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Development of structured zeolitic catalysts for the process of hydroisomerization of *n*-hexane

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Abstract

The hydroisomerization of linear or low branched alkanes through alkenes is a significant process for the refining of C_5 to C_6 hydrocarbon fractions to increase the octane number of automotive fuels. The hydroisomerization leads to the conversion of linear alkanes with a low octane number to branched isomers with a sufficiently high octane number. The bifunctional heterogeneous catalysts are a combination of an acid catalyst consisting of oxides containing acidic active centers and a metal cluster, where the hydrogenation and dehydrogenation of hydrocarbon reactants take place. The zeolite-based catalysts are significant in petroleum industry for the hydroisomerization of alkanes, especially the MOR zeolite type. However, availability of active sites for the *n*-hexane molecule in MOR zeolite is restricted by slow diffusion in narrow channels, and overall efficiency of the catalytic process is thus limited by transport of molecules. Branched alkanes diffuse even more slowly than linear *n*-alkanes due to of the higher kinetic diameter. The access of acidic active sites in current industrial catalysts is typically increased by partial dealumination of zeolites, where the aluminum atoms are extracted from the framework of zeolite resulting in positive textural changes in the channel structure of the zeolite but at the same time lowering the concentration of active acidic Brønsted centers. For these reasons, various post-synthesis methods of zeolites such as desilication, dealumination and fluoridation have been used in this work. The texture parameters of zeolites are adjusted by combination of these methods and allow easier transport of the hydrocarbon molecules to the active sites, therefore achieving a substantial increase in the rate of hydroisomerization reaction and shifting the reaction conditions to lower temperatures where the thermodynamic equilibrium is inclined to forming of multi-branched alkanes. Another important parameter for the hydroisomerization of C_6 is the amount of acidic centers contained in the zeolites. The analysis of the role of increased

density of strongly acidic protons showed that the high density of non-interacting but close and strongly acidic structural hydroxyl groups significantly lower the activation barrier in the isomerization reaction compared to far-distantacid sites and can provide higher reaction rates compared to state-of-the-art Pt/H-zeolite catalysts.

Abstrakt

Hydroizomerizace lineárních nebo málo větvených alkanů, prostřednictvím alkenů, je významným procesem pro rafinaci C_5 až C_6 uhlovodíkových frakcí s cílem zvýšit oktanové číslo automobilových paliv. Hydroizomerizace vede k transformaci lineárních alkanů s nízkým oktanovým číslem na větvené izomery s dostatečně vysokým oktanovým číslem. Pro hydroizomerizaci alkanů se osvědčilo použití bifunkčních heterogenních katalyzátorů, které jsou kombinací kyselého katalyzátoru složeného z oxidů obsahujících kyselá aktivní centra a klastrů kovu, kde probíhá hydrogenace a dehydrogenace uhlovodíkových reaktantů. V ropném průmyslu jsou pro hydroizomeraci alkanů významné katalyzátory na bázi zeolitu, zejména typu MOR. Nicméně, dostupnost aktivních center pro molekulu C_6 v MOR zeolitu je omezena pomalou difuzí úzkým kanálem a celková účinnost katalytického procesu je tak limitována transportními jevy. Větvené alkany vzhledem k vyššímu kinetickému průměru difundují ještě pomaleji než lineární *n*-alkany. Dostupnost kyselých aktivních center v současných průmyslových katalyzátorech je typicky zvyšována částečnou dealuminací zeolitů, kdy dochází k extrakci části atomů hliníku ze strukturní mřížky, což vede k pozitivním texturním změnám v kanálové struktuře zeolitu, ale zároveň ke snížení koncentrace aktivních kyselých Brønstedovských center, jejichž přítomnost v zeolitu je podmíněna přítomností hliníku ve strukturní mřížce zeolitu. Z těchto důvodů byly v této práci použity různé post-syntézní úpravy zeolitů jako je desilikace, dealuminace a fluoridace. Jejich kombinací se upraví texturní parametry zeolitů, což umožní snadnější transport molekul uhlovodíků k aktivním centrům, a tím se dosáhne podstatného zvýšení rychlosti hydroizomerizační reakce, a posunu reakčních podmínek k nižším teplotám, kde je termodynamická rovnováha nakloněna k tvorbě vícerozvětvených alkánů. Dalším důležitým parametrem pro hydroizomerizaci C_6 je množství kyselých center obsažených v zeolitech. Analýza role zvýšené hustoty silně kyselých protonů ukázala, že vysoká hustota neinteragujících, ale blízkých a silně kyselých strukturních hydroxylových skupin, významně snižuje aktivační bariéru v izomerizační reakci ve srovnání se vzdálenými aktivními centry, a

poskytuje vyšší reakční rychlost ve srovnání k nejmodernějšími Pt/H-zeolitovými katalyzátory.

Keywords
hydroisomerization, *n*-hexane, dealumination, desilication, fluorination, shape selectivity, mordenite (MOR), beta zeolite (*BEA), hierarchical zeolite

Klíčová slova
hydroizomerizace, *n*-hexan, dealuminace, desilikace, fluoridace, tvarová selektivita, mordenit (MOR), beta zeolit (*BEA), hierarchické zeolity

CONTENTS

INTRUDUCTION

The gasoline contains predominantly the hydrocarbons with 4 - 10 atoms of carbon, higher hydrocarbons are present only in a trace amount.

The C_6 alkanes are present in significant amount in the crude oil and form an important part of gasoline. However, these hexanes occur predominantly in the linear form characterised by very low octane number (only about 25) in contrast to branched C_6 isomers having high octane number (up to about 90). The basic processes how to increase the octane number are methods of the reforming, catalytic cracking, alkylation or hydroisomerization. The hydroisomerization of light gasoline fractions has recently become one of the most widely used processes in the petroleum industry due to its relevance to environmentally friendly and economical production of gasoline [1].

This hydroisomerization reaction is become a key reaction for the production of automotive fuels focusing to transform the linear C_6 alkanes with low octane number into the branched isomers: 2, 2-dimethylbutane, 2, 3-dimethylbutane, 3-methylpentane and 2-methylpentane with sufficiently high octane numbers.

This complex catalytic hydroisomerization reaction consists of several steps. Hydroisomerization of linear C_6 alkanes start with dehydrogenation of a linear alkane to an alkene on a noble metal, and followed by skeletal isomerization of the formed alkene via protonization and a cyclopropyl intermediate on a strongly acidic site and re-hydrogenation of the branched alkene to the alkane [2-7].

Currently, the most used catalysts for hydroisomerization of C_5 and C_6 hydrocarbon fraction are based on chlorinated alumina, sulfated oxides or zeolites. The chlorinated alumina has several disadvantages, since the chlorination occurs by reversible chemical exchange of the surface hydroxyl groups of the alumina support. That is the reason why the use of this catalyst is associated with constant supply and formation organochlorine compounds during the hydroisomerization reaction [1], which leads to serious questions about the environmental impact. Created organic chlorines have to be removed using scrubbers. The neutralization of fluegases and ellimination of environmentally harmful wastes raises the cost of operating[1]. Advantage of chlorinated alumina catalysts is their high activity at temperatures as low as 150 °C [8-9]. For the aforementioned reasons, the development is focused on enviromentaly friendly catalysts based on zeolites. Zeolites are used primarily as catalysts for catalytic cracking and hydrocracking in the petrochemical industry, for the production of chemicals

(e.g. ethylbenzene, cumene, cyclohexanone) or fuels, for the oligomerization of olefins, xylene synthesis and isomerisation, production of gasoline and synthesis of light olefins from methanol.

1.1 Zeolites as heterogenous catalysts in hydroisomerization of *n*-hexane

More than 150 commercial catalysts based on zeolites were proposed for refining processes (e.g. isomerization of paraffins and aromatics, hydro-cracking, aromatization reactions). The high activity and selectivity of zeolites and lower coke formation relative to the previous generation of catalysts (amorphous silica–alumina's) allowed refiners to increase gasoline output [10]. The success of zeolites in the industrial catalytic reactions is due to their relatively high acidity or mild basicity, stable structure at high temperatures (>400–800 °C) allowing use in the very harsh conditions, their channels pore system for optimum management of the molecular transport, their shaping (extrudates, spheres, microspheres) making them easy to handle and to separate in various catalytic reactor configurations, their non-corrosive and non-toxic character, their versatile composition (Si/Al ratio) and properties adaptable using the ion-exchange [10].

The unique catalytic properties of zeolites are based on the concurrent interaction of a hydrocarbon molecule with the acidic site [11] and adsorption in the confined reaction space of zeolitic channels [12-13]. The acidic sites in zeolitic channels of similar dimensions to hydrocarbon molecules provide high activity and selectivity in a wide range of relevant acid-catalysed reactions not available in other non-zeolitic catalysts [14-15].

For hydroisomerization are used bifunctional Pt/H-zeolite catalysts. The acid active sites in zeolites catalyse the skeletal isomerization reaction and Pt particles have dehydrogenation/hydrogenation functions. The reaction scheme of the hydriozomerization of C_6 alkanes using H/Pt zeolites is shown in **Chyba! Nenalezen zdroj odkazů.**. The first step of hydroisomerization reaction is dehydrogenation of the linear *n*-hexane to *n*-hexene on the Pt particles. This dehydrogenation reaction provides a low and stable concentration of *n*-hexene. From the *n*-hexene, the branched isomers are formed on strongly acidic active sites in the zeolite via cyclic carbocation intermediate. The presence of hydrogen gas blocks the formation of carbon deposits on catalysts [1]. Dehydrogenation is a very fast reaction and do not limit overall reaction rate of the process at proper dispersity and concentration of platinum. The reaction rate of the process is controlled by acid catalysed reaction steps.

Zeolites are crystalline microporous aluminosilicates and their frameworks are built from TO_4 tetrahedra (T= Si or Al atoms), where every oxygen atom is shared between two T atoms. The chemical composition of a zeolite framework can be therefore expressed as a combination of the SiO_2 and AlO_2 units. SiO_2 units are neutral, but every AlO_2 unit has one negative charge which is normally compensated by a cation, e.g. Na^+ or K^+. These metal cations can be exchanged by other cations, including protons forming the Brønsted acid centers. Lewis acid centers are associated with the presence of coordinated unsaturated metal cations, e.g., aluminum cations or network defects [16]. These acid centers of zeolite play a dominant role in the catalysis. The strength of the centers depends on the structure of the zeolites, but it is known that the strongest centers are isolated centers. The creation of the acidic centers in the zeolite structure and incorporation of precious metals into the zeolites led to the forming the classical catalysts with dehydrogenation and hydrogenation functions and the formation of bifunctional catalysts. These catalysts are used for technological processes such as hydrocracking or hydroisomerization of *n*-alkanes.

1.1.1 Types of zeolites

The strong development of zeolite chemistry has led to the fact that currently 235 unique structures can be distinguished (for the IZA Structural Committee, April 2018). In spite of this large amount, it is important to realize that only a few types of zeolites are used in the industrial scale. The most important types of zeolites include FAU, *BEA, ZSM-5, MOR and FER [17].

Mordenite zeolite (MOR) is one of the most industrially important catalyst based on zeolites for hydroisomerization of C_6 alkanes working at temperature about 220-290°C [1]. This zeolite has the two types of channels: large 12-memberedd-ring (12-MR) channels (7.0 × 6.7 Å) and small 8-MR side pockets located between 12-MR channels. The hydroisomerization of C_6 alkanes was suggested to be controlled by the concentration of acid sites in the channels of MOR zeolite. It has been proved that the active sites located in the 8-MR channels provide five times higher catalytic activity compared to the active sites located in the 12-MR channels [18]. However, the accessibility of these 8-MR side pockets compared to 12-MR channels is limited. Diffusion limitations due to restricted access for *n*-hexane [19-22] and slow transport to/from the active site decrease catalyst efficiency and support further transformations of desired products [19, 23].

Beta zeolite (BEA) is ranked between industrially catalyst based on zeolites used usually for alkylation of aromatics or hydrocracking [10]. But, in this work we wanted shown the potencial of this zeolite for the hydroisomerization of *n*-hexanes. The BEA network is crystallized in a tetragonal system and its elementary unit consists of 64 tetrahedral atoms. This zeolite has 3D structure containing the large 12-MR channels with size of opening window 7.6 x 6.4 Å.

Zeolite ZSM-5 (Zeolity Socony Mobil 5) was first synthesized in Mobil Oil laboratories in 1972. The unit cell of ZSM-5 zeolite consists of the 96 tetrahedrons. The three-dimensional zeolite pores system consists of two types of channels that lead into the 10- section windows. The channels have a straight section of 5.3 x 5.6 Å parallel to the direction [010], and channels elliptical 5.1x 5.5 Å elongation in the direction [100]. The wide range of ZSM-5 zeolite in catalytic applications includes the reforming of gasoline, the MTG process (methanol to gasoline) as well as isomerization or separation of the aromatic compounds [10].

1.1.2 Hierarchical zeolites

In recent years, considerable efforts have been devoted to improve pore accessibility and molecular transport of reactants to active sites in micropores, namely in ZSM-5 zeolites, to enhance the activity to desired products in major chemical processes. Diffusion limitations due to restricted acces and slow transport to/from the active sites decrease catalyst efficiency and support further transformation of desired products. These facts represent a major drawback in most indrustrial reactions catalysed by zeolites in hydrocarbon cracking, hydroisomerization, alkylation, transalkylation and esterification.

Several approaches to minimize diffusion limitations and enhance the catalyst effectiveness were developed. Synthesis of zeolites by using nanosheets [24], methods creating larger micropores [25] and the synthesis of zeolite prepared by confined crystal growth [26-27] or with using polymers as mesoporogens [28] were suggested . These strategies can overcome some diffusional limitations.

Nevertheless, the most of these methods are not really applied in the industry due to of demanding technical and synthetic operations. Therefore, we tried find such the synthesis of hierarchical zeolites which will be easier, cheaper, enviromentaly friendlier and can be really used in the industry.

The potentially suitable strategy to obtain resulted products is to synthesize hierarchical zeolites that combine the primary micropore and a secondary system which is consisted of

mesopores (2–50 nm) inside the microporous zeolite crystals, through using post-synthesis desilication and dealumination processes[21, 29-33]. The advantage of the presence of mesopores in the zeolite crystals for reaction rate is accompanied by the formation of the non-shape selective enviroment of the acid sites in the mesopores. These are easily accessed by reactants but behave like non-selective sites on open surfaces.

The current industrial catalysts use acid-treated partially dealuminated MOR of improved textural properties. But the dealumination leads to a loss in the concentration of Brosted sites, formation of Lewis sites and small changes of micropores. The intruduction of secondary mesoporosity into MOR provides opportunity for much dramatic enhancement of accessibility of active sites with preservation of a vast amount of acid sites.

1.1.3 Synthesis of Hierarchical zeolites

As already mentioned, it is possible to create zeolites with micromesoporous structure using special dealumination or desilication leaching procedures leading to the enhanced access to the active sites located in the inner part of zeolites with secondary mesoporous structure and thus eliminate the problem with diffusion of reactants and products to these active sites.

1.1.3.1 Desilication of zeolites

The principles of desilication of zeolites were described by Groen at al. with H-ZSM-5 zeolite crystals by their treatment in alkaline solution. Their group stressed the importance of Si/Al ratio in the zeolites and that the presence of Al atoms in zeolite framework is important for stabilization a neighbouring siliceous parts of the crystal zeolite [29].

It was found that the optimal Si/Al ratio for development of mesoporosity with preserved Al centers inside zeolite framework is 25-50. Lower Si/Al ratios (Si/Al<20) enable limited formation of mesopores becouse the desilication is restricted by higher concentration of aluminum atoms (the negatively charged AlO_4^- tetrahedra were found to prevent the Si extraction). On the other side, Si/Al ratios > 50 lead to the excessive and unselective Si dissolution which can lead to formation of relative large pores but also to destruction or completly dissolution of zeolite structure. For these reasons, conditions of desilication have to be optimized carefully for each type of zeolite [21].

1.1.3.2 Dealumination of zeolites

It has also been found that for the preparing hierarchical zeolites with using dealumination is better applied to zeolites with a higher Si/Al ratio. The higher Si/Al ratio is beneficial for stability during dealumination of zeolite and forming acid sites with higher strength [34].

Dealumination can be done with using hydrolysis at steamtreatment or by direct application of acids of a proper concetration. Special dealumination with adding water steam is used for syntehsis of zeolite Y with higher Si/Al ratio (USY zeolite). On the other side, dealumination can be applied on the other zeolites such as MOR, *BEA, ZSM-5 or FER. However, the mesopores are created by direct acid treatment with strong acid such as acetic, oxalic, tartaric acid or nitric, sulfuric or hydrochloric acid at different concentrations. Their concentration is highly dependent on the nature a types of zeolite.

1.1.4 Post-synthesis modification of zeolites by fluorination

A fairly young method of achieving the hierarchical structure of zeolite is a combination of a desiccation and fluoridation method which allows the controlled extraction of Al and Si from the zeolite to form a micromesoporous structure. This method was described for the ZSM-5 zeolite by Yu at el. [35] using the NaOH leaching and impregnation by NH_4F solution. The insertion of the fluorination as step prior to desilication allows the creation of secondary mesoporous structure formed by the extraction of both Si and Al atoms at the same time. The process allows the formation of interconnected opened channel structures with accessible acidic active sites of zeolites without large decrease in their concentration. This post-synthesed modification is optimal for different types of zeolites for creation of secondary mesoporosity [36] (Si rich zeolites) and forming of supermicroporosity [37] (Al-rich zeolite). It is expected that these modified zeolites can provide the hierarchical structure more accessible for reactants and with high concentration and availability of Brønsted active sites, thus providing a significantly higher catalytic activity in the hydroisomerization of C_6 alkanes [36-38].

2 AIM OF THE THESIS

The aim of this dissertation thesis is to understand relations between the local arrangement of active sites in microporous and micromesoporous zeolites and skeletal isomerization of *n*-hexane in order to adapt the structure of zeolite catalysts to increase their activity and selectivity for branched C_6 alkanes. The major objective was rational design of isomerization zeolite catalysts providing superior activity and shifting the window of operating temperatures to the thermodynamically more suitable area for the formation of di-branched isomers.

Two approaches were employed for this purpose in these studies focusing on enhancement of the concentration and/or the accessibility of active sites. The studies attempted to enhance the accessibility of the active sites by introducing secondary mesoporosity into mordenite zeolites coupled while attempting to preserve a large number of acid sites. The objective was attainment of the enhanced accessibility of acid sites using post-synthesis methods which are easy for application and really usable in industry. The aim was to explore potential for effective formation of secondary mesoporosity through postsynthesis alkaline, alkaline−acid, acid−alkaline−acid, and fluorination−alkaline leaching procedures of conventional microporous mordenite zeolites. The aim was also the modification of the structure of mordenite zeolite to provide an increase in the dimensions of the microporous channel openings, enlargement of the micropores and 3D interconnection of the micropores by postsynthesis concurrent extraction of Si and Al atoms from the framework using fluorination-alkaline-acid treatments. The objective of this paper was also analysis of the effect of a micromesoporous structure on the shape selectivity.

A synthesis of zeolites of *BEA structural topology with unique density and distribution of strongly acid sites was exploited to increase the concentration of active sites. This approach was used with the aim to examine of the extent to which the isomerization reaction is affected by high density and close proximity of strongly acidic centers.

3 EXPERIMENTAL PART

3.1 Preparation of hierarchical zeolites using post-synthesis treatment

The several types of parent zeolites were used in this work (Table 1). Two parent zeolites of the MOR structure (Table 2), designated as MOR/A/12 and MOR/B/5.8, and four parent zeolite of ZSM-5 structure (Table 3), designated as ZSM-5/A/25, ZSM-5/B/25, ZSM-5/C/15 and ZSM-5/D/22.5 were used for preparation of their hierarchical structure using postsynthesis treatment. Two zeolite of *BEA structure, designated as *BEA/A/11.3, Al-rich *BEA sturucture, designated as *BEA/B/4.2 and one zeolite of faujasite structure, designated as USY/6 were used for analysis and comparing of the catalytic properties (Table 1).

Table 1. List of parent microporous zeolites

Sample	Synthesis
ZSM-5/A/15	Microporous ZSM-5 (Zeolyst Int., CBV 3020, Si/Al = 15)
ZSM-5/B/25	Microporous ZSM-5 (Zeolyst Int., CBV 5524G, Si/Al = 25)
ZSM-5/C/25	Microporous ZSM-5 (Zeolyst Int., CBV 5020, Si/Al = 25)
ZSM-5/D/22.5	Microporous ZSM-5 (Alsi Penta, SM-55, Si/Al = 22.5)
MOR/A/12	Microporous MOR (Zeolyst Int., CBV 20A, Si/Al 12.1)
MOR/B/5.8	Microporous MOR (Zeolyst Int., CBV 10A, Si/Al 5.8)
BEA/A/4.2	Microporous Al-rich BEA (synthesised, Si/Al 4.2)
BEA/B/11	Microporous BEA (Zeolyst Int., CP814B-25, Si/Al 11.3)
USY/6	Microporous USY (Zeolyst Int., CBV 712, Si/Al = 6)

Schema of preparation of micro-mesoporous mordenite zeolites using postsynthesis alkaline-acid (Series I), acid-alkaline-acid (Series II), and fluorination-alkaline-acid (Series III) leaching procedures is illustrated in Figure 1. One of the parent MOR zeolite, denoted as MOR/A/12 (Figure 1 and Table 2) was used for preparation of micromesoporous mordenites using postsynthesis treatment: alkaline-acid leaching (Series I), acid-alkaline-acid leaching (Series II), and fluorination-alkaline-acid leaching (Series III) procedures [36]. The Ist series (Figure 1), micromesoporous mordenites were prepared using alkaline-acid treatments by leaching MOR/A/12 in an alkaline solution (30 ml 0.2 M NaOH per 1 g mordenite stirred in a beaker at 85 °C for 2 h, sample mm-MOR/A/8) and subsequent leaching in acid solutions (30 ml 0.1 M oxalic acid per 1 g alkaline treated zeolite stirred in a beaker at 85 °C for 20 h,

sample deAl-mm-MOR/A/9, or 40 ml 0.1 M HNO_3 per 1 g alkaline treated zeolite stirred in a beaker at 50 °C for 15 min, sample deAl-mm-MOR/A/9.5). The IInd series (Figure 1) was prepared using acid-alkaline-acid treatments with dealumination of MOR/A/12 (30 ml 3 M HNO_3 per g mordenite stirred and heated under reflux at 80 °C for 40 min, sample deAl-MOR/A/16), subsequent desilication (30 ml 0.2 M NaOH per 1 g dealuminated zeolite stirred in a beaker at 85 °C for 2 h, sample mm-deAl-MOR/A/9.1), and finally mild dealumination (30 ml 0.1 M HNO_3 per 1 g zeolite at 50 °C for 15 min, sample deAl-mm-deAl-MOR/A/13; or 30 ml 0.1 M $(COOH)_2$ per 1 g zeolite at 85 °C for 20 h, sample deAl-mm-deAl-MOR/A/30). The IIIrd series (Figure 1) was prepared by fluorination of MOR/A/12 (5 g mordenite were impregnated by 15 ml 0.36 M NH_4F at room temperature, stored at RT for 8 h, and subsequently dried at 120 °C for 12 h), subsequent desilication (30 ml 0.2 M NaOH per 1 g fluorinated mordenite stirred in a beaker at 85 °C for 30 min) and calcination at 550 °C for 3 h (sample mm-MOR/A-0.36F/9.4), with subsequent leaching in acid solutions (30 ml 0.1 M HNO_3 per 1 g zeolite at 50 °C for 15 min, sample deAl-mm-MOR/A-0.36F/13.6) [36].

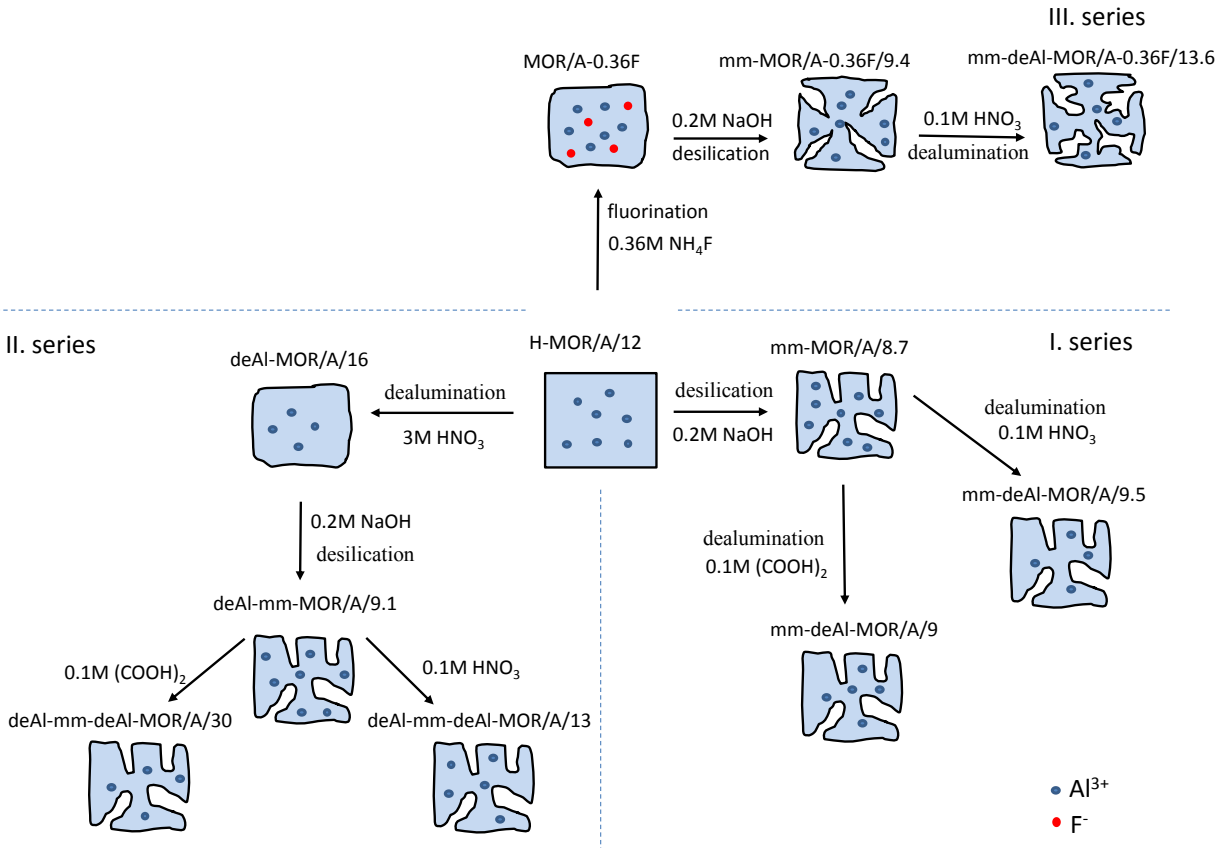

Figure 1. Schema of preparation of micro-mesoporous mordenite zeolites using postsynthesis alkaline-acid (Series I), acid-alkaline-acid (Series II), and fluorination-alkaline-acid (Series III) leaching procedures.

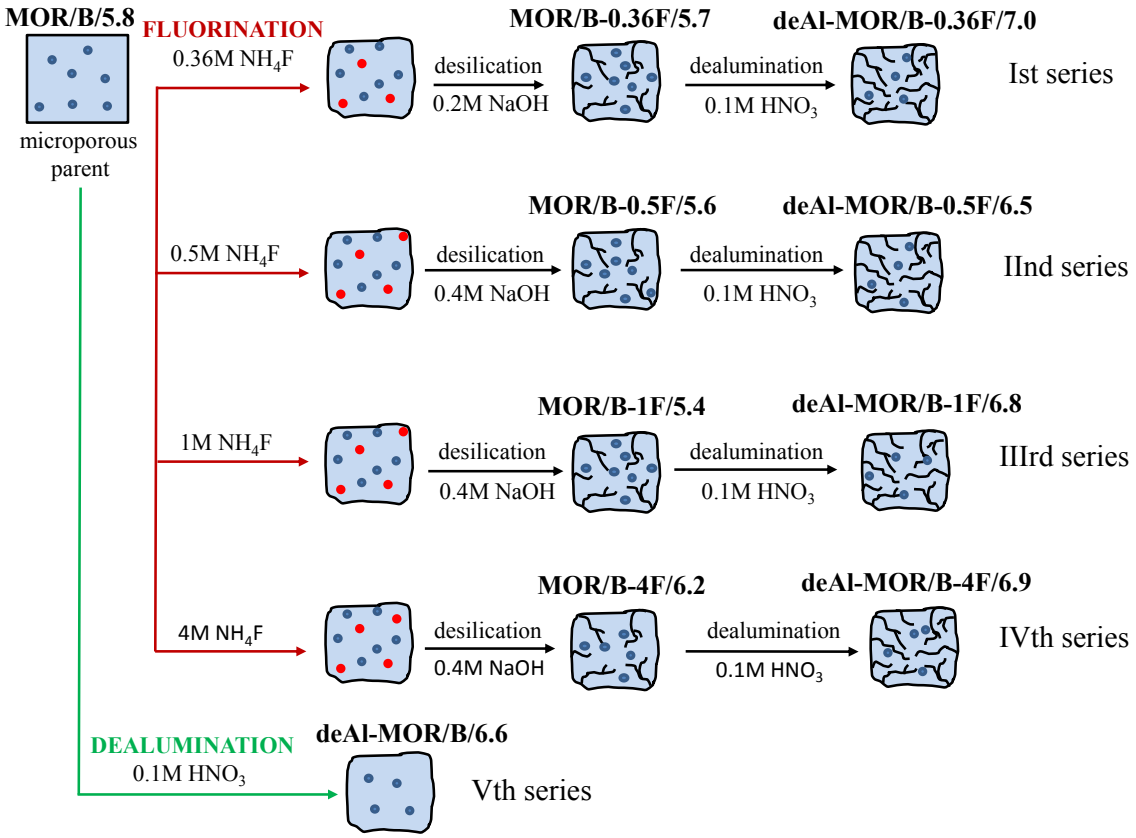

Figure 2. Scheme of the preparation of the supermicroporous mordenites using postsynthesis fluorination-alkaline-acid (Series I-IV), and acid (Series V) treatments.

The second parent MOR zeolite (Table 2 and Figure 2), denoted as MOR/B/5.8, was used for preparation of mordenites with enhanced accessibility of micropores using postsynthesis fluorination-alkaline-acid leaching procedures (Figure 2). The MOR/B/5.8 was treated by fluorination-alkaline leaching with various concentrations of NH_4F and NaOH and subsequently by mild dealumination [37]. Typically, 5 g of MOR zeolite was impregnated with 15 ml aqueous solutions of NH_4F at room temperature, kept at RT for 8 h and was then dried at 120 °C for 12 h and calcined at 550 °C for 3 h. The alkaline treatments were applied on the fluorinated zeolites (1 g of fluorinated MOR per 30 ml NaOH solution stirred in a beaker at a temperature of 85 °C for 30 min). In the Ist series (Figure 2) concentrations of 0.36 M NH_4F and 0.2 M NaOH solutions were used and the sample was denoted as MOR/B-0.36F/5.7. The IInd series was prepared using 0.5 M NH_4F and 0.4 M NaOH solutions and the sample denoted as MOR/B-0.5F/5.6. For the preparation of the IIIrd series (Figure 2), 1 M NH_4F and 0.4 M NaOH solutions were used and the sample was denoted as MOR/B-1F/5.4. The IVth series was prepared using 4 M NH_4F and 0.4 M NaOH solutions and the sample was designated as MOR/B-4F/6.2. Finally, after fluorination and alkaline treatment, the samples

were mildly dealuminated by adding 30 ml of 0.1 M HNO_3 per 1 g prepared MOR at 50 °C for 15 min and the samples were designated as deAl-MOR/B-0.36F/7.0, deAl-MOR/B-0.5F/6.5, deAl-MOR/B-1F/6.8 andBdeAl-MOR/B-4F/6.9 (Table 2). For the Vth series, the parent MOR zeolite was treated only by dealumination with HNO_3 (1 g parent MOR zeolite was added to 30 ml 0.1 M HNO_3 at 50 °C for 15 min) and the sample was denoted as deAl-MOR/B/6.6 [37].

Table 2. List of prepared micromesoporous MOR zeolites using postsynthesis treatment

Sample	Synthesis
MOR/A/12	**Microporous parent MOR**
mm-MOR/A/8	+ 0.2M NaOH
deAl-mm-MOR/A/9	+ 0.2M NaOH + 0.1M $(COOH)_2$
deAl-mm-MOR/A/9.5	+ 0.2M NaOH + 0.1M HNO_3
deAl-MOR/A/16	+ 3M HNO_3
mm-deAl-MOR/A/9.1	+ 3M HNO_3+0.2M NaOH
deAl-mm-deAl-MOR/A/13	+ 3M HNO_3 + 0.2M NaOH + 0.1M HNO_3
deAl-mm-deAl-MOR/A/30	+ 3M HNO_3 + 0.2M NaOH + 0.1M $(COOH)_2$
mm-MOR/A-0.36F/9.4	+ 0.36 M NH_4F + 0.2M NaOH
deAl-mm-MOR/A-0.36F/13.6	+ 0.36 M NH_4F + 0.2M NaOH + 0.1M HNO_3
MOR/B/5.8	**Microporous parent MOR**
MOR/B-0.36F/5.8	+ 0.36 M NH_4F + 0.2 M NaOH
deAl-MOR/B-0.36F/7.0	+ 0.36 M NH_4F + 0.2 M NaOH + 0.1 M HNO_3
MOR/B-0.5F/5.6	+ 0.5 M NH_4F + 0.4 M NaOH
deAl-MOR/B-0.5F/5.6	+ 0.5 M NH_4F + 0.4 M NaOH + 0.1 M HNO_3
MOR/B-1F/5.4	+ 1M NH_4F + 0.4 M NaOH
deAl-MOR/B-1F/6.8	+ 1 M NH_4F + 0.4 M NaOH + 0.1 M HNO_3
MOR/B-4F/6.2	+ 4 M NH_4F + 0.4 M NaOH
deAl-MOR/B-4F/6.9	+ 4 M NH_4F + 0.4 M NaOH + 0.1 M HNO_3
deAl-MOR/B/6.6	+ 0.1 M HNO_3

Several types of parent ZSM-5 zeolites (Table 3) were used for preparation of their micromesoporous analogues using fluorination−alkaline leaching procedures according to procedures reported by Yu et al. [35]. 5 g of ZSM-5 zeolite was impregnated with 15 ml of aqueous solution of 0.36 M NH_4F at room temperature, stored at RT for 8 h, then dried at 120 °C for 12 h, and subsequently calcined at 550 °C for 3 h. The calcined zeolite was than leached in an alkaline solution (30 ml 0.2 M NaOH per 1 g of fluorinated ZSM-5 stirred in a

beaker at 85 °C for 30 min). The obtained samples were denoted as mm-ZSM-5/A-F/10.2, mm-ZSM-5/B-F/15.9, mm-ZSM-5/C-F/15.1, and mm-ZSM-5/D-F/13.4 (Table 3). The synthesis steps of fluorination and alkaline treatments were subsequently repeated on modified micromesoporous ZSM-5 samples under the same conditions yielding samples designated as mm-ZSM-5/A-F/6.9 and mm-ZSM-5/B-F/12.9 (Table 3) [38].

All types of prepared zeolites were ion-exchanged with 0.5 mol.dm^{-3} NH_4NO_3 solutions at RT (1 g of a zeolite per 100 cm^3 of solution, three times over 12 h) to obtain the ammonium form of the zeolites. All parent zeolites of MOR, ZSM-5, *BEA and USY structure (Table 1) were used as a standard for comparing catalytic properties.

For the reaction of hydroisomerization of *n*-hexane, the Pt was introduced into the zeolites in the NH_4^+ forms by incipient wetness impregnation of pre-dried (105 °C/2 h) powdered material by H_2PtCl_6 solution to yield 1.5 wt. % of Pt. The amount of aqueous solution of H_2PtCl_6 and its concentration used for the impregnation were calculated based on the porous volume of each zeolite [36-38].

Table 3. List of prepared micromesoporous ZSM-5 zeolites using postsynthesis treatment

Sample	Synthesis
ZSM-5/A/15	Microporous parent ZSM-5
mm-ZSM-5/A-F/10.2	+ 0.36 M NH_4F + 0.2 M NaOH
mm-ZSM-5/A-F/6.9	+ 0.36 M NH_4F (2x) + 0.2 M NaOH (2x)
ZSM-5/B/25	Microporous parent ZSM-5
mm-ZSM-5/B-F/15.9	+ 0.36 M NH_4F + 0.2 M NaOH
mm-ZSM-5/B-F/12.9	+ 0.36 M NH_4F (2x) + 0.2 M NaOH (2x)
ZSM-5/C/25	Microporous parent H-ZSM-5
mm-ZSM-5/C-F/15.1	+ 0.36 M NH_4F + 0.2 M NaOH
ZSM-5/D/22.5	Microporous parent ZSM-5
mm-ZSM-5/D-F/13.4	+ 0.36 M NH_4F + 0.2 M NaOH

3.2 Characterization of prepared zeolites

The prepared samples of zeolites was characterised by the several methods. Texture parameters of modified zeolitic materials were determined at the ASAP 2010 apparatus (Micromeritics) by the analysis of N_2 adsorption isotherms at liquid nitrogen temperature (77 K). The SEM images were obtained on a field emission scanning electron microscope Hitachi S-4800. Sputter coating of samples with a noble metal was needless. The HR-TEM

micrographs were obtained on a JEOL JEM 3010 microscope equipped by LaB6 cathode, operated at 300 kV. The FTIR spectra of H-forms zeolites were measured on a Nicolet nexus 670 FTIR apparatus, where from the zeolite samples were made self-supporting wafers and inserted into the metal holder in the IR cell. The wafers of zeolites were evacuated at 450 °C during 3h and then recorded at RT by collecting 256 scans at 2 cm^{-1} resolution for each spectrum. The diffraction patterns of zeolites were collected on the Bruker AXSD8 Advance diffractometer with Cu Kα radiation with a graphite monochromator and a position sensitive detector (Våntec-1) was used to record the XRD patterns in Bragg–Brentano geometry. The UV–Vis spectra of *BEA zeolites dehydrated at 500 °C in a vacuum after interaction with HMB at 200 °C for 1, 2 and 3 h and after subsequent interaction with NH_3 were measured in the range from 20 000 to 45 000 cm^{-1} using a Perkin-Elmer Lambda 950 spectrometer equipped with a Spectralon integration sphere. The solid state ^{27}Al MAS NMR method was used for characterization of the Al species with different coordination in the zeolite. The experiments were performed on a Bruker Avance 500 MHz Wide-Bore spectrometer (11.7 T) equipped with a 4 mm double-resonance MAS NMR probe head. The ^{29}Si MAS NMR single pulse spectra of hydrated zeolites were measured at a rotation speed of 7 kHz, with a π/6 (1.7 μs) excitation pulse and relaxation delay of 30 s for single pulse spectra.

3.3 Hydroisomerization of *n*-hexane

The catalytic activity in hydroisomerization of linear C_6 to the branched isomers was performed in U-shaped glass through-flow reactor with catalyst loading of 0.5 g on a porous glass septum. Before each catalytic experiment, activation of the Pt/H-zeolite was performed in an oxygen stream at 450 °C for 3 h and then cleaned with pure nitrogen for 15 min. After calcination, the temperature was lowered to 250 °C and the catalyst was reduced in a mixture of 80 mol % H_2 + 20 mol % N_2 at 250 °C for 1 h. Then 1 mol % of *n*-hexane was fed into this mixture using a glass saturator kept at the selected temperature. The total gas flow was thus set at 66 $cm^3.min^{-1}$, and this corresponded to GHSV 5 000 and WSHV 0.25 h^{-1}. The reactor temperature was kept in the desired range of 125 – 325 °C, controlled by an inserted K-thermocouple. The final product containing: n-C_6, iso-C_6 and low molecular products (i.e.: C_1, C_2, C_3, C_4 and iso-C_4, C_5 and iso-C_5) was analysed by an on-line connected GC (Finnigan 9001), furnished with a capillary column (Al_2O_3/KCl) and TCD detector. A steady-state regime was typically attained during approx. 0.5 - 1 h of time-on-stream.

4 RESULTS AND DISCUSSION

4.1 Enhancement of accessibility of acid sites in micromesoporous zeolites

This chapter describes the methods for effective formation of secondary mesoporosity through postsynthesis alkaline, alkaline-acid, acid-alkaline-acid and fluorination-alkaline leaching procedures of conventional mordenite zeolites. These syntheses attempted to enhance the accessibility of the active sites by introducing secondary mesoporosity into mordenite zeolites coupled while attempting to preserve a large number of acid sites. In contrast to dealumination, controlled alkaline-based treatments of the mordenite framework lead to better preservation of the concentration of Brønsted sites and formation of well-developed secondary mesoporosity.

Selective dissolution of silicon-rich areas of the framework and the extraction of aluminum are inherent parts of the acid and alkali treatments of zeolites, respectively. Results of this study [36] clearly show that, for the formation of micromesoporous mordenite with Brønsted active sites readily accessible in non-restricted micropores, it is necessary to extract both silicon and aluminum atoms in a controlled way ensuring the formation of mesopores and preservation of micropores and the majority of the framework Al. Particularly for desilication of mordenites with a high concentration of aluminum in the framework (Si/Al ~ 12), the extraframework tetrahedrally coordinated $AlO_x/(OH)_y$ species, formed by hydrolysis and dislodgment of a small fraction of framework Al, block a significant part of the pseudo-monodimensional 12-ring channels and/or accessibility of the acid sites in 8-ring side pockets.

Desilication of mordenite surprisingly does not lead to greater accessibility of the acid sites; to the contrary, a significant part of the micropores is diffusion-limited even for nitrogen molecules. However, subsequent acid leaching under specific conditions, characterized by a low concentration of oxalic or nitric acid, leads to efficient removal of the extra-framework and/or perturbed framework Al species formed in mesopores after desilication and blocking part of the micropores. The concentration of the Brønsted sites determined by d_3-acetonitrile and their accessibility for *n*-hexane as a relevant molecular probe for the hydroisomerization reaction indicate that the prevailing amount of the framework Al atoms is not dislodged during either the dissolution of silicon-rich areas of the framework or the selective extraction of the extraframework Al. Thus the alkaline removal of parts of the Si-rich framework and subsequent selective acid leaching of extraframework Al and only small amount of framework Al resulted in a micro-mesoporous mordenite structure with high concentration of

strongly acidic Brønsted sites readily accessible in both 12-ring and 8-ring channels. The desilication with subsequent removal of only extraframework Al creates a number of new channel openings in mesopores effectively shortening of the main 12-ring channels. However, the dealumination of a small fraction of the framework Al atoms is indispensable for significant enhancement of the accessibility of the OH groups in 8-ring side pockets. It should be also mentioned that the increase in the concentration of Lewis centres and an intense signal of internal Si-OH groups suggests that the massive changes in the texture of the zeolite towards a well-developed mesoporous structure leads to the disruption of part of the regularly arranged atoms originally present in the low-defective zeolitic structure.

The alkaline leaching of mordenite pre-impregnated with a solution of NH_4F appeared to be the most efficient approach for creating the secondary mesoporous structure in mordenite zeolite with a high concentration of readily accessible Brønsted sites. This procedure enabled controlled extraction of Si atoms and concomitantly the framework F-bearing tetrahedral Al species. The dissolution of tetrahedrally coordinated $Al(FO_3)$ and SiO_4 entities during alkaline treatment resulted in secondary mesoporosity and opened non-restricted channel openings of the preserved microporous structure with high concentration of Brønsted sites readily accessible for *n*-hexane. A difference was observed in the modes of formation and types of mesoporous structures obtained by desilication-acid treatment and desilication of fluorinated mordenite. With desilication-acid treatment, circular mesopores 5-20 nm in size were predominant while desilication of fluorinated mordenite yielded small mesopores combined with mesopores formed along crystal boundaries and intergrowths.

4.2 Enhancement of accessibility of acid sites in supermicroporous zeolite

In continuity with the previous study [36], we applied the fluorination method on MOR zeolite containing a high concentration of aluminium and corresponding concentration of acid sites readily accessible for the *n*-hexane molecules. For this purpose, structure of mordenite zeolite with a high content of lattice aluminium (Si/Al 5.8) was modified by postsynthesis concurrent extraction of Si and Al atoms from the framework using fluorination-alkaline-acid treatments in several series I-IV (Figure 2).

Fluorination-alkaline treatment with concentrations of 0.36 M NH_4F in the Ist series and 0.5 M NH4F in the IInd series resulted in slight increase in the micropore volume mainly by an increase in the number of micropores with dimensions of about 0.7 nm. This enhancement could be ascribed to enlargement of the narrow openings of the 8-ring channels. It is also

reflected in an increase in the accessibility of the OH groups in the 8-ring channels for the n-hexane molecule in the originally inaccessible pores. The significant increase in the micropore volume, the increase in the size of some micropores and only minor formation of mesopores observed for the samples in series I and II prepared from Al-rich MOR (Si/Al ~ 5.8) show that the high concentration of Si-O-Al in the framework increases the resistance to alkaline treatment, as also reported for ZSM-5 [29]. The degree of susceptibility of the parent MOR/5.8 zeolite towards alkaline leaching after fluorination results in controlled concurrent extraction of both Al and Si atoms, leading to desirable development of microporosity without excessive formation of mesopores.

The fluorination-alkaline treatment with a concentration of 1M NH4F (series III) resulted in a decrease in the micropore volume compared to the parent zeolite, but the subsequent mild acid leaching increased the micropore volume. Previous studies showed that hydrolysis of framework Al at harshened conditions of desilication lead to formation of extraframework Al species which can easily block the openings the pseudo-monodimensional channel structure of MOR [33, 39]. A slight increase in the molar Si/Al ratio and the significant increase in the micropore volume after the mild acid leaching indicate that the extraframework Al blocking part of the micropores was removed. The size distribution of micropores shows a further increase in their dimensions associated with supermicroporosity and 3D interconnection of the monodimensional mordenite channels [23, 36, 40-42].

The harshest fluorination treatment by 4 M NH_4F in the IVth series has led to partial destruction of crystalline structure displayed by a significant decrease in XRD intensity.

The V. series was prepared by acid treatment of MOR/5.8 providing mildly dealuminated deAl-MOR/6.6. However, a small microporous volume and a low accessibility of the OH groups for n-hexane in the mildly dealuminated deAl-MOR/6.6 sample indicate that the desirable changes in the channel structure require a removal of larger proportions of Al from the framework.The 27Al MAS NMR analysis and the adsorption measurements clearly showed that the acid treatment does not extract all the atoms removed from the framework and various extra-framework species partially block the pores. In contrast, the fluorination-alkaline-acid treatment (series I – III) provides much larger increase in the volume in supermicropores when a similar amount of Al is extracted from the zeolites.

The principle of the fluorination-alkaline-acid treatment is similar to the coupling of dealumination with desilication employed for flexible tailoring of the concentration of aluminum related acid sites in micromesoporous zeolites [33, 36, 43-44]. The uniqueness of the fluorination-alkaline-acid procedure lies in the effective formation of 3D connected

supermicroporous channels enhancing the accessibility of the acid sites without the formation of a significant proportion of the secondary mesoporosity. The combination of the supermesoporosity and the occurrence of highly active acidic sites dramatically increases the activity of mordenite zeolites in the hydroisomerization of *n*-hexane to the branched isomers. The high activity shifts the window of operating temperatures to the thermodynamically more suitable area for the formation of di-branched isomers [37].

4.3 Enhancement of concentration of acid sites in microporous zeolite

In pursuing the present work on the isomerization of linear alkanes over zeolites [36-37], we wanted to specify the role of an increase in the density of the strongly acidic protons countering the negative charge of the framework in the H-forms of zeolites in relation to the occurrence of Al-Si-Al sequences, inevitably formed at high concentration of Al in the zeolite framework. We wanted to determine the effect of variations in the distribution of aluminum providing charge balance for the corresponding high concentration protons located in the close vicinity on the reaction rate and selectivity. We therefore employed zeolite *BEA topology, which can be prepared in a broad range of Al concentrations and which offers fast intra-crystalline diffusion of reactants and products through channels with three-dimensional architecture and 12-MR openings. We exploited recent progress in the synthesis of the beta zeolite that opened a new potential to manipulate the framework aluminum content in a very broad range and employed Al-rich beta zeolites with very high concentration of aluminum (Si/Al $\geq$ 4) with highly predominant tetrahedrally coordinated Al in the framework [45-57]. This approach enabled us to examine the extent to which the isomerization reaction is affected by close proximity of strongly acidic centers. We found that the high density of non-interacting strongly acidic sites facilitates extraordinarily high reaction rates due to a synergetic effect significantly decreasing the activation barrier of the reaction. This enabled more rational design of isomerization zeolite catalysts providing superior activity.

It is well established that mordenite zeolites with strongly acidic bridging Si-OH-Al sites are the most active and selective among all the types of investigated zeolitic hydroisomerization catalysts [4, 18, 23, 40-41]. However, considerably lower activity of mordenite zeolites compared to chlorinated alumina necessitates isomerization at higher temperatures leading to unfavorable thermodynamic equilibrium for branched isomers. An essential solution of the problem lies in significant enhancement of the isomerization activity that enables reaching high conversions at lower temperatures in a favorable area of the

thermodynamic equilibrium. The remarkable increase in the yield of branched isomers and an increase in the selectivity for the desired products limiting cracking reactions over Al-rich Pt/H-*BEA enables a shift of the operation window to lower temperatures. To analyze the potential of the Al-rich *BEA zeolite as an environmentally sustainable low/medium temperature hydroisomerization catalyst, the activity, selectivity and durability of Al-rich Pt/H-*BEA were compared with state-of-the-art microporous and micromesoporous mordenite zeolites [36] under model reaction conditions and also the relevant conditions of the hydroisomerization process, i.e. at elevated pressure and at high concentrations of n-hexane in the reaction stream. The yield of branched isomers was approximately 7 times higher (at 175 °C) over Al-rich *BEA than over MOR, while the yield of C_1-C_5 by-products was comparable or lower to that over mordenite catalysts. The performance of the mordenite catalysts was comparable to Si-rich *BEA catalysts.

A threefold increase in the concentration of the active sites and the synergetic effect clearly resulted in the desired increase in activity and selectivity. The Al-rich Pt/H-*BEA/A/4.2 gives an isomer yield of 51.1% at a temperature of 200 °C, whereas the Si-rich Pt/H-zeolites lead to isomers yields from 10.1 to 12.1% at the same temperature. Stable values of the yields of isomers ~77% and by-products ~1.2% as a function of time-on-stream were obtained at 215 °C for 72 h that indicates stability of the Al-rich Pt/H-*BEA. It is clear that the unique density and distribution of the strongly acidic sites are ultimately connected with catalytic performance highly exceeding that of state-of-the-art Si-rich zeolite catalysts. There is no evidence in the scientific literature that the strength of the acidity of the Al-rich H-*BEA zeolite is significantly weakened due to its high aluminum content, at least with respect to acid-catalysed transformations of hydrocarbons. On the contrary, acid-catalysed reactions requiring strongly acidic centers like alkylation and hydroamination of aromatics [56, 58], and cracking and hydrocracking of aromatics and alkanes [50, 52, 56] are substantially improved over Al-rich H-*BEA exceeding significantly the Si-rich H-*BEA zeolites. Thus, the Al-rich H-*BEA provides the unique concentration of strongly acidic sites in the three-dimensional channel system with 12-MR openings. Such density of the acid sites is not available in zeolites with the three-dimensional channel system with 10-MR openings, e.g. ZSM-5 structural topology, due to the absence of a synthesis procedure for the preparation of zeolite with molar Si/Al ratio <10. Al-rich H-*BEA is also advantageous to USY zeolites, wherein the protonic sites are mutually affected due to the presence of Al-Si-Al sequences in the framework and exhibit much lower acid strengths [59]. The three-dimensional channel system with 12-MR openings of Al-rich H-*BEA is also a significant advantage over traditional

mordenite based isomerization catalysts where the pseudo-monodimensional channel structure and the restricted accessibility of acid sites located in 8-MR channels limit the efficiency of the catalytic process by mass transfer effects [23].

4.4 Effect of shape selectivity in hierarchical zeolites

This study was performed to analyse the shape selectivity of zeolites with well-developed mesoporous surface in hydroisomerization of *n*-hexane as a representative acid-catalysed transformation of hydrocarbons. The objective of this study was not a detailed analysis of the specific activity and structure of the active acid sites on a molecular level in micromesoporous zeolites, or an analysis and understanding of mechanism and entropy and enthalpy changes during a catalytic reaction, but rather to evaluate the effect of a micromesoporous structure obtained by common methods on the shape selectivity. The initial intuition was that the shape selectivity of zeolites, depending on how reactant/transient state/product fit the spatially defined local reaction environments, will be altered by the non-shape-selective reactions on the surface of mesopores with an open reaction environment lacking the molecular confinement. However, a careful analysis of the relationships between the variation in the microporous/mesoporous zeolitic structures and the distribution of the individual reaction products has taught us that the shape selectivity of zeolites is predominantly controlled by acid sites in the microporous channels with steric constraints and tight confines of reactant molecules regardless of the presence of a well-developed secondary mesoporous structure.

In this work, the microporous and micromesoporous zeolites of ZSM-5 and MOR structures and microporous *BEA and USY zeolites was prepared for analysis of the effect of the secondary mesoporous structure on the shape selectivity (Table 2 and Table 3). Microporous parent zeolites (Table 1) were used to reflect the effects of zeolite structure on the catalytic properties enabling comparison of the shape selectivity for various dimensions of the channel systems and differing in the secondary mesoporosity. Three ZSM-5 zeolites with a similar molar Si/Al ratio of about 23 (Table 3) but largely differing in the crystal size from 50 to 5000 nm were used to analyse the possible effects of textural parameters on the structure of prepared micromesoporous analogues and to analyse the effect of the external surface of microporous zeolites. The secondary mesoporosity was introduced into the ZSM-5 (Table 3 and **Chyba! Nenalezen zdroj odkazů.**) and mordenite zeolites (Table 2 and **Chyba! Nenalezen zdroj odkazů.**) by desilication and dealumination methods using post-synthesis

alkaline, alkaline-acid [36, 39], acid-alkaline-acid [36, 39], and fluorination-alkaline [35] leaching to obtain zeolites with a wide range of mesoporous volume and various mesopore sizes [38].

The high yields of di-branched isomers over *BEA and faujasite (Figure 44A) show that a small increase in the size of channels from 10-ring to 12-ring openings mitigates the shape selectivity effects and the mono- and di-branched isomers can be formed. The yield of di-branched isomers is about ten times higher for *BEA and faujasite than for ZSM-5 and increases with the total yield.

It is obvious that the distribution of isomers is completely unaffected by the presence or absence of the secondary mesoporous structure. The reaction of hydroisomerization of *n*-hexane over both microporous and micromesoporous ZSM-5 is highly selective in the mono-branched isomers. The shape selectivity of all the micromesoporous ZSM-5 samples is thus fully preserved without the formation of an increased amount of the di-branched hexanes at the expense of mono-branched hexanes. Comparison of the obtained yields of di-branched hexanes for microporous and micromesoporous mordenites also does not exhibit any clear differences. Thus the transformation of *n*-hexane into the mono- and di-branched isomers depends on how the hydrocarbon molecules fit the zeolitic channel in the microporous part of the micromesoporous structure irrespective of the presence of a large surface area of the mesopores, in principal forming an extension of the external surface of the zeolitic crystal. To rule out the explanation that the acidic centres on the mesoporous surface differ from the acid centres on a regular external surface of microporous zeolites due to the preparation process, we also analysed the hydroisomerization of *n*-hexane over a series of microporous ZSM-5 fundamentally differing in crystal size (from 50 nm to 5 000 nm), yielding very different external surface areas. The identical yields of the mono- and di-branched isomers obtained on all the catalysts clearly show that the acid sites on the external surface do not contribute to the overall isomerization reaction. The formation of individual isomers is thus exclusively controlled by the reactions in the shape-selective environment in the inert voids of the microporous channels [38]. Based on comparison of contributions of the interaction of *n*-C_6 molecules with Brønsted acid sites and the van der Waals interactions between *n*-C_6 molecules and the inert walls,it is obvious that the interaction of the hydrocarbon molecule in the confined reaction space with the inner walls of the zeolite channels is an important factor controlling the apparent activation energy of isomerization and the corresponding reaction rate, while the presence of strongly acidic active sites is a necessary condition for the occurrence of the reaction. The concurrent interaction of the reactant molecule with the acid

sites and the lateral interaction with the walls of the zeolite channels are thus responsible for the isomerization reaction.

4.5 Effect of Pt on hydroisomerization of *n*-hexane

The mechanism of the hydroisomerization of *n*-hexane over Pt/H-zeolites (**Chyba! Nenalezen zdroj odkazů.**) consists of dehydrogenation of *n*-hexane to *n*-hexene on metallic platinum, skeletal isomerization of the formed *n*-hexene into *iso*-hexene via a cyclopropyl intermediate on a Brønsted acid site and re-hydrogenation of the *iso*-hexene to *iso*-hexane [2-7]. The dehydrogenation and hydrogenation reactions are performed in the presence of a sufficient amount of well-dispersed metallic platinum in thermodynamic equilibrium and the acid-catalysed reaction steps control the isomerization [5, 60-61]. We showed in our studies on hydroisomerization of *n*-hexane over microporous Pt/*BEA and Pt/H-USY [39] and micromesoporous Pt/H-MOR [36, 39] and Pt/H-ZSM-5 [38] zeolites that the dehydrogenation-hydrogenation reactions at a metal loading ~ 1.5 wt. % Pt under the employed reaction conditions (high H_2/*n*-hexane ratio) do not limit the overall alkane hydroisomerization. This is consistent with Ribeiro et al. [61] and Van de Runstraat [60], who demonstrated that the hydrogenation-dehydrogenation reactions are much faster than the skeletal isomerization on acid centres over a variety of Pt/H-zeolites metal loading of ~ 1.5 wt. % Pt. Platinum was introduced into all the zeolitic samples (Table 2 and Table 3) by a standard procedure and its dispersion and the metallic form were confirmed using HR-TEM and a CO sorption followed by FTIR spectroscopy (**Chyba! Nenalezen zdroj odkazů.**). The incorporation of mesoporosity can lead to the alteration in the proximity between metallic sites (sites for dehydrogenation-hydrogenation) and acid sites (sites for isomerization). The effect of the "distance" between these two types of active sites and its influence on this sequential reaction was recently assessed for Pt/H-mordenite zeolites in our recent studies [36-37, 39]. The effect of nanoscale proximity was recently analysed in detail by Zecevic et al. [62]. The yields of the individual isomers were practically identical for mordenite zeolites with both close and distant Pt^0 and H^+ centres [39]. That the hydrogenation-dehydrogenation function of the platinum clusters present in the mm-deAl-MOR/A/9.5 and deAl-mm-deAl-MOR/A/13 does not limit the acid-catalysed isomerization was demonstrated in our previous study [36]. The sufficient concentration of functional clusters of metallic platinum available in the bifunctional Pt/H-zeolites thus enables analysis of the essential features of the isomerization reaction catalysed by the Brønsted acid sites.

5 CONCLUSION

Doctoral thesis was devoted to the study of hydroisomerization reaction of *n*-hexane which is one of the most important catalytic reactions for production of automotive fuels. The hydroisomerization of linear C_6 alkanes into the branched isomers with suficiently high octane number, was analysed over hierarchical micromesoporous zeolites, supermicroporous zeolites and microporous zeolites with various densities of active sites. The zeolites were prepared by hydrothermal synthesis and post-synthesis methods using combinations of desilication, dealumination or fluorination.

The critical function of the micromesoporous structure and the concentration and accessibility of Brønsted sites for hydroisomerization of linear hexane was elucidated by using three series of micro-mesoporous mordenite zeolites differing in their mesoporosity and concentration and the accessibility of acid sites (Chapter **Chyba! Nenalezen zdroj odkazů.**). The hydroisomerization of *n*-hexane over microporous Pt/H-mordenite is limited by mass transfer effects due to the low accessibility of acid sites in 8-ring channels structure. The introduction of secondary mesoporosity into mordenite using the alkaline-acid, acid-alkaline-acid, and fluorination-alkaline postsynthesis treatments effectively shortens the length of the 12-ring main channels, opens the side 8-ring channel-pockets, provides the high concentration of Brønsted sites and enhances the accessibility of the acid sites for hexane molecules. The shortening of the main 12-ring channels and a larger number of channel openings provide an increase in the selectivity, limits the nonselective subsequent cracking reactions and consequently increases the yield of the desired products at higher temperatures. The micro-mesoporous mordenite structure with the Brønsted sites in the environment of the micropores and accessible through mesopores alleviates the limitations of transport of molecules to/from the active site, resulting in a significant increase in the catalyst efficiency and improvements in the selectivity in skeletal hydroisomerization of *n*-hexane.

It was demonstrated that the simultaneous extraction of Al and Si from the Al-rich MOR framework using fluorination-alkaline-acid treatment leads to high micropore volume, enlargement of the micropores and interconnection of the channels (Chapter 4.2). The re-organization of the mono-dimensional channel system of the MOR zeolite into a three-dimensional supermicroporous zeolite structure with connectivity of the pore network providing good accessibility to the acid sites allows the preparation of catalytic materials providing strongly enhanced hydroisomerization properties. These findings highlight the essential role of the 3D supermicroporous structure in the catalytic activity, selectivity of the

transformation of *n*-hexane into the corresponding branched isomers without excessive participation of consecutive cracking reactions, and long-term catalytic stability. In general, the concept provides opportunities for the creation of accessible Brønsted and Lewis active sites in Al-rich zeolites for diffusion-restricted reactions.

The role of the density of the acidic protons for hydroisomeroization of *n*-hexane was elucidated using the H-forms of the beta zeolites with a very high concentration of aluminum (Si/Al $\geq$ 4) with highly predominant tetrahedrally coordinated Al atoms in the framework (Chapter 4.3). Analysis of the relationships between the density and distribution of strongly acidic sites and *n*-hexane isomerization identified a specific arrangement of Brønsted acid sites directing the reaction toward higher reaction rates. A high density of strongly acidic non-interacting close OH groups in the Al-rich H-*BEA zeolite lowers the activation barrier in the isomerization reaction and results in multiplying the reaction rates by a factor of six compared to the hitherto most active Si-rich zeolite catalysts. The arrangement of Brønsted acid sites is unique for the Al-rich H-*BEA zeolite and is given by the arrangement of Al atoms in the Al-Si-Al sequences charge-balanced by two H^+ ions located in different zeolite channels. In conclusion, the achievement of the high concentration of non-interacting acidic protons in the zeolite catalyst allowed a significant increase in the isomerization activity and a shift of the operation temperature window into the thermodynamically more favourable region for desired di-branched isomers.

Hydroisomerization of *n*-hexane is very sensitive to changes in the spatial arrangement of the reaction environment and accurately detects the degree of the shape selectivity of zeolites. The formation of di-branched hexane isomers is hindered in ZSM-5 as their molecular dimensions exceed the internal voids of the 10-ring channels imposing strong the product shape selectivity. An increase in the size of the channels from 10-ring to 12-ring openings mitigates the shape-selectivity effects and the mono- and di-branched isomers can be formed with high yields over *BEA and faujasite. The analysis of the hydroisomerization over a series of micromesoporous ZSM-5 zeolites showed selective formation of the mono-branched isomers regardless of the presence or absence of the mesoporous structure. The spatial confinement of reactants in the internal voids of the zeolitic channel is essential for the course of the isomerization reaction and the external surface (or mesoporous surface) does not contribute significantly to the catalytic reaction. Thus, the product-shape selectivity of micromesoporous zeolites is virtually unaffected and the advantages of the presence of the secondary mesoporous structure can be fully exploited for tailoring of functionality in the catalytic proces (Chapter 4.4).

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PUBLISHING ACTIVITIES

- Skowerski, K.; Pastva, J.; Czarnocki, S. J.; Janoscova, J. *Org. Process Res. Dev.* **2015**, *19* (7), 872–877.

- Petr Sazama, Dalibor Kaucky, Jaroslava Moravkova, Radim Pilar, Petr Klein, Jana Pastvova, Edyta Tabor, Stepan Sklenak, Ivo Jakubec, Lukasz Mokrzycki; *Applied Catalysis A*: *General*, **2017,** 533, 28–37.

- Jana Pastvova, Dalibor Kaucky, Jaroslava Moravkova, Jiri Rathousky, Stepan Sklenak, Maryna Vorokhta, Libor Brabec, Radim Pilar, Ivo Jakubec, Edyta Tabor, Petr Klein, Petr Sazama; *ACS Catal.*, **2017**, 7, 5781–5795.

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- Petr Sazama, Jana Pastvova, Cristina Rizescu, Alina Tirsoaga, Vasile I. Parvulescu, Hermenegildo Garcia, Libor Kobera, Jürgen Seidel, Jiri Rathousky, Petr Klein, Ivan Jirka, Jaroslava Moravkova, Vaclav Blechta; *ACS Catal.*, **2018**, 8, 1779−1789.

CONFERENCE ABROAD

- ZMPC 2015 (International Symposium on Zeolite and Microporous Crystals); 28.6 - 2. 7. 2015; Sapporo, convention center, Japan; Preparation of 3D porous nanocarbon materials using USY zeolite as a hard template; autoři: **Jana Janoščová**, Petr Sazama, Jiří Rathouský, Libor Brabec, Galina Sádovská

- CIS6 (6th Czech-Italian-Spanish Conference on Molecular Sieves and Catalysis); 14. – 17. 6. 2015; Amantea, Itálie; Micro-mesoporous zeolites with tailored structure and distribution of active sites for hydroisomerization of linear C_5-C_6 alkanes; autoři: **Jana Janoscova**, Dalibor Kaucky, Edyta Tabor, Alena Vondrova, Jiri Rathousky, Petr Klein, Petr Sazama

- CIS6 (6th Czech-Italian-Spanish Conference on Molecular Sieves and Catalysis); 14. – 17. 6. 2015; Amantea, Itálie; Experimental overview of catalysts for HT-DEN_2O; autoři: G. Sadovská, P. Sazama, Z. Sobalík, E. Tabor, A. Vondrová, M. Bernauer, **J. Janoščová**

- CIS6 (6th Czech-Italian-Spanish Conference on Molecular Sieves and Catalysis); 14. – 17. 6. 2015; Amantea, Itálie; Modeling of high temperature DEN_2O laboratory scale reactor; autoři: M. Bernauer, G. Sádovská, P. Sazama, Z. Sobalík, E. Tabor, A. Vondrová**, J. Janoščová**, B. Bernauer

- CIS6 (6th Czech-Italian-Spanish Conference on Molecular Sieves and Catalysis);

14. – 17. 6. 2015; Amantea, Itálie; Enhancement of density of active sites and reaction rates for acid and redox catalysed reactions over zeolite catalysts; autoři: P. Sazama, **J. Janoščová**, L. Mokrzycki, V I. Parvulescu, E. Tabor, A. Vondrová, D. Kaucký, P. Klein

- ZMPC 2015 (International Symposium on Zeolite and Microporous Crystals); 28.6 - 2. 7. 2015; Sapporo, convention center, Japan; Unprecedented Acid and Redox Activity of Template-free Al-rich BEA Zeolite; autoři: Petr Sazama, Lukasz Mokrzycki, Blanka Wichterlová, Galina Sadovská, Vasile I. Parvulescu, Jiří Dědeček, **Jana Janoščová**, Petr Klein

- AMMM 6th Symposium (6th International Symposium on Advanced Micro and Mesoporous Materials); 6. - 9. 9. 2015; Burgas, Bulharsko; Hydroisomerization of Hexane over Micro-mesoporous Zeolites with Tailored structure and Distribution of Active Sites; autoři: Dalibor Kaucký**, Jana Janoščová**, Edyta Tabor, Jiří Rathouský, Petr Klein, Petr Sazama

- 18th IZC (International Zeolite Conference); 19. - 24. 6. 2016, Rio de Janeiro, Brazílie
  Název: Preparation of hierarchical mordenite zeolites with tailored texture and accessibility of acid sites
  Autoři: **Jana Pastvová**, Jaroslava Morávková, Dalibor Kaucký, Jiří Rathouský, Ivo Jakubec, Petr Sazama

- 18th IZC (International Zeolite Conference); 19. - 24. 6. 2016, Rio de Janeiro, Brazílie
  Název posteru: Hydroisomerization of n-hexane over micro-mesoporous zeolites
  Autoři: Dalibor Kaucký, Jaroslava Morávková, **Jana Pastvová (Janoščová),** Petr Klein, Edyta Tabor, Petr Sazama

- 18th IZC (International Zeolite Conference); 19. - 24. 6. 2016, Rio de Janeiro, Brazílie
  Název přednášky: Dramatic improvement of n-hexane hydroisomerization over zeolites with mutual close vicinity and high accessibility of strongly acidic centers
  Autoři: Jaroslava Morávková, Dalibor Kaucký, **Jana Pastvová**, Alena Vondrová, Edyta Tabor, Radim Pilař, Petr Sazama

- 13th European Congress on Catalysis (EUROPACAT 2017); 27. – 31. 8. 2017, Florencie, Itálie
  Název přednášky: Synthesis and structural analysis of micro-mesoporous mordenite with tailored structure and accessibility of active sites
  Autoři: **Jana Pastvová**, Dalibor Kaucký, Jaroslava Morávková, Jiří Rathouský, Ivo Jakubec, Petr Klein, Libor Brabec, Petr Sazama

- 13th European Congress on Catalysis (EUROPACAT 2017); 27. – 31. 8. 2017, Florencie, Itálie
  Název přednášky: Enhancement of hydroisomerization activity by high density of well-accessible acid sites in zeolites
  Autoři: Jaroslava Morávková, Dalibor Kaucký, **Jana Pastvová**, Edyta Tabor, Radim Pilař, Jiří Rathouský, Petr Klein, Ivo Jakubec, Petr Sazama

- 13th European Congress on Catalysis (EUROPACAT 2017); 27. – 31. 8. 2017, Florencie, Itálie

Název přednášky: Hydro-isomerization of n-hexane over fluoridation-route prepared hierarchical micro-mesoporous zeolites
Autoři: Dalibor Kaucký, **Jana Pastvová (Janoščová),** Petr Klein, Jaroslava Morávková, Jiří Rathouský, Edyta Tabor, Petr Sazama

- 10th International Conference on Environmental Catalysis & the 3rd International Symposium on Catalytic Science and Technology in Sustainable Energy and Environment; 22. – 26. 9. 2018, Tianjin China
  Název: Superior activity of Al-rich Pt/H-*BEA zeolites in hydroisomerization of *n*-hexane
  Autoři: Jaroslava Moravkova, Radim Pilar, Dalibor Kaucky, **Jana Pastvova**, Petr Sazama

- 8th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT8) and International Symposium on Zeolites and Microporous Crystals; 5. - 10. 8. 2018, Yokohama, Japan
  Název: Enhanced functionality of Al-rich zeolite beta catalysts in industrially relevant acid- and redox-catalysed reactions
  Autoři: Petr Sazama, Radim Pilar, Vasile Parvulescu, Galina Sadovska, Jaroslava Moravkova, Dalibor Kaucky, **Jana Pastvova**, Stepan Sklenak, Alena Vondrova

- 8th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT8) and International Symposium on Zeolites and Microporous Crystals; 5. - 10. 8. 2018, Yokohama, Japan
  Název: Controlled synthesis of the Al-rich zeolites of *BEA structure
  Autoři: Radim Pilar, Galina Sadovska, Dalibor Kaucky, **Jana Pastvova**, Petr Sazama

HOME CONFERENCE

- 12th Pannonian Symposium on Catalysis; 16. – 20. 9. 2014; zámek Třešť, ČR; Synthesis of 3D porous nanocarbon with defined structure; **Jana Janoščová**, Petr Sazama, Jiří Rathouský, Alena Vondrová, Petr Klein, Dalibor Kaucký

- 12th Pannonian Symposium on Catalysis; 16. – 20. 9. 2014; zámek Třešť, ČR; Enhancement of activity and selectivity in acid-catalyzed reactions by dealuminated hierarchical zeolites; autoři: Petr Sazama, Zdenek Sobalík, Petr Klein, Dalibor Kaucký, Milan Bernauer, Ivo Jakubec, Vasile Parvulescu, **Jana Janoščová**, Jiří Rathouský, Alena Vondrová

- Seminář studentů ÚFCH JH 2015; 4. – 6. 5. 2015; KC AV ČR Liblice; Synthesis of micro-mesoporous materials with defined structure; autoři: **J. Janoščová**;

- 47th Symposium on Catalysis; 2. – 4. 11. 2015, ÚFCH JH AV ČR, Praha
  Název přednášky: Hydroisomerization of hexane over micro-mesoporous MOR and ZSM-5 zeolites
  Autoři: Dalibor Kaucký, **Jana Pastvová (Janoščová),** Jiří Rathouský, Jaroslava Morávková, Petr Klein, Petr Sazama

- Seminář studentů ÚFCH JH 2016; 10. – 11. 5. 2016; KC AV ČR Liblice; Preparation of hierarchical mordenite zeolites; autoři: **Jana Pastvová**

- 48th Symposium on Catalysis; 7. – 9. 11. 2016, ÚFCH JH AV ČR, Praha
  Název přednášky: Synthesis of hierarchical mordenite by postsynthesis modification using flourination
  Autoři: **Jana Pastvová**, Dalibor Kaucký, Jaroslava Morávková, Jiří Rathouský, Petr Klein, Petr Sazama

- 48th Symposium on Catalysis; 7. – 9. 11. 2016, ÚFCH JH AV ČR, Praha
  Název přednášky: Enhanced hydroisomerization activity of non-interacting close acidic protons in Al-rich Pt/H-*BEA zeolite
  Autoři: Jaroslava Morávková, Dalibor Kaucký, Radim Pilař, Štěpán Sklenák, **Jana Pastvová**, Barbara Supronowicz, Lukasz Mokrzycki, Petr Klein, Edyta Tabor, Petr Sazama

- 49th Symposium on Catalysis; 6. – 7. 11. 2017, ÚFCH JH AV ČR, Praha
  Název přednášky: Micromesoporous mordenites with tailored structure and accessibility of active sites
  autoři: **Jana Pastvová**, Jaroslava Morávková, Dalibor Kaucký, Jiří Rathouský, Ivo Jakubec, Petr Klein, Libor Brabec, Petr Sazama

- 49th Symposium on Catalysis; 6. – 7. 11. 2017, ÚFCH JH AV ČR, Praha
  Název přednášky: Hydroisomerization activity of hierarchical micromesoporous zeolites obtained by fluoridation-route
  autoři: Dalibor Kaucký, **Jana Pastvová**, Jaroslava Morávková, Edyta Tabor, Petr Sazama

- 49th Symposium on Catalysis; 6. – 7. 11. 2017, ÚFCH JH AV ČR, Praha
  Název přednášky: Hydroisomerization activity enhancement via high density of well-accessible acid sites in zeolites
  autoři: Jaroslava Morávková, Dalibor Kaucký, **Jana Pastvová**, Edyta Tabor, Radim Pilař, Jiří Rathouský, Petr Klein, Ivo Jakubec, Petr Sazama