressures (Table 1), corresponds to the strength of interaction between CO_2 molecule and alkali metal cation expressed by means of isosteric heat of adsorption. As mentioned above, the number of CO_2 molecules per cation at 10 torr equals to 0.43 for Na-MCM-22/15, while for K-MCM-22/15 it reaches 0.99. For samples Na-MCM-22/15, Na-MCM-22/20 and Na-MCM-22/40 the isosteric heats of adsorption decrease with decreasing cation content in the whole range of amount adsorbed (Fig. 5). It is obvious from data in Table 1 that this decrease correlates with adsorption properties of sodium MCM-22 forms.

4 Conclusions

In the sodium forms of MCM-22 zeolite the amount of adsorbed CO_2 expressed as number of molecules per one cation at low equilibrium pressure does not depend on the number of cations. This effect is probably caused by the interaction with the most accessible cations regardless of total amount of cations. As the number of CO_2 molecules per one cation decreases with increasing number of sodium cations in the unit cell, the accessibility of cations for CO_2 molecule gradually decreases.

The experimental study of temperature dependence of carbon dioxide adsorption on various forms of MCM-22 zeolite provides detailed information on the interaction of carbon dioxide molecule with alkali metal cations. Isosteric heats of adsorption attain the highest values with potassium form of MCM-22; the lowest values were found with sodium forms. For these forms of MCM-22 zeolite the isosteric heats of adsorption decrease with decreasing cation content in the whole range of amount adsorbed.

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