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Synthesis of macro- and mesoporous supports prepared by alkali-activation of aluminosilicate components and their post-synthesis modification

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Abstract

The dissertation thesis deals with the synthesis, detailed characterization and subsequent testing of new materials based on zeolite foams prepared by alkali-activation of natural zeolites, and the possibilities of these materials for using in the chemical industry, especially as catalysts, catalyst supports or adsorbents. The basic feedstock (natural zeolite), where the main component is the clinoptilolite zeolite, is almost exclusively mesoporous material with a small specific surface area and with a small pore volume. For this reason, its use is mainly limited to wastewater and gas treatment applications. Alkali activation of this easy and affordable aluminosilicate component by using mixed activators based on potassium hydroxide and sodium silicate and subsequent foaming by aluminium or hydrogen peroxide produces the macroporous material - solid inorganic foam. The properties of this foam can be modified by post-synthesis modifications to allow the materials to be used in other than the building industry where are the alkali-activated materials commonly used. These materials also meet the requirements for ecological and economic materials.

Abstrakt

Dizertační práce se zabývá syntézou, podrobnou charakterizací a následným testováním nových materiálů na bázi zeolitových pěn, připravených alkalickou aktivací přírodních zeolitů, a možností využití těchto materiálů v chemickém průmyslu, zejména jako katalyzátorů, katalyzátorových nosičů nebo adsorbentů. Základní vstupní surovinou, kterou je přírodní zeolit, jehož hlavní složkou je zeolit klinoptilolit, je téměř výlučně mezoporézní materiál s malým měrným povrchem a malým objemem pórů. Jeho využití je z tohoto důvodu omezeno především na aplikace v oblasti čištění odpadních vod a plynů. Alkalickou aktivací této, snadno a cenově dostupné, aluminosilikátové složky, pomocí směsného aktivátoru na bázi hydroxidu draselného a křemičitanu sodného, a následným napěněním této směsi, např. pomocí hliníku nebo peroxidu vodíku, vzniká makroporézní materiál - tuhá anorganická pěna, jejíž vlastnosti lze modifikacemi upravit tak, aby bylo možné materiály využít i v jiném než stavebním průmyslu nebo průmyslu žáro-izolací, pro které jsou alkalicky aktivované materiály běžně používány. Tyto materiály zároveň splňují i požadavky na ekologické a ekonomické materiály.

Keywords:

natural zeolite, clinoptilolite, alkali-activation, inorganic foam, acid leaching, catalyst

Klíčová slova:

přírodní zeolit, klinoptilolit, alkalická aktivace, anorganická pěna, kyselé loužení, katalyzátor

CONTENT

LIST OF SYMBOLS AND ABBREVIATIONS

C-S-H	Binder matrix $CaO\text{-}SiO_2\text{-}H_2O$
D1	0,1M HCl leached sample (80 °C/6 h)
D2	3M HCl leached sample (80 °C/6 h)
EDX	Energy-dispersive X-ray spectroscopy
HDO	Hydrodeoxygenation
DIE	Direct Ion Exchange
KLI	Natural zeolite Klinofeed®
MAS-NMR	Magic Angle Spinning - Nuclear Magnetic Resonance
MK	Metakaolin
Ms	Silicate modulus
Na(K)-A-S-H	Binder matrix $Na_2O(K_2O)\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$
S	Alkali-activated Klinofeed sample
SCR	Selective Catalytic Reduction
SEM	Scanning Electron Microscopy
SimDis	Simulated distillation
TGA	Thermogravimetric analysis
TPD	temperature programmed desorption of CO_2 and NH_3
w	Water coefficient of mixture
XRF	X-ray fluorescence
XRD	X-Ray Diffraction
ZF	Zeolite foam

1 INTRODUCTION

Alkali-activated materials are a group of materials that are mainly used in the construction industry as various types of concrete and thermal and heat-insulating materials. However, their properties predetermine them for much wider use, for example in the chemical industry, such as catalysts, sorbents and catalyst supports.

Alkali-activated materials are not new. Their history goes back to the distant past, when the civilizations of ancient Mesopotamia (today's territory of Iraq) were probably already able to use material prepared by alkali-activation. Prof. Davidovits presented the theory that Egyptian pyramids were built with similar technologies.[1] These materials were forgotten for a long time and were rediscovered in the 20th century when the German chemist and engineer H. Kühl patented materials based on a slag and alkali carbonates and hydroxides/oxides of alkaline earth metals (US 900 939). Later, these materials were intensively studied by A. O. Prudon (1940). [2-4]

In the 1960s V. D. Glukhovsky presented the possibility of preparing a new inorganic binder from natural aluminosilicates (mainly clay minerals) and alkaline compounds (carbonates, hydroxides, silicates) for which he used the designation gruntosilicate, gruntocement, geocement.[5,6] In 1979 prof. J. Davidovits patented, under the name "geopolymers", alkaline cements formed by mixing alkaline solutions with a mixture of calcined kaolinite, limestone and dolomite.[7]

2 ALKALI-ACTIVATED MATERIALS

Alkali-activation is an inorganic polycondensation reaction where dissolved particles of the starting solids react and subsequently condense into larger clusters. The precursors are units of the monomers $Si(OH)_4$ and $[Al(OH)_4]^-$ which condense into di-, tri- until to oligomers, which further polycondensate. Unbridged O atoms are converted by polycondensation to bridged atoms. In the maximum degree of polycondensation, the ratio of the bridging and non-bridging O atoms is stabilized. The structure consists of building units, which are described as poly(sialates), poly(siloxo-sialates) and poly(disiloxo-sialates).[8]

The precise reaction mechanism of alkaline activation is very complex and proceeds through a series of simultaneous reactions (dissolution of the aluminosilicate material in alkaline conditions, the formation of oligomers and formation of a gel phase). These reactions are also highly dependent on the raw materials used (type and structure).[9] The course of the reaction is currently described as a sequence of three parallel events (Fig. 1):

1. Solvation of the surface and dissolution of active ingredients to monomers,

2. Formation of oligomers by condensation or self-condensation,

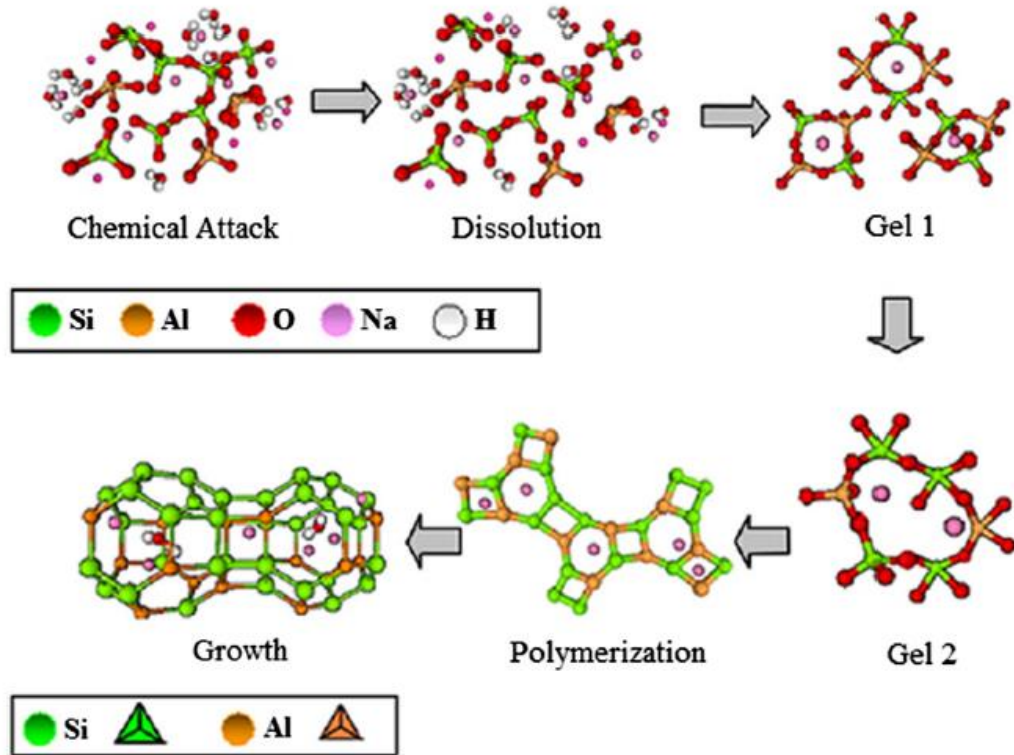3. Polycondensation with gradual networking of the whole system.[7]

Fig.1 The formation of alkali activated phase [10]

The molecular structure of an alkali-activated matrix is sometimes compared to zeolites, but the method of formation is different because zeolites crystallize from hot and dilute solutions.[11] Alkali-activated materials are systems at the interface between conventional hydrated inorganic binders, ceramic and glass materials. The structure comprises Si and Al tetrahedra randomly distributed along polymer chains, which are crosslinked to provide cavities of sufficient size to store hydrated sodium (or potassium and other) charge-compensating ions.[12] In materials based on amorphous aluminosilicates with a low calcium content (such as fly ash or metakaolin), alkali-activation is the main reaction, which leads to the formation of Na(K)-A-S-H gel.[13-15]

Over time, several models of the structure of alkali-activated materials have been proposed. A new structural model was designed by M. R. Rowles based on more detailed measurements using ^{29}Si, ^{27}Al, ^{1}H a ^{23}Na MAS-NMR (Fig. 2c).[16] The measurements showed disordered cavities in contrast to the channel structures observed with zeolites. In the matrix, Al remains predominantly in the coordination 4 (the tetrahedra form). The ^{23}Na MAS-NMR data indicates predominantly hydrated Na^{+} ions. However, some of these cations are not hydrated and form structures where the cation is partially bound to the aluminate (Fig. 2a) or to the bridging oxygen (Fig. 2b). [16,17,18]
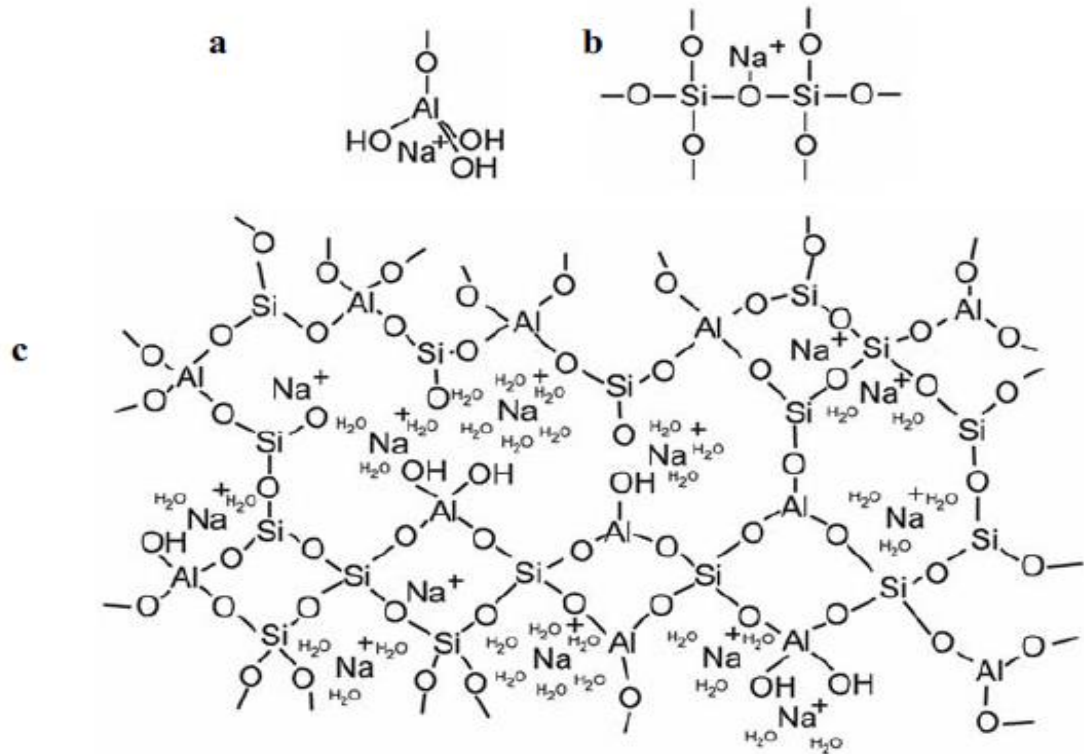
Fig. 2 The aluminate (a), bridge oxygen (b) and overall model by M. R. Rowles (c)[16]

In the synthesis of alkali-activated systems, the ratio of oxides of the starting materials, which is different for the each feed material, is important. While for the alkali activation of clinkers and the slag, it is sufficient to use alkali solutions of carbonates as activators, for the activation of fly ash and metakaolins using of hydroxides is necessary (most often in a mixture with silicates). At the same time, the phases present in the material change. Clinker and slag contain a large proportion of calcium and these materials then contain a larger amount of C-S-H phase. In contrast, activation of metakaolin provides exclusively the N(K)-A-S-H phase.[19]

The initial content of Si, Al and Na (possibly K) controls the transformation of the amorphous and the crystalline phase.[18,20,21] The most important ratios are the Si/Al and Me/Al ratios, where Me = Na or K, leading to high strength and resistent materials. The Si/Al ratio has a great effect on dissolution, hydrolysis, condensation reaction and consequently strength since micro-cracks can occur in the material, which reduces the strength. The optimum ratios are highly dependent on the aluminosilicate feedstock used.[10] The water content is particularly important for the transport of ions and monomers, and for the proper homogenization of the mixture. Excess of water can cause dilution of the reaction mixture or leaching of soluble components from the reaction zone [12] or formation of crystalline zeolites in the structure of materials.[13,22]

The starting material for geopolymer formation is metakaolin, alternatively it is possible to alkali activate a wide range of aluminosilicate materials: slag, fly ash, red bauxite sludge, mine tailings, used

catalysts (zeolites from FCC unit), ash, paper production sludge, waste glass, waste from ceramics and natural minerals e.g. albite, volcanic ashes, tuffs, pozzolans, bentonite, phonolite, illite etc.[13,23,24] When some minerals are used, their original structure is preserved after alkali-activation (zeolite tuffs - natural zeolites, bentonite, phonolite, illite, etc.).[13]

The solid inorganic foams containing macropores are obtained by foaming of the alkali-activated mixture. The presence of larger pores (macro and mesopores) in the structure usually has a beneficial effect on the transport of the reactants but also reduces the weight of the catalytic bed, which is important for column design.

The inorganic foams can be prepared in various ways. The so-called template method is often used [25-28], another possibility for the preparation of foam materials is the use of surfactants as foaming agents [29,30] or metals (Al, Mg, etc.) which produce hydrogen by the reaction in an alkaline medium.[31] It is also possible to use peroxides, releasing oxygen upon decomposition, or silicon/silica fume releasing the hydrogen. The use of these foaming agents (H_2O_2, Si) allows longer handling of the prepared mixture, as these reactions proceed much more slowly than with Al powders.[31-35] The foaming process can be further modified by adding of vegetable oils (rape, sunflower, olive). The reaction of the oil with a strongly alkaline activator leads to the formation of soaps, which in turn contribute to the formation of finely and regularly dispersed bubbles in the matrix of the material.[36,37]

Alkali-activated materials have a wide range of uses depending on the aluminosilicate feedstock used and reaction conditions. These materials are mainly used in the construction industry. The addition of natural zeolite and bentonite to alkali-activated fly ash and slag-based materials improves certain properties such as stability of mixtures and hydration kinetics. Natural zeolite acts as a source of nucleation centres and brings the seeds of future phases of the system and improves the compactness of the materials because fine particles dissolve well.[13,38-40] The use of the microporous texture of these materials is possible in the field of catalysts or catalyst supports, adsorption of substances, molecular sieves, filters and other functional materials. For these applications, alkali-activated materials can be used up to approx. 600 °C before the matrix shrinks significantly. No material changes are observed even at extremely low temperatures, eg liquid nitrogen (-197 °C).[11]

Due to the high affinity for the ammonium ion, alkali-activated zeolites have also been studied in water purification.[41] Geopolymers prepared by alkali-activation of metakaolin have been studied in the selective catalytic reduction of NO_x and NH_3 (SCR process) [42] or alkali-activated hyalite clays were studied in Friedel-Crafts alkylation.[43,44]

8

3 AIMS OF THE THESIS

The main aim of the work was to show new possibilities and directions in the utilization of alkali activated materials, which are currently used primarily in the construction industry, but have a great potential for a use in the chemical industry (heterogeneous catalysts, catalyst supports, filter layers protecting catalytic bed or as adsorbent and filter materials for gases and liquids).

In the first phase, the aim was to optimize the method of preparation and mixtures composition to obtain materials with appropriate textural, chemical and mechanical properties. This phase was followed by the development and optimization of the forming process, which allow the zeolite foams (ZF) to be formed into pellets of different diameters and cross-sections and will be also applicable to industrial production.

The prepared pellets were further modified by post-synthesis processes such as acid leaching, ion exchange or calcination to obtain detailed information on the effect of each process on the texture, chemical and mechanical properties. These post-synthesis modifications lead to obtaining materials suitable for other applications.

The last goal was to prepare real catalysts or adsorbents, to optimize processes and methods of preparation and to verify properties and usability in real catalytic/adsorption applications. Last but not least to detail characterize of all prepared samples of zeolite foams, catalysts/adsorbents using a wide range of analytical methods.

4 ALKALI-ACTIVATED FOAMS

The study of alkali-activated fly ash-based materials was primarily aimed at replacing Portland cement-based concrete with more environmentally friendly materials that do not produce such high CO_2 emissions. In the case of fly ash as an aluminosilicate component, a used material has a very limited secondary utilization and is largely landfilled for the time being. For the time being, the use of geopolymer fly ash concretes encounters some problems that prevent their mass spread (solidification control, efflorescence, etc.), however the first direct applications in the construction industry already exist. Another possible evaluation of these alkali-activated fly ash materials is the production of lighter versions by foaming of the alkali-activated mixture. The obtained materials would find application in the construction industry as a substitute for aerated concrete, but due to very good thermal insulating properties also in the thermal and heat-insulations. Work was carried out using fly ash from the Opatovice brown coal power plant, whose alkali activation with a mixed activator of sodium hydroxide and sodium silicate (Na-water glass) and foaming with an aluminium powder were used for samples synthesis and these materials were used for further mechanical and thermal tests.

The use of aluminium powder has proven advantageous in terms of the macropores distribution in the material, but unfortunately, it has not been advantageous in terms of material preparation itself, since the reaction between the activator and the powdered aluminium is strongly exothermic and very fast.

Another important parameter is the water coefficient of the mixture, which had to be optimized in view of good mixing of the aluminium powder in the alkali-activated mixture, but at the same time, the formed foam had to be stable after foaming to prevent the structure from collapsing. The strength and the thermal conductivity of the prepared foams in this way are fully comparable to commonly used concrete foam or Ytong-type materials, and these materials provide very low shrinkage up to 800 °C. At higher temperatures, larger volume changes and partial sintering start to occur. The calcined material does not exhibit mechanical defects and, unlike the foam of the concrete, is stable as it does not break down the binder phase (the rehydration of calcined concretes leads to the collapse of the structure over time).

The used aluminosilicate component - fly ash containing mainly glass phase accompanied by minority quartz, mullite and hematite, is not suitable for catalytic and adsorption applications because of poor texture properties. Therefore, natural zeolite was chosen as the aluminosilicate raw material for the following works. It contains mainly clinoptilolite zeolite (Heulandite group) and other accompanying minerals such as feldspar, mica, hematite, quartz, etc. Natural zeolite is a very easily available material with large deposits worldwide (Greece, Iran, Cuba, Japan, Slovakia).[45,46]

4.1 ZEOLITE FOAM PREPARATION

Natural zeolite is a raw material very different from the previously used fly ash. It is a microcrystalline material with a completely different chemical composition (Si/Al ratio, presence of other elements, especially alkalis) and very different rheological properties of the prepared mixtures. In the first phase, it was necessary to optimize the composition of the alkali-activated mixture as well as the actual activation conditions. The actual synthesis of materials proceeded according to the same scheme, ie. first, the corresponding alkaline activator (in this case a mixture of $KOH + Na_2SiO_3$) was prepared and added to the aluminosilicate component (ground natural zeolite). Foaming agent (Al powder) was added to the homogenized mixture and allowed to activate.

In the first syntheses of zeolite foams, the aluminum powder was used to foam the mixture, but due to the same problems encountered in the preparation of fly ash foams, this was later replaced by a solution of hydrogen peroxide, whose decomposition in alkaline medium is gradual and is not so much exothermic.

The outputs of the first phase of the research of alkali-activation of natural zeolite were optimized values of mixture parameters:

- Silicate modulus of alkaline activator (M_s), defined as molar ratio SiO_2/Me_2O, where Me is Na or K: 1.2 - 1.8.
- Mixture water coefficient (w), defined as the weight ratio of the total amount of water to the aluminosilicate component in the mixture: 0.4 - 1.0.
- Total alkali content (Me_2O, Me = Na and K): 5 - 15 wt%.
- Molar ratio Na_2O/K_2O: 0.3 - 0.9.
- Foaming agent content: up to 2 wt%.
- Activation temperature: 20–80 °C.
- Time of activation: up to 24 hrs.
- Ageing: 1 month.

The optimal composition and conditions for the used natural zeolite (Klinofeed®) are roughly in the middle of the defined intervals (Ms = 1.5; w = 0.7; Me_2O = 8.2 and Na_2O/K_2O = 0.56), except for activation, which was extended to 48 hours in subsequent preparations to better activating of the entire volume of the foam.

The using of heterogeneous catalysts, catalyst supports, adsorption and filter materials in the chemical industry requires shaped materials since powdered materials cannot be used in the flow units widely used in the chemical industry. Conventional techniques such as tabletting, extrusion or casting cannot be used for shaping. For this reason, another aim was to develop a method of shaping these materials applicable on an industrial scale. For the shaping and preparation of pellets of different diameters and cross-sections (trilobes, tetralobes, etc.), the method "foaming into the matrix" was used. The method consists of inserting a matrix with a dense network of holes with the desired size and shape into an alkali-activated mixture mixed with a foaming agent. During the foaming, the individual holes of the matrix are filled with the resulting zeolite foam, which is solidified by the activation. The pellets can be easily removed from the holes thanks to the partial shrinkage. This method can also be used for mixtures without added foaming agent, especially for the preparation of small pellet diameters (2-3 mm). The pellets having a circular cross-section of 3 to 8 mm were obtained in an amount of more than 1000 g, thereby it verifying the applicability of the process to larger scales. For complicated, non-circular cross-sections (tetralobes), the 3D printing method was used to manufacture the matrix (Fig. 3).
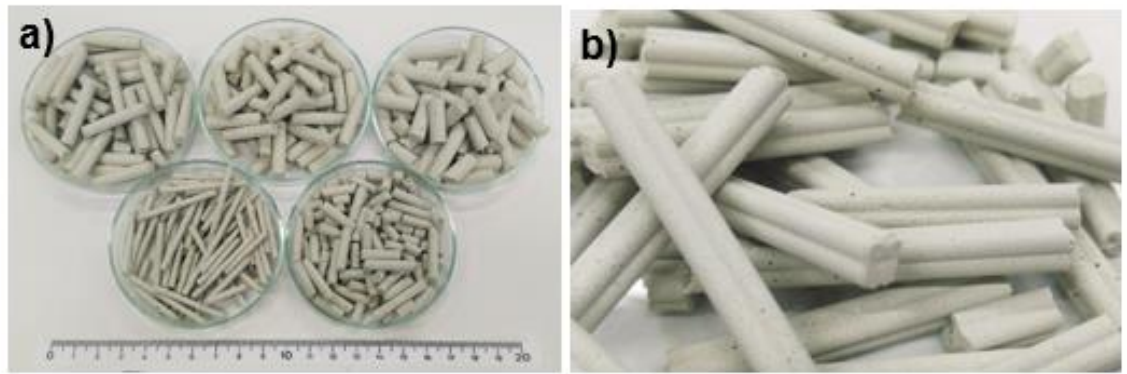
*Fig. 3 Pellets of zeolite foams with circular cross-section (diameter from 3 to 8 mm)(left) and „tetralob"
cross-section (diameter 5 mm)(right)*

Another important parameter for use on a larger scale is the highest possible strength of the prepared materials. This problem was solved by adding an additive to the alkali activated mixture. The first tests were carried out with the addition of metakaolin, which serves to prepare of geopolymers, but its use did not lead to an improvement in strength. In the alkaline activation of the fly ash, CaO is added as a solidification accelerator, which forms partially the C-S-H phase in the binder system, resulting in improved mechanical properties.[47,48] The CaO addition to zeolite foams showed very good results (CaO addition up to 2.5 wt%). The high CaO content in the mixtures led to the rapid reaction between CaO and the activator, the Ca-silicates were formed, and the resulting pellets were damaged by a number of cracks. The pellet edge strength with 2.5 wt% CaO in the dried state is about 2 times higher than the basic zeolite foam. Significant increases in the strength were also observed in post-synthesis modified pellets by acid leaching.

Based on the obtained results, MgO addition was tested as additive, which caused a similar increase in the strength as in the case of CaO, but much more MgO could be added to the mixture without affecting the processability of the mixture in terms of solidification rate, because MgO reacts with the silicates significantly slower. The different addition of MgO to the mixture mainly affects the textural properties.

4.2 POST-SYNTHESIS MODIFICATIONS

The basic requirement in the post-synthesis treatment of the obtained foam pellets was to modify the chemical and textural properties simultaneously with preservation of the appropriate mechanical properties guaranteeing subsequent applicability in larger applications.

The zeolite foams contain, after synthesis, a part of the unreacted activator, which causes the formation of a glass phase formed by sodium and potassium silicates after calcination. This glass phase increases the strength of the pellets, but subsequently prevents effective acid treatment of the surface during leaching. For this reason, the leaching must be carried out before pellet calcination.

The first tests also showed that only the water wash can not be used to remove this excess activator, as there is a large increase of pH on the surface and inside the pellets. That results loss of the strength and "chalking" of the surface due to the binder matrix attacking. This can be effectively prevented by using a weak acid (0.01 M HCl - hereinafter referred to as "D1 leaching") in a large excess (zeolite to solution ratio = 1:20 to 1:30) to neutralize the alkali present. As the results show, after this step, the material has very similar chemical and acid-base properties as the raw material - natural zeolite, but from the texture point of view, the macropores that are almost absent in the natural zeolite have been added to the material. The presence of macropores, on the one hand, improves permeability and thus reduces diffusion problems and on the other hand, significantly reduces the weight of the sprinkled bed.

During D1 leaching, most of the sodium and a portion of potassium, calcium and magnesium are removed. The use of acids with a higher concentration leads to the gradual elimination of other components - aluminium, iron and potassium, which in turn has an impact on the textural and acid-base properties. The gradual leaching of the other components was monitored by leaching with 0.1 to 6M HCl or by leaching with 3M HCl (hereinafter referred to as "D2 leaching") at increasing temperature or at increasing leaching time. In the course of the tests, the occurrence of cracks in samples leached with concentrated acids (6M, partly also 3M), which are likely to be caused by relaxed stress after removal of the excess activator and other components, was observed. This process can be eliminated by using a two-step leaching, in which the first step (D1 leaching) removes the excess alkaline activator and the second step (D2 leaching) removes other components and clean the micro and mesopore system. In this procedure, the structure is not so abruptly stressed and the occurrence of cracks was not observed.

As the XRD results show, there is no significant change in the crystalline structure. During the alkali-activation, there was a partial decrease in crystallinity, which was caused by the presence of an amorphous alkaline activator or a binder matrix and partial disruption of the zeolite structure during activation. During acid leaching, crystallinity increases up to the concentration of 1M HCl then decreases again with the gradual formation of defects due to the loss of aluminium. The zeolite structure collapses completely when 6M HCl was used and only the structures of accompanying aluminosilicate minerals (feldspar, quartz) are visible in the diffractogram.

The most significant changes were observed in the texture of zeolite foams, where the pores presented in the material were gradually released and cleaned. Alkali activation leads to a decrease in the pore volume by half compared to natural zeolite and the total pore area decreased four times compared to the original value. During the leaching, the mesopores are cleaned, whose volume increases only slowly during the increasing concentration of leaching acid (up to 3 M HCl) and then is almost constant. On the contrary, there is a significant increase in the volume of micropores and their gradual differentiation into pores of 0.8–0.9 nm; 1.0–1.1 nm and 1.3–1.5 nm. The observed collapse of the zeolite structure using 6M HCl is evident in the changes in the microporous structure of the material. The Hg porosimetry results show the presence of meso- and macropores with dimensions ranging from 3 to 200 nm and a maximum of about 45 nm in the natural zeolite. After alkali activation, the pore distribution curve fluently continues from 3 nm up to macropores with a dimension of 950 nm. Another group of pores present in the material are macropores with a size of 950–3450 nm, followed by "super-macro" pores with the size of tens to hundreds of μm.

The proportion of individual pore sizes is significantly changed by the addition of foam-enhancing strength additives. While in the case of metakaolin addition, the change is not so significant (only the maximum for pores of 8–10 μm was observed), a completely different pore distribution is evident in samples with MgO and especially CaO addition. The different pore distribution is probably related to the partial formation of the different binder matrix. D1 and D2 leaching removes the magnesium and calcium from the structure and it resulting in a pore volume increasing for pores of 3–50 nm by 50 % for MgO and by 200 to 350 % for CaO (Fig. 8) compared to the no-additived zeolite foam.

The structure of obtained activated materials (zeolite foam/binder matrix) and natural zeolite were investigated in detail using the ^{29}Si MAS-NMR (Fig. 4a) and ^{27}Al MAS-NMR (Fig. 4b) methods. The measurements were performed on the raw natural zeolite and zeolite foam samples S, D1, D2. In terms of silicon structure (Fig. 4a), it is evident that the natural zeolite contains predominantly $Si[SiO]_4$ units (112 ppm position), $Si[AlO][SiO]_3$ units (107 ppm position) and $SiO[SiO]_3$ units (101 ppm position). After alkali-activation, an increase in the signal intensity at 101 ppm was observed. This signal returns to its original position after D1 leaching and the modified material has the same spectrum as the natural zeolite. In the case of D1 leaching of the natural zeolite, there are also no significant changes and only a small signal increase with a 112 ppm position is observed. Leaching with concentrated acid (D2 leaching) already leads to significant structural changes in the natural zeolite and alkali activated material. There is a decrease in the signal at 107 ppm and an increase in the signals at 112 ppm and 101 ppm. The changes are related to the removal of aluminium from the structure and the subsequent formation of silanol groups.[15,49-51]
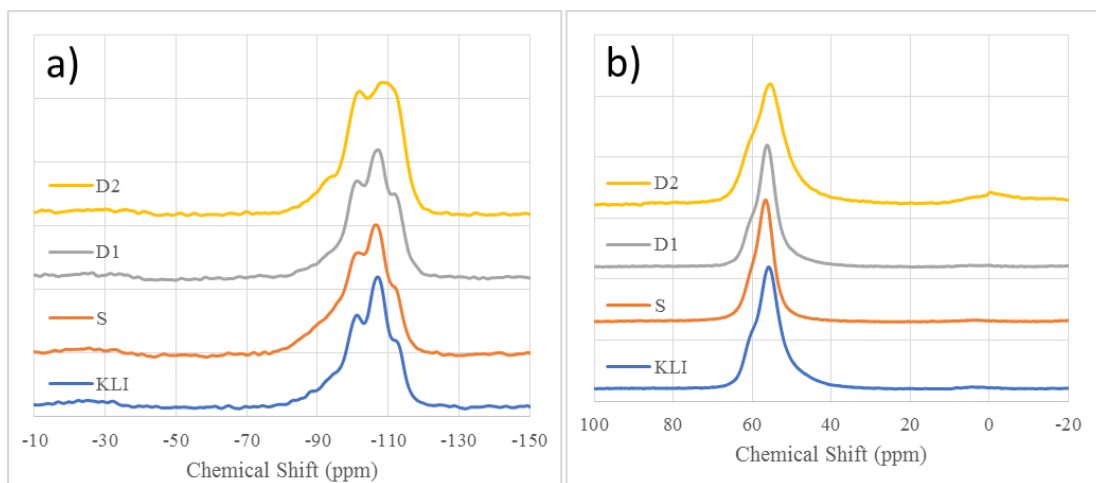
Fig. 4 ^{29}Si-MAS NMR (a) and ^{27}Al-MAS NMR (b) of natural zeolite (KLI) and zeolite foam (S) after acid treatment (D1 and D2 leaching)

The ^{27}Al MAS-NMR spectra (Fig. 4b) show that Al in the alkali-activated material is present solely in the tetrahedral coordination with a 55 ppm position corresponding to the poly(sialate-siloxonate) Al[SiO]$_4$ units.[9,15,49,50] The spectra show a broadening of the peak towards 60 ppm, which corresponds to units in which one position is free (containing the aluminol group AlO[SiO]$_3$). During alkali activation, this peak is reduced due to the binding of silicon from the alkaline activator to the terminal aluminols. After D1 leaching, the material again has the spectrum identical to the natural zeolite, and some of the silicon is removed. The more significant removal of Al is evident in the D2 leached sample, where apart from the extension to 60 ppm, the formation of octahedral units [AlO$_6$] at the 0 ppm position is also evident.

The obtained results showed that the material after D1 leaching is the same as the raw natural zeolite or the alkali activated foam. In the case of D2 leaching, damage of the zeolite structure is evident, and the material shows the predominance of units containing Lewis centre consisting of AlO$^+$, Al(OH)$_2$$^+$ and Al(OH)$^{2+}$ groups. The original assumption that the binding matrix is an N(K)-A-S-H gel formed by partial dissolution of the zeolite or accompanying aluminosilicates from a number of clays, feldspars and mica has not been confirmed The measured data showed that the binder matrix is almost exclusively composed from bridges or short chains formed by tetrahedra [SiO$_4$], which are bound to the surface aluminols of natural zeolite (clinoptilolite). The aluminols are presented on the surface of zeolite grains. Part of the Si chains contains free ends with two OH groups.

In the next work, the leached foam materials were used as a basic framework for subsequent modification consisting in the deposition of oxidic (Al$_2$O$_3$, TiO$_2$, SiO$_2$) and other (MoC$_x$, MoN$_x$) layers serving as modified catalyst supports or directly as catalysts.

The possibility of applying further layers has been verified by various techniques based on commonly available procedures, such as homogeneous precipitation, where a layer of Al hydroxides was precipitated on the surface of zeolite foam due to the decomposition of urea at higher temperatures

(95 °C). Thus treated support was impregnated with a mixed aqueous solution of nickel nitrate, ammonium fluoride, and ammonium metatungstate to the target content of 5 wt% Ni, 1 wt% F and 10 wt% W. The commercial support γ-Al_2O_3 and D2 modified zeolite foam were also impregnated, and all the obtained catalysts were used for deoxygenation of waste fats. The possibility of preparation of composite catalysts and supports by impregnation and precipitation methods was also verified. The TiO_2/ZF composite support was prepared by the impregnation method using a peroxide solution of TiO_2 and a silica modified support (SiO_2/ZF) was prepared by the precipitation method for the SBA-15 synthesis.

By the method according to the patent CZ 307 632 (Tišler et al., Molybdenum catalyst production method) were prepared catalysts containing as active phase molybdenum carbide or nitride. Molybdenum nitride and carbide were in the form of layers placed inside macropores of zeolite foam in order to obtain composite material with large cavities containing on the walls molybdenum carbides and nitrides particles. This was due to the fact that larger carbide and nitride phase particles have better stability during the reactions, and thus increase resistance to deactivation of the active phase by oxidation.[52,53] The MoN_x/ZF and MoC_x/ZF composite catalysts will be used in hydrodeoxygenation (HDO) catalytic applications to replace older types of sulfide or precious metal based HDO catalysts.[54-56]

The cobalt catalysts prepared by using zeolite foams as supports were prepared for catalytic decomposition of N_2O. The cobalt catalysts were prepared i) on zeolite foam pellets with a diameter of 5 mm (AA-S), ii) on modified pellets by D2 leaching (AA-D) and iii) on ion-exchanged pellets (AA-N) using 1M NH_4NO_3 (80 °C/6 hrs). Catalysts on commercial γ-Al_2O_3 supports (Sasol) and kieselguhr (Eurosupport Manufacturing, referred to as SiO_2) were also prepared for comparison. The solution of cobalt nitrate was used for impregnation of supports to target cobalt content of 5 wt%. To complement the series, there were additionally prepared two catalysts (AA-IE-Co and AA-IE-CoMn; 80 °C/6 hrs) by direct ion exchanging (DIE) of unmodified ZF pellets with i) 0.25M $Co(NO_3)_2$ solution or with ii) mixed $Co(NO_3)_2$ and $Mn(NO_3)_2$ solution (c_{Co} = 0.2 moldm^{-3} + c_{Mn} = 0.05 moldm^{-3}) . An interesting phenomenon was observed with these catalysts, namely that the active metal (cobalt or cobalt with manganese) is not evenly distributed in the cross-section of the pellet, but forms a thin layer to a depth of approx. 0.5–1 mm below the surface of the pellet.

Mapping of the catalyst pellet cross-section using the SEM-EDS method showed that cobalt was distributed uniformly over the surface when modified zeolite foam supports were used (AA-N and AA-D). In the case of impregnation of the AA-S support, an area is not loaded completed by cobalt due to precipitation of Co hydroxide during impregnation by the alkaline present in the zeolite foam. This resulting layer prevents further penetration of the impregnation solution into the interior of the pellet. A similar effect was observed in the direct ion exchange preparation method. The cobalt was only observed

on the outer surface of the pellet in the form of a ring, the penetration depth of Co into the pellet was about 0.7 mm. The distribution of manganese shows a decrease of the content from the surface to the centre, but unlike of cobalt, there is no such marked boundary line. In terms of alkali content, there is a decrease in the content of Na and K in the order AA-S-Co, AA-IE-Co/AA-IE-CoMn, AA-N-Co and AA-D-Co and their uniform distribution throughout the pellet cross-section.

The process of active metal-enriched layer formation was further studied in detail for a number of cations (Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, etc). The metal concentration in the cross-section was determined by SEM-EDX analysis using line mapping of the element from the surface of the pellet to the centre. The effect of solution concentration, temperature or time of DIE was performed and the effect of component ratio for cation mixtures was also studied.

The results showed that with increasing concentration, as well as temperature or DIE time, the layer line moves towards the centre and the line was not so sharp. For cation mixtures, the line movement was also dependent on the ratio of the components. The SEM-EDX profiles and photos of cuts pellet (Fig. 5) show that for each cation the boundary and its sharpness is different. While for Cu, Ni, Ag, Co and Mn the boundary is sharp, the Fe concentration decrease in the profile is gradual. A very interesting profile has Cr, which has formed an interlayer at a depth of 250 to 800 μm. On the other hand, Mg do not show a significant maximum and are evenly distributed throughout the cross-section. Thus, the explanation of the formation of the layers is the gradual precipitation of the cation due to the diffusion of alkalines from the pellet. At some depth, a layer is formed which further prevents the cation from entering the interior of the pellet. The shape and location of the profile also depend on the pH at which precipitation of the cation occurs. For this reason, maximum for eg. Mg, whose precipitation occurs only at a relatively high pH, is not observed.
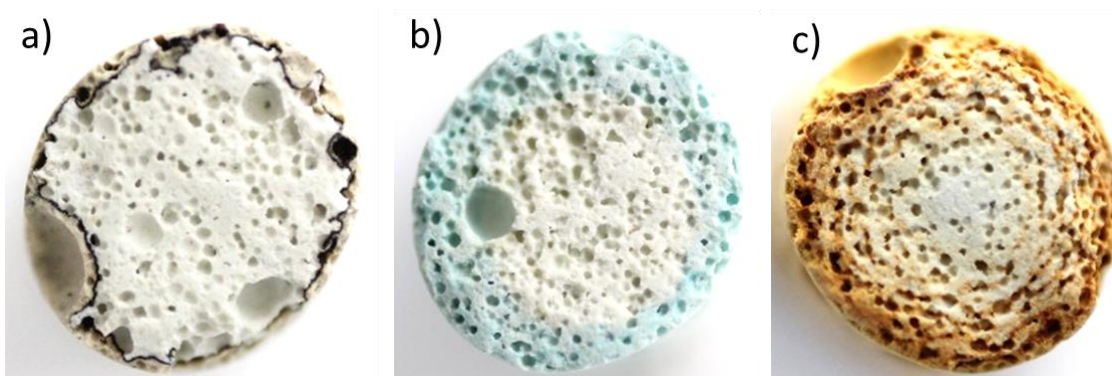

Fig. 5 „Egg-shell" pellets of zeolite foams with manganese (0,05M)(a), copper (0,25M)(b) and iron (0,25M)(c) layers

4.3 APLICATIONS OF ZEOLITE FOAMS

The zeolite foams have a considerable application potential as can be seen in the preparation and modification section. The newly prepared materials have been monitored in several different applications and the research will continue to develop in partial or individual research projects and in cooperation with other partners.

Adsorption applications

The results of the NH_3-TPD and CO_2-TGA experiments characterizing the acid-base properties of these materials show that, as with natural zeolites, adsorption applications for various gases may be the basic application. Here it is possible to assert the acidity of the zeolite and, on the other hand, the basicity of the material due to the presence of an excess activator. A significant advantage over natural zeolite is the lower bulk density of the material, which reduces the costs of the equipment, but also the higher volume of meso- and macropores.

The modified alkali-activated natural zeolites were studied during adsorption of Zn^{2+} ions (Fig. 6) in cooperation with the bachelor thesis (M. Kočí, University of Pardubice). The obtained results show practically identical adsorption curves for natural zeolite and D1 modified zeolite foam and thus again confirm that these materials are almost identical in many aspects. The D2 leached material has sorption properties significantly worse, which corresponds to changes in the clinoptilolite structure due to strong acid leaching. On the other hand, several times better adsorption properties of the raw alkali-activated foam were observed. This increase is due to the precipitation of $Zn(OH)_2$ by the alkali present in the material. This is the same process that leads to the formation of hydroxide layers in the zeolite pellets described in the previous chapter.
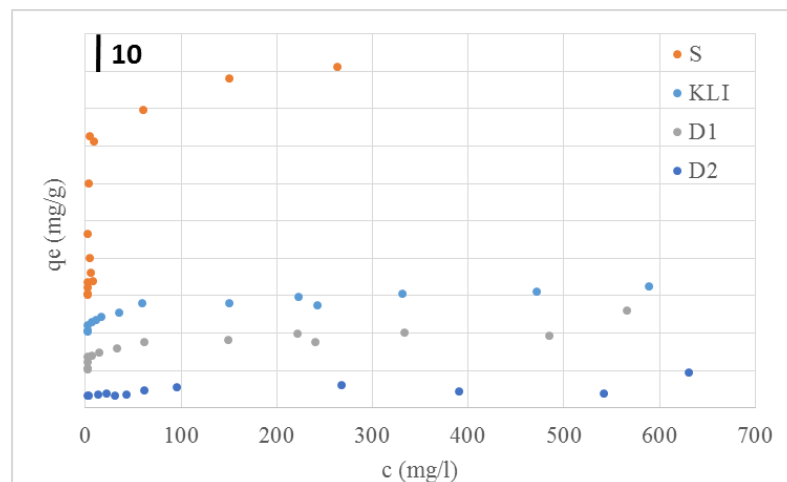

Fig. 6 The adsorption properties of natural zeolite (KLI) and zeolite foams (S, D1, D2) for Zn^{2+}

These results indicate the possibility of using these materials as adsorbents in emergency situations where, for example, water contamination has occurred and it is necessary to quickly remove and fix larger amounts of a contaminant in the form of insoluble hydroxide or oxide.

Catalytic applications

The catalytic applications have been verified for materials based on alkali-activated zeolite foams in deoxygenation of waste (rendered) fats (NiWF catalysts) and in catalytic decomposition of N_2O (Co catalysts).

The waste (rendering) fats are currently of limited use and represent another possible substitute for fuels (petrol, diesel) produced from oil. As the results have shown, zeolite foam catalysts are able to compete with commercial catalysts in activity despite very small specific surfaces (Fig. 7).
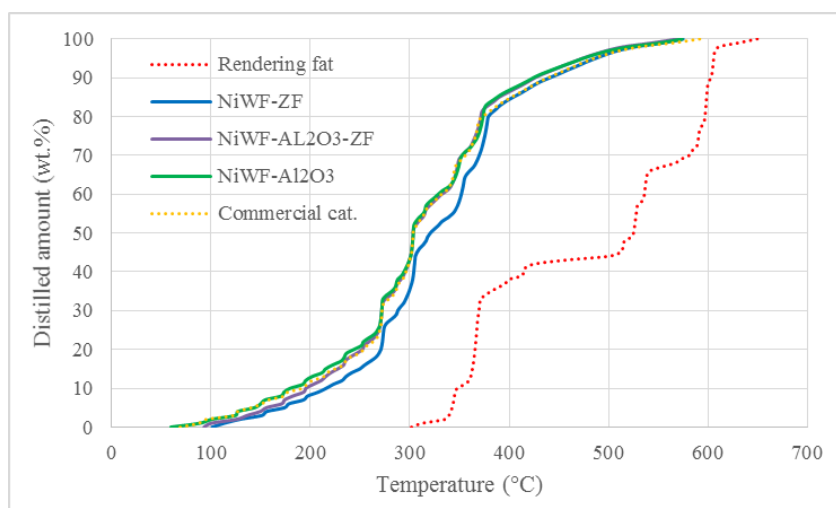

Fig. 7 SimDis curves of raw material (rendered fat) and deoxygenation products

The NiWF/Al$_2$O$_3$/ZF catalyst showed the best activity and converted more than 74 % of the original waste fat mass to liquid products, where 48 % of products were with the boiling point at 220–340 °C (it corresponds to the C_5-C_{19} fraction useful as motor fuels - gasoline, diesel) and 14% of products were with the boiling point of 50–200 °C (it corresponds to the composition of fraction C_5-C_{12}). 11 % of the total waste fat input was converted to gaseous products. The presence of the gaseous products and products with the boiling point below 220 °C is due to hydrocracking and deoxygenation activity by the presence of tungsten and nickel, respectively. The main constituent of the gaseous products is CO_2 because of decarboxylation reactions and C_1–C_4 hydrocarbons formed as a result of hydrocracking reactions.

The second catalytic application verifying the applicability of zeolite foams prepared by alkali activation of natural zeolite or catalysts prepared from them respectively was the catalytic decomposition of nitrous oxide (N_2O). The N_2O is an important pollutant contributing to the greenhouse effect. The largest source of N_2O emissions are waste gases from nitric acid plants. One of the possibilities of N_2O removal is low-temperature catalytic decomposition into nitrogen and oxygen. This procedure offers an attractive solution to reduce of N_2O emissions in the tail gas from the plant, allows existing technologies to be used and the process itself does not require the addition of a reducing agent.[57] Cobalt-based catalysts show very good results and the use of zeolite foam catalysts offered a suitable alternative to existing deN_2O catalysts.

The cobalt catalysts were tested in laboratory units under defined conditions (1000 ppm N_2O in N_2, 300–450 °C). The results of temperature dependencies of N_2O conversions using catalysts pellets (Fig. 8a) show significant differences in the activity between catalysts due to different properties (chemical composition, texture, acid-base properties, reducibility).
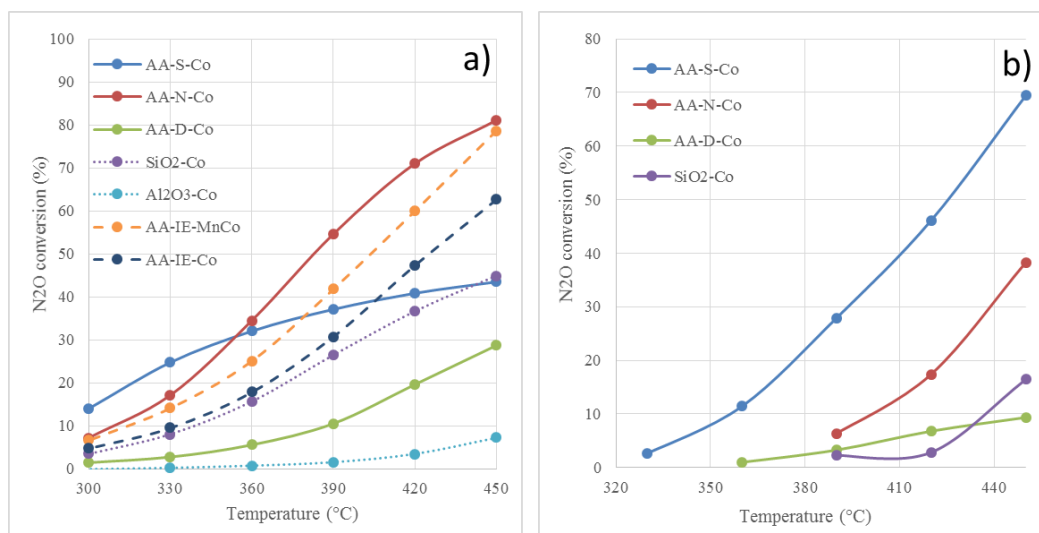

Fig. 8 N_2O conversion for catalysts pellets (a) and for crushed catalysts (b)

The catalyst prepared on commercial γ-Al_2O_3 support (Al_2O_3-Co) exhibits very low N_2O conversion (only 7 % at 450 °C) even though it has the highest specific surface area from all of catalysts. As shown H_2-TPR, the low catalytic activity is due to the formation of hardly reducible particles, which cannot participate in the N_2O decomposition. In contrast, the second catalyst on commercial kieselguhr support (SiO_2-Co) exhibits a relatively high activity (the conversion of N_2O at 450 °C is almost 45 %) due to the better reducibility of the cobalt particles. The conversion of N_2O on cobalt catalysts prepared on differently modified zeolite foams increases in the order of AA-D-Co → AA-S-Co → AA-N-Co with N_2O conversions of 29 %, 43 % and 81 % at 450 °C respectively. The order of samples by activity correlated with the reducibility of cobalt species obtained from TPR. The presence of acid centres was

confirmed by NH$_3$-TPD analyzes. The amount of acid centres was the highest of all monitored catalysts in the case of AA-N-Co, followed by AA-IE-Co and AA-IE-CoMn, where their activity were also high in N$_2$O decomposition (63 % and 79 % conversion at 450 °C respectively).

The different shape of the conversion curve of the AA-S-Co catalyst indicates a possible textural effect, which has been verified on catalytic tests carried out in a small laboratory reactor using a crushed catalyst at a fraction of 160–315 μm. The order of obtained N$_2$O conversions curves for catalysts was differed for using of the pellets (Fig. 8a) and for using of the crushed catalysts (Fig. 8b). It indicates that the reaction kinetics is influenced by the textural properties of the catalysts and the intrinsic diffusion has a significant effect.

The obtained results show that the active phase deposited on a support with a high specific surface area (γ-Al$_2$O$_3$) may not be the most advantageous solution due to the presence of poorly reducible cobalt species. A good alternative can be macroporous foamed supports based on alkali-activated natural zeolites with suitable post-synthesis modification or with a suitable process for preparing the catalyst itself. Last but not least, the advantage of these materials is their ease of synthesis and low cost, which meets the requirements of the industry and the possibility of later application on a larger scale.

5 CONCLUSION

Alkali-activation of aluminosilicate components is widely used in the construction industry and its widespread use is prevented in particular by the cost requirements associated with raw materials for the alkaline activator, while the aluminosilicate component is usually based on waste components or commonly available minerals and rocks. So far, the use of these materials in the chemical industry, specifically in catalysis and sorption applications, has been limited to only a few studies focused primarily on geopolymers (materials prepared by the alkali-activation of metakaolin). This work significantly extends and refines the view of these materials and their applicability in these fields. The study showed the unique properties of alkaline-activated zeolite foams prepared from natural zeolites and the huge potential for the subsequent use in catalytic and adsorption applications. The uniqueness of the results was confirmed by granting of three patents for the production, modification and shaping of zeolite foams and filing of another patent application, which deals with the specific preparation of catalytic/adsorption materials.

Alkali-activation of the natural zeolite with a mixed activator consisting of potassium hydroxide and sodium silicate results in the production of solid and heat resistant foam materials which partially retain the structure of the clinoptilolite natural zeolite and additionally provide meso- and macropores that opened up the entire interior surface of the catalyst/adsorbent. The presence of these pores is important not only for the transport of the components but also significantly reduces the weight of the bed, which is important for possible larger-scale use in terms of column and adsorber designs.

Acid leaching of materials leads to a modification of textural properties (cleaning and creation of new pores) and reduction of the content of accompanying elements (Al, Na, K, Fe, Ca, Mg), which were contained in the natural zeolite and the Si/Al ratio also increased. The acid-base properties (the strength and the number of active sites) can be controlled by synthesis procedures along with other modifications. Thus, the prepared materials can be modified for the specific application.

During the study, the usability of these materials was verified in two different catalytic applications i) deoxygenation of waste fats and ii) catalytic decomposition of N_2O. The obtained results unambiguously show the applicability of these materials in catalytic applications and the prepared catalysts are able to compete with commercial or other previously studied catalysts in the processes studied. Of course, the long-term testing and stability control is a long way to transfer to industrial applications, but one of the important parameters in industrial applications is price, which is very favourable due to the used raw materials and subsequent procedures. These materials are so interesting that the research will continue to improve the properties, but especially to their wider use and industrial-scale application.

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7 LIST OF PUBLISHED WORKS AND CONFERENCE CONTRIBUTIONS

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Oral and poster presentation at conferences

Posters

I. Z. Tišler, D. Kubička, R. Bulánek, Alkali activated zeolite foams – New structured materials for adsorption and catalysis, 48th Symposium on catalysis, 7-9 November 2016, Prague, Czech Republic

II. Z. Tišler, K. Marklová, Y. Ghrib, J. Vaculík, R. Bulánek, Surface chemistry of modified geopolymers: amount and nature of acid sites, Solid State Chemistry 2018 (SSC 2018), September 16-21, 2018, Pardubice, Czech Republic

Oral presentation

I. Z. Tišler, R. Bulánek, New foam materials synthesised by alkali activation of natural zeolite, ICCT 2017, April 10-12, 2017, Mikulov, Czech Republic

II. J. M. Hidalgo, Z. Tišler, J. Horáček, A. Vráblík, J. Lederer, Acid-modified phonolite and foamed zeolite as supports for NiW catalysts for deoxygenation of waste rendering fat, 1st International Conference on Reaction Kinetics, Mechanisms and Catalysis, June 6-9, 2018, Budapest, Hungary

III. Z. Tišler, R. Bulánek, The influence of acid treatment on properties of alkali activated zeolite foams, Solid State Chemistry 2018 (SSC 2018), September 16-21, 2018, Pardubice, Czech Republic

Published results without connection to the topic of dissertation thesis (2014 – 2019)

Druh výsledku	Main author	Co-author	Published	In print
Patent	8	0	4	4
Functional sample	1	3	4	0
Utility model	0	3	1	2
Article with IF	2	28	27	3
Presentation	0	> 20	18	2
Posters	0	> 15	13	2