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Carbonylic species in alkali-metal exchanged zeolites

ANNOTATION OF Ph.D THESIS

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Abstract

The subject of this doctoral thesis was the study of behaviour of small molecules trapped in a confined space of zeolitic channels and interacting with cations coordinated to zeolite. The properties of zeolites as a complex system are given by a combination of several factors. For this purpose, carbon monoxide was used, acting as a so-called "probe" molecule. This thesis describes the interaction of carbon monoxide with extraframework alkali-metal cations in different zeolites matrixes (MFI, FER and BEA) to give CO adsorption complexes, especially so-called bridged complexes.

Using IR spectroscopy, several carbonyl species have been described in literature, which can be divided to three classes of adsorption complexes: complexes on a single cation site coordinated by a carbon atom (C-down complex, carbonyl), or by an oxygen atom of CO (O-down complex, isocarbonyl), and complexes on a dual (or multiple) cation site (bridged complexes). Also geminal polycarbonyl species have been identified. In this thesis, bridged complexes attracted special attention. Such types of complexes have been studied in MFI, FER and LTA zeolites, but no complete information has been gained. There has also been no study about CO adsorption complexes on other important industrial zeolite, such as zeolite BEA. The main aim of this thesis was to complete the characterization of carbonylic complexes in alkali-metal exchanged BEA zeolite and obtain advanced information on these complexes in previously studied zeolites (MFI, FER).

To meet these goals, a combination of IR spectroscopy, measurement of volumetric adsorption isotherms and calorimetric heat of adsorption was used. This thesis reports on the estimation of molar absorption coefficient for bridged carbonyl, isolated carbonyls and isocarbonyls formed in Na- and K- forms of MFI and FER zeolites, allowing to calculate the amount of each complex and their population. For the first time ever, the thesis determined the adsorption heats and vibrational characteristics of CO adsorption complexes on the zeolite alkali-metal exchanged BEA. Further, the thesis reports on the experimental determination of adsorption heat of CO in bridged complexes on K-FER zeolites.

Keywords: Bridged carbonyls, quantitative analysis, carbon monoxide, zeolite, FER, MFI, BEA, microcalorimetry, IR spectroscopy, molar absorption coefficient.

List of papers:

This doctoral thesis is written in the form of a commented set of scientific papers. The publications presented here were composed in years 2010-2017 at the Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice.

I)   Eva Koudelkova, Roman Bulanek, Eva Frydova, Karel Frolich
     Quantitative IR characterization of bridged adsorption complexes of CO in Na-FER zeolite
     Topics in Chemistry and Material Science (Advanced Micro- and Mesoporous Materials – 11) 6 (2011) 77 – 86, ISSN 1314 – 0795

II) Roman Bulánek, Eva Koudelková,
     Carbon monoxide adsorption on alkali-metal exchanged BEA zeolite: IR and thermodynamics study
     Microporous Mesoporous Mat. 151 (2012) 145-156

III) Roman Bulánek, Eva Koudelková
     Determination of adsorption heats of individual adsorption complex by combination of microcalorimetry and FTIR spectroscopy
     J. Therm. Anal. Calorim. 113 (2013) 97-103

IV) Roman Bulánek, Eva Koudelková
     Quantitative analysis of IR spectra of carbonylic species in alkali-metal exchanged ZSM-5 and FER zeolite
     Catal. Today 243 (2015) 62-68

Further publications (published during the doctoral study, but not including this thesis):

V)   Frolich Karel; Koudelkova Eva; Frydova Eva, Roman Bulanek
     The quantity of Cu^+ ions forming isolated and bridged carbonyl complexes in FER zeolites determined by IR spectroscopy
     Vibrational spectroscopy 58 (2012) 146-152

VI) Rajesh Kodiyath, Gubbala V. Ramesh, Eva Koudelkova, Toyokazu Tanabe, Mikio Ito, Maidhily Manikandan, Shigenori Ueda, Takeshi Fujita, Naoto Umezawa, Hidenori Noguchi, Katsuhiko Ariga and Hideki Abe
     Promoted C–C bond cleavage over intermetallic $TaPt_3$ catalyst toward low-temperature energy extraction from ethanol
     Energy Environ. Sci. 8 (2015) 1685-1689

VII) Noelia M. Sanchez-Ballester, Gubbala V. Ramesh, Toyokazu Tanabe, Eva Koudelkova, Jia Liu, Lok Kumar Shrestha, Yuri Lvov, Jonathan P. Hill, Katsuhiko Ariga and Hideki Abe
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     J. Mater. Chem. A 3 (2015) 6614-6619

VIII) Smoláková Lucie, Kout Martin, Koudelková Eva, Čapek Libor
Effect of Calcination Temperature on the Structure and Catalytic Performance of the Ni/Al$_2$O$_3$ and Ni-Ce/Al$_2$O$_3$Catalysts in Oxidative Dehydrogenation of Ethane,
Ind. Eng. Chem. Res. 54 (2015) 12730-12740

IX) M. Rubeš, M. Trachta, E. Koudelková, R. Bulánek, V. Kasneryk, and O. Bludský
Methane adsorption in ADOR zeolites: A combined experimental and DFT/CC study
Phys. Chem. Chem. Phys. 19 (2017) 16533-16540

X) Luděk Hromádko, Eva Koudelková, Roman Bulánek, Jan M. Macak
SiO$_2$ fibers by centrifugal spinning: beating up traditional sorbents
ACS Omega – submitted

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1. Introduction

The zeolite chemistry has been a fast-developing area of material research, adsorption and catalytic applications. Everything started with Swedish mineralogist Axel Frederick Cronstedt in 1756, but the main interest in zeolites in non-scientific public had yet to come. In 1974 Henkel introduced zeolite A in detergents as a replacement for environmentally harmful phosphates. Since then, we have known a large number of zeolites structures, are able to synthesize a new structure, or have innovated a well-known structure, and we have applied zeolite in our lives, and found new applications of these materials in industry.

Nowadays zeolites play an important role in material chemistry and industry. They are used as adsorbents, catalysts, separators etc. The responsibility for uppermost properties (such as catalytic and adsorption properties) of zeolites have the extraframework cations. In recent years, a great attention of many research groups has been devoted to alkali-metal exchanged zeolites due to their potential usage as a model system for a detailed study of cation localization within extraframework positions.

There are many ways to characterize the extraframework position in zeolites. The easiest is the usage of infrared spectroscopy; it is a very powerful way to account for the surface site properties. Carbon monoxide is often used as a probe molecule for the characterization of active sites of catalysts and adsorption site of adsorbents by means of IR spectroscopy. Stretching frequency of CO molecule is highly sensitive to the nature and the local environment of adsorption sites. The factor modulate the C-O stretching frequency of the CO adsorbed on cation-exchanged zeolites is well understood today.

Several carbonyl species have been described in literature by using IR spectroscopy, which can be divided to the three types of adsorption complexes: species on a single cation site coordinated by a carbon atom (C-down complex, carbonyl) or by an oxygen atom of CO (O-down complex, isocarbonyl), and complexes on a dual (or multiple) cation site (bridged complexes), where a CO molecule interacts with two cations at the same time. Also geminal polycarbonyl species have been identified.

Literature has described the formation, nature and location of CO adsorption complexes on extraframework cations for zeolite FER and MFI. Carbonyl complexes formed in zeolite BEA and MOR have been first described in this thesis, and also the quantification of so-called dual cation sites is a new phenomenon in zeolite chemistry. Our study would help to

advance the knowledge of the specific behaviour during a so-called "host-guest" (electrostatic) interaction of CO in a confined space of zeolite pore system. We suppose that our research can widen the fundamentals of the molecule interaction with these promising materials, and help to accelerate the research of the synthesis of new tailored solids being designed for particular purposes.

2. Zeolites

Silicate minerals are divided into several main groups from the mineralogical point of view. The basic building units are silicon-oxygen tetrahedrons $[SiO_4]^{4-}$, in which a silicon cation is in the centre, and oxygen anions are in the top of a tetrahedron. Part of silicon atoms can be substituted with aluminium atoms (rather some $[SiO_4]^{4-}$ can be replaced by tetrahedral $[AlO_4]^{5-}$) in the structure of these materials (so-called aluminosilicates).

Zeolites belong to a group of the most interesting part of silicate minerals for us, so-called "tectosilicates". Only tectosilicates have a 3-D structure built of tetrahedral $[SiO_4]^{4-}$ units. These silica tetrahedrons are connected to each other via shared oxygen anions, and the tops of tetrahedrons are connected by T-O-T bridges (where T stands for Si, Al, B, Fe, Ga). It means that each oxygen atom is shared by two neighbouring buildings units. Its binding capacity is fully used, so that is why the structure of these materials is really stable. Zeolites are composed of interconnected channels and cavities, in which molecules of water and cations of alkali metals (Na, K, Li, Cs) and alkaline earth metals (Ca, Mg, Ba, Sr) are fixed very weakly. These cations are localized in extraframework positions and compensate the negative charge of the zeolite framework. They are responsible for the uppermost properties of zeolites, such as catalytic and adsorption properties and also the ion exchange ability.

2.1 Zeolite structure

Nowadays, about 232 various zeolite structures are known and described.[9] General formula of zeolitic materials can be expressed as follows:

$$M_{z/n}O . Al_2O_3 . x\,SiO_2 . p\,H_2O \qquad\qquad (1)$$

It this formula:

i)   M stands for a cation compensating the negative charge of the lattice (the most common are cations Na^+, K^+, Ca^{2+}, Mg^{2+}, or from synthesis NH_4^+),

ii) n is the charge of cation,

iii) z stands for the binding capacity of cation,

iv) x ≥ 2, because there is no possibility to connect two $[AlO_4]^-$ tetrahedrons by one shared oxygen atom. It means that bond Al-O-Al is forbidden in the zeolite structure and this is described by Lowenstein rule[10]. This fact also reveals that the minimal molar Si/Al ratio is equal to 1. Many zeolites were prepared in a wide range of Si/Al ratios, but no structure was prepared in all range of Si/Al ratios (from 1 to ∞).

v)   p represents the degree of hydratation of zeolite. Zeolites are able to keep a lot of reversible adsorbed water (so-called zeolite water), which can be desorbed from material in a wide range of temperature interval, namely from 110 to 350°C. At room temperature and humidity the reverse hydratation occurs.

These secondary structures forming a microporous system of zeolites can be composed in many ways, which leads to a broad range of zeolite structure types. The organization of primary building units affects the diameter of particular channels and cavities and also influences the size of entrance windows in zeolites. From the technological point of view, there are two main interesting groups of zeolitic materials, which have so-called "sodalite" and "pentasil" substructural units. The "sodalite" type of materials has typical large cavities connected by channels with a lower diameter compared to these cavities. The diameters of particular parts of substructural units can be various among materials belonging to this group of structures.

This dissertation thesis deals with the characterization of extraframework cationic sites in the pentasil zeolite group of materials. To these "pentasil zeolites" belong several structures with a variety of framework properties. In contrast to sodalites, pentasil zeolite frameworks do not contain large cavities and they are built by the system of channels having various diameters and shapes (they can be straight or tortuous). In some materials the framework could reveal the intersection of channels.

The framework of zeolite consists of channels and cavities with regular geometry and diameters from 3 to 15 Å. The structure can be described as a complex space (matrix) having

high internal surface and volume (specific area 250-800 m^2/g, volume 0.1-0.35 cm^3/g), which gives high sorption capacity of these materials. Dimensions of channels and entrance windows limit the diameter of a molecule, which can pass through, and define molecular sieve effect. The ability to adsorb preferentially certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene by silicalite. The geometry and diameter of channels and cavities influence size of molecules, which can be produced by chemical reaction taking place inside the zeolitic matrix. The shape and size of a particular pore system exert a steric influence on the reaction, controlling the access of reactants and products. Thus zeolites are often said to act as shape-selective catalysts. Increasingly, attention has focused on fine-tuning the properties of zeolite catalysts in order to carry out very specific syntheses of high-value chemicals, e.g. pharmaceuticals and cosmetics. The chemical composition of zeolite framework (namely molar Si/Al ratio) determines the concentration of negative charge and so the amount of coordinated charge balancing cations.

2.2 Zeolite in application

Zeolites (natural or synthetic) are used in many applications in the industry. World production was estimated to be in the range of 2.7 to 3.2 million metric tons (Mt). Around 2 million metric tons of natural zeolites per year is used worldwide. Prices for natural zeolites vary with zeolite content and processing and it ranged from $110 to $440 per metric ton[19]. The main applications of natural zeolites are in agriculture as additives to fertilizers and feeds. The presence of zeolites in agricultural fertilizers increases the pH of tilth and also holds ammonium and potassium ions, and that's why the activity and efficiency of fertilizers increase. Natural zeolites find only limited usage in industrial applications due to inhomogeneity and also impurities. Major part is used as additive to the concrete and construction materials.

Synthetic zeolites are topologically homogeneous and prepared in a very clean state. The consumption of these materials is about 1.5 million tons per a year.[6] As was mentioned

in previous chapter, specific features of zeolitic materials give them variable adsorption, catalytic,[20] and ion exchange properties[21] of paramount importance in the chemical industrial field. Moreover, interest is growing on the study of new zeolite applications related to process intensification,[22] hybrid materials,[23] medicine,[24] animal food uses,[25] optical- and electrical-based applications, [26] and nanotechnology[27]. The newest application for zeolite is in green chemistry,[28] as a single gas sensor for detection of wide spectrum of sensing targets[29] or as a controlled drug release[30].

2.3 Importance of alkali metals in zeolites

In recent years, big attention of many research scientist groups has been devoted to alkali-metal exchanged zeolites due to their potential usage as a model system for detail study of cation localization in extraframework positions. Extraframework alkali-metal, which interacts with oxygen atoms near framework aluminium, represents Lewis acid site, while neighbouring oxygens act as Lewis basic site (the basicity of these oxygens is decreasing with increasing distance from framework aluminium). It is now widely accepted that the extra-framework metal cations play a key role in the gas adsorption and catalysis on zeolites. The adsorption characteristics of zeolites depend not only on the nature of the extra-framework cation and its localization and coordination, but also on the character of the confined space of the zeolite channels and cavities and spatial distribution of cations inside this space.

Fundamental for understanding of sorption and catalytic mechanisms occurring in zeolite system is the information about the structure of the active adsorption centre and its proximate surrounding. Due to a close connection of cation site nature with localization of framework aluminium, the sorption behaviour of a given zeolite matrix is influenced by the distribution of aluminium among possible crystallographic positions in framework.[32]

The experimental techniques, often used for the characterization of cation coordination in zeolites are, among others, microcalorimetry and IR spectroscopy of selectively adsorbed probe molecules. Both methods are regular methods for the characterization of the active centre in zeolite. FTIR is the most common application to identify adsorbed species and to study the way in which these species are physisorbed onto the surface of zeolite, and microcalorimetry is useful thanks to the possibility of direct measuring of adsorption heat of

these species. These experimental techniques can be combined with theoretical studies performed by periodic DFT calculations.

3. Carbonyl complexes on zeolites

CO stretching frequencies and CO adsorption enthalpy are highly sensitive to the nature and environment of the adsorption site. Based on the previous knowledge about the location of extraframework cations, experimental results and ever-increasing insight from theoretical quantum-chemical studies, it was found, that CO interacting with extra-framework cations in zeolite forms the following adsorption complexes:[36,43-46]

(i) mono- and dicarbonyl C-down complexes formed on isolated cation sites, so-called SCS (single cation site)

(ii) isocarbonyl (O-down) complexes, in which the metal cation coordinates the CO molecule through the oxygen atom, called ISO (isocarbonyl cation site).

(iii) bridged $M^+...CO...M^+$ complexes formed between a pair of nearby M^+ ions, called DCS (dual cation site)

(iv) multiple complexes can be formed in sites involving more than two cations.

A general model of CO vibrational dynamics in porous systems has been recently proposed by Nachtigall et al.,[45] the C-O stretching frequency of CO adsorption complexes depends on: i) *effects from bottom*, which depends on the nature of the CO adsorbing cation and its coordination to the framework. This effect is site-specific; this specificity decreases with increasing cation size; ii) *effects from top,* arising from CO interaction with the oxygen atoms of the zeolite framework on the opposite channel wall or with other cations siting in a nearby cationic site.

Effects from bottom mainly reflect the cation coordination with oxygen atoms of the zeolite framework, which depends on the zeolite topology and on the position of the nearby framework Al atom(s). Both, the CO stretching frequency and the adsorption enthalpy decrease when the coordination number and strength of interaction of the extra-framework cation with oxygen atoms of the framework increase.

There are two types of effects from top. When there is no secondary extra-framework metal cation in the vicinity of the adsorbed CO molecule, this molecule interacts through its

oxygen atom with the zeolite framework. Such an interaction shows an increase of the C-O stretching frequency and a small stabilization of the adsorption complex due to electrostatic and dispersion interactions.

The effect of the secondary cation on the properties of the CO adsorption complex makes the energy stabilization effect and the decrease of υ(CO) as a function of the distance between primary and secondary cations, r (M...M). The secondary metal cation, which faces the oxygen atom of the CO molecule, partially counteracts the polarization exerted on the CO molecule by the primary cation, which results in a decrease of the C–O stretching frequency.

This bridged M^+...CO...M^+ complexes appear whenever two alkali metal cations are at the right distance apart from each other, and such a pair of metal cations was termed a dual-cation site (DCS). The right distance depends on the cation and structure. For the individual alkali-metal cation it is 5-7, 6-8 and 7-9 Å for Li^+, Na^+ and K^+, respectively. The most suitable cation for probing the site-specificity due to the effects from the bottom is the small Li^+ cation, on the other hand the large cations, as K^+, are likely candidates for probing the site-specificity due to the effects from the top. Firstly, due to the small radius of the Li^+ cation, the probability of the existence of dual sites (a pair of two Li^+ cations about 5.5 Å apart from each other[45]) is rather low; secondly, because Li^+ ions often fit well in the plane of surrounding framework anions (e.g. 6-member oxygen rings), and that renders them less adapted for CO bridging.[47]

The type of adsorption complexes that can be formed depends on (i) the zeolite topology, Si/Al ratio (that determines cation concentration) and cation size, and (ii) size, geometry and electronic structure of the adsorbed molecule.

For alkaline zeolites, the dual cation sites usually adsorb gas molecules more strongly than single cation sites, and advancing knowledge of the factor determine gas adsorption energy can be exploited for technological application of zeolites in gas separation and gas storage[48-50] as well as for some applications in heterogenous catalysis. [51,52] The bridged complexes could be formed in zeolites other than alkaline, as well as in a larger range of adsorbed molecules (CO, CO_2, acetonitrile, ...) [34,41,46,53-56]

4. Aims of thesis

This dissertation thesis is focused on the studies of the coordination of extraframework alkali-metal cations in zeolites (mainly FER, MFI and BEA topology) using CO as a probe molecule, especially on the characterization of so-called dual cationic sites, which were recognized in Na-, K- and Rb-forms of MFI and FER zeolites previously. [43-45,57,70] The CO molecule was chosen as a probe molecule due to (i) its sensitivity to changes in local environment; (ii) well-known vibration behaviour of a CO molecule inside the zeolite channels and (iii) unambiguous distinguishing of single and bridged carbonylic species in the IR spectra of the CO/M-zeolite system. The aims of this thesis can be summarized as follows:

1) **Quantitative analysis of single and dual cationic sites in Na- and K-FER and MFI zeolites**. These zeolites had been studied previously; individual types of cationic sites had been described by means of vibrational bands in IR spectra, but the real population of these complexes on zeolites had not been estimated. For this purpose, a combination of two methods (IR spectroscopy of adsorbed CO molecules and volumetric estimation of CO total amount adsorbed) was used. Molar absorption coefficients of individual types of carbonylic species were estimated, used for quantitative analysis of the IR spectra and discussed in a broader context.

2) **Investigation of cationic sites and occurrence of dual cationic sites in Na- and K- BEA.** These zeolites together with MFI and FER zeolites belong to industrially important zeolitic materials. The motivation for this study is the fact that the information on the existence of dual cationic sites in BEA zeolite have been missing in literature. Cationic sites of sodium and potassium cations were explored by FTIR spectroscopy of CO adsorbed on the mentioned cations. The previous experience and knowledge from the study of MFI and FER zeolitic system could be utilized in this study.

3) Estimation of heat of adsorption of CO on individual cationic sites. The interaction energy of a molecule with cations has a decisive role in the adsorption behaviour of the zeolite. The stabilization effect of the interaction with a secondary cation in the dual cationic sites can dramatically change the separation performance of such adsorbent. Therefore, the determination of adsorption heats is a crucial task. The heat of the adsorption of CO on Na- and K-BEA zeolites was determined by the isosteric method

from optical adsorption isotherms constructed based on the IR spectra of the systems investigated at different temperatures. Also the microcalorimetric method was used in combination with a quantitative analysis of the IR spectra (see task 2) in the case of K-FER zeolites. The advantages and disadvantages of using microcalorimetry and isosteric method are discussed in the context of the reported data.

5. Results and discussion

5.1 Quantitative analysis of single and dual cationic sites in zeolites

The Na- and K-ion exchange zeolites FER and MFI had been previously studied in detail by means of vibrational IR spectroscopy and quantum chemistry, as it was summarized in Chapter 5.1. However, the real population of SCS and DCS had not been determined from the IR spectra due to unknown molar absorption coefficients in the previous studies. Just a rough comparison of the intensities of individual IR bands can result in the misinterpretation of them, because the prediction of molar absorption coefficient is very raw, and especially in the case of such a different interaction, as single and bridged carbonyls are, it cannot be generalized. The question about the population of bridged complexes is fundamental for the examination of these centres relevance for usable properties of zeolites. The IR spectroscopy is enormously qualitative in nature, but very rarely does the technique bring information about quantitative aspects of the surface phenomena. The quantitative information can be obtained only by a combination of IR spectroscopy with other analytical techniques as gravimetry, thermogravimetry or adsorption volumetry.

This thesis deals with the analysis of the FTIR spectra of carbonyl complexes on Na^+- and K^+-FER zeolite and Na^+- and K^+-MFI with varying Si/Al ratio in order to calculate the corresponding molar absorption coefficient and quantity of individual carbonyl types (I, IV). The quantitative analysis was made on the basis of a combination of FTIR spectroscopy and volumetric adsorption isotherms measurement at the same temperature. The areas of particular vibrational bands were obtained by the deconvolution of IR spectra. The extinction coefficients of adsorbed species were determined based on the regression analysis and the population of individual carbonyl species was calculated.

The resulting molar absorption coefficients obtained for individual zeolites and the deconvoluted spectra are shown in Fig. 1. Fit of experimental adsorption isotherms of adsorption of CO on K-FER zeolite by IR spectra using estimated ε_i values is depicted in Fig. 2A. The very good agreement between both sets of data is apparent.

A

ε_{SC} = 0.8 cm/µmol
ε_{DS} = 7.9 cm/µmol
ε_{iso} = 4.1 cm/µmol

B

ε_{SC} = 1.2 cm/µmol
ε_{DC} = 3.7 cm/µmol
ε_{iso} = 3.5 cm/µmol

C

ε_{SC} = 1.5 cm/µmol
ε_{DC} = 5.4 cm/µmol
ε_{iso} = 3.2 cm/µmol

D

ε_{SC} = 1.0 cm/µmol
ε_{DC} = 3.5 cm/µmol
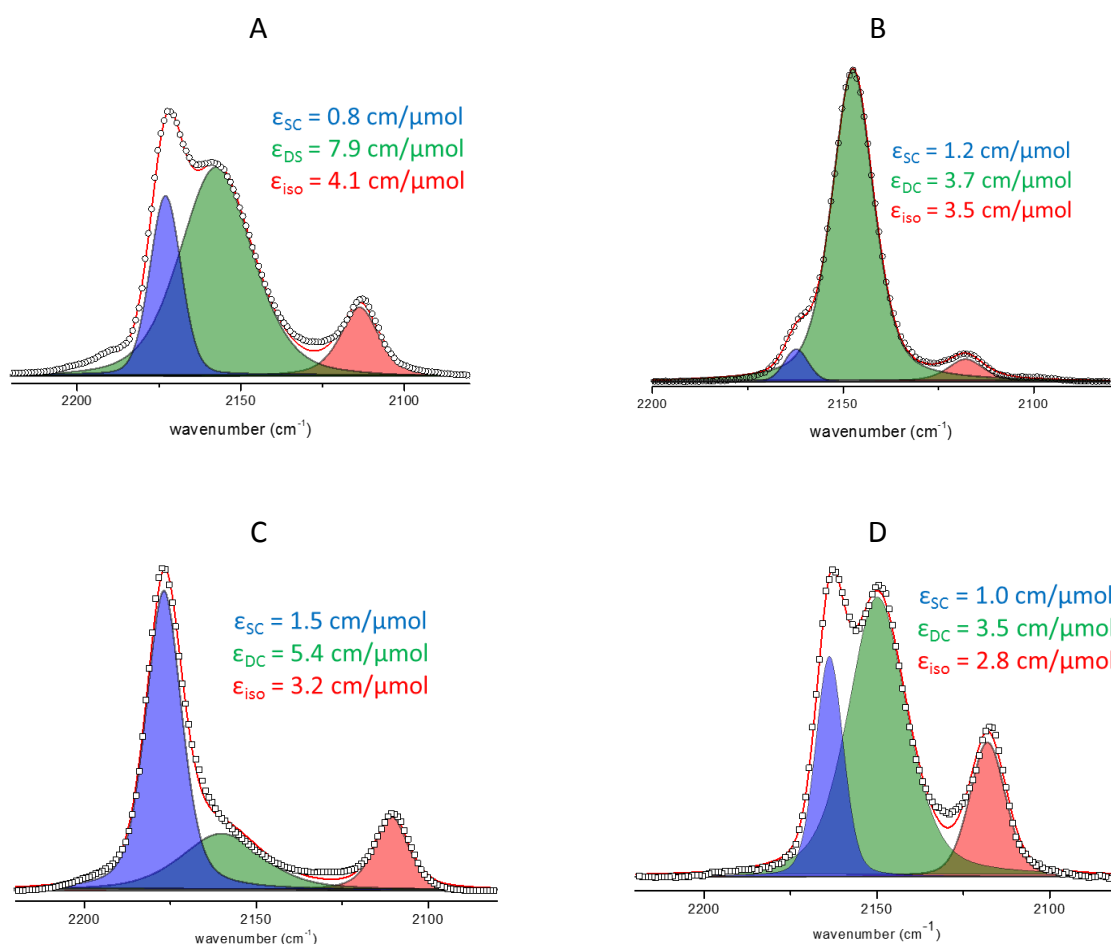ε_{iso} = 2.8 cm/µmol

Fig. 1. The example of the deconvoluted spectra of Na- and K-FER with Si/Al=8.6 (A, B, resp.) and Na- and K-MFI with Si/Al=11.5 (C, D, resp.) under study, and absorption coefficient of intrazeolitic carbonyls. SC, DS and ISO abbreviations stand for isolated carbonyl on a single cationic site, bridged carbonyls on dual cationic sites and isocarbonyls, respectively.

It is evident that a simple electrostatic model is not convenient for the interpretation of absorption coefficient of bridged carbonyl complexes on DCS. The band of bridged carbonyl on DCS in all investigated systems is slightly blue-shifted compared with free gaseous CO and red-shifted compared with the carbonyl on SCS and, therefore, the lower absorption coefficient would be expected considering the electrostatic model.

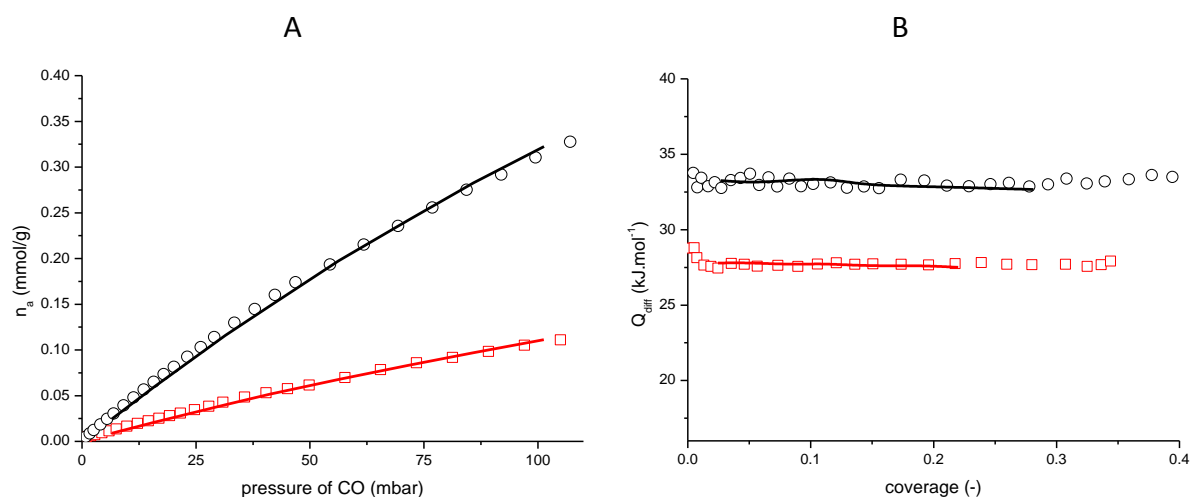A   B

Fig. 2 Adsorption isotherms (A) and heats (B) of CO at 300 K of K-FER zeolites. Symbols correspond to experimental data from volumetry and calorimetry; curves represent fits based on the quantitative analysis of IR spectra using integral absorption coefficients.

In spite of the position, bridged carbonyl complexes exhibit the highest absorption coefficients from all the complexes in a given zeolite. Therefore, it can be concluded that the increase of ε value for bridge carbonyl species is a general phenomenon and can be expected also in other zeolitic systems, including various zeolite structures and cations. According to bridged complexes, other absorption complexes are not the same for the same type of complex in FER and MFI zeolites. It has to be mentioned that we tried to calculate united values of absorption coefficients for both types by the same approach, but without satisfaction. We conclude that the absorption coefficient of a given complex differs across zeolite structures is different and cannot be generalized. The distance of two cation formed DCS and geometry of $M^+...CO...M^+$ complex have an effect on the broad range of values.

Cation		Na				K			
Zeolite structure		FER		MFI		FER		MFI	
Si/Al		8.6	27.5	11.5	30	8.6	27.5	11.5	30
Relative population (%)	SC	81.9	91.0	79.2	84.4	16.5	65.0	46.8	67.3
	DC	13.3	3.4	11.7	6.1	80.1	22.3	43.0	18.2
	ISO	4.8	5.4	9.1	9.5	3.4	12.7	10.2	14.4

Table 1 Relative population of individual carbonyl complexes calculated from the analysis of appropriate IR spectra corresponding to coverage of 10% (molar ratio of CO adsorbed to a number of extraframework cations) using molar absorption coefficients resulted from the regression analysis. SC, DS and ISO abbreviations stand for isolated carbonyl on a single cationic site, bridged carbonyls on dual cationic sites and isocarbonyls, respectively.

On the basis of the knowledge of absorption coefficients of SCS, DCS and ISO complexes, their population can be calculated from IR spectra. The population of bridged carbonyl complexes depends strongly on both Si/Al ratio (thus the concentration of cations in the zeolite) and the type of cation and also the type of zeolite structure. Table 1 clearly shows (IV) that bridged complexes are more populated in the potassium zeolites due to a larger size of the K^+ cation resulting in a longer distance of two K^+ cations suitable for CO molecule stabilization in bridged complex, and thus higher probability of such cation pair existence.[45] Another interesting fact is seen from the spectra or from the population of bridged complexes (III), the population of bridged complexes for frameworks having approximately three times higher Si/Al ratio (8.6 to 27.5 for FER and 11.5 to 30 for MFI) is more distinct for the FER zeolite (four times lower population) than for MFI (only twice lower population) in both cationic forms of zeolites. It could be partially caused by the distribution of Al atoms in the framework, which is non-statistical and depends on the conditions of zeolite synthesis.

5.2 Investigation of cationic sites in BEA zeolite

Zeolites FER and MFI together with BEA are the key zeolitic materials of several industrial processes. There is no study of the existence of dual cationic sites on zeolite BEA. The aim was to find and characterize the bridged complexes in those zeolites. The same principles and approach were applied to those zeolites using IR spectroscopy, volumetry and microcalorimetry together. The interpretation of individual spectral bands is discussed and adsorption enthalpies of CO in individual surface complexes are characterized by distinct IR bands. They are estimated by the means of isosteres constructed from a set of optical adsorption isotherms obtained at different temperatures.

Zeolite BEA has a large pore size, surface area, and pore volume with controllable Si/Al ratios accompanied by ion exchange capacity, so it is a very good candidate for catalytic and adsorption applications. The character of intrazeolitic carbonyls on alkali-metal exchanged BEA brings experimental evidence of the existence of dual cationic sites in BEA and the thermodynamic characteristic of carbonyl complexes formed on them is described in detail in article (II).

We collected the IR spectra of Na and K-BEA zeolite at 77 K. We found in Na-BEA three adsorption bands: the main absorption bands at 2180 cm^{-1} and 2161 cm^{-1}, and weaker bands at about 2130 and 2112 cm^{-1}. Similar spectra of CO adsorbed on Na-zeolites were reported

previously.[43,44,57,73,79,80] The main band at 2180 cm^{-1} is assigned to the SCS based on a very similar position of the band in other Na-zeolites, and based on fact that it exhibits low-frequency counterpart at 2112cm^{-1}. According to the reports on CO adsorbed on Na-zeolites in literature[44,57,73,79,80], the minor band at 2112 cm^{-1} is ascribed to the O-down complexes (ISO). The low intensity of this band is a consequence of temperature-dependent equilibrium between M$^+$...CO and M$^+$...OC species (M=alkali-metal cation) and it is well documented in the literature.[73] The band at 2130 cm^{-1} by its intensity and position corresponds to isotopic ^{13}CO counterpart of the main band at 2180 cm^{-1}. The band at 2161 cm^{-1} exhibits a smaller blue shift than monocarbonyls, therefore, it should correspond to the C-O stretching vibration of CO molecules bridging two Na$^+$ cations in dual cationic sites. Futhermore, no partner component related to the corresponding CO species adsorbed via O-end is observed. According to the previous reports dealing with bridged carbonyls on the other Na-zeolites, the larger adsorption enthalpy is expected for this type of CO complex, as was evidenced (see Chapter 5.3).
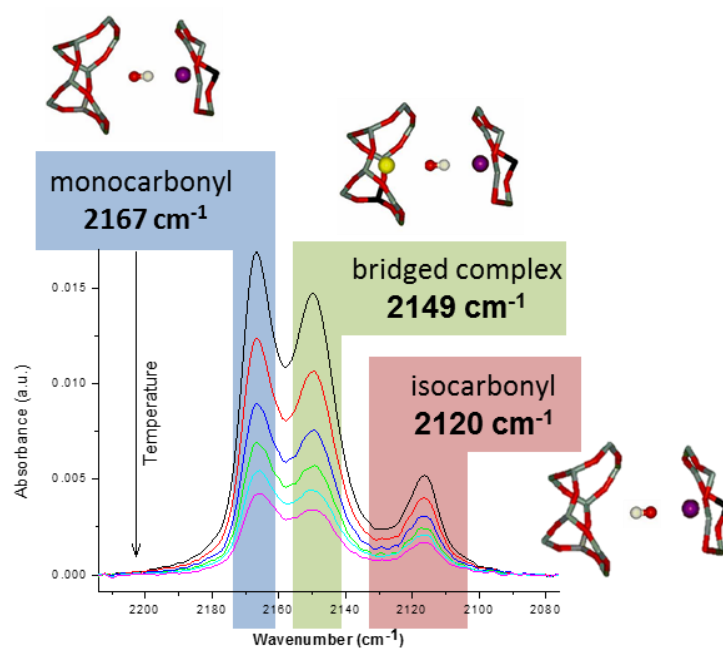

Fig. 3 VTIR spectra of CO adsorbed on K-BEA zeolite in the temperature range from -49.2 °C to -22.5 °C (p~3mbar). The colour-highlighted wavenumber regions correspond to each carbonyl species.

5.3 Determination of adsorption heat of individual CO-complexes on zeolite

From the practical point of view, the thermodynamic characterization of CO adsorption complexes, involving heat of adsorption, is very important. The adsorption heat is related to the energy of the bonds between CO and a cation site. In addition, stretching frequencies and adsorption enthalpies of adsorbed CO are complex specific, therefore the single carbonyls and the bridged carbonyls can be clearly discerned in the spectra.

The adsorption heats of CO adsorption complexes had not been estimated for the zeolite BEA previously. Further, an experimental determination of adsorption heat of CO in bridged complexes on K-FER zeolites has not been measured and prediction of the theoretical calculation has not been experimentally confirmed up to now.

The simplest way to get adsorption heat is to use a calorimeter. Our used apparatus is a heat-flow microcalorimeter of the Tian Calvet type. The heat generated in the system during adsorption flows from the calorimetric cuvette to the calorimetric block and is accurately measured by a large number of identical conductive thermocouples (a thermopile). The differential adsorption heat of CO adsorption on zeolites is defined as a numerical differentiation of the integral adsorption heat versus data of adsorbed amount, therefore using high-sensitive calorimeters and sensitive volumetric apparatus we can determine accurately the adsorbed amounts and measure direct adsorption heats (which is equal to the isosteric heat) at the same time. Unfortunately, the determination of adsorption heats by microcalorimetry was complicated by simultaneous formation of several types of adsorption complexes. In our study we measure K-FER zeolite with two different Si/Al ratios (8.6 and 27.5) (III). Calorimetric curves of K-FER zeolite with different Si/Al ratio are constant and equal to 33 and 27.5 kJ/mol, it is usually considered as an indication of adsorbent homogeneity. But from the IR spectra we know, that CO stretching region consist of three vibrational bands at 2163, 2148 and 2116 cm^{-1}. It is important to mention, that the changes in the ratio of vibrational band are very small, in other words, the population of all types of adsorbed species is not changing significantly, which is given by a relatively narrow measured range of coverage and Boltzmann distribution at relatively high temperature compared with the interaction energies of CO. Therefore the heat is constant – the average heat for all adsorption complexes formed in a particular adsorption step. All spectral

characteristic have been previously interpreted based on IR spectroscopy and DFT modelling. Garrone et al. [43] interpreted the high- and low-frequency band as C-down complex on SCS and O-down complex, resp., while the intermediate frequency band is due to the CO adsorption complexes on DCS.

The comparison of calorimetric and spectroscopic results led to a conclusion that the difference between calorimetrically determined differential adsorption heats for both samples is given by variation in bridge carbonyl species population. The constancy of differential adsorption heats depending on coverage is caused by simultaneous formation of all three types of complexes with the nearly constant probability, which is given by Boltzmann distribution law in the case of DCS and SCS complexes, and by thermodynamical equilibrium in the case of SCS and ISO complexes.

For the estimation of the adsorption heats of individual complexes and the solution of the problem with their estimation we should: i) measure a significantly lower temperature for a better separation of probability of carbonyl formation on SCS and DCS, or ii) combine experimental data from different experimental techniques, which can bring other information. Therefore, we must use a sophisticated methodology combining information form IR spectroscopy, home-made volumetry and microcalorimetry.

The knowledge of the actual amount of individual carbonyls on zeolitic samples (it means also the knowledge of adsorption complexes) combined with the knowledge of calorimetric heats offers a possibility to calculate the adsorption heat of individual adsorption species, and compared it with a value determined by another method, for example by VTIR spectroscopy. It could be another verification method of the meaningfulness of determined absorption coefficients (IV, I). The adsorption heat of individual adsorption complexes can be obtained on the basis of a regression analysis of calorimetric data, if we assume the Langmuir type of adsorption isotherm on each adsorption site. Differential adsorption heat at a given overall coverage degree ($Q_{diff}(\Theta)$) recorded by a calorimeter can be expressed as follows:

$$Q_{diff}(\Theta) = \left(\frac{dQ(\Theta)}{dn(\Theta)}\right) = \left(\frac{\sum_i dn_i(\Theta) \cdot Q_{diff}^i}{\sum_i dn_i(\Theta)}\right) \tag{6}$$

where $dn_i(\Theta)$ is a change of actual molar amount of i-th type of carbonyl at given coverage, calculated from a quantitative analysis of IR spectra, and Q^i_{diff} is molar adsorption heat of i-th type of carbonyl, which can be estimated by a regression analysis.

A regression analysis of calorimetric data results in adsorption heats of 21.5, 26.2 and 34.8 kJmol⁻¹ for ISO, SCS carbonyls on isolated K⁺ cation and bridged carbonyls in dual cationic sites, respectively. All of the estimated adsorption enthalpies are summarized in the Table 2. Fig. 2B clearly shows an agreement between the estimated and experimentally obtained adsorption heats.

Zeolite	SC	DC	ISO	Ref.
	$-\Delta H$	$-\Delta H$	$-\Delta H$	
Na-MFI	33.5	35.8	28.5	[43,44,73]
Na-FER	30.5	34.6	24.2	[57]
Na-BEA	29.3	33.5	24.2	(II)
K-MFI	28.2	31.6	24.5	[43,74]
K-FER	26.2	34.8*	21.5	[43] *(IV)
K-BEA	25.7	28.4	21.4	(II)

Table 2 Adsorption enthalpies ΔH (kJmol⁻¹) of intrazeolitic carbonyl complexes on alkali metal zeolites reported in literature (references provided in the last column)

Another method for the estimation of adsorption heats is variable temperature infrared spectroscopy (VTIR).[35] The VTIR approach is based on recording infrared spectra over a wide temperature range in a closed system with a constant amount of an adsorptive in the cell with simultaneous measurement of IR absorbance, temperature and equilibrium pressure. Due to our constraints with a precise determination of the maximum absorbance corresponding to coverage equal to one (A_M), we modified this approach for the estimation of adsorption ethalpies of CO adsorbed on Na- and K-BEA (II). We combined the methods of the measurement of the spectra of VTIR (several sets of IR spectra varying in initial equilibrium CO pressure were recorded over a temperature range from -70°C to -20°C) and the theoretical background of isosteres.

The isosteric enthalpy obtained for the monocarbonyl species in the Na-BEA zeolite characterized by band at 2180 cm⁻¹ was ΔH = -29.3 kJmol⁻¹, for isocarbonyl species (band at 2112 cm⁻¹) the value of ΔH = -24.2 kJmol⁻¹ was obtained, while bridged CO species (formed

on dual cationic sites) exhibited ΔH = -33.5 kJmol[-1]. It can be noted that the variation of values of ΔH with band intensity (corresponding to coverage) was random and in a narrow range of ± 2 kJmol[-1]. This is a consequence of a limited range of coverage no more than 0.5. In the case of zeolite K-BEA, the isosteric enthalpy for monocarbonyl species was ΔH = -25.7 kJmol[-1]. Bridged carbonyl species on dual cationic sites exhibited isosteric enthalpy of ΔH = -28.4 kJmol[-1].

It should be mentioned that for all three types of CO adsorption complexes (monocarbonyls, bridged carbonyls, and isocarbonyls), and the estimated isosteric enthalpies are found to be systematically smaller for K-BEA than for Na-BEA, as expected. The same trend was also found for CO adsorbed on potassium cations in MFI and FER zeolites as compared with CO adsorbed on sodium MFI and FER.[43,57,72] The results shown here for Na-BEA and K-BEA can be understood in terms of the recently proposed concept of vibrational dynamics of adsorbed molecules in a confined space of zeolites.[45]

The adsorption enthalpies of sodium exchanged zeolites of monocarbonyls in SCS are in the range from 29.3 to 33.5 kJmol[-1], the lower is associated with the Na-BEA, than Na-FER, and the highest have the zeolite Na-MFI. The same sequences of zeolites are in the case of bridged complexes on DCS, the range is from 33.5 kJmol[-1] for Na-BEA to 35.8 kJmol[-1] for the zeolite MFI, respectively. The difference in the heats between DCS and SCS is around 4 kJmol[-1] in the case of FER and BEA and around 2 kJmol[-1] in MFI. The bridged carbonyl complexes on Na-BEA and FER were found to be about 4 kJmol[-1] and the Na-MFI around 2 kJmol[-1], respectively, more stable than the appropriate C-down monocarbonyl complexes.

K-exchanged zeolites show a similar trend as in the case of Na-exchanged zeolites. The range of SCS is gradual from 28.2 to 25.7 kJmol[-1] for zeolites MFI, FER and BEA. The adsorption enthalpy of bridged complexes on DCS is the highest in K-FER zeolite, 34.8 kJmol[-1], than in the K-MFI with 31.6 kJmol[-1] and the lowest value of adsorption heat is in K-BEA zeolite (28.4 kJmol[-1]). The stability of the bridged carbonyl complexes compared to the corresponding monocarbonyls increase in the sequence BEA, MFI and FER zeolite.

6. Conclusion

Nowadays, the chemistry of zeolite and structural molecular sieves is a very important subject of material research, adsorption and catalytic applications. The number of zeolite structures rises every year, the synthesis of new structures or innovation of well-known structures is now very successful and new applications of these materials in industry were found.

The present thesis summarizes data from the literature about the CO adsorption on zeolite FER, MFI, complements missing information about experimentally determined adsorption heat of bridged complexes on DCS, and shows new measured data for zeolite BEA using a new approach for the "traditional" technique (microcalorimetry and FTIR) by combining both of them.

The main results can be summarized as follows:

(i)   For the first time a quantitative analysis was provided, made using obtained absorption coefficients and the population of each CO complexes (especially bridged complexes) in sodium and potassium form of MFI and FER zeolites was determined. The identification and quantification of dual cationic sites and complexes formed on such sites are important for understanding the adsorption behaviour of zeolites, and it has a relevance to a practical use of zeolites in such fields as gas separation and purification, gas storage and heterogeneous catalysis.

(ii)   Calculated absorption coefficients of a given type of a carbonyl complex in different zeolite structures are not the same and cannot be generalized.

(iii)   Isocarbonyls, monocarbonyls on SCS and bridged complexes on DCS were identified on Na- and K-BEA zeolites using IR spectroscopy. By the means of isosteric method in combination of optical isotherms the adsorption enthalpies, each complexes were estimated. It was found that the adsorption enthalpy of a CO molecule bonded via a carbon atom with a single sodium and potassium cation was -29.3 and -25.7 kJmol^{-1}, respectively, whereas the interaction via an oxygen atom let to adsorption enthalpy of -24.2 kJmol^{-1} and -21.4 kJmol^{-1}. The bridged carbonyl complexes on Na- and K-BEA were found to be about 4.2 kJmol^{-1} and 2.7 kJmol^{-1} more stable than suitable monocarbonyl complexes on SCS.

(iv)   The adsorption heats of bridged complexes on DCS of K-FER were obtained for the first time. The heat is 34.8 $kJmol^{-1}$, which is higher than the interaction energy of bridged complexes in the K-MFI with 31.6 $kJmol^{-1}$. The lowest value of adsorption heat of DCS is in K-BEA zeolite (28.4 $kJmol^{-1}$). The stability of the bridged carbonyl complexes compared to the corresponding monocarbonyls increase in the sequence BEA, MFI and FER zeolite.

(v)   We combine the experimental method from VTIR with the methodology of isosteric heats. With this approach we can estimate the heats of adsorption without knowledge of complicated and difficult-to-established parameter A_M from VTIR spectroscopy.

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