Adsorption (2013) 19:381–389
DOI 10.1007/s10450-012-9461-8

Study of thermodynamic characteristics of CO adsorption on Li exchanged zeolites

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Received: 31 October 2012 / Accepted: 21 December 2012 / Published online: 8 January 2013

Abstract The experimental thermodynamic characteristics of CO probe molecule adsorption on lithium exchanged zeolites of MFI, FAU, MCM-58, MCM-22, MCM-36 and MCM-49 structure was investigated by joint volumetry-calorimetry method. Consideration was given to the interpretation of the heat evolved when a probe molecule was adsorbed on the surface. In particular, the number and strength of adsorption sites were discussed as functions of zeolite structure and concentration of extra-framework cation. In addition, the obtained thermodynamic data and energy distribution functions were discussed together with results obtained from FTIR spectroscopy and theoretical DFT calculations.

Keywords Carbon monoxide · Zeolites · Regularization · Calorimetry · Volumetry

1 Introduction

The amount and localization of Al atoms and other extra framework atoms strongly influence the adsorption characteristics of zeolites together with their textural characteristics. Only zeolites with low Si/Al ratio can be directly characterized from this point of view using XRD or neutron scattering analysis (Mortier 1982; Olson 1995). The localization and coordination of extra framework atoms cannot be studied directly in the case of high silica zeolites and the indirect methods based on the adsorption of small probe molecules could be used for the characterization of such materials (Zecchina and Arean 1996; Hadjiivanov and Vayssilov 2002; Garrone and Arean 2005; Bolis et al. 2004; Arean et al. 2007).

The thermodynamic characteristics of the formation of probe molecules adsorption complexes can bring useful information about the character and localization of cations in the zeolite framework. The thermodynamic data of the adsorption are usually obtained from the direct calorimetric measurements or indirectly from the evaluation of adsorption isosteres (Zukal et al. 2011; Zukal et al. 2012; Carniti et al. 1994). Coupling of measurement of calorimetric data with the measurement of the adsorption isotherms brings the possibility to obtain the dependence of differential adsorption heat on the cover degree from one experiment. The dependence of adsorption heat (q_{diff}) on coverage degree (Θ) brings some information about heterogeneity of adsorption sites but these data are rather "smoothed" by thermal effects.

The task of obtaining the original distribution function of the adsorption energy from experimental data can be formulated as a solution of Fredholm integral equation of first kind (Von Szombathely et al. 1992; Jagiello 1994; Kowalczyk et al. 2002). Solution of this equation is possible only when (i) we can expect an uniform "stoichiometry" of the formed adsorption complexes, (ii) no subsequent occupancy of one adsorption site by another adsorbate molecule occurs and (iii) no adsorbate–adsorbate interactions takes place. Nevertheless this problem belongs to the "inverse problem" tasks which are usually ill posed. The Tikhonov regularization (Tikhonov 1943) of adding of some information about the smoothness of expected solution is often used to solving such ill posed problems. When we wish to use the methodology based on the regularization method for the evaluation of the adsorption experimental data, we must properly choose the experimental

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conditions and materials for which the above mentioned limiting conditions are fulfilled.

Carbon monoxide can be used as a suitable probe molecule due to its high sensitivity to nature and local environment of the adsorption site. The interaction energy of CO adsorption on the zeolitic cation site is affected either by the character of cation, its coordination and the local composition of the adsorption site (effects from bottom) or by the interaction of adsorbed CO with charge on opposite side of the zeolitic channel or cavity (effects from top) (Nachtigallova et al. 2006). It was reported that the small Li^+ cation is the most suitable cation for probing of the site-specificity due to the effects from the bottom while the effect from the top is not site specific in the case of the Li^+ cations (Nachtigall et al. 2007; Nachtigall and Bulanek 2006). Since lithium cationic sites in the zeolites differ in coordination of Li^+ cations, experimental determination of the CO stretching frequency and the adsorption enthalpy for a particular zeolite can provide information on type of the cationic adsorption sites present in the investigated zeolite.

However, adsorption of CO on the alkali-metal cations in zeolites (including Li^+ cations) is complicated by the fact that the CO molecule is able to interact with the cation in the zeolite matrix by both ends forming either the "M^+…CO" adsorption complexes (also denoted as "C-down" complexes) or the "M^+…OC" adsorption complexes (denoted as "O-down" complexes or "isocarbonyl" complexes) (Arean et al. 2001; Arean et al. 2007). Both types of adsorption complexes can be formed freely on the same adsorption site and probability of their abundance is controlled by the temperature and difference of adsorption energy connected with the appearance of both type species. Possibility of occurrence of both type complexes must be hence included in all models attempting to describe the adsorption of CO on alkali metal cations in zeolite matrices. Moreover, the formation of polycarbonyl species or significant contributions of adsorbate–adsorbate interactions to experimental data also start to play significant role at higher values of cover degree over Li exchanged zeolites and must be taken into account in the models.

In this contribution we report our results of testing of applicability of the regularization method for the evaluation of the coupled volumetric-calorimetric data from the CO adsorption on various Li exchanged zeolites differing in the structure and character of inner space. MFI zeolite represents three-dimesional system of interconnected and crossed channels. MCM-22 and MCM-49 represent zeolites combining 10-MR channels with a large cavity, whereas its layered form (MCM-36) represents hierarchical zeolitic material combining micro- and mesoporosity. IFR zeolite represents one dimensional zeolitic channel system of the parallel non-crossing tubular pores. FAU zeolite represents low-silica zeolite with a very high concentration of cations providing not channel but cavity system of the inner space. Suggested model of CO adsorption is assuming possibility of formation of two types of adsorption complexes Li^+…CO and Li^+…OC on each lithium cation. Employed model of the adsorption assumed that solving the integral Fredholm equations for description of both the adsorption and the calorimetric isotherms should provide the same solution of distribution function of adsorption energy.

2 Experimental

2.1 Sample preparation and characterization

The faujasite (zeotype FAU) and ZSM-5 (zeotype MFI) samples were supplied by the Zeolyst Corp. Samples MCM-58 (zeotype IFR), MCM-22, MCM-36 and MCM-49 (all of zeotype MWW) were supplied by the J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic. All zeolites were obtained in their ammonium forms and transferred by calcination at about 673 K to H^+ forms.

The lithium forms of zeolites were obtained by an ion exchange repeated five times in a 0.1 M aqueous solution of LiCl for 5 days at 313 K. Complete ion exchange was checked by the disappearance of the IR band in the 3,600–3,620 cm^{-1} region, where Brønsted-acid hydroxyl groups appeared in the protonic form of the zeolites.

The structure of investigated materials, after the ion exchange and calcinations, was checked by a Bruker D8 Advance X-ray powder diffractometer with Cu Kα radiation. XRD patterns evidenced a well-developed structure of all investigated materials. The XRD patterns of all investigated zeolite samples exhibited the presence of only a zeolite-type framework structure characteristic for the particular zeolite structures (Treacy and Higgins 2001) (not shown here).

2.2 FTIR spectroscopy measurement

For the FTIR measurements, thin self-supported sample wafers were activated at 673 K under dynamic vacuum overnight (residual pressure of 10^{-4} Torr). CO (purity of 99.997 % Linde gas corp.) was further purified before the adsorption by a freeze–pump–thaw cycle. CO was dosed to the IR glass cell to equilibrium pressures of about 0.1 and 140 Torr for experiments at liquid nitrogen and room temperature, respectively. The absorption bands of liquid CO and dicarbonyl species appeared in the spectra collected at 77 K. Therefore the IR cell was slowly evacuated until these bands disappeared. The spectra were collected with a resolution of 2 cm^{-1} on a Nicolet FTIR 6700 spectrometer equipped with an MCT/A cryodetector. The spectrum of sample taken before the CO dosage was used as a background, and it was subtracted from all spectra shown in this work.

VTIR experiments were carried out at temperature ranging from 243 to 278 K. The mixture of ethanol and isopropanol (vol. ratio 4:1) cooled down by liquid nitrogen was used as a cooling agent. The starting temperature of the mixture was about 233 K and then it was added to a cooling part of the cell. The temperature change of the cooling mixture was monitored by thermocouple through the experiment. The collection of the spectra started when the temperature increased to 243 K and repeatedly after each 5 K till the temperature of 278 K was reached.

The positions and areas of individual absorption bands in the obtained spectra of the carbonyl species were evaluated by fitting to Gaussian shape functions using the MicroCal Origin software.

2.3 Coupled adsorption-microcalorimetric measurements

Prior to each adsorption experiment, the sample of the weight 400 mg was outgassed by slowly increasing temperature of the sample with the simultaneous careful evacuation up to residual pressure 10^{-4} Pa at 700 K. The temperature program was running: from the 298 K temperature raised with the slope of 1 $K^{-1}.min^{-1}$ to 380 K, isotherm was then keep for 30 min, and subsequently the temperature of sample was increased with the heating rate 3 $K^{-1}.min^{-1}$ to the final temperature of 700 K. The whole sample pretreatment procedure was carried outside of the calorimeter in glassy calorimetric cell. The microcalorimetric—volumetric experiments were carried out in the isothermal Tian-Calvet type microcalorimeter (BT 2.15 from SETARAM) combined with a homemade volumetric-manometric device. The experiments were measured at temperature 173 K. The adsorption isotherms and heats of adsorption were measured by step-by-step introduction of the adsorptive into the cell. The CO (the same purity as for FTIR experiments) was introduced via a system of electrically operated vacuum valves controlled by PC with the software developed at our laboratory. After the stabilization of the pressure in the dosing volume, the valve separating dosing volume from a sample cell was opened and the system was equilibrated at each dose for the 50 min. Each dose was accompanied by the exothermic effect detected by the microcalorimeter until the equilibrium was 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 the integral adsorption heat were determined for each step of the experiment. The dependence of differential adsorption heat versus adsorbed amount of CO was obtained by numerical differentiation of the dependence of the adsorption heat versus adsorbed amount data.

2.4 Calculation methodology

The distribution function of the adsorption energy $\chi(\varepsilon)$ can be under fulfillment of some conditions obtained by the regularization method (Von Szombathely et al. 1992; Kowalczyk et al. 2002; Jagiello 1994) which allows us to determine unknown energy distribution given by function $\chi(\varepsilon)$ from Fredholm integral equations of the first kind (1a, 1b), usually defined as:

$$\Theta(\mathrm{p}) = \int_0^\infty \theta(\mathrm{p},\varepsilon) \cdot \chi(\varepsilon) \cdot \mathrm{d}\varepsilon \tag{1a}$$

$$\mathrm{Q_{int}}(\mathrm{p}) = \int_0^\infty \varepsilon \cdot \theta(\mathrm{p},\varepsilon) \cdot \chi(\varepsilon) \cdot \mathrm{d}\varepsilon \tag{1b}$$

In our case the local isotherms $\theta(p, \varepsilon)$ as a function of pressure p and adsorption energy ε (temperature T is given as a constant parameter) can be of the Langmuir type due to relatively isolated and independent character of the adsorption sites but we must consider that the formation of isocarbonyl species ($Li^+ \ldots O = C$) can occur simultaneously on the same adsorption sites as the formation of carbonyls ($Li^+ \ldots C = O$) occurs. Therefore we used two local adsorption isotherms (2a, 2b) in the form:

$$\theta_{\mathrm{CO}}(\mathrm{p},\varepsilon) = \frac{\mathrm{K_{CO}}(\varepsilon) \cdot \mathrm{p}}{1 + (\mathrm{K_{CO}}(\varepsilon) + \mathrm{K_{OC}}(\varepsilon + \Delta \mathrm{H_{iso}})) \cdot \mathrm{p}} \tag{2a}$$

$$\theta_{\mathrm{OC}}(\mathrm{p},\varepsilon) = \frac{\mathrm{K_{OC}}(\varepsilon + \Delta \mathrm{H_{iso}}) \cdot \mathrm{p}}{1 + (\mathrm{K_{CO}}(\varepsilon) + \mathrm{K_{OC}}(\varepsilon + \Delta \mathrm{H_{iso}})) \cdot \mathrm{p}} \tag{2b}$$

The K_{CO} and K_{OC} values denote the equilibrium constants of adsorption for C-down and O-down complexes. The value ΔH_{iso} is change of the enthalpy connected with the switching of the both mentioned adsorption complexes. If we assume that both types of adsorption complexes interact similarly with the cationic site and the change of the entropy of adsorption is hence the same for both types of adsorption complexes, we can write the equilibrium constants of adsorption as functions of the adsorption energy in the form:

$$\mathrm{K_{CO}} = \exp\left(\frac{\Delta \mathrm{S_{ads}}}{\mathrm{R}}\right) \cdot \exp\left(-\frac{\varepsilon}{\mathrm{RT}}\right) \tag{3a}$$

$$\mathrm{K_{OC}} = \exp\left(\frac{\Delta \mathrm{S_{ads}}}{\mathrm{R}}\right) \cdot \exp\left(-\frac{\varepsilon + \Delta \mathrm{H_{iso}}}{\mathrm{RT}}\right) \tag{3b}$$

The ΔS_{ads} denotes a change of the entropy of adsorption and R is a gas constant. Hence energy distribution functions $\chi(\varepsilon)$ were obtained by regularization of weighted sum of both sets of the experimental data i.e. Θ degree and Q_{int} versus CO pressure using following equations:

$$\Theta(p) = \int_0^\infty (\theta_{CO}(p,\varepsilon) + \theta_{OC}(p,\varepsilon)) \cdot \chi(\varepsilon) \cdot d\varepsilon \tag{4a}$$

$$Q_{int}(p) = \int_0^\infty (\varepsilon \cdot \theta_{CO}(p,\varepsilon) + (\varepsilon + \Delta H_{iso}) \cdot \theta_{OC}(p,\varepsilon)) \cdot \chi(\varepsilon) \cdot d\varepsilon \tag{4b}$$

We assumed that the distribution function can be written as a piecewise defined set of trapezoidal functions. Because both sets of experimental data share the same distribution function of the energy we can rewrite the weighted sum of the Eqs. (1a, 1b) in matrix form:

$$\mathbf{A} \cdot \chi(\varepsilon) \approx \text{weight} \cdot \Theta(\mathbf{p}) + (1 - \text{weight}) \cdot Q_{int}(\mathbf{p}) = \mathbf{g}(\mathbf{p}) \tag{5}$$

where **A** is a matrix representing weighted sum of integral kernels of (1a, 1b) equations in matrix form (Von Szombathely et al. 1992; Kowalczyk et al. 2002). The Eq. (5) hence represents the transformation of Eqs. (1a, 1b) into the set of linear equations.

Because such equations represents the ill posed problem we solved it by the regularization procedure by adding the second term for the minimization $\lambda\|\mathbf{C}.\chi(\boldsymbol{\varepsilon})\|^2$ which controls the smoothness of the solution (λ chosen to be 1.10^{-6}) (Tikhonov 1943). To solve this problem we used the non-negative least square (NNLS) solver which is a standard part of the SciPy library of the Python programming language. Used method is based on the algorithm of Lawson et al. (Lawson and Hanson 1987). Hence we solved this set of the equations in the form:

$$\begin{array}{l} \textit{Minimize} \quad \|\mathbf{A} \cdot \chi(\varepsilon) - \mathbf{g}(\mathbf{p})\|^2 + \lambda\|\mathbf{C} \cdot \chi(\varepsilon)\|^2 \\ \quad \textit{with respect to } \chi(\varepsilon) \geq \mathbf{0} \end{array} \tag{6}$$

All calculations were preformed assuming the energy values ranging from −60 to −10 kJ.mol^{-1} with a step of 0.5 kJ.mol^{-1}.

3 Results and discussions

FTIR spectra of CO molecule adsorbed on Li exchanged zeolites at 77 K are presented in the Fig. 1a. Positions of absorption bands found in region 2,165–2,210 cm^{-1} for particular samples are also included in the Table 1. The blue shift of CO absorption bands corresponding to lithium C-down carbonyls from wavenumber of free gaseous CO (2,143 cm^{-1}) is caused by the CO polarization effect and can be used as characteristics for particular types of cationic positions.

Previously, on the basis of a good agreement between experimental IR spectra and theoretical calculations obtained for a number of different Li exchanged zeolites, four main types of stable Li$^+$ sites in the zeolites were discussed and characterized by the stretching frequency of the corresponding C-down carbonyl complexes (Nachtigall et al. 2007): (i) Li$^+$ ions coordinated only to two oxygen atoms at the intersection of two 10-ring channels denoted type II in the Ref. (Nachtigall et al. 2007); corresponding monocarbonyl complexes are characterized by $\nu_{CO} >$ 2,190 cm^{-1} (ii) Li$^+$ ions coordinated to three oxygen atoms of 8-ring or Li$^+$ cation located on top of 5- or 6-rings on the channel walls with the aluminium at the corner of the ring and coordinated to three or four oxygen atoms [denoted type Ia in the Ref. (Nachtigall et al. 2007)]; corresponding monocarbonyl complexes are characterized by $\nu_{CO} \sim$ 2,187 cm^{-1}. (iii) Li$^+$ cations located in the plane of 6-ring and coordinated to four oxygen atoms of this ring with the aluminum atom at the centre of longer side of the ring [denoted type I in the Ref. (Nachtigall et al. 2007)]; corresponding monocarbonyl complexes are characterized by $\nu_{CO} \sim$ 2,182 cm^{-1} and (iv) Li$^+$ cations in the vicinity of two framework aluminium atoms [denoted in the Ref. (Nachtigall et al. 2007) “Al-pair”]; corresponding monocarbonyl complexes are characterized by the band at $\nu_{CO} \sim$ 2,170 cm^{-1}.

The information about zeolitic structure of the particular sample and previously published (Nachtigall et al. 2007) information allow us to attribute the observed positions of CO adsorption bands to the presence of the most likely adsorption centers which can be expected in these samples.

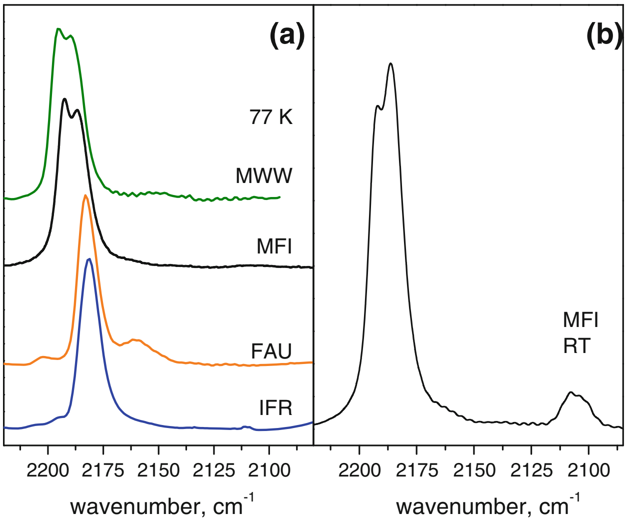

Fig. 1 **a** FTIR spectra of CO adsorbed on zeolite samples at 77 K. **b** FTIR spectrum of adsorbed CO on the ZSM-5 zeolite adsorbed at room temperature

Table 1 Studied lithium exchanged zeolite samples and their FTIR and adsorption characteristics

Sample	Zeotype	Si/Al ratio	$-E_{ads}$, kJ.mol^{-1} (abundance)	FTIR peaks, cm^{-1}	Li$^+$ in position by FTIR*	$E_{int,DFT}$, kJ.mol^{-1}**
Faujasite	FAU	2.6	27.5	2,183	I	9–18
MCM-58	IFR	17.0	36, 30.5	2,181	I	17
			(79 %), (21 %)		"Al pair"	12
MCM-22	MWW	24.5	41.5	2,195	II	25–32
				2,190	Ia	21–24
MCM-36	MWW	29.9	42	-/-	-/-	
MCM-49	MWW	16.7	41	-/-	-/-	
ZSM-5	MFI	30.0	41	2,192	II	25–32
				2,187	Ia	21–24

* Nomenclature of cationic positions from Ref. (Nachtigall et al. 2007)

** Values of interaction energy from Ref. (Nachtigall et al. 2007) calculated on the DFT level i.e. dispersive forces interactions are not considered

Results of this attribution for the all samples are presented in the Table 1.

Figure 1b shows the spectrum of adsorbed CO measured at room temperature over the ZSM-5 zeolite. It is clearly seen that spectrum of CO adsorbed on Li-ZSM-5 at RT moreover exhibits other absorption bands in region 2,090–2,120 cm^{-1}. This vibrational absorption band can be ascribed to the presence of isocarbonyl species i.e. to complexes with structure Li$^+$…OC. The intensity of these bands is lower than intensity of absorption bands belonging to Li$^+$…CO species due to lower interaction energy of these species. Lower interaction energy of these species compared to the Li$^+$…CO species also causes the fact that absorption bands according to these species are not observed or have very low intensity in the spectra measured at 77 K. Moreover the shape of this absorption bands is a "mirror image" of bands of Li$^+$…CO species because the change of polarization of these species causes the opposite red shift effect than for the Li$^+$…CO species.

Because the low temperature spectrum of CO adsorption on the MCM-58 sample apparently exhibited lowest distribution of the absorption bands, the FTIR measurement of the CO adsorption at variable temperatures (VTIR) was performed over this sample. This technique measuring the FTIR spectra under constant or quasi-constant pressure with variation of the temperature was recently used to determine thermodynamic characteristics of the adsorbed CO species (Garrone and Arean 2005) assuming the Langmuir's character of the adsorption. Representative spectra obtained by this experiment for the dose of 21 m bar are presented in the Fig. 2. In the closed cell the total area of the obtained spectra is decreasing with the increasing of the temperature as it can be expected (CO pressure is only slightly changing during measurement). The ratio of area of bands at ca. 2,180 cm^{-1} to the area at ca. 2,115 cm^{-1} is proportional to the equilibrium constant of the exchange between Li$^+$…CO and Li$^+$…OC carbonyl species so the van't Hoff plot (the inset of Fig. 2) can provide the value of change of the isomeration enthalpy ΔH_{iso}. The obtained value ca. 6 kJ.mol^{-1} is only slightly lower than the value 7.8 kJ.mol^{-1} previously reported by Bonelli and coworkers for Li-ZSM-5 (Bonelli et al. 2003) and our value was subsequently used as one of input parameters for our evaluation of the calorimetric-volumetric data by the regularization method.

The interaction of CO with the alkali metal cations is relatively weak and is caused mainly by the electrostatic interaction of cation charge with the dipole of CO molecule. Moreover the unsaturated coordination sphere of the cation in the certain zeolitic position facilitates the successive formation of dicarbonyls or higher polycarbonyls over these adsorption sites. Dicarbonylic complexes exhibit vibrational bands red-shifted by 3–13 cm^{-1}. Dicarbonyls

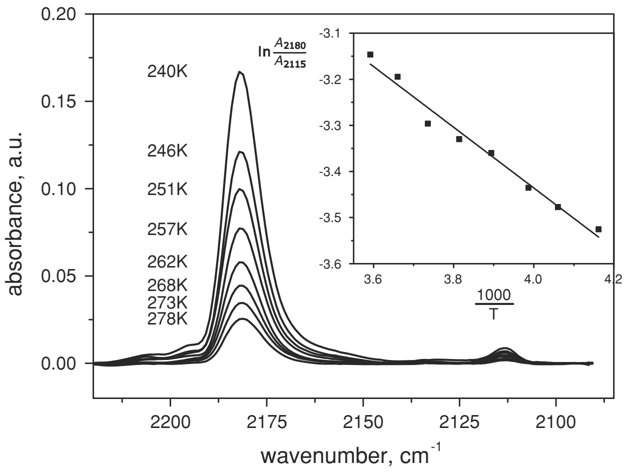

Fig. 2 FTIR spectra of CO adsorbed at MCM-58 sample measured during the VTIR experiment at various temperatures. In inset of figure is van't Hoff's plot from data obtained during this experiment

can be formed mainly on the Li cations at the channel intersections (it means type (i) defined above) with the adsoption enthalpy for the second CO molecule being only about 50–75 % of adsorption enthalpy of the first CO molecule. Therefore, dicarbonyl adsorption complexes formation can be expected at higher levels of the cover degree and thus at the higher CO pressure. The appearance of the dicarbonyl species is shifted to the higher cover degree values over measured Li exchanged zeolite samples at lower temperatures (173 K in our case) in comparison with the adsorption at RT. Considering the complications with including formation of dicarbonyl species into mathematical model, we used for calculations the experimental data only for cover degree lower than 0.5. Both the obtained adsorption and calorimetric isotherms are presented in Fig. 3. Presented data corresponds to the cover degree in range 0–0.5 where the formation of dicarbonyls over our samples can be neglected.

The value of entropic term in equilibrium constant of adsorption was estimated from fit of experimental adsorption isotherm data of FAU sample to Langmuir isotherm model because this sample exhibited relatively flat dependence of q_{diff} value on the cover degree. The obtained value of $\Delta S_{ads} \sim -165$ J.K^{-1}.mol^{-1} agree very well with values of entropy change upon adsorption of CO on various alkali-metal cations in the different zeolites (ranging from -136 to -179 J.K^{-1}.mol^{-1}) estimated by VTIR method and overviewed in the paper of Arean and Garrone (Arean et al. 2001; Arean et al. 2007; Bonelli et al. 2003). Main part of this value can be attributed to loss of translational degree of freedom ($S_{trans,CO} \sim 140$ J.K^{-1}.mol^{-1} at 173 K, $p = 100$ kPa). Moreover, it was shown in the past that result of the regularization procedure is relatively insensitive to the used value of adsorption entropy and Heuchel (Heuchel et al. 1993) shown on the analysis of simulated data that the increasing or the decreasing of the preexponential part of adsorption constant 100 times (in our case change of entropy ~35 J.K^{-1}.mol^{-1}) led to change of the value of the adsorption energy in the range ±3 kJ.mol^{-1}. Therefore our experimentally estimated value for Li-FAU sample was subsequently used in process of evaluation for all remaining data, assuming that formation of C-down and O-down complexes is accompanied by the same change of entropy at first approximation.

Both the adsorption isotherm and the calorimetric isotherm data were evaluated by methodology described in the experimental section taking into account simultaneous formation of Li^{+}…CO and Li^{+}…OC complexes and the values of the distribution of adsorption energy were obtained. Figure 4 shows “fit” of the obtained calculated curves to our experimental data (only sample MCM-58 for sake of brevity). Dashed lines in Fig. 4 represents typical simultaneous “fit” of both data sets obtained without considering the Li^{+}…OC species formation. It is clearly seen that these dependences exhibit a systematic shift from the experimental data points. We can therefore conclude that our suggested model which includes isocarbonyl adsorption complexes formation is able sufficiently describe the experimental data from both the volumetry and the microcalorimetry by one set of parameters using one distribution function of the adsorption energy shared for the both sets of data.

Results of regularization procedure i.e. maxima of adsorption energy and their distribution are summarized in the Table 1 and presented together with the dependency of calorimetric differential heat on the cover degree in the Fig. 5. The dependences in Fig. 5 clearly indicate that distribution of adsorption energy obtained from regularization

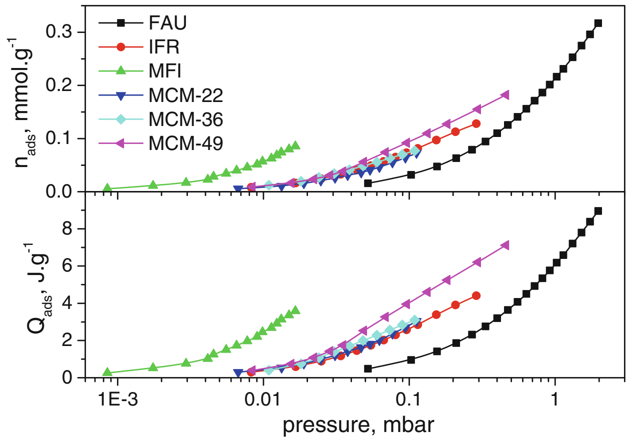

Fig. 3 **a** CO adsorption isotherm obtained at 173 K over zeolite samples. **b** Adsorption heat evolved during the measurement of CO adsorption over zeolite samples at 173 K. Only data corresponding to cover degree less than 0.5 are shown

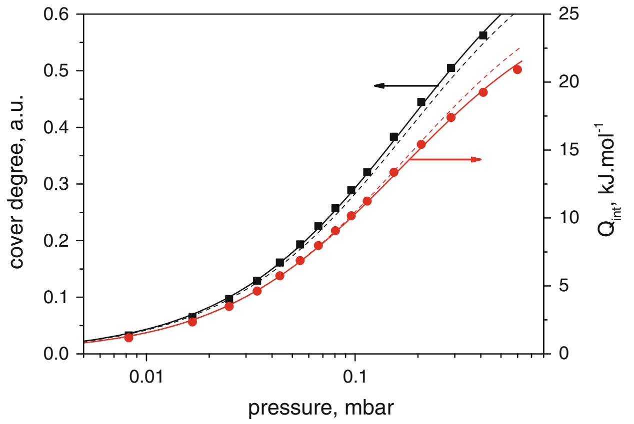

Fig. 4 Comparison of experimental data from coupled volumetry and calorimetry with course of calculated dependence of adsorption and calorimetric isotherm from model including the formation of isocarbonyls (*solid lines*) and not including formation of isocarbonyls (*dashed lines*)

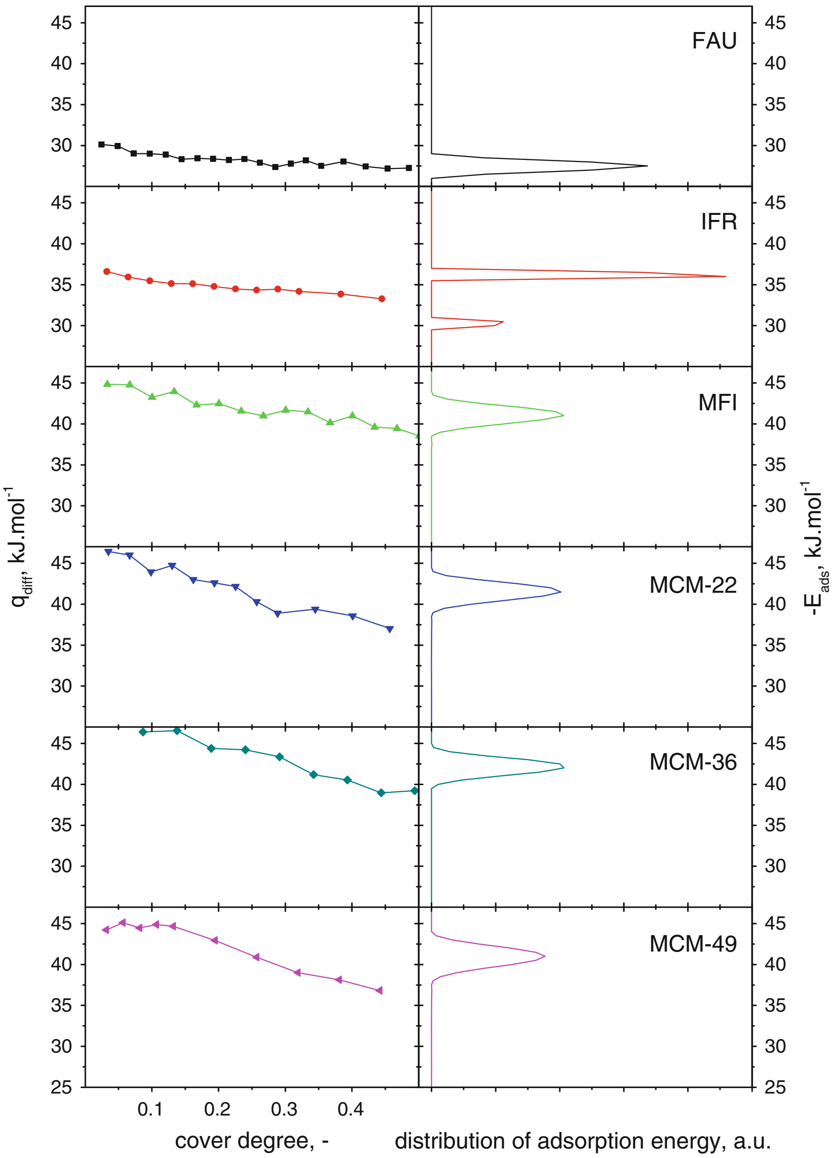

Fig. 5 Obtained dependences of differential adsorption heat on the cover degree and corresponding distributions of adsorption energy obtained from regularization procedure

procedure are in good agreement with the experimentally observed differential heat values q_{diff} and reasonably correspond to the dependence of q_{diff} on the cover degree. The adsorption energies corresponding to maxima on its distribution function obtained from regularization decreases for tested sample in the order MFI ~ MCM-22 ~ MCM-49 ~ MCM-36 > IFR > FAU.

This result is quite surprising for the MFI zeolite, because the position of its adsorption and calorimetric isotherms in the Fig. (3a, b) is shifted to the lower pressure values in the comparison with the other samples. This shift can be caused either by the energetic or entropic influence. As we used the same entropy of adsorption in our calculation hence, it can be expected that observed effect is caused by the different energy of adsorption. Nevertheless we also mentioned above, that the result of the regularization procedure is not very sensitive to the accurate value of adsorption entropy but must correctly describe the course of both the adsorption and calorimetric isotherm. Because both these dependences contain the information about the heat of adsorption we can assume that regularization procedure using both sets of data can provide results about the distribution of the adsorption energy which correspond to the results from calorimetry even if not exact value of the adsorption entropy is used as a parameter for this method. Therefore we assume that observed shift to the lower values of pressure for the MFI zeolite can be ascribed to the entropic effects of CO adsorption in this type of zeolite.

Based on the position of the vibrational band of monocarbonyl complexes in the FTIR spectra reported in the Fig. 1, it is possible to obtain the same sequence of the values of the predicted $Li^{+}\ldots CO$ interaction energy values based on the quantum chemistry calculations on the DFT level of theory published in Ref. (Nachtigall et al. 2007).

The distribution function of the adsorption energy for MFI and MWW samples obtained by the regularization is broader than the distribution functions of FAU and IFR samples. This effect can be caused by the fact that MFI and MWW zeolites contain channel intersections, therefore provide cationic positions for cations of the all above mentioned types, whereas IFR and FAU possess only cationic sites of the channel wall types. The materials MCM-22, MCM-49 and MCM-36 belong to the zeotype family MWW which can crystallize from the hydrogel directly (MCM-49) or via lamellar precursor (MCM-22) which can be swollen and pillared (MCM-36). The same distribution of the CO adsorption energy obtained over all these samples indicates that way of the synthesis or the modification of the original MCM-22 structure by pillaring of this structure by amorphous SiO_2 (MCM-36) do not change significantly the distribution, amount and characteristics of the present cationic positions in this type of materials. Therefore the potential differences in catalytic behavior of these zeolites can be ascribed only to their different textural properties.

We should notice that all results summarized in Fig. 5 and Table 1 were obtained when the regularization procedure was performed with the same value of Tikhonov λ parameter controlling the smoothness of the solution for all samples. It means that predicted both the position and the "width" of expected CO interaction energy values over cationic position of these types reflects true properties of the real samples.

Although the ordering of CO interaction energies obtained from the regularization agrees with the theoretical prediction, the absolute values of obtained adsorption energy are by 10–15 $kJ.mol^{-1}$ higher than the values predicted from the quantum chemistry DFT calculation. This difference is caused by the fact that the DFT methods have not included the contribution of the dispersive forces to its calculated interaction energy values. We should hence shift these theoretic values by some correction term and we can expect that the contribution of dispersive forces can increase the theoretic value in range 8–17 $kJ.mol^{-1}$ which corresponds to limits of the $\Delta H_{subl,CO}$ (Stephenson and Malanowski 1987) and experimentally obtained interaction energy of CO with the silicalite (pure siliceous MFI zeolite structure without any cationic sites) (Savitz et al. 2000). If we use the average of these values to be approximately 13 $kJ.mol^{-1}$ and add this value to the DFT interaction energy values we can obtain nearly perfect agreement of our values with the theoretically predicted values.

4 Conclusions

The applicability of the regularization method of evaluation data obtained from volumetric to calorimetric measurement of CO adsorption on Li exchanged zeolite samples was tested. The above discussed data allow us to draw the following conclusions:

- Possibility of formation of both the $Li^+ \ldots CO$ and the $Li^+ \ldots OC$ adsorption complexes on one adsorption site must be considered during the formulation of model of adsorption over lithium exchanged zeolites.
- Model of CO adsorption on the cation site of zeolite suggested in this article is able simultaneously describe the both experimental data from coupled volumetry and calorimetry i.e. adsorption and calorimetric isotherm. Nevertheless this methodology of evaluation of data is limited only for data measured at relatively low cover degree values when the formation of dicarbonyl species does not occur.
- The adsorption energy values obtained from the regularization procedure for particular zeolitic samples were in good agreement with data obtained for these materials from FTIR experiments and published results of theoretical calculations.
- Zeolites from the zeotype MWW family exhibited nearly same results of obtained distribution of CO adsorption energy at least for adsorption sites which can be characterized by developed method i.e. for cover degree less than 0.5. It means that at least for part of adsorption sites the modification of zeolite structure do not change their CO adsorption characteristics.

Acknowledgments A financial support of the Czech Science Foundation under the project No. P106/12/G015 is highly acknowledged.

References

Arean, C.O., Manoilova, O.V., Delgado, M.R., Tsyganenko, A.A., Garrone, E.: Formation of several types of coordination complexes upon CO adsorption on the zeolite Li-ZSM-5. Phys. Chem. Chem. Phys. **3**(19), 4187–4188 (2001)

Arean, C.O., Nachtigallova, D., Nachtigall, P., Garrone, E., Delgado, M.R.: Thermodynamics of reversible gas adsorption on alkali-metal exchanged zeolites—the interplay of infrared spectroscopy and theoretical calculations. Phys. Chem. Chem. Phys. **9**(12), 1421–1436 (2007). doi:10.1039/b615535a

Bolis, V., Barbaglia, A., Bordiga, S., Lamberti, C., Zecchina, A.: Heterogeneous nonclassical carbonyls stabilized in Cu(I)- and Ag(I)-ZSM-5 zeolites: thermodynamic and spectroscopic features. J. Phys. Chem. B **108**(28), 9970–9983 (2004). doi:10.1021/jp049613e

Bonelli, B., Garrone, E., Fubini, B., Onida, B., Delgado, M.R., Arean, C.O.: Two distinguishable lithium sites in the zeolite Li-ZSM-5 as revealed by adsorption of CO: an infrared spectroscopic and thermodynamic characterisation. Phys. Chem. Chem. Phys. **5**(13), 2900–2905 (2003). doi:10.1039/b303613h

Carniti, P., Gervasini, A., Auroux, A.: Energy-distribution of surface acid sites of metal-oxides. J. Catal. **150**(2), 274–283 (1994). doi:10.1006/jcat.1994.1346

Garrone, E., Arean, C.O.: Variable temperature infrared spectroscopy: a convenient tool for studying the thermodynamics of weak solid-gas interactions. Chem. Soc. Rev. **34**(10), 846–857 (2005). doi:10.1039/b407049f

Hadjiivanov, K.I., Vayssilov, G.N.: Characterization of oxide surfaces and zeolites by carbon monoxide as an IR probe molecule. In: Gates, B.C., Knozinger, H. (eds.) Advances in Catalysis, vol 47, pp. 307–511. Elsevier Academic Press, San Diego (2002)

Heuchel, M., Jaroniec, M., Gilpin, R.K., Brauer, P., von Szombathely, M.: Energetic heterogeneity of reference carbonaceous materials. Langmuir **9**(10), 2537–2546 (1993). doi:10.1021/la00034a011

Jagiello, J.: Stable numerical-solution of the adsorption integral-equation using splines. Langmuir **10**(8), 2778–2785 (1994). doi: 10.1021/la00020a045

Kowalczyk, P., Terzyk, A.P., Gauden, P.A., Gun'ko, V.M., Solarz, L.: Evaluation of the structural and energetic heterogeneity of microporous carbons by means of novel numerical methods and genetic algorithms. J Colloid Interf Sci **256**(2), 378–395 (2002). doi:10.1006/jcis.2002.8680

Lawson, C.L., Hanson, R.J.: Solving Least Squre Problems. Prentice-Hall, Englewood Clifss (1987)

Mortier, W.J.: Compilation of Extra-Framework Sites in Zeolites. Butterworks, London (1982)

Nachtigall, P., Bulanek, R.: Theoretical investigation of site-specific characteristics of CO adsorption complexes in the Li^+ -FER zeolite. Appl. Catal. A Gen. **307**(1), 118–127 (2006). doi: 10.1016/j.apcata.2006.03.020

Nachtigall, P., Frolich, K., Drobna, H., Bludsky, O., Nachtigallova, D., Bulanek, R.: FTIR study of CO interactions with Li^+ ions in micro- and mesoporous matrices: coordination and localization of Li^+ ions. J. Phys. Chem. C **111**(30), 11353–11362 (2007). doi:10.1021/jp0716785

Nachtigallova, D., Bludsky, O., Arean, C.O., Bulanek, R., Nachtigall, P.: The vibrational dynamics of carbon monoxide in a confined space—CO in zeolites. Phys. Chem. Chem. Phys. **8**(42), 4849–4852 (2006). doi:10.1039/b612238h

Olson, D.H.: The crystal-structure of dehydrated NaX. Zeolites **15**(5), 439–443 (1995). doi:10.1016/0144-2449(95)00029-6

Savitz, S., Myers, A.L., Gorte, R.J.: A calorimetric investigation of CO, N-2, and O-2 in alkali-exchanged MFI. Microporous Mesoporous Mat. **37**(1–2), 33–40 (2000). doi:10.1016/s1387-1811(99)00190-0

Stephenson, R.M., Malanowski, S.: Handbook of the Thermodynamics of Organic Compounds. Elsevier, New York (1987)

Tikhonov, A.N.: On the stability of inverse problems. Dokl. Akad. Nauk SSSR **39**(5), 195–198 (1943)

Treacy, M.M.J., Higgins, F.M.: Collection of Simulated XRD Powder Patterns for Zeolites. Elsevier, Amsterodam (2001)

Von Szombathely, M., Brauer, P., Jaroniec, M.: The solution of adsorption integral-equations by means of the regularization method. J. Comput. Chem. **13**(1), 17–32 (1992)

Zecchina, A., Arean, C.O.: Diatomic molecular probes for mid-IR studies of zeolites. Chem. Soc. Rev. **25**(3), 187 (1996). doi: 10.1039/cs9962500187

Zukal, A., Arean, C.O., Delgado, M.R., Nachtigall, P., Pulido, A., Mayerova, J., Cejka, J.: Combined volumetric, infrared spectroscopic and theoretical investigation of CO2 adsorption on Na-A zeolite. Microporous Mesoporous Mat. **146**(1–3), 97–105 (2011). doi:10.1016/j.micromeso.2011.03.034

Zukal, A., Zones, S.I., Kubu, M., Davis, T.M., Cejka, J.: Adsorption of carbon dioxide on sodium and potassium forms of STI zeolite. ChemPlusChem **77**(8), 675–681 (2012). doi:10.1002/cplu.201200089