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Acid-base properties of zeolites

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Abstrakt

Zeolity jsou kyselé heterogenní katalyzátory hojně využívané v širokém spektru průmyslových aplikací. Jejich katalytická aktivita je spjata se silou, koncentrací a typem kyselých center v zeolitické struktuře. Existuje řada technik, které byly, a stále jsou využívány pro ohodnocování kyselosti zeolitů. Mezi některými těmito technikami jsou však jisté diskrepance.

V této disertační práci je věnováno úsilí rozklíčování těchto diskrepancí a určení spolehlivější metody. Dále je tato práce věnována výzkumu vlivu transformace 3D zeolitu na 2D strukturu a vliv této transformace na výslednou kyselost zeolitu. Rovněž je posuzováno, zda je možné experimentálně studovat pouze externí nebo intrazeolitická centra. V práci je studována i modelová katalytická reakce (dehydratace ethanolu) jako možný deskriptor pro posuzování síly kyselosti zeolitů.

Abstract

Zeolites are widely used as a heterogeneous catalysts in large field of industry applications. Their catalytic activity is related to the strength, concentration and nature of their acid sites. There are lots of techniques to evaluate zeolite acidity, but there exist a discrepancy between few of them.

Aim of this dissertation is to solve this discrepancy and determine the more reliable technique. This work is also focused on the influence of 3D to 2D structural transformation on acidity of given structure and also on the possibility to study separately intrazeolitic and surface acid sites. In this work also the model reaction of dehydration of ethanol is used as a descriptor of acidity.

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Introduction

Zeolites as heterogeneous acid catalysts have an irreplaceable position in many industrial applications, especially in the processing of petroleum products. The catalytic activity of these materials is closely related to the acidity of their structure, ie to the strength, concentration and type of acidic centers contained in the structure of the zeolite. There are a number of experimental techniques for evaluating the acidity of zeolites, but discrepancies have been found between some of these techniques. The question also arises as to whether acidity is affected by the transformation of a 3D structure into a 2D analogue and also whether external and intrazeolitic acid centers can be studied separately. It is also determined whether a model chemical reaction (ethanol dehydration or H/D isotopic exchange with ethane) can be used as an acid descriptor.

1. Theory

1.1. Zeolites

Zeolites are inorganic crystalline materials with a precisely defined microporous structure consisting of basic primary building blocks, tetrahedra SiO_4 and AlO_4 , which are interconnected by common bridged oxygen atoms to form secondary and more complex structures[1]. Each aluminum tetrahedron carries one negative charge, so the Si/Al ratio also expresses the negative charge of the framework, which must be compensated by extra-framework cations (organic or inorganic cations or protons). If the cation compensating for the negative charge of the framework is a proton which is located on the oxygen bridge between the silicon and oxygen atoms (Si - O - Al), an acidic Brønsted center (BAS) is formed (*Fig. 1*) - the reason why zeolites are acidic. If the negative charge is compensated by another inorganic cation, or a structural defect has occurred, a Lewis acid center (LAS) is formed[2] (*Fig. 2*).

Natural zeolites were already known at the turn of the 18th and 19th centuries, however, synthetic zeolites were prepared in the laboratory after the 1940s and only 20 years later began to be used commercially. The number of newly synthesized zeolites is still growing rapidly, as of March 2022, according to the official database of zeolite structures, 255 unique zeolite structures[3] are known, and this number will certainly continue to grow.

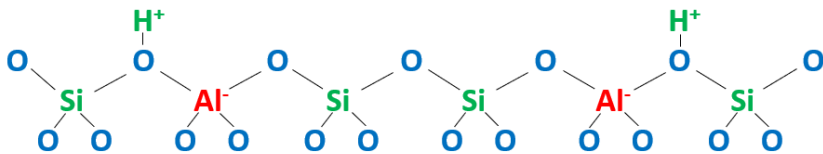


Fig. 1: Typical Brønsted acid site[4]

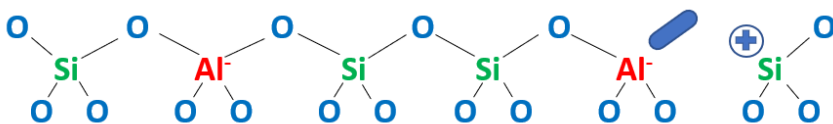


Fig. 2: Typical Lewis acid site[5]

Zeolites are highly specific materials with amazing and original properties, for which they are essentially irreplaceable in industrial use. They have a very low refractive index, about 1.47 - 1.54. Their hardness is low to medium, which corresponds to a value of around 3-5 on the Mohs scale. Zeolites are environmentally friendly, they are also important inorganic adsorbents and ion exchangers with high selectivity for cations. They are used as molecular sieves and driers, have a high affinity for radioactive cations (eg ^{90}Sr , ^{137}Cs) and are used in the treatment of wastewater from nuclear power plants[6]. Zeolites, which have a low Si/Al ratio and thus a high content of aluminum and compensating cations in the structure, are often used as ion exchangers due to their high exchange capacity[7], for example in water softening washing powders. The uniqueness of zeolites is further enhanced by the so-called molecular sieve effect, which is due to the specific character of the structural pores in the zeolite crystal. Each type of zeolite has a different but precisely defined and unique microporous structure with precisely given pore/channel dimensions, usually in the range 0.3 - 1.2 nm. Zeolites find perhaps the greatest use in a variety of acid catalyzed reactions. However, the catalytic reaction on conventional zeolites containing only micropores (also called 3D materials) is considerably limited by the transport of reactants to the active centers, and thus an effort was made to obtain a zeolitic structure containing a combination of wider pores (mesopores) and micropores. These dual porosity materials are also called hierarchical.

1.2. Hierarchical structures

Due to the presence of mesopores in the hierarchical structure, the transport routes are much wider and more voluminous, and therefore their eventual blocking with carbon deposits and thus deactivation takes a significantly longer time. Another advantage of hierarchical materials is the significantly higher proportion of active centers involved in the reaction (occurring in the reaction zone) compared to conventional 3D zeolites. The advantage of hierarchical structures is the shortening of the diffusion path length and thus the reduction of mass transport[8, 9]. The first hierarchical structures of zeolites were prepared as composites on a pre-prepared matrix,

such as porous glass or silicon oxide in the late 1990s[10, 11]. In practice today, there are a number of ways to prepare a hierarchical zeolitic structure[8, 12]. In general, the synthesis of mesoporous materials can be divided into two main groups - the "bottom-up" and "top-down" techniques (Fig. 3).

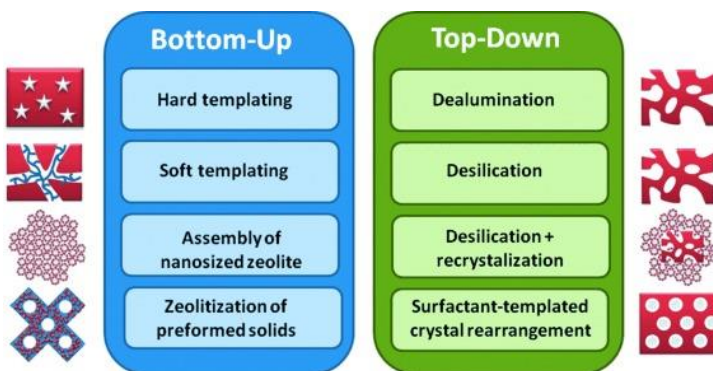


Fig. 3: Top-down and bottom-up techniques used to prepare hierarchical material[13]

The "bottom-up" technique is a process in which a hierarchical material can be assembled by condensing a precursor around a template (structure-determining substance)[14]. The template is then removed, most often by calcination in oxygen and cavities - mesopores - are formed at the place where the template particles were. Template types can be divided into hard, which uses solid nanoparticles (spherical particles, tubes, fibers etc.) and soft, which uses micelle solutions[14]. The "top-down" technique works essentially in the opposite way - by creating mesopores in the zeolite by removing parts of the material without completely destroying its microporous structure[15]. As mentioned, the catalytic activity of zeolites is directly related to their acidity, so it is necessary to outline the basic idea of acidity of solids and how to measure it.

1.3. Acidity of zeolites

To understand the catalytic activity of zeolites, it is essential to be able to characterize the strength, concentration and type of their acidic centers and to compare individual types of zeolitic materials. The significance lies in understanding the influence of the structure and composition of the zeolite lattice on the character and properties of acid centers. This would then make it possible to estimate the acidity of the newly prepared structures or to design a suitable zeolite for the given industrial process, which has the required properties. While the concentration and type of (Lewis/Bronsted) centers are relatively easy to achieve experimentally, it is experimentally challenging to express the strength of the acidic centers in the zeolite. The types of individual centers and their concentrations are most easily determined by IR spectroscopy, with the help of adsorption of specific molecules and knowledge of their extinction coefficient. Other possibilities of determination are the use of eg TPD, MAS NMR, etc.). The acidity of zeolites can be studied by the interaction of acidic centers with a weak or strong base. Weak basic molecules interact with the acidic center by electrostatic forces, which

do not lead to proton detachment, but the formation of a hydrogen bond. Usually, the vibration of the OH group shifts due to the binding of the CO molecule. Strongly basic molecules, which form a conjugated ion pair with the acid center, are also often used to measure the strength of acid centers. The acidity of a solid is defined by the energy required to split a proton from a given acid center of the acidic material and convert it to the gas phase - deprotonation energy, or also negative proton affinity. However, the interpretation of experimentally determined adsorption heats is not entirely straightforward due to other interactions, often schematically represented by the so - called Born – Haber scheme[16] shown at *Fig. 4* and discussed in more detail in the full text dissertation.

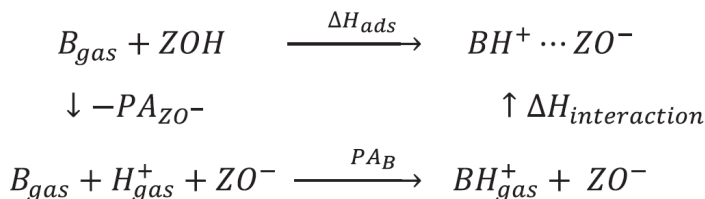


Fig. 4: Born – Haber scheme of elementary steps in the interaction of the Brønsted acid center with a basic molecule.

The interaction with a strongly basic molecule, most often ammonia, can be monitored, for example, by temperature-programmed desorption, where the activation energy of ammonia desorption is determined by changing the position of the desorption peak maxima depending on the heating rate of the material. Test reactions can also be used to describe the acidity of zeolites. In this work, two model test reactions were selected, namely ethanol dehydratate and H/D isotopic exchange using ethane. The crucial question is how the acidity is affected when converting a 3D form to a 2D analog, and also how the acidity of the external and intrazeolitic centers differs. Much more detailed description of the aspects, history and the techniques used to the study of zeolite acidity are described in the full text dissertation in Chapter 4.

2. Aims of Doctoral Dissertation

Despite the great attention paid to Brønsted acidic centers in zeolites (and their industrial significance), the question of their strength and comparison between different zeolites remains open. Even more is the gap between the observed catalytic activities of hierarchical and 2D zeolites in different reactions and our knowledge of the influence of the location of the acid center (on the outer surface or surface of the mesopore and inside the structural micropore) on its strength. Based on these facts, the following questions were defined, which were sought answers within the dissertation.

- Is ethanol dehydration a suitable model reaction for studying the acidity of Brønsted acid centers?

- A recently observed discrepancy between the frequency shift of OH vibration during weak base (CO, N₂) interaction and the adsorption enthalpy of these molecules on **MWW** zeolite [46, 47] raised the question whether the strength of Brønsted acid centers of **MWW** zeolite is lower than **MFI** zeolite, what does the adsorption enthalpy of CO look like, or higher, as would correspond to the frequency shift value?

- Is the strength of Brønsted acid centers affected by the transformation of a 3D material into a 2D/hierarchical material?

- Is the different strength of the Brønsted acid centers inside the micropores of the zeolite structure and on its surface or the surface of the mesopores of the hierarchical form of the zeolite?

3. Results and discussion

3.1. Selection of a suitable test reaction

Alcohol dehydration is a frequently investigated reaction to evaluate the acidity of a catalyst. Therefore, we chose ethanol dehydration, which was performed in a flow arrangement in a fixed bed reactor, but because experimental tests clearly showed the complexity of the reaction and the large effect of diffusion, in the following research, we chose isotopic exchange of deuterium and proton, which was performed in batches in a static arrangement with detection by IR spectroscopy and which yielded results whose interpretation and relationship to acidity seemed much clearer. Zeolites **MFI** (Si/Al = 30 and 34.6), **MWW** (Si/Al = 24.5 and 29.9) and **CHA** (Si/Al = 7.5 and 14) were selected for the test reaction, the basic characterization of which is given in Tab. 1.

Tab. 1: Basic material characterization

Sample	S _{BET} [*] , m ² .g ⁻¹	S _{EXT} ^{**} , m ² .g ⁻¹	V _{micro} ^{**} , cm ³ .g ⁻¹	H ⁺ from NH ₃ - TPD, μmol per 10 mg	E _A of H/D exchange, kJ.mol ⁻¹
MFI -30	408	24.8	0.124	5.31	104 ± 1
CHA -7.5	478	2.9	0.244	11.97	130 ± 1
CHA -14	510	51.5	0.234	6.69	109 ± 3
MCM-22	547	158	0.178	-	-
MCM-36	637	380	0.113	-	-

Ethanol dehydration was studied in both flow continuous and dynamic configurations under temperature-programmed desorption conditions associated with the reaction. A 10 mg sample was used to study the dehydration of ethanol in a continuous arrangement in a fixed bed flow U-reactor, which was calcined in oxygen at 450°C for 16 hours before the actual catalytic test. A mixture of 1 and 10 mol was used for the catalytic tests themselves. The catalytic test was then performed in the temperature range 120 - 200°C. A 10 mg sample was also used in a non-stationary TPSR catalytic assay in an AutoChem 2920 tubular U-reactor (Micromeritics Instrument Cor., Norcross, GA, USA). The sample was calcined in a helium flow at 480°C for 10 minutes, then cooled to 40°C. A dose of the ethanol was then allowed to flow through the helium through a loop, allowing the ethanol to interact with the sample. Subsequently, the sample was heated in a controlled manner with a defined heating rate and the TPSR experiment itself was performed. In the continuous mode, the catalytic tests of the mentioned zeolites in ethanol dehydration clearly showed differences in the behavior of narrow- and medium-porous zeolites. Both zeolite types differ significantly in the rate of deactivation. The stability of the catalytic activity of the zeolites in the dehydration of ethanol as a function of the time spent in the reaction (TOS) is shown in Fig 5. This deactivation is due to the deposition of carbon deposits formed from ethanol by its condensation on longer chains, as demonstrated by TG/DTA analysis. This strong deactivation is the main reason why data from the initial phase of the reaction were used to evaluate the catalytic behavior of all zeolites, when the catalytic data are not yet so much affected by deactivation (in TOS = 2 minutes). The obtained data are then summarized in Tab. 2.

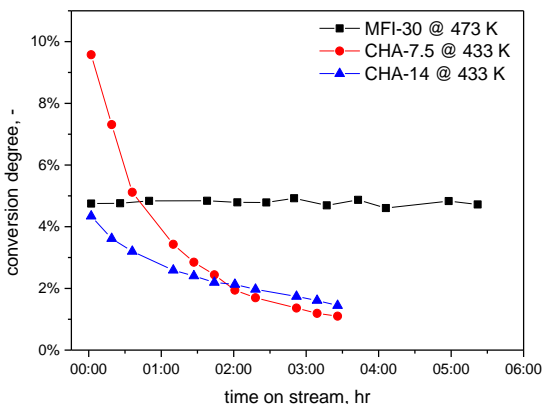


Fig. 5: Ethanol dehydration - TOS stability of samples at 10% ethanol at the reactor inlet

Tab. 2: Catalytic data of studied zeolites, TOS = 2 minutes

Sample	1 % of etanol					10 % of etanol				
	T K	S _{DE,0} %	X ₀ %	TOF ₀ min ⁻¹	E _A kJ.mol ⁻¹	T K	S _{DE,0} %	X ₀ %	TOF ₀ min ⁻¹	E _A kJ.mol ⁻¹
MFI-30	413	99.8	1.1	0.09		413	99.8	0.1	0.08	
	433	99.8	2.9	0.24		433	99.8	0.4	0.34	
	453	99.4	6.1	0.51		453	99.7	1.4	1.18	
	473	98.0	12.8	1.08	66	473	99.3	4.7	3.95	104
CHA-7.5	393	98.5	9.3	0.35		393	98.5	1.1	0.41	
	413	94.1	26.3	0.98	70	413	93.6	3.7	1.38	
	433	91.3	44.2 ⁾	1.65		433	92.4	9.6	3.58	77
CHA-14	393	94.5	5.7	0.38		393	95.1	0.9	0.60	
	413	93.6	12.0	0.8		413	94.8	2.0	1.33	
	433	92.4	23.8	1.59	51	433	93.3	4.3	2.87	55

The main products of ethanol dehydration are diethyl ether (DE), while ethylene appears only as a minor by-product. The dominant DE shows a selectivity of 91-99% in all continuous bed catalytic experiments in the continuous mode. The apparent activation energies, determined from the temperature dependences of the ethanol conversions, reach 66 and 104 kJ/mol for the **MFI** zeolite, depending on the input ethanol concentration in the reaction (1 and 10% by volume), which clearly indicates the effect of internal diffusion. According to the theory, the strong effect of internal diffusion can reduce the value of the apparent activation energy of the reaction by up to half of the actual activation energy. The determined values of the activation energies are shown in *Fig. 6*.

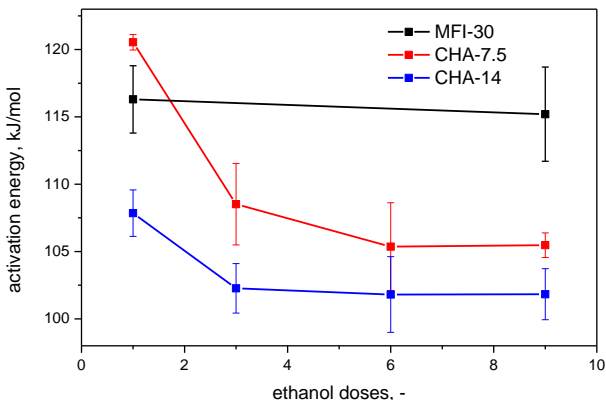


Fig. 6: Apparent activation energies obtained from TPSR depending on the amount of ethanol

The failure of the dehydration reaction led to a series of experiments with isotopic H/D exchange between zeolitic acid centers and ethane monitored by IR spectroscopy. This process has been considered as a suitable model response for acidity testing in the literature several times. The design of the experimental protocol chosen for this dissertation is based on a recent study by Kubota et al.[95]. This is a simple elementary process, which is the first step in activating hydrocarbons. In this dissertation we chose detection by IR spectroscopy. The zeolite in the form of a thin self-supporting plate was placed in an AABspec # 2000-A Multi-mode cell, which allows in situ monitoring of the sample by IR spectroscopy as a function of temperature. The sample was first evacuated at 450°C for 2 hours, then cooled to 150°C. At this temperature, several pulses of D₂O were repeatedly admitted to the sample, which caused quantitative deuteration of the OH centers to OD and partial deuteration of SiOH to SiOD. Excess D₂O was then evacuated and the sample was heated to the experimental temperature at which H/D isotopic exchange was monitored (usually in the range of 330 - 475°C). Once the temperature had stabilized, 50 mbar of ethane was admitted to the sample. The IR spectra of zeolites in deuterated form in contact with ethane gas show several characteristic regions of vibrations - (i) region 2800 - 2600 cm⁻¹ belonging to OD vibrations, (ii) CH vibrations of ethane in the range 3100 - 2800 cm⁻¹ and (iii) OH vibration in the range of 3750 - 3550 cm⁻¹. It is very important to always use the same and sufficiently high ethane partial pressure in each experiment to ensure that its excess is significant enough for its concentration to be considered constant, thus including it in the formal rate constant of the pseudo-first order kinetic equation. The resulting temperature dependences of the isotopic exchange rate constants performed on physically the same samples as the dehydration of ethanol are shown in Fig. 7.

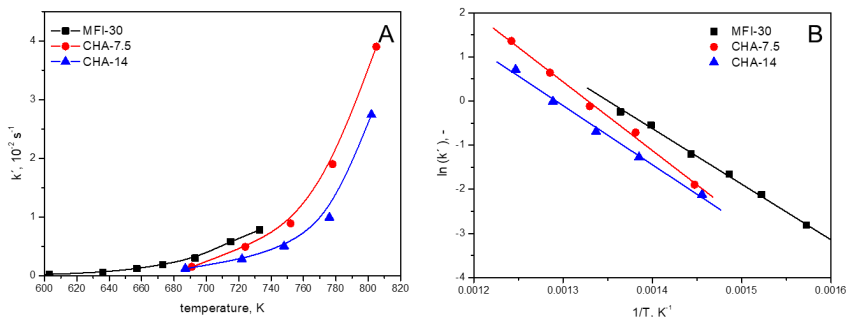


Fig. 7: H/D isotopic exchange rate constants between 50 mbar ethane and deuterated zeolite expressed as a function of temperature (A) and the Arrhenius dependence obtained from these rate constants in Figure A (B)

The activation energy of the H/D exchange for zeolite **MFI 30** is 104 kJ/mol, while for **CHA 7.5** and **CHA 14** they are 130 and 108 kJ/mol. These values are very close to the Kissinger activation energy values from the TPSR experiments with the lowest amount of pre-adsorbed ethanol (due to the suppressed effect of internal diffusion) and also correspond very well to the activation barriers for hydrocarbon activation predicted by quantum chemical calculations performed by Rybicki and Sauer[17]. The conclusion of this part of the dissertation can be summarized in the statement that H/D isotopic exchange in a static arrangement and monitored by IR spectroscopy by monitoring the change in deuterioxy concentration over time is a more robust and straightforward tool for studying acidity in zeolites compared to ethanol dehydration. Therefore, the H/D isotopic exchange was chosen in further research as a suitable test reaction for scaling the acidity of zeolites. The results obtained by this experimental approach were compared and discussed with other, often used acid descriptors, such as adsorption heats of weak and strong bases, frequency shifts of OH bond vibrations, etc., which are summarized in the following chapters.

3.2. Comparison of the acidity of zeolites **MWW** topology with other zeolite materials

At the end of the previous chapter, the reasons why the H/D isotopic exchange was chosen to characterize the acidity of individual centers in zeolites were mentioned. This chapter summarizes the results of characterization and acidity evaluation of **MWW** type zeolites using NH_3 -TPD, IR spectroscopy of carbonyls and H/D isotopic exchange and their comparison with the characteristics of other zeolitic structures (**MFI**, **FER**, **FAU**). The **MWW** topology zeolites were available in two configurations a) as 3D material MCM-22 and b) layered 2D analog MCM-36. The strength of the **MWW** zeolite acid centers was experimentally evaluated using (i) H/D isotopic exchange, (ii) carbon monoxide adsorption and (iii) temperature-programmed ammonia desorption. These strength characteristics of the **MWW** zeolite acid centers were compared and discussed with the values of the same descriptors characterizing the **BAS** centers of the **MFI**, **FER** and **FAU** zeolites. H/D isotopic exchange kinetics were measured in the temperature range of 325 to 475°C. The interpretation of activation energies is not, in our

opinion, simple, because the adsorption enthalpy of the hydrocarbon cannot be considered independent of temperature and its values at isotopic experiment temperatures are not known. In our opinion it is most reliable to directly compare rate constants for given materials at one particular temperature than uncorrected or vaguely corrected activation energies. Isotopic experiments under completely identical conditions were performed for zeolites **MWW**, **MFI**, **FER**, **FAU**. The H/D isotopic exchange rate at 425°C is highest for **MFI** material with a rate constant value $3.3 \cdot 10^{-3} \text{ s}^{-1}$, followed by **FER** ($1.2 \cdot 10^{-3} \text{ s}^{-1}$) zeolite, **MWW** ($4.5 \cdot 10^{-4} \text{ s}^{-1}$) and finally **FAU** ($2.4 \cdot 10^{-4} \text{ s}^{-1}$). Since the **FAU** type zeolite has the largest inlet windows, while the **FER** has the smallest, the magnitude of the rate constant does not appear to be controlled or affected by the diffusion of ethane through the channel system but by the reactivity of the acid centers. It follows that the acidity of the **MFI** material is considerably higher than the acidity of the **MWW** topology, among which the **FER** is still present, while the **FAU** has the lowest exchange rates and therefore the lowest strength of the acid centers. These results are also consistent with the values of carbon monoxide adsorption enthalpy measured by VTIR (variable temperature infrared) spectroscopy for **MWW**, **MFI** and **FER** materials[18], where the value of carbon monoxide adsorption enthalpy was much higher for standard **MFI** and **FER** zeolites compared to **MWW** (see Fig. 8).

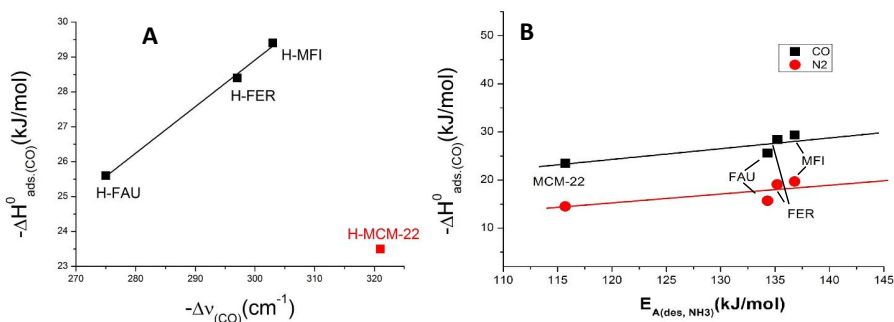


Fig. 8: A) discrepancy for MCM-22 between carbon monoxide adsorption enthalpy and OH vibration frequency shift in carbon monoxide adsorption and (B) correlation between carbon monoxide and nitrogen adsorption enthalpy results and ammonia desorption activation energy values determined by TPD.

In addition to isotopic exchange, the TPD ammonia technique was used for independent comparison of zeolite acids. Zeolite MCM-22 and **MFI** were compared. Two experimental methods of temperature-programmed experiment were chosen - (a) at constant flow of inert gas and variable heating rate of sample and (b) at constant flow rate of sample and variable flow of inert[19], whose mathematical model also includes the effect of readsorption. Activation energy values were determined in both ways. In constant gas flow experiments, the activation energy was calculated by knowing the temperature maximum of the desorption peak and the heating rate of the sample from Kissinger's equation. The Katada equation was used for constant sample rate heating experiments[90]. The average value of the ammonia desorption activation energy determined by a set of different heating rates (method (a)) was 127 kJ/mol for MCM-22, while from the variable inert flow technique (method (b)) 111 kJ/mol. The accuracy of determining the values of activation energies is usually in the range of 10 - 20 kJ/mol. The difference of 16 kJ/mol obtained by us shows that both methods are more or less comparable. **MFI**, has a value

of ammonia activation energy of about 137 - 160 kJ/mol, at the lower limit of this range lies the value of 137 kJ/mol. For other materials measured by us, we obtained values of 135 kJ/mol for **FER** and 134 kJ/mol for **FAU**.

3.3. Influence of 3D/2D structural transformation on zeolite acidity

In this dissertation, we tried to investigate the changes in the character of the acid centers of hierarchical zeolites in comparison with purely microporous zeolites using our acid center evaluation procedures. We decided to focus on 2D forms of zeolites, as their controlled synthesis leads to materials showing fewer defects compared to desilicated or dealuminated hierarchical zeolites. 3D and 2D forms of **MFI** zeolites were selected for this study, as one of the most important industrial catalysts, **MWW**, which is widely studied in this work, and **PCR** as a new zeolitic material obtained by modification of the original **UTL** germanosilicate by ADOR technique[14]. The IR spectra of adsorbed carbon monoxide and its interaction energies and H/D exchange kinetics (for **MWW** and **MFI** zeolites) were investigated in detail for all three materials. The tool for determining the acidity of **PCR**, **MFI** and **MWW** zeolites in 3D and 2D configurations was IR spectroscopy of a carbon monoxide molecule adsorbed at low temperatures on acid sites. When comparing the frequencies of C-O bonding in OH ... CO carbonyls, for both forms of **MWW** zeolite, the carbonyls are exactly the same frequency, while in the case of **MFI** a low frequency arm can be observed, for carbonyls on the 2D form of zeolite. In the case of **PCR** zeolite, the vibrating carbonyl band in 2D (IPC-1P) shows completely shifted maxima of the vibrating bands, see *Fig. 9*.

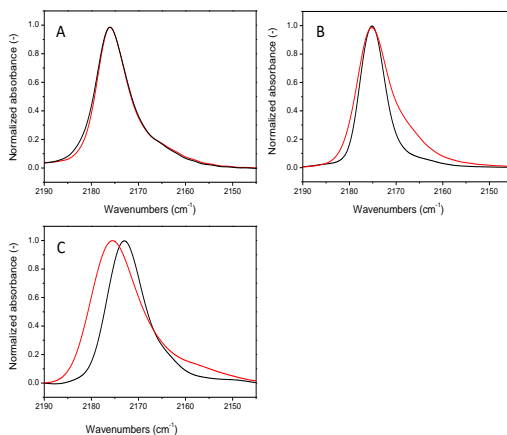
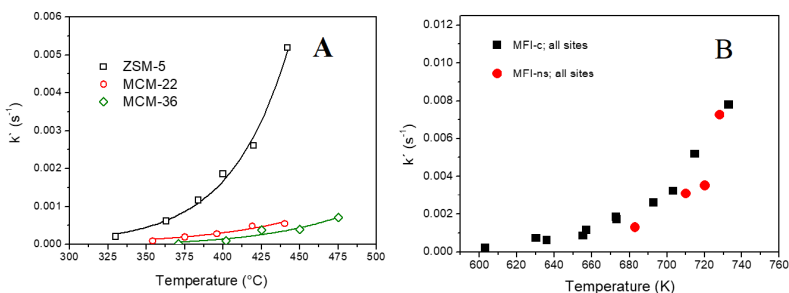


Fig. 9: Normalized carbonyl vibration IR spectra for (A) **MWW**, (B) **MFI** and (C) **PCR** zeolites. The 2D form is red and the 3D form black.

A comparison of OH ... CO adsorption complexes formed in 3D and 2D forms of zeolites shows that carbon monoxide complexes can be divided into two categories, (a) a carbon monoxide molecule bound to the acid site within the layer, and (b) a carbon monoxide molecule bound to

the external acid site. If a carbon monoxide molecule is bound inside a layer, it is characterized by a vibration frequency equal to that in 3D bulk material - for **PCR** and **MFI** these values are 2176 and 2178 cm^{-1} , while for complexes on the surface of individual layers (ie the second category of complexes) slightly lower, for **PCR** and **MFI** 2172 and 2171 cm^{-1} . Furthermore, in addition to these two types, a third type of vibration and a wavelength below 2170 cm^{-1} can be identified. In this type of adsorption complexes, carbon monoxide interacts with the acid site by means of a carbon atom and with the proton of the terminal silanols by means of oxygen, thus forming a so-called "bridge". This "bridge" complex is characterized by a weaker interaction of carbon monoxide and a lower wavelength of its vibration. The average value of the adsorption enthalpy of a carbon monoxide molecule decreases slightly when converting 3D to 2D material, similar to the vibration frequency of carbon monoxide molecules. The highest decrease in adsorption enthalpy was recorded for 3D/2D **PCR** material (-33/-29 kJ/mol), followed by **MFI** (-31/-28 kJ/mol) and only a very slight change was observed for **MWW** material (-30.5/30 kJ/mol). Both the vibrational frequencies of the adsorbed carbon monoxide on the acid site, the frequency shift of the OH vibration during the adsorption of the carbon monoxide molecule and the adsorption enthalpies of the carbon monoxide show only small differences, so it can be said that the effect of 3D structural transformation on 2D material has very little effect on the resulting acidity. The maxima of the carbon monoxide vibration spectral bands differed by less than 5 cm^{-1} for the 3D and 2D form of the given topology. These results are also consistent with the conclusions obtained by H/D isotopic exchange, where the acidity of MCM-22 and MCM-36 as 3D and 2D representatives of **MWW** topology was very comparable (see Fig. 10).



Obz. 10: (A) comparison of the temperature dependence of the rate constant H/D of the isotopic exchange for **MFI** materials (black), **MCM-22** (red) and **MCM-36** (green) and (B) comparison of the temperature dependence of the rate constant for **MFI** material for pure microporous form (black) and hierarchical form (red)

The same conclusion also follows from the TPD experiments, where in addition to the MCM-22 material, the activation energy of ammonia desorption was measured for the MCM-36 material with a value of 118 kJ/mol. Thus, all techniques used have shown that the acidity of the 3D and 2D forms of a given zeolite topology depends on the flexibility of the lattice and the thickness of the layer. This has led us further to find a way to distinguish between internal and surface acidic centers and to examine their acidity separately.

3.4. Determination of acidity of external and intrazeolitic acid sites separately

One of the possible approaches to the determination of acidity is the blocking of individual acid centers and subsequently their partial characterization. As part of the dissertation, it was possible to design an experimental protocol for the treatment of the studied material so it is possible to study the H/D exchange only at the surface or only at the inner centers. The principle of our developed procedure consists in shielding external acid centers by a specific bulk molecule, which due to steric barrier cannot diffuse into the zeolitic channel and interacts only with external centers (in this case 2,6-di-tert-butylpyridine), and also interacts with acid sites more strongly than water vapor, so that the occupied centers protect against water adsorption and thus the exchange of H for D at these centers. This enabled us to selectively achieve only deuteration of internal or external acid centers, on which a kinetic study of H/D exchange using ethane was performed. There is no information in the literature on a similar approach, and thus our method is unique in this respect. To verify this concept, we chose the **MFI** zeolite prepared in the form of the so-called nanosponge, which provides a large proportion of acid centers located on the outer surface (in our case about 1/3). The molecule 2,6 di-tert-butylpyridine (DTBP) has a kinetic diameter of 0.8 nm, and is therefore large enough not to diffuse into the structure of the **MFI**. Because DTBP binds more strongly than water, it can be used to block external acid sites. To study the external centers themselves, all centers can be deuterated first, then the external deuterated acid centers can be blocked by DTBP, and then the intrazeolitic centers can be protonated with redistilled H₂O. This is followed by the desorption of all bound molecules and thus the release of blocked external OD acid centers. The individual process steps are described in the detail in the full text dissertation and illustrated in Fig. 11.

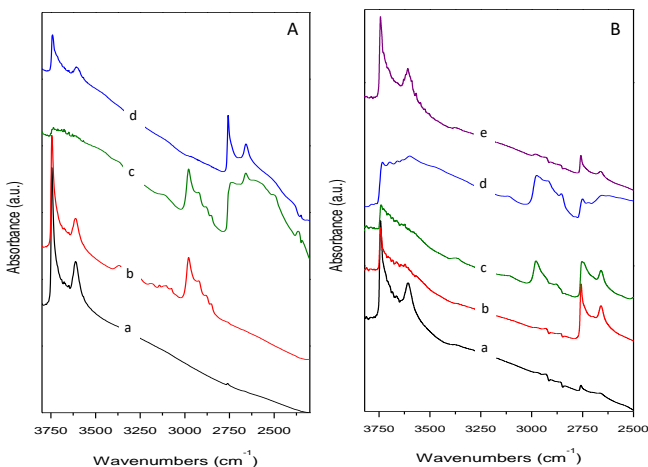


Fig. 11: IR spectra of nanosponge **MFI** in various experiments - (A) H/D exchange of intrazeolitic acid centers, a - fresh degassed sample, b - pre-adsorbed DTBP, c - pre-adsorbed DTBP in contact with D₂O, d - partially deuterated sample after removal of DTBP and D₂O. (B) H/D exchange of external acid centers, a - fresh degassed sample, b - fully deuterated sample, c - fully deuterated sample with bound DTBP, d - sample from c in contact with H₂O, e - partially deuterated sample after removal of all molecules.

The rate constants on the external BAS were slightly higher than on the internal centers and the activation energy of the external centers was 113 ± 7.5 kJ/mol. The illustrative spectra of the deuterated sample in contact with ethane, the linear dependences of the OD vibration intensity on time for individual temperatures, the dependence of the obtained rate constants on temperature and the Arrhenius dependence are shown in Fig. 12.

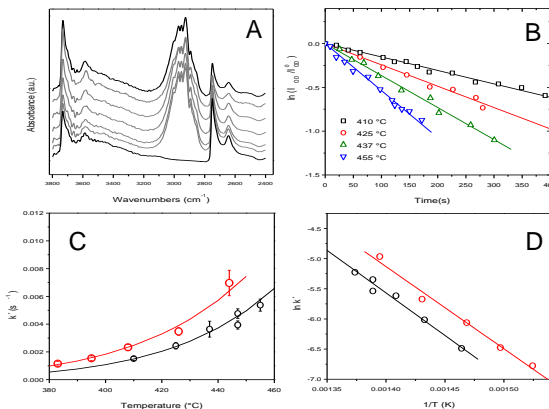


Fig. 12: *H/D isotopic exchange on nanosponge MFI material. (A) - typical IR spectra of deuterated nanosponge MFI in contact with ethane, 400°C, 0 - 400 seconds, (B) - natural logarithm of the relative intensity OD of the vibrating belt as a function of time at different temperatures, (C) - change of the internal rate constant (black) and external (red) centers in temperature, (D) - Arrhenius dependencies from data (C)*

When comparing the kinetics for 3D and 2D MFI at chosen temperature 425°C, at which the rate constants have values of $3.2 \cdot 10^{-3}$, $3.8 \cdot 10^{-3}$ and $2.4 \cdot 10^{-3} \text{ s}^{-1}$ for classical 3D MFI, for external acid centers and for intrazeolitic acid centers, respectively. The experimental value of the activation energy for the 3D MFI showed a slightly lower value, 97 ± 5 kJ/mol than for the 2D MFI, which indicates that diffusion will have some small effect here. Also, the pre-exponential factor obtained from fitting the linearized Arrhenius dependencies for external and internal acid centers differs slightly ($1.09 \pm 0.79 \cdot 10^6$ and $1.45 \pm 0.88 \cdot 10^6 \text{ s}^{-1}$ for external and internal centers). This may be related to the different entropic state of the ethane molecule at the outer surface and the molecule inside the zeolitic channel. However, the differences are so small that it is not possible to draw any conclusions from them.

4. Conclusions

The main results of this dissertation can be summarized as follows:

- The use of catalytic dehydration of ethanol as a test reaction proved to be problematic, especially due to the strong influence of diffusion, a number of side reactions of leaders to deactivate some materials (especially **CHA** zeolite) and complicated a mechanism that leads to different products by changing the reaction conditions (ethylene/diethyl ether).
- H/D isotopic exchange between the deuterated sample and the ethane molecule conducted in static arrangement was recognized as a more appropriate response. The advantage is very simple mechanism, which also acts as the first step in the catalytic activation of hydrocarbons at acid centers in various catalytic reactions, the possibility of in situ monitoring with high time resolution, the possibility of specific in situ sample pretreatment.
- Study of Brønsted acid centers in **MWW** zeolite using temperature programmed ammonia desorption and H/D isotopic exchange confirmed the fact that Brønsted acid centers of the **MWW** zeolite are weaker than the centers in the **MFI** or **FER** of the zeolite. These results again indicated that the method of evaluating acidity on the basis of frequency shift of OH vibration during adsorption of a weakly basic molecule introduced by Paukshtis and Yurchenko is not generally valid, but the reason why it leads to erroneous results in particular in evaluating the strength of Brønsted acid centers in zeolite **MWW** topology so far remains unclear.
- Systematic study of properties of Brønsted acid centers in 3D and 2D forms zeolites **MFI**, **MWW** and **PCR** through vibrational shifts CO and OH, adsorption CO heat interacting with an acidic proton and H/D isotopic exchanges led to the finding that with the total strength of the Brønsted acid centers (meaning averaged over all popular crystallographic positions of aluminum in a given measured sample) 3D forms of zeolites do not differ from their 2D analogues.
- The most important result of this dissertation can be considered the development of a unique methodology to distinguish external (localized on the outer surface of crystallites) Brønsted acidic centers from intrazeolitic and study of their acidic properties using H/D isotopic exchanges separately. This procedure, based on blocking external BAS large molecule of DTBP, allowed to monitor the rate of isotopic exchange on each of the types of acid centers in isolation and thus evaluate the strength of intrazeolitic centers independently external and vice versa. The obtained results show that the strength of external Brønsted acid centers are not fundamentally different from intrazeolitic Brønsted acid centers. Analysis of the H/D exchange rate constants showed the same activation barrier for both types of centers and a slightly different value of the Arrhenius frequency factors. It can be explained by small differences in the entropic states of molecules in external ones centers compared to intrazeolitic.

I believe that this research has helped to at least partially fill the gap in knowledge about the strength of acid centers in hierarchical or 2D zeolites and that they represent a valuable basis for further study of these structured porous materials.

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