

Thermodynamics of CO probe molecule adsorption on Cu–FER-zeolite comparison of TPD, FTIR, and microcalorimetry results

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Abstract The existence of the new type of the adsorption complexes of carbon monoxide, where CO molecule interacts simultaneously with both copper and potassium cation, formed on so-called heterogeneous dual adsorption sites was detected by the FTIR spectroscopy and temperature programmed desorption technique (TPD) in the Cu, K–FER zeolite samples. The time-resolved IR spectroscopy and TPD experiments also proved their lower stability in the comparison with the classical monodentate adsorption complexes. The TPD curves of these materials exhibited low temperature desorption peak which was ascribed to these sites. The energetic parameters (i.e., energy and entropy of adsorption) as well as distribution of all present Cu^+ sites were obtained by the fitting of TPD data to the phenomenological model. Obtained results suggest that the heterogeneous dual sites are special form of the adsorption sites localized on the wall of channels destabilized due to significantly higher change of the entropy of adsorption. Direct microcalorimetric measurement proved energetic equality of single and heterogeneous dual sites together with the validity of the adsorption energy values obtained from TPD.

Keywords Ferrierite · Copper · TPD · FTIR · Microcalorimetry · Heterogeneous dual sites

Introduction

Detailed characterization of high-silica zeolites is crucial for understanding of these interesting materials with unique properties which offer possibility to employ them in wide range of important catalytic and adsorption processes. Nevertheless the complicated structure of these materials limits or hinders the applicability of conventional methods of structural research and the methods based on the evaluation of interaction of proper probe molecules with these materials are employed instead of them [1–7]. The carbon monoxide is frequently used as a probe molecule for zeolite characterization due to its high sensitivity of adsorption interaction to nature of zeolite extra framework cations and their environment. The interaction of carbonyl species with extra framework cation is usually analyzed and interpreted within the concept of single cation sites. This concept, which works well in the case of flat surface with low concentration of adsorption sites, cannot be uncritically used without reserve in the case of zeolites due to very complex inner texture a confined space of zeolite channels and cavities. Several authors referred to that some CO molecules interact with more than one cationic center in alkali metal zeolites [8–10]. This hypothesis has been later supported by series of detailed studies combining infrared (IR) spectroscopy with computational studies on carbon monoxide adsorption on sodium and potassium form of FER [11, 12] and MFI [13] zeolites. These bridged $\text{M}^+\cdots\text{CO}\cdots\text{M}^+$ complexes appear whenever two cations are at the proper distance apart from each other, and such a pair of metal cations was termed a dual cation site. These adsorption complexes showed red shifted C–O stretching frequencies and larger adsorption heats, with respect to CO adsorption on isolated sites ($\text{M}^+\cdots\text{CO}$).

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The monovalent copper ion-exchanged zeolites are promising catalysts for the direct NO_x decomposition [14] as well as for the selective reduction of NO_x by hydrocarbons. The detailed localization of Cu^+ ions was widely studied by the CO probe molecule adsorption using the FTIR, EXAFS, EPR, UV-Vis, microcalorimetry, and TPD techniques [15–27] assuming the presence of several distinguishable types of Cu^+ -CO adsorption complexes. The finding of bridged species on alkali-metal exchanged zeolites prompted the question of whether similar complexes would also occur in zeolites with other cations and whether they can be behind some peculiar features of CO IR spectra. Very recently, the authors reported preliminary results of CO interaction with cations in $\text{Cu}_x\text{M-FER}$ zeolites, which brought evidence of existence of bridged $\text{Cu}^+\cdots\text{CO}\cdots\text{M}^+$ complexes, where M stands for alkali-metal cations. [28] In this article the authors report about these so-called heterogeneous dual sites in more details. Newly, it was report the data on stability and thermodynamic characteristics of these complexes obtained by temperature programmed and isothermal desorption measurements and by direct calorimetric measurements as function of copper concentration which allows with previously published structure and stability of CO adsorption complexes in $\text{Cu}_x\text{M-FER}$ at the periodic DFT level [28], to create a picture of these species at atomistic level and then better understand to the CO adsorption in cation exchanged zeolites.

Experimental

Preparation of samples

Ferrierite sample having nominal Si/Al ratio 8.6 was supplied by the Research Institute of Inorganic Chemistry, Ústí nad Labem. Firstly, the starting ammonium form of zeolite was calcined in dried O_2 at 450 °C for 5 h for decomposition of the rest of template and ammonium ions, yielding protonic form of the zeolite. The alkali metal forms of zeolite were prepared by the one step procedure taken at RT in the 1 M aqueous solution of NaCl or KCl. After washing, filtration and drying of resulting solids, complete ion exchange to alkali metal form was checked by the absence of IR absorption band corresponding to the Brønsted acid $\text{Si}(\text{OH})\text{Al}$ groups in the samples. Samples, in both alkali metal form, were then contacted with $5 \cdot 10^{-4}$ – $1 \cdot 10^{-2}$ M aqueous solution of CuCl_2 or $\text{Cu}(\text{acetate})_2$ at RT in order to obtain the zeolite sample containing demanded amount of Cu ions. The resulting solution was filtered, three times washed by re-distilled water, and final powder was dried at 120 °C in air.

Analysis of sample composition

The amount of copper content in prepared samples was determined by WD XRF spectroscopy by Spectroscan U (Spectron Optel, St. Petersburg, Russia) [29] and they are summarized together with the conditions of preparation in Table 1. It must be noted that all samples prepared from alkali-metal form of parent zeolite contain certain amount of protons. These protons were ion-exchanged into zeolite during Cu ion-exchange procedure in aqueous solution (pH ca 5.5) or were produced during reduction of Cu^{2+} to Cu^+ ions. The zeolites are labeled as $\text{Cu}_x\text{M-FER-Cu/Al}$ ratio, where M indicate co-cation (it means the original cation in the zeolite before Cu ions introduction, M = Na or K).

FTIR experiments

For IR spectroscopic measurements, thin self-supported wafers (around 5 mg/cm^2) were prepared, activated by oxidation in 100 Torr O_2 at 450 °C and subsequently reduced in 100 Torr CO at 470 °C inside glass IR-cell. The spectra reported and discussed in this paper were obtained by adsorption of 10 Torr of CO at 25 °C and subsequent short evacuation at 25 °C for 1 min for removal of dicarbonyl complexes (process was checked by disappearance of the symmetric vibration band of this complex at 2177 cm^{-1}). Measurement of IR spectra was done by using the Nicolet Protégé 460 spectrometer equipped by MCT-A detector. All spectra were measured in the range 400–4000 cm^{-1} with the resolution 0.5 cm^{-1} as a sum of 256 scans. Due to remarkable difference in adsorption energy of first and second CO molecule on the Cu^+ site is reasonable to assume that all reported spectra represent the C-O stretching vibration mode of Cu^+ -CO mono carbonyls. In addition, it can be assumed that these spectra correspond to sample coverage close to monolayer. Additional evacuation by turbomolecular pump leads to desorption of CO from mono-carbonyl complexes. IR spectra corresponding to different coverage were measured after

Table 1 Chemical composition of $\text{Cu}_x\text{M-FER}$ zeolites and conditions of ion exchange at RT

Zeolites	Ion exchange parameters			
	Cu/Al ^a	$w_{\text{Cu}}/\text{wt}\%$	Solution	Time/h
Cu,Na-FER-0.31	0.31	2.70	1×10^{-3} M CuCl_2	24
Cu,K-FER-0.09	0.09	0.83	5×10^{-4} M CuCl_2	24
Cu,K-FER-0.18	0.18	1.60	5×10^{-4} M CuAc_2	36
Cu,K-FER-0.30	0.30	2.64	1×10^{-2} M CuAc_2	24

^a Atomic ratio

continuous evacuation of samples by turbomolecular pump for time in the range from 1 to 180 min.

CO-TPD experiments

In order to investigate stability and thermodynamic characteristics of mono-carbonyl complexes of CO on investigated samples, temperature programmed desorption (TPD), and microcalorimetry were measured. CO-TPD experiments were measured in the through-flow device equipped by quadrupole mass spectrometer Balzers OmniStar GSD 300 monitoring masses 4, 18, 28, and 32 amu. The copper in samples was reduced to Cu⁺ in the CO/He gas mixture (5 vol% of CO in He) at 450 °C for 2 h and the samples were subsequently saturated by CO for 40 min at RT and then purged in flow of He (flow rate 25 ml/min) for 20 min in order to desorb physically adsorbed CO. The CO-TPD experiments were carried out in the temperature range from RT to 550 °C with the heating rate 10 °C/min. The intensities of each mass fraction were registered every 3 s, i.e., every 0.5 K. 100 mg of sample was used in each experiment.

Microcalorimetry experiments

Microcalorimetric determinations of the adsorption heat of CO were performed on isothermal Tian-Calvet calorimeter (BT 2.15, from Setaram) equipped with a standard Sievert adsorption—desorption volumetric apparatus controlled by PC. The samples (approximately 400 mg) were outgassed in dynamic vacuum at 400 °C, reduced in 100 Torr CO at 450 °C overnight and subsequently evacuated at the same temperature for 1 h. Pretreatment of samples were carried out outside of calorimeter in an external oven. After pretreatment, cell with sample was mounted into the calorimeter under vacuum. Measurement of the heat of adsorption and adsorption isotherm was carried out at 25 °C by step-by-step dosing of known amount of CO up to 10 Torr of equilibrium pressure. The establishment of adsorption equilibrium was monitored by both the pressure and the heat-flow measurement after each dose minimally for 45 min.

Methodology of CO-TPD evaluation

The thermodynamic characteristics of CO adsorption complexes were determined using the formal kinetics based model similar to the models previously published [30, 31]. This model was based on few assumption: (i) desorption is strongly affected by reabsorption of CO on unoccupied Cu⁺ ions (ii) due to expected high values rate constant of both adsorption and desorption the adsorption quasi-equilibrium state is the good approximation for the

description of temperature programmed desorption experiment. (iii) A non-dissociative Langmuir type of adsorption isotherm defined by eqs. (1), (2) was assumed for the description of CO adsorption on the Cu⁺ sites in zeolite, without considering lateral interactions among adsorbed molecules.

$$\Theta_i = \frac{K_i c}{1 + K_i c}, \quad (1)$$

$$K_i = \exp\left(-\frac{\Delta H_{ads,i} - T \Delta S_{ads,i}}{R T}\right) \quad (2)$$

The Θ_i is a dimensionless coverage degree of i -th adsorption site and c is molar concentration of CO in the gas phase. (iv) A complete coverage of all Cu⁺ sites at the beginning of experiment was assumed in the TPD simulations. (v) The K_i value is an equilibrium adsorption constant related to i -th adsorption site at temperature T and $\Delta H_{ads,i}$ and $\Delta S_{ads,i}$ the values of adsorption enthalpies and entropies for this site are treated as constants. (vi) Only the formation of mono-carbonyls during the TPD process is considered. This assumption is in good agreement with the mass balance of the Cu⁺ content in samples and the amount of the desorbed CO during the TPD experiments. (vii) A presence of four independent sites was considered in zeolites, because three site models were able to describe TPD experiments in the Cu–Na–MFI and Cu–Na–FER zeolites without considering the presence of the heterogeneous dual sites previously [31–33]. (viii) Diffusion of CO in the zeolite channels is sufficiently fast and the amount of sample is small what implies that the continuously stirred tank model reactor is sufficient for description of the sample layer in the TPD experiment.

Within these assumptions the TPD spectra simulation method leads to the one differential eq. (3) for the time change of CO concentration which was solved numerically.

$$\frac{dc}{dt} = -\frac{(1 - \varepsilon) \cdot c_{Smax} \cdot \sum_{i=1}^4 \left(\frac{K_i x_i}{(1 + K_i c)^2} \left(\frac{\Delta H_{ads,i}}{RT^2} \right) \beta \right) + \frac{F T}{T_0 V}}{\varepsilon + (1 - \varepsilon) \cdot c_{Smax} \cdot \sum_{i=1}^4 \left(\frac{K_i x_i}{(1 + K_i c)^2} \right)} \cdot c \quad (3)$$

The x_i is a relative population of adsorption site of type i in the sample and c_{max} is the Cu⁺ ions concentration in the sample of the catalyst related to its volume V . F is the rate of flow of the carrier gas, ε is a porosity of the layer of the catalyst bed. The β value is rate of temperature change. The population x_i of the Cu⁺ site types and both desorption energies and desorption entropies for all Cu⁺ site types were optimized to obtain the best fit with the experimental data. The values of both adsorption energies and entropies obtained from the previous results were used as starting values in fitting. All experimental Cu–K–FER TPD curves

were fitted at once together with all Cu–Na–FER measured TPD curves constraining the parameters $\Delta H_{ads,i}$ and $\Delta S_{ads,i}$ to be the same values for all samples.

Results and discussion

FTIR study

In order to investigate stability of individual IR band in the spectra of Cu,M–FER samples, the series of time-resolved spectra (Fig. 1) were measured in dependence on time of sample evacuation at 25 °C. The spectra of Cu,Na–FER-0.31 sample displayed in Fig. 1a exhibit only single, slightly asymmetric band at 2155 cm⁻¹ and very small band at 2107 cm⁻¹ whose position is in good agreement with theoretical position of the band of isotopic ¹³CO–Cu⁺ carbonyl complex as a counterpart of band at 2155 cm⁻¹. The IR spectra of CO molecules adsorbed on Cu,K–FER zeolites contains the intense and well-distinguished bands at 2155, 2138, and 2112 cm⁻¹ (see Figs. 1b, 3b). The relative intensity of bands at 2138 and 2112 cm⁻¹ observable in spectra of Cu,K–FER samples is decreasing for samples with the higher loading of copper as it is presented in the Fig. 3b, and these bands were ascribed to the vibration of CO adsorbed on the new type of adsorption site. Previously published [34] correlation between the vibrational frequency and the CO bond length suggests the

presence of the specie modifying the complex Cu⁺...CO properties located close to oxygen atom. Based on this assumption we can attribute the vibrational bands at 2138 and 2112 cm⁻¹ to some type of heterogeneous dual site species Cu⁺...CO...M⁺ whose presence was previously suggested by DFT calculations [28].

Only small changes of intensity of the band at 2155 cm⁻¹ are apparent in the case of the desorption from Cu,Na–FER-0.31 sample presented in the Fig. 1a where only spectra taken in the first 45 min are presented because after reaching this time, no decreasing of intensity of spectra was observed on this sample. Figure 1b display changes in the spectra of Cu,K–FER-0.09 sample within 180 min of evacuation. This sample was chosen due to well-discernible bands at 2138 and 2112 cm⁻¹. It is clearly seen that intensity of spectra decrease in time due to desorption of CO molecules from adsorption complexes. Deconvolution of the spectra (shown in the inset plots) to individual bands led to dependences presented in Fig. 2 whose clearly indicate that intensity of individual band decreased during 180 min to ca 60, 45, and 18% of original intensity of band at 2155, 2138, and 2112 cm⁻¹ in the case of Cu,K–FER sample, respectively, and the authors can conclude that presence of second cation destabilizes the heterogeneous dual sites and it means that desorption rate from these sites is much higher than the desorption rate from the conventional adsorption site and should be detected at significantly lower temperature at CO-TPD

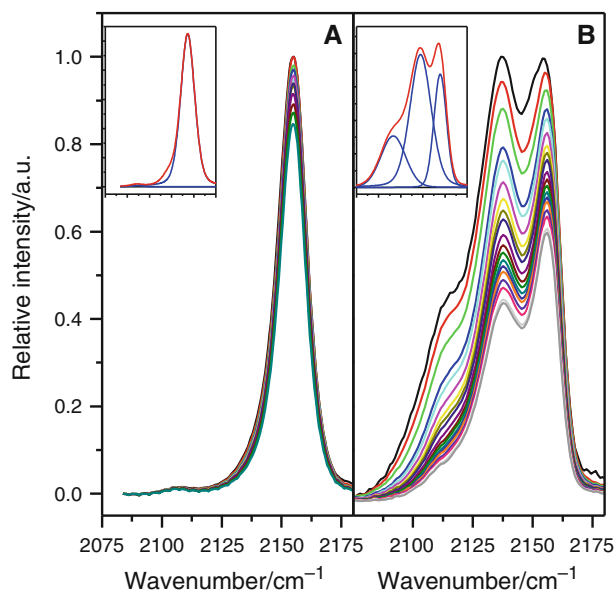


Fig. 1 a Time-resolved IR spectra of Cu,Na–FER-0.31 measured under dynamic vacuum at 25 °C for 1–45 min. *Inset plot* show deconvolution of the spectra into individual bands. b Time-resolved IR spectra of Cu,K–FER-0.09 measured under dynamic vacuum at 25 °C for 1–180 min. *Inset plot* show deconvolution of the spectra into individual bands

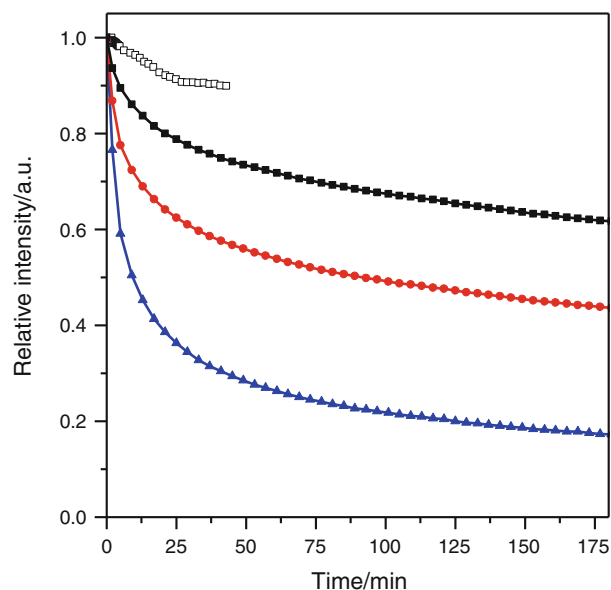


Fig. 2 Time dependence of relative intensity of absorption bands of Cu,Na–FER-0.31 sample (*open square*—wavenumber 2155 cm⁻¹, 0–45 min) and Cu,K–FER-0.09 (wavenumbers *filled square* 2155, *filled circle* 2138, and *filled triangle* 2112 cm⁻¹ for 1–180 min) measured under dynamic vacuum at 25 °C

experiment. The absorption band at 2155 cm^{-1} can be found in both type materials and can not be fitted by one exponential decay curve what implies that presence of more adsorption complexes with different stability is responsible for presence of this absorption band and generally this vibration is not site specific for usual $\text{Cu}^{+\cdots}\text{CO}$ complexes [35]. Similar results were obtained also in the case of analysis desorption rate of site with absorption bands at 2138 and 2112 cm^{-1} .

TPD study

However, it is well-known from previous studies [32, 33, 36] that IR bands of mono-carbonyls in Cu-MFI and Cu-FER are not in generally site-specific and they consist of various type of mono-carbonyls. Therefore, the methodology of CO-TPD curves analysis was developed by our laboratory for discrimination and characterization of individual mono-carbonyl complexes [31–33, 37]. CO-TPD experiments on Cu,Na-FER were in detail reported previously [32]; in this article the authors focused on CO-TPD data obtained on Cu,K-FER samples which exhibit unusual IR bands at 2138 and 2112 cm^{-1} . Figure 3 show CO-TPD curves (part A) and corresponding IR spectra of mono-carbonyls (part B) of Cu,K-FER samples. CO-TPD pattern and IR spectrum of Cu,Na-FER-0.31 sample is depicted for comparison too. It is evident that the all TPD curves obtained for Cu,K-FER samples exhibited the high desorption rate at low temperature (below $100\text{ }^{\circ}\text{C}$) and overall desorption is shifted to lower temperature in

comparison with Cu,Na-FER sample. In the case of Cu,K-FER sample with Cu/Al ratio 0.09, approximately 40% of carbon monoxide was desorbed at this low temperature desorption region. Comparison of TPD curves with IR spectra led to conclusion that the higher is intensity of IR bands at 2138 and 2112 cm^{-1} the higher is desorption rate of CO at low temperature and the lower is temperature of the end of TPD peak. It means that presence of these IR bands in the spectra is directly connected with low-temperature desorption in TPD. This is in agreement with behavior of IR bands at $25\text{ }^{\circ}\text{C}$ under dynamic vacuum.

Deconvolution of experimental TPD curves by means of mathematical model based on formal kinetics was used, for obtaining of more details about adsorption sites in Cu,K-FER samples. Due to the presence of low-temperature desorption peak in the TPD curves of Cu,K-FER samples, early used three-site model was not sufficient and a new adsorption site had to be included to phenomenological model of TPD experiments previously used for the description of the Cu,Na-FER samples [32]. However, it is clear from IR spectroscopy, that the desorption of CO occurs from several adsorption sites, the all these sites were represented into the TPD model by only one adsorption site to avoid the numerical over-determination of model. The fit of experimental TPD curves was performed in order to obtain adsorption energies, changes in entropy during adsorption and populations for individual site types: sites denoted “A” (Al pair), “B” (sites for Al at T1 or T2 positions), “C” (sites for Al mainly at T3 or T4 positions), and “D” (newly introduced site). The new four-site model

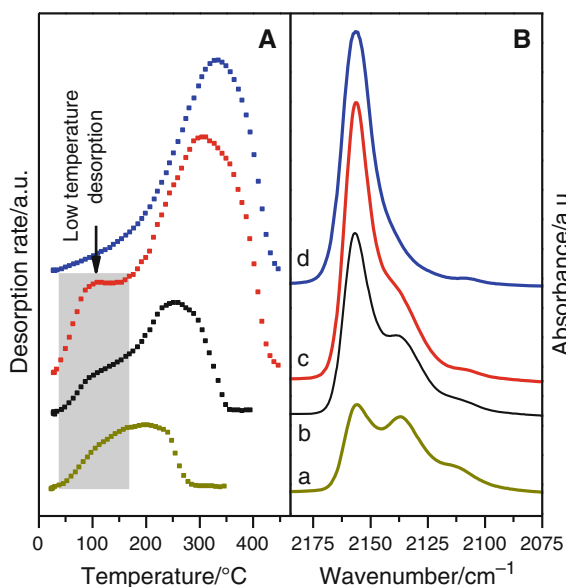


Fig. 3 Comparison of CO-TPD curves (a) and IR spectra obtained after 1 min evacuation at $25\text{ }^{\circ}\text{C}$ (b) of Cu,Na- and Cu,K-FER samples. (a) Cu,K-FER-0.09, (b) Cu,K-FER-0.18, (c) Cu,K-FER-0.30, and (d) Cu,Na-FER-0.31

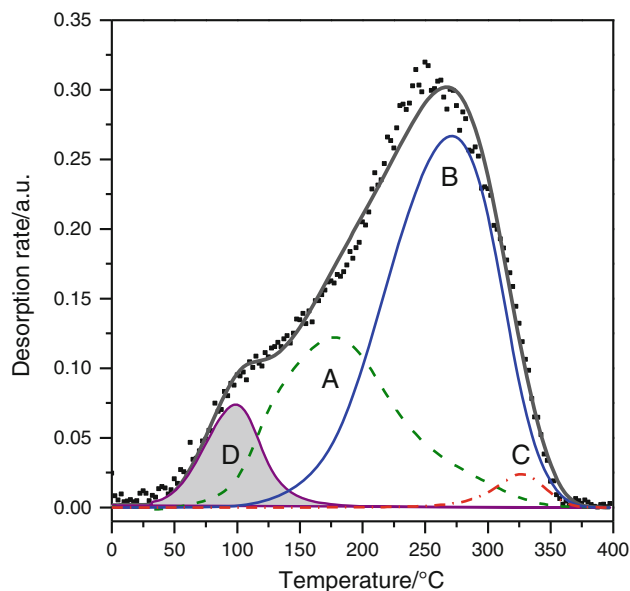


Fig. 4 Experimental (points) and calculated (thick solid line) TPD of sample Cu,K-FER-0.18. Calculated desorption rates from sites: A (dashed line), B (solid line), C (dash dotted line), D (gray filled solid line)

Table 2 Result of the TPD fitting procedure—obtained thermodynamics data

TPD site	$\Delta S_{ads}/J\ K^{-1}\ mol^{-1}$	$\Delta H_{ads}/kJ\ mol^{-1}$	$E_{DFT}\ [38]/kJ\ mol^{-1}$	Site details
“A”	−44	−62	−59	Al pair
“B”	−70	−84	−76	Adsorption complex on P6/T1 site
“C”	−80	−121	−122	Adsorption complexes on M7/T3, P7/T4, and I2/T4 sites
“D”	−130	−82	-76 ± 4	Heterogeneous dual site in Cu-K-FER zeolite

was able to reproduce experimental TPD curves well as it is demonstrated in the Fig. 4. Values of thermodynamic parameters are summarized in Table 2. Parameters corresponding to adsorption processes “A”, “B”, and “C” is essentially the same as the ones for Cu,Na-FER samples (cf. ref [32]). The adsorption energy of new site “D” is *ca.* $-82\ kJ\ mol^{-1}$. This value is rather close to adsorption energy of $-86\ kJ\ mol^{-1}$ found for the site “B”, however, the adsorption entropy obtained for sites “B” and “D” are rather different: $-67\ J\ K^{-1}\ mol^{-1}$ and $-130\ J\ K^{-1}\ mol^{-1}$ for sites “B” and “D”, respectively. Values of adsorption energy of site “B” and “D” are nearly the same what allow us to adopt the assumption that the heterogeneous dual site is some variant of the “B”. The assumption is also supported by the Fig. 5 where is clearly perceptible that the sum of population of “B” and “D” site obtained on the Cu,K-FER samples fits well previously obtained population of “B” site on the Cu,Na-FER zeolite. The destabilization of heterogeneous dual sites is in the agreement with obtained larger value of adsorption entropy whose value reflects well the more rigid and “less probable” structure of such adsorption complex when compared to CO molecule bonded to one Cu^{+} ion.

Microcalorimetry study

In order to verify results of TPD fitting, the differential heat of CO adsorption was directly measured by microcalorimeter coupled with volumetric adsorption apparatus. Calorimetry was measured on the sample Cu,Na-FER-0.31 (red curve in the Fig. 6), which exhibits only usual IR band at $2155\ cm^{-1}$, and on sample Cu,K-FER-0.09 (black curve in the Fig. 6), which contains significant amount of monocarbonyl complexes in unusual IR bands at 2138 and $2112\ cm^{-1}$. Initial heat of CO adsorption on Cu,Na-FER sample is $105 \pm 3\ kJ\ mol^{-1}$ and it is constant until *ca.* 40–45% coverage. Then differential heat of adsorption decrease to value $88 \pm 4\ kJ\ mol^{-1}$ and this value remains constant until coverage about 90%. With approaching of coverage to monolayer capacity, the differential adsorption heat start to decrease and this fall continue to values at about $45\ kJ\ mol^{-1}$. These results are in good agreement with previously published results [32] obtained from TPD. First region of adsorption is possible to attribute to

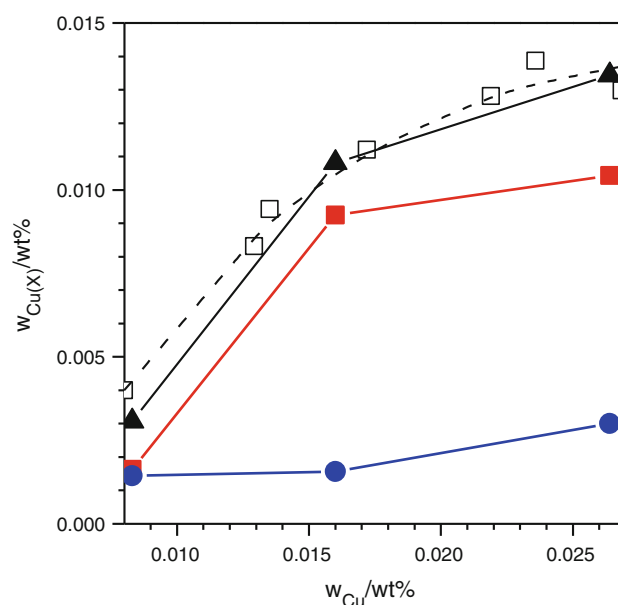


Fig. 5 Dependence of calculated adsorption site concentration on the copper loading: open square “B” site in Cu,Na-FER samples, filled square “B”, filled circle “D”, and filled triangle “B” + “D” sites in Cu,K-FER samples

adsorption of CO molecule to Cu^{+} ions localized in Al atom in T3 and T4 position of FER zeolite (DFT binding energy values $M7/T3 = -120\ kJ\ mol^{-1}$, $P7/T4$ and $I2/T4 = -115\ kJ\ mol^{-1}$ [38]) whose relative population was determined to 48%. The second plateau on the adsorption curve is attributed to adsorption of CO to copper ions localized to Al atoms on T1 and T2 positions (DFT energy $P6/T1 = -85\ kJ\ mol^{-1}$, $I2/T2 = -100\ kJ\ mol^{-1}$ [38]) with the adsorption energy *ca.* $85\ kJ\ mol^{-1}$ determined also by TPD experiments. Final stage of the adsorption can be ascribed to formation of CO complexes with copper ions on so-called Al pairs and to formation of di-carbonyls. Contrary to Cu,Na-FER sample, the calorimetric curve of the Cu,K-FER sample exhibits significant differences. The differential heat of CO adsorption is fairly constant with CO loading up to coverage close to monolayer capacity. This plateau of heat at $83 \pm 3\ kJ\ mol^{-1}$ is then followed by decrease to the value *ca.* $40\ kJ\ mol^{-1}$. It must be noted that the initial heat of the adsorption is somewhat higher than plateau ($92\ kJ/mol$), but it very quickly decrease; only

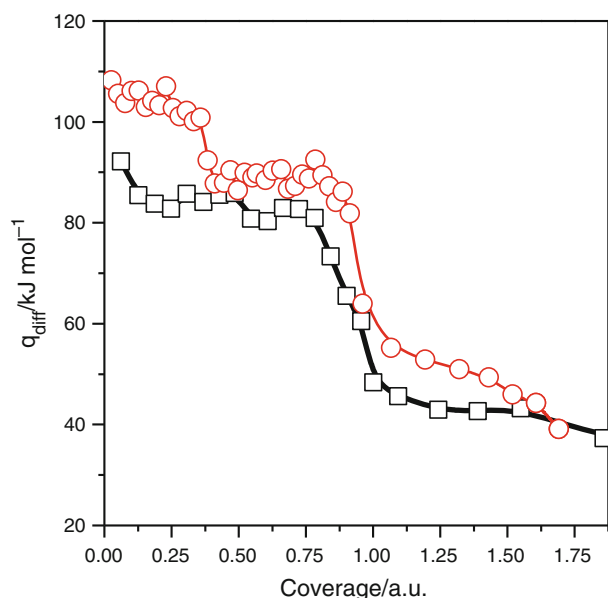


Fig. 6 Differential heat of adsorption of CO at 298 K on the Cu, K-FER-0.09 (squares) and Cu,Na-FER-0.31 (circles)

first doses of CO, resulting to coverage 6%, exhibits this higher value. The observed effect can be explained by the fact that copper preferentially coordinates to Al atoms in positions T1 and T2 which was proved by TPD analysis of Cu,Na-FER samples [32]. This fact causes rapid disappearance of the CO adsorption complexes with adsorption energy at about 100–120 kJ mol⁻¹ in the case of sample with small degree of ion exchange. The sample Cu,K-FER-0.09 contain remarkable amount of heterogeneous dual sites (ca. 50%) based on the FTIR and TPD results and therefore the dependence of the differential heat of adsorption on the coverage degree should contain remarkable contribution of adsorption heat from these sites. Nevertheless the relatively constant adsorption heat of the first stage of calorimetric experiment indicates that the adsorption to the conventional site and the heterogeneous dual sites occurs on the sites with similar adsorption energy what is also in agreement with result of TPD experiments. The authors can conclude that observed destabilization of these sites can be ascribed to change of the entropy of adsorption as it was already suggested by analysis of TPD experiments.

Conclusions

The authors can summarize results of this study of CO adsorption on Cu,K-FER zeolite in few subsequent points.

- The IR spectroscopy proved presence of new type adsorption complexes in the Cu,K-FER samples, called heterogeneous dual sites, and presence of these sites is

especially remarkable at low degree of Cu⁺ ion exchange. Measurement of the desorption rate proved that those sites are destabilized in comparison with conventional adsorption sites.

- The CO TPD experiments performed on Cu-K-FER can be described by the four-site adsorption model based on the reaction kinetics. The low-temperature peak in TPD was attributed to adsorption complexes formed on the heterogeneous dual cation sites. Adsorption energies obtained from the fit of TPD are in good agreement with the results obtained for Cu-Na-FER samples previously and with the results of DFT calculations.
- The CO adsorption energy on the heterogeneous dual sites in Cu,K-FER zeolite is comparable to adsorption of CO on the “B” site of Cu,Na-FER zeolite. Destabilization of these adsorption complexes is caused by the change the entropy of adsorption when compared to site B of the “normal” adsorption site. The comparison of population “B” site of Cu,Na-FER zeolite with the sum of “B” and “D” site in the case of Cu,K-FER zeolite suggests that the heterogeneous dual sites are formed as a special form the “B” site.
- The direct microcalorimetric measurement of adsorption heats provided results consistent with results obtained from the TPD including the entropic reason of destabilization of heterogeneous dual sites.

Data presented in this article clearly evidence the usefulness of both TPD and calorimetry techniques for characterization of metal-exchanged zeolites. However, it must be noticed that complete image of adsorbed CO molecule properties can not be elucidated by using only one of those techniques but the combination of results of several methods whose are capable to verify at least a part of results obtained by other methods is necessary.

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