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# Lokalizace a distribuce atomů hliníku ve skeletu křemíkem bohatých zeolitů

**Komise pro obhajoby doktorských disertací v oboru FYZIKÁLNÍ CHEMIE**

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# Academy of Sciences of the Czech Republic

**Summary of Doctor of Science Thesis in
CHEMICAL SCIENCES**

# Siting and distribution of aluminum atoms in the framework of silicon-rich zeolites

**Commissions for Defending Doctor of Science Theses in PHYSICAL
CHEMISTRY**

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## ABSTACT

In this Thesis is summarized recent research of siting and distribution of Al atoms in the framework of Si-rich zeolites. Zeolites are crystalline microporous aluminosilicate molecular sieves with three dimensional frameworks formed by $SiO_4$ and $AlO_4^-$ tetrahedra sharing corners. The enormous variability of the arrangement of $Si(Al)O_4$ tetrahedra results in more than two hundred framework topologies with different architectures and dimensions of the zeolite inner pore/cavity system. The isomorphous substitution of Al atoms in the silicate framework results in the potential ability of the framework negative charge to stabilize well-defined counter-ion species, i.e. acidic protons, bare metal ions, metal-oxo and metallic species inside the defined pore system which act as highly active sites for acid- and redox-catalyzed reactions or as specific adsorption centers in numerous chemical processes. At the present time, zeolite-based catalysts represent the widest group of industrial heterogeneous catalysts. Zeolite base Si-rich zeolites with low concentrations of Al atoms in the framework (Si/Al > 8), yield protons with high acid strength employed in highly selective hydrocarbon processing, and counter cation species exhibiting extraordinary redox and catalytic properties, not found with counter ions in Al-rich zeolites and metal oxides supported on amorphous oxides. The low concentration of Al atoms in the framework of Si-rich zeolites together with the high number of crystallographically distinct $Si(Al)O_4$ tetrahedra results in significant variability of their positions in the individual rings and distances in the framework. As the negative charge of the $AlO_4^-$ tetrahedra in zeolites is localized at these $AlO_4^-$ entities, it could be suggested that the location and distribution of the framework $AlO_4^-$ tetrahedra are crucial parameters controlling the location, distribution and structure of the counter-ion species.

Our development of method for analysis of Al distribution in the framework of Si-rich zeolites, which still remains the only one for analysis of the distribution of Al atoms in zeolites, represents a substantial step forward in the analysis of the distribution of Al atoms. We have shown for the first time that single Al atoms and Al pairs (Al-O-(Si-O)$_2$-Al sequences in one ring) predominate in the framework of Si-rich zeolites, Al distribution between these two Al species is not random or controlled by simple rules and zeolites with the same topology can exhibit different Al distribution. We have demonstrated that Al distribution in the framework can be tuned by the control of zeolite synthesis in industrially important zeolites of ZSM-5, ferrierite and beta structures. Our priority in the elucidation of the effect of selected synthesis parameters on control of the Al distribution in the framework enabled us to develop methods for the synthesis of Si-rich zeolites with the close to monomodal distribution of Al atoms even in the conditions for larger scale synthesis. We clearly demonstrated in a number of

studies that the distribution of Al atoms in the framework between single Al atoms and Al pairs represents a key parameter controlling the incorporation, structure, concentration and redox properties of TM ion species in Si-rich zeolites, dramatically affecting the activity/selectivity of the redox reactions (NO decomposition, selective catalytic reduction of $NO/NO_2$) in which Si-rich metallo-zeolite catalysts exhibit unique activity. In the case of hydrocarbon transformations over protonic zeolite forms, we showed that cooperating and single protons are connected with different reaction pathways and that the Al distribution can affect the selectivity of hydrocarbon transformations over zeolites.

The application of our method for the analysis of Al siting in framework of Si-rich zeolites based on the $^{27}$Al 3Q MAS NMR experiment supported by quantum chemical calculations provided the first and unambiguous evidence that the siting of Al atoms in Si-rich zeolites is not random and depends on the synthesis conditions. Moreover, the siting of framework Al atoms in ZSM-5 (with 24 different T sites) was partly solved and the occupation of 7 T sites by Al atoms was suggested for the first time. With ferrierite, we provided the first and so far the only complete analysis of the siting of framework Al atoms in Si-rich zeolites.

In the field of the distribution of Al atoms in Si-rich zeolites, it can be concluded that we introduced Al distribution as a key parameter into zeolite science, developed methods for Al analysis, demonstrated the significant effect of the distribution of Al atoms on the catalyst activity and rounded out our work by development of methods for tuning the Al distribution in zeolites up to a scale suitable for technical applications. In the field of the siting of framework Al atoms in Si-rich zeolites, it can be concluded that we have developed methods for the analysis of the siting of single Al atoms. Our results clearly demonstrate non-random, hydrothermal synthesis-controlled Al siting and provide new opportunities for the development of highly active and selective catalysts. We demonstrated the significant effect of the location of the Al pairs on the catalytic activity of zeolites, which can be exploited up to technical applications.

**Content**

# 1.    Introduction

Zeolites are crystalline aluminosilicate molecular sieves with molar Si/Al composition of $1 - \infty$ and three dimensional frameworks formed by $SiO_4$ and $AlO_4^-$ tetrahedra sharing corners.[1,2] The enormous variability of the arrangement of $Si(Al)O_4$ tetrahedra results in more than two hundred framework topologies with different architectures and dimensions of the zeolite mono- up to tri-dimensional inner pore/cavity system with the channel diameter ranging from 3.5 to 15 Ǎ.[3] The isomorphous substitution of Al atoms in the silicate framework results in the potential ability of the framework negative charge to stabilize well-defined counter-ion species, i.e. strongly acidic protons, bare metal ions, metal-oxo and metallic species inside the defined pore system. Due to the local negative framework charge, these counter-ion species exhibit unique acidic or redox properties, which enable them to act as highly active sites for acid- and redox-catalyzed reactions or as specific adsorption centers.[2] The combination of the variability of well-defined active sites and the variability of the well-defined channel/cavity system with large inner surface area has led to the potential use of zeolites as catalysts or sorbents in numerous chemical processes. At the present time, zeolite-based catalysts represent the widest group of industrial heterogeneous catalysts.

Aluminum-rich zeolites (Si/Al $1 - 6$) of faujasite and A-type structure have found broad application as catalysts in processes of catalytic cracking and fuel reforming, and as adsorbents and detergents.[2] In recent decades, research has been focused particularly on pentasil ring silicon-rich zeolites with low concentrations of Al atoms in the framework (Si/Al > 8), which yield protons with high acid strength and are employed in highly selective hydrocarbon processing.[4] Later, attention was devoted to the extraordinary redox and catalytic properties of counter cation species in Si-rich zeolites, not found with counter ions in Al-rich zeolites and metal oxides supported on amorphous oxides.[4-7] In addition, Si-rich zeolites exhibit a wide range of pore dimensions, from small and medium sizes (~ 3.5 – 5.5 Ǎ) up to large ones (~ 15 Ǎ),[3] offering shape-selective effects in reactions in the synthesis and transformation of hydrocarbons. The remarkable properties and catalytic activity of protons and counter metal ion species in Si-rich zeolites stimulated analysis of their structure, location and the consequent relationship to their extraordinary catalytic activity. We have devoted substantial efforts to analyzing the coordination of bare divalent transition metal cations and cations bearing extra-framework oxygen atom(s).[8-20] Our analysis of the location and coordination of TMI in zeolites has been accepted and is now generally used in the literature. While bare divalent cations are clearly connected with two negative charges in the framework,[21] some metal-oxo structures have been assumed to be related to the presence of single Al atoms in the framework, but without any experimental evidence.[22,23] However, very slow progress in analysis of the

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positions of Al atoms in the framework T(Si,Al) sites has long prevented at least estimation of the siting and distribution of framework Al atoms.

Nevertheless, the low concentration of Al atoms in the framework of Si-rich zeolites together with the high number of crystallographically distinct $Si(Al)O_4$ tetrahedra[3,4] results in significant variability of their positions in the individual rings and distances in the framework. As the negative charge of the $AlO_4^-$ tetrahedra in zeolites is not delocalized over the framework but, to the contrary, is localized at these $AlO_4^-$ entities, it could be suggested that the location and distribution of the framework $AlO_4^-$ tetrahedra control the location, distribution and structure of the counter-ion species (protons, bare cations, oxo-cations or cation-ligand species in general).[21]

Although the structures of counter-ion species and their relationship to their performance in catalysis have been studied intensively, there has been no analysis of the effect of the siting and distribution of framework Al atoms on the structure, properties and activity of the counter-ion species. Bare metal ions coordinated only to framework oxygen atoms and counter-ion species containing extra-framework oxygen atom(s) (including metal oxygen-bridged structures) were suggested as the active sites. The counter metal ions have been shown to be coordinated to specific structural rings with specific spatial distribution in the zeolite. To ensure local charge balance, the metal counter-ion species must be related to the siting of Al and its distribution in the framework. Thus, the local negative charge in the framework rings and defined structural arrangements can be assumed to be decisive for the location, structure and charges on the counter-ion species. Accordingly, the arrangement of the zeolite pore system and the total Al content, as well as the siting and distribution of framework Al atoms in Si-rich zeolites, are crucial parameters controlling the structures, properties and activities of counter-ion species.

The development of methods for analysis of Al-O-(Si-O)$_n$-Al sequences and Al - Al "visible" distances in the framework of Si-rich zeolites in our laboratory based on the use of Co(II) ions as probes of closed Al atoms and monitored by various spectroscopic techniques, together with $^{29}Si$ MAS NMR, represented a substantial step forward in the analysis of the distribution of Al atoms, i.e. the local negative charge in the framework.[21,24,25] It was shown that single Al atoms and Al pairs (Al-O-(Si-O)$_2$-Al sequences in one six-membered ring) predominate in the framework of Si-rich zeolites. Moreover, high variability of the distribution of Al atoms in zeolites with the same topology was observed for a wide range of Al contents in the framework.[24-26] The conclusion that the distribution of Al atoms in the framework of Si-rich zeolites is not random and is thus not controlled by statistical rules suggested that it might be possible to control the distribution of Al atoms in the framework by the conditions of the zeolite synthesis. Our recent experiments have clearly shown that the synthesis conditions lead to different distributions of

Al atoms in the framework of Si-rich zeolites, and the distribution of Al atoms between Al pairs and single Al atoms in the framework of ZSM-5, ferrierite, beta and MCM-22 zeolites can be tuned in a wide range.[27,28] The effect of selected synthesis parameters on control of the Al distribution in the framework was elucidated and knowledge of the synthesis of Si-rich zeolites with the desired distribution of Al atoms even in the conditions for larger scale synthesis was established.[29] It has been shown that the distribution of Al atoms in the framework dramatically and specifically affects the activity and selectivity of H- and metallo-zeolite catalysts in both acid and redox catalyzed reactions.[21,27,30,31]

In obtaining a complete picture of the Al location in the zeolite framework, analysis of the siting of Al atoms in the crystallographically distinct framework T sites in Si-rich zeolites remains a great challenge. We achieved significant progress in the analysis of Al siting in Si-rich zeolites by using a combination of $^{27}$Al (3Q) MAS NMR experiments with the prediction of $^{27}$Al isotropic chemical shifts in the individual T sites employing high accuracy DFT calculations. The Al siting in the ferrierite structure and partly also in ZSM-5 frameworks has been resolved.[32-34] Moreover, it has been revealed that the siting of Al-O-(Si-O)$_2$-Al sequences in the individual rings of the framework is a parameter that can be accessed indirectly, without knowledge of the occupation of the individual T sites by Al atoms, by means of a combination of $^{29}$Si MAS NMR and quantitative analysis of the location of defined divalent counter cations provided by spectral and diffraction techniques.[15-18,21,24,25] The results obtained for ZSM-5 and ferrierite zeolites clearly showed that the siting of the Al atoms in the individual framework T sites and of Al-O-(Si-O)$_2$-Al sequences is also not random or controlled by simple rules, but depends on the conditions of the zeolite synthesis.[26,28]

Attempts have also been made to control the siting of Al atoms in the framework by using various organic structure-directing agents (SDA) in the synthesis, and thus location of protonic sites in different channels of the ferrierite. Moreover, it has been shown that the Al siting in the framework, both of isolated Al atoms in T sites and of Al pairs, can be significantly varied by synthesis in the presence of an inorganic cation or by the nature of the Si and Al sources. Despite this significant progress in experimental analysis of Al siting in Si-rich zeolites, the relationship between the Al siting and activity and selectivity of zeolite catalysts was analyzed only by theoretical calculations for selective carbonylation of methanol or dimethyl ether.

Progress in the last few years in the area of siting and distribution of Al atoms in the framework of Si-rich zeolites seems to represent a dramatic step forward, both in analysis of the siting and distribution of Al atoms in the framework and in tuning of Al siting and distribution in the frameworks by zeolite hydrothermal synthesis. These achievements open the pathway for tuning the

properties of the protons and metal counter-ion species in Si-rich zeolites and for designing a new generation of highly active and selective zeolite catalysts for the individual transformations.

The Thesis describes efforts and achievements in the analysis and evaluation of the location of Al atoms in the framework T sites and their distribution between Al pairs and single Al atoms in the framework of Si-rich pentasil ring zeolites, centered in the most important zeolite structures of ZSM-5, ferrierite, mordenite, beta and MCM-22 zeolites. Evidence has been found indicating that the siting and distribution of framework Al atoms in Si-rich zeolites is not random and is not controlled by statistical rules. Successful tuning of the framework Al parameters has been achieved by the originally developed hydrothermal synthesis of Si-rich zeolites. Tailoring of the distribution of framework Al atoms in zeolites, providing different local negative charges on the framework available for balancing counter-ion species of various structures and locations, enabled synthesis of proton- and metallo-zeolites exhibiting specific catalytic activity and selectivity documented in reactions of transformation of hydrocarbons, selective reduction of $NO/NO_2$, and NO decomposition.

## 2. Distribution of Al atoms in the framework of Si-rich zeolites
## 2.1. History of the problem and strategy for its solution

Surprisingly, the aspect of the distribution of Al atoms in Si-rich zeolites and its relation to zeolite properties has been practically ignored in the zeolite science. There existed a dichotomy in assumptions on Al distribution in Si-rich zeolites. In the case of acid-catalyzed reactions over protonic forms of Si-rich zeolites, the exclusive presence of isolated protonic sites balancing single Al atoms was assumed and the presence of close protonic sites was not discussed.[21] In contrast, in the area of redox catalytic reactions over metallo-zeolites containing TM ions, the concentration of close framework Al atoms balancing the charge of divalent species up to molar ratio M/Al = 0.5 was assumed by analogy with Al-rich zeolites. The occurrence of far distant single Al atoms in the framework of Si-rich zeolites and their role was not taken into account.

The problem of the distribution of Al atoms in the framework of Si-rich zeolites was introduced by our papers on the nature and properties of Cu ions in Si-rich zeolites in connection with their extraordinary, unique activity in NO decomposition.[10,12,14,35] We suggested that the Cu ions in ZSM-5 are located in the vicinity of one or two framework Al atoms, whose local negative charge governs their reducibility and sorption and catalytic properties. In connection with the high interest in Si-rich metallo-zeolites, this finding attracted attention to the distribution of Al atoms in zeolite frameworks. However, no method was available for analysis of the distribution of Al atoms in Si-rich zeolites. Initially, random distribution of framework Al atoms in Si-rich zeolites was generally assumed in

the absence of any experimental support. Monte Carlo simulations were attempted to predict Al distribution in Si-rich zeolites and to explain the properties of metallo-zeolites.[36-40] However, this approach failed to match experimental differences in catalytic performance of zeolite catalysts with the same topology and similar Si/Al compositions.

The development of an experimental approach enabling analysis of the distribution of framework Al atoms in Si-rich zeolites by our group represented a breakthrough providing a realistic basis for analysis of Al in the framework and its impact on the properties of counter-ion species. In this approach, we utilized our extensive experience in the preparation and structural analysis of Co-zeolites of mordenite, ferrierite and ZSM-5 structures: the Co(II) ions exchanged into the zeolite were used as a probe of the distribution of framework Al atoms.[21,24,25] It should be pointed out that this method still remains the only one for analysis of the distribution of Al atoms in zeolites. From the very beginning, application of this approach unambiguously provided evidence that the distribution of Al atoms in ZSM-5 is not random or controlled by some simple rules, and that only experimental data obtained for the framework of individual zeolites can serve as a base for understanding the redox and catalytic properties of TMI species in zeolites.[41-43] This pioneering work on Al distribution in ZSM-5 was later extended to all industrially important Si-rich zeolites, such as ferrierite, mordenite, MCM-22, beta zeolite structures.[27,29,34,41,44] It was clearly shown that the nonrandom distribution of Al atoms in zeolites is a general property and that zeolites with the same topology and Al content can exhibit different distributions of Al atoms between far-distant single Al atoms and Al-O-(Si-O)$_2$-Al sequences occurring in one ring.

Solution of the siting of probe Co$^{2+}$ ions in zeolites also encompasses solution of the location of Al pairs in the framework. Thus, siting of Al pairs in zeolite rings will be discussed together with distribution of Al atoms. Our analysis of the Co$^{2+}$ siting in ferrierite, ZSM-5, mordenite and beta zeolites was based on the suggestion that the Vis spectrum of the d-d transitions of bare Co$^{2+}$ ions is highly sensitive to the Co$^{2+}$ ligand field and thus to the geometrical arrangement of the cationic sites of the (alumo)silicate framework.[15,21] Three cationic sites were suggested for Co$^{2+}$ ions (and thus for Al pairs) in mordenite, ferrierite, ZSM-5 and beta zeolites.[15-20] Analysis of the Co$^{2+}$ siting in these matrices represented the first information on the siting of divalent cations in Si-rich zeolites (note that diffraction studies were performed on mordenite with Si/Al 5). For ferrierite, our suggestion for the Co$^{2+}$ sites was later confirmed by x-ray diffraction studies[45-48] but, for ZSM-5 and beta zeolites, our results to date represent the only structural information on the siting of Al pairs and divalent metal ion species in these matrices. Our suggestion on siting of divalent cations in ferrierite, ZSM-5 and beta zeolites is generally accepted and our site notation is generally used. Similarly to

the distribution of Al atoms in the framework, the siting of Al pairs in zeolites is not random or controlled by simple rules, but depends on the synthesis conditions.[21,28]

The observed variability of the distribution of Al atom and location of Al pairs in zeolites directed our work in two related directions: (i) elucidation of the effect of the distribution of Al atoms and location of Al pairs on the zeolite properties and its impact on catalysis and, (ii) understanding of the processes controlling the Al distribution in the framework in order to prepare zeolites with controlled distribution of the Al atoms.

Ad (i) We clearly demonstrated in a number of studies that the distribution of Al atoms in the framework between single Al atoms and Al-O-$(Si-O)_2$-Al sequences in one ring represents a key parameter controlling the incorporation, structure, concentration and redox properties of TM ion species in Si-rich zeolites, dramatically affecting the activity/selectivity of the redox reactions. In this area, we focused on environmentally important "deNOx" reactions (NO decomposition, selective catalytic reduction of $NO/NO_2$) in which Si-rich metallo-zeolite catalysts exhibit unique activity.[21,27,41-43,49-51] These unambiguous results led to the introduction of the distribution of Al atoms into a general discussion in the area of redox catalysis. In the case of hydrocarbon transformations over protonic zeolite forms, we showed that cooperating and single protons are connected with different reaction pathways and that the Al distribution can affect the selectivity of hydrocarbon transformations over zeolites.[30]

There can be no doubt that the siting of the Al pairs controls the coordination of the divalent metal ions and thus their properties. The siting of the Al pairs is also reflected in the catalytic properties of metallo-zeolites and, in combination with the Al distribution, represents a key parameter for the unique activity of Fe-ferrierite in $N_2O$ decomposition.[50-56] This finding served as a starting point for the development of zeolite catalysts up to a scale suitable for technical applications.

It should be mentioned that we are still the leading laboratory in the analysis of the effect of the distribution of Al atoms on catalysis over Si-rich zeolites, as a result of our significant comparative advantage over other laboratories consisting in the controlled synthesis of zeolites with defined the distribution of Al atoms (note that commercial zeolites exhibit quite similar Al distributions), which is typically missing in other laboratories, where analysis of the relationship between the distribution of Al atoms and the zeolite catalytic activity tends to be speculative.

Ad (ii) Evidence for the dramatic impact of the distribution of Al atoms in the framework on the catalytic properties of zeolites resulted in our attempt to understand the parameters controlling the distribution of Al atoms in order to synthesize zeolites with the desired distribution of Al atoms. Owing to the

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complexity of the hydrothermal synthesis of Si-rich zeolites, there is no simple answer regarding the mechanism of formation of the structural units, their ordering and nuclearity in amorphous gels, and the crystal growth. No investigations have been performed on the distribution of Al atoms either in the nuclei of the amorphous phase, in the pre-crystallized gels or in the crystalline products. Analyses in other laboratories were concerned only with the total degree of Al incorporation. The screening work resulted in the identification of the parameters of the synthesis affecting the distribution of Al atoms in the framework,[26] and it served as a base for the first controlled preparation of zeolites with significantly prevailing single Al atoms or Al-O-(Si-O)$_2$-Al sequences in one ring of the framework.[21,27] Detailed analysis of the synthesis of gels with respect to Si-Al sequences performed for the first time in our laboratory allowed us to suggest mechanisms through which the individual synthesis parameters control the incorporation of Al atoms into the framework in the form of single Al atoms or Al-O-(Si-O)$_2$-Al sequences in one ring.[28] The obtained knowledge represented a base for development of the syntheses of zeolites with the desired distribution of framework Al atoms up to a larger scale under industry-like conditions.[29]

In the field of the distribution of Al atoms in Si-rich zeolites, it can be concluded that we introduced Al distribution as a key parameter into zeolite science, developed methods for Al analysis, demonstrated the significant effect of the distribution of Al atoms on the catalyst activity and rounded out our work by development of methods for tuning the Al distribution in zeolites up to a scale suitable for technical applications. Our knowledge and experience in this area was recently summarized in detail in a review paper by Ref..[21]

## 2.2. Definition of the distribution of framework Al atoms

Two types of Al species are most important for the coordination of metal ions and metal-oxo species in zeolites and are also the most populated in Si-rich zeolites: (i) Al-O-(Si-O)$_2$-Al sequences in one ring (denoted as Al pairs) and, (ii) single Al atoms in these Si-Al sequences that are able to charge-balance only monovalent ions or monovalent metal-oxo complexes.[21] In addition to these Si-Al sequences, the framework also contains other types of Si-Al sequences, but they are much less populated and will not be discussed in detail. The selection of types of Si-Al arrangements suggested here to describe the distribution of Al atoms in the framework is based on knowledge of the importance of specific types of distribution of Al atoms for the location and structure of the counter ion (proton or metal) species, and the methods available for analysis of the Al siting in the framework.

The arrangement of Al atoms in Al-O-(Si-O)$_n$-Al sequences represents the first approach to description of the Al arrangement in zeolites. There is only one strict rule for the aluminum distribution in the zeolite framework excluding

sharing of an oxygen atom by two $AlO_4$ tetrahedra.[57] Thus, *Al-O-Al sequences* are not present in the zeolite framework.

The closest Al atoms, *Al-O-Si-O-Al sequences,* are well-known for Al-rich materials, but are very rare in Si-rich frameworks.[21] On the other hand, close Al atoms of *Al-O-(Si-O)$_2$-Al sequences in one six-membered ring (6-MR)* (denoted *Al pairs,* $Al_{2Al}$) in Si-rich zeolites represent substantial and, in some Si/Al compositions, the predominant fraction of Al atoms.[21,24,25] The Al-O-(Si-O)$_3$-Al sequence can exist in an 8-MR in mordenite. The Al-O-(Si-O)$_3$-Al sequence is unique for the mordenite structure and exhibits the same properties as Al pairs in 6-MRs.[15,21] When occupied by the above sequences, the 6- and 8-MRs represent cationic sites for bare divalent cations bound exclusively to framework oxygen atoms in dehydrated zeolites.

*Al-O-(Si-O)$_n$-Al* with n=2 or 3 with Al atoms *located in different rings* is also a possibility for the distribution of Al atoms. This is the only condition for these Al atoms, albeit there is no way of differentiating amongst the numbers of $(Si-O)_n$ groups. If close enough, the Al-O-(Si-O)$_{2,3}$-Al sequences with Al atoms in the different rings can balance the charge of the divalent hexaquo-complex in hydrated zeolites, whereas they are unable to coordinate bare divalent cations in dehydrated zeolites.[8,18,21] The arrangement of Al atoms in the zeolite is schematically depicted in Figure 1.

Two Al atoms separated by a large number of Si atoms in the Al-O-(Si-O)$_n$-Al chain (n > 3) can also exhibit rather short inter-atomic distances. In contrast, when the two Al atoms of the Al-O-(Si-O)$_{2,3}$-Al sequence are separated by a zeolite wall consisting of a double $TO_4$ layer, despite the short distance between these Al atoms, they will behave as single Al atoms unable to coordinate a divalent cation, but only monovalent species.

The *visible distance of Al atoms* is defined as a sufficiently short geometric distance (Al-O-(Si-O)$_{1,2}$-Al in one ring and Al-O-(Si-O)$_n$-Al in different rings), but excluding two close Al atoms separated by the double-layer wall. The visible distance of two Al atoms represents an important parameter, which affects the accommodation and properties of the polyvalent counter-ion species, and cooperation of two close monovalent centers. These facts also suggest that this siting/distribution of the Al atoms could to some extent be monitored indirectly by using the specified counter ions as probes.

*Unpaired Al atoms* ($Al_{UNPAIR}$) include two Al atoms located in different rings, close enough to balance a hexa-aquo complex of divalent $Co^{2+}$ cation, i.e. at a visible distance, but unable to accommodate bare divalent ions.[21]

*Single Al atoms* ($Al_{1Al}$) represent the opposite of close Al atoms in various Al-O-(Si-O)$_n$-Al sequences with consideration of their location in a single ring or in different rings at geometrical and visible distances. Single Al atoms are understood to be two distant Al atoms (distant local charges), each exclusively

balanced by a monovalent cation. A single Al atom is separated from another Al atom by a long $(Si-O)_n$ sequence with $n > 2$ or the interaction of their counter ions is geometrically restricted. Their population cannot be experimentally determined and is calculated from the balance of framework Al atoms.[21]
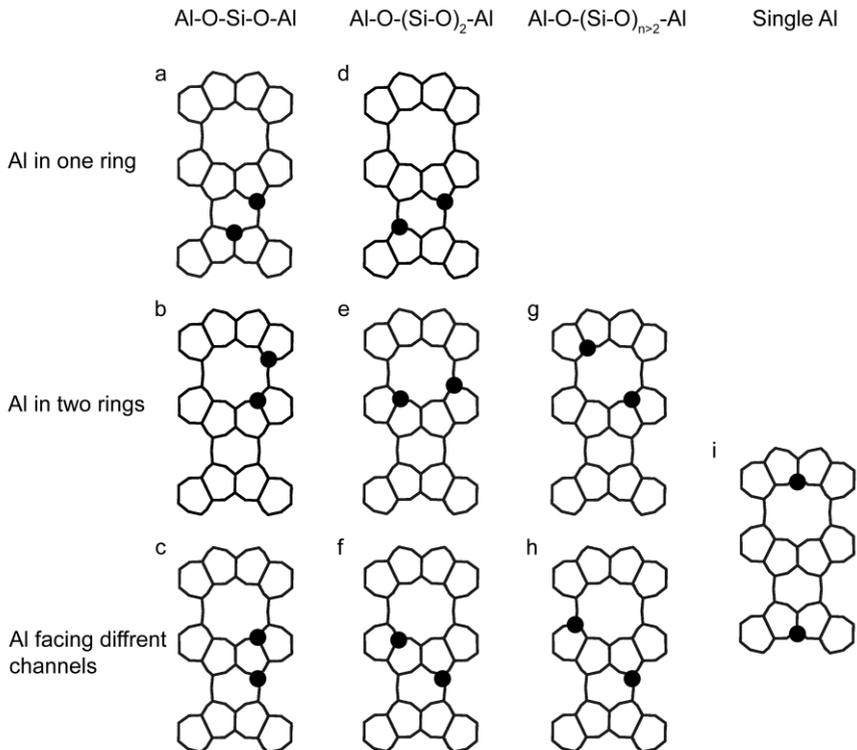


**Figure 1.** Variability of the distribution of Al atoms in the framework of Si-rich zeolite. Al-O-Si-O-Al sequences (a-c), Al pair (d), Al-O-(Si-O)$_{n>1}$-Al sequences with Al in different rings (e - h), unpaired Al atoms (b, e, g), and single Al atoms (f, h, i).

## 2.3. Analysis of the distribution of Al atoms and siting of Al pairs in the framework

$^{29}$Si MAS NMR allows identification of only Al-O-Si-O-Al sequences, which are not present in Si-rich zeolites.[21] We employed our experience in the characterization of metallo-zeolites to develop a method enabling analysis of the distribution of Al atoms between Al pairs and single Al atoms in Si-rich zeolites. The $Co^{2+}$ ions were used as a probe of the distribution of the Al atoms in the

framework as they exhibit: (i) high stability of their valence state, both in solution and in the dehydrated zeolite, (ii) low tendency towards complexation in solutions, which enables us to prepare aqueous solutions with the exclusive presence of $[Co^{2+}(H_2O)_6]^{2+}$ complexes coordinated to the zeolite framework and, (iii) characteristic d-d spectra of $Co^{2+}$ ions coordinated in zeolites composed of a large number of transitions in the Vis region unambiguously reflecting changes of their coordination.[15] In Si-rich zeolites, $Co^{2+}$ ions exhibit highly unusual but characteristic coordinations that have never been reported for other compounds. These coordinations result from specific arrangement of the zeolite framework and reflect the location of the Al pairs,[15-18,45-48,58-65] see Section 3.

The *single Al atoms* are those which could not accommodate the $[Co^{2+}(H_2O)_6]^{2+}$ complex. Their molar concentration, $[Al_{1Al}]$, is given by relationship:

$$[Al_{1Al}] = [Al_{FR}] - 2\,[Co^{2+}(H_2O)_6] \qquad\qquad (EQ\ 1)$$

where $[Al_{FR}]$ is the concentration of framework Al atoms and $[Co^{2+}(H_2O)_6]$ represents the maximum concentration of $[Co^{2+}(H_2O)_6]^{2+}$ complex in the zeolite. The concentration of $Co^{2+}(H_2O)_6$ is obtained by chemical analysis and the maximum loading of the zeolite by $[Co^{2+}(H_2O)_6]^{2+}$ is reached by its repeated equilibration with $Co^{2+}$ nitrate solution. The exclusive presence of $[Co^{2+}(H_2O)_6]^{2+}$ complexes both in the solution and in the exchanged zeolite, monitored by Vis spectroscopy,[15] is guaranteed by an $Co^{2+}$ concentration in solution of less than 0.1 mol/l, the ambient temperature and the Na-form of the parent zeolite.[21,24,25]

The concentration of Al atoms in *Al pairs*, $[Al_{2Al}]$ is given by the equation:

$$[Al_{2Al}] = 2\,([Co_\alpha] + [Co_\beta] + [Co_\gamma]) \qquad\qquad (EQ\ 2)$$

where $[Co_\alpha]$, $[Co_\beta]$ and $[Co_\gamma]$ are the molar concentrations of the bare Co ions in the $\alpha$-, $\beta$- and $\gamma$-type sites of mordenite, ferrierite, ZSM-5 and beta zeolites. Quantitative analysis of the d-d spectra of bare $Co^{2+}$ ions of the maximum $[Co^{2+}(H_2O)_6]^{2+}$-exchanged and dehydrated zeolite in the Vis region are characteristic for the individual cationic sites; the extinction coefficients of $Co^{2+}$ were reported elsewhere,[15-18] see Section 3. The use of bare $Co^{2+}$ as a probe for Al pairs is based on our assumption that bare $Co^{2+}$ ions are accommodated in dehydrated zeolites exclusively in rings containing two Al atoms, while unpaired Al atoms were suggested to accommodate Co-oxo species formed due to the high reactivity of $Co^{2+}$ ion in the vicinity of one Al atom in rings.[21,24,25] This assumption was based on the similar properties of $Co^{2+}$ ions in Al- and Si-rich zeolites and was confirmed by theoretical calculations and our observation of predicted Co-oxo

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species in ZSM-5, MCM-22 and beta zeolites.[8,18,21,27,44,66] As Al-O-Si-O-Al sequences are not present in Si-rich zeolites, six-membered rings (6-MR) represent a majority of the cationic sites in these zeolites.

The concentration of ***unpaired Al atoms*** (accommodating the $[Co^{2+}(H_2O)_6]^{2+}$ complex, but not bare $Co^{2+}$ ions) is given by the equations:

$$[Al_{UNPAIRED}] = 2\,[Co^{2+}(H_2O)_6] - [Al_{2Al}] \hspace{2cm} (EQ\ 3)$$

$$[Al_{UNPAIRED}] = 2\,[Co^{2+}(H_2O)_6] - 2\,([Co_\alpha] + [Co_\beta] + [Co_\gamma]) \hspace{1cm} (EQ\ 4)$$

Bare $Co^{2+}$ ions in dehydrated zeolites with maximum loading of $Co^{2+}$ ions (evacuated at 450 $^{o}$C), monitored by Vis spectroscopy, were successfully used as a probe for the ***location of Al pairs***. The d-d spectra of bare $Co^{2+}$ ions in the Vis region of the dehydrated zeolites are characteristic for the individual cationic sites as the energy of the d orbitals of the $Co^{2+}$ ions is highly sensitive to the local arrangement of the ligand field stemming from the topology of the cationic site. The cationic sites of $Co^{2+}$ ions with similar d-d spectra were identified for the individual zeolite topologies in analogy with the arrangement of the $Co^{2+}$ sites in mordenite.[15] The siting of $Co^{2+}$ ions in mordenite was suggested on the basis of the known siting of non-transition divalent cations in this zeolite and the d-d spectra corresponding to the $Co^{2+}$ ions were identified by employing the effect of various mono- and divalent co-cations with known preferred siting on the spectra of CoM-mordenite (M = Ba, Ca, H, Na, K, Rb, Cs).[59-65] Three cationic sites, denoted as the α-, β- and γ-types, were distinguished for each of the mordenite, ferrierite, ZSM-5 and beta zeolites and 6-MRs of these sites accommodated Al pairs (the 8-MR of the β-site of mordenite is an exception).[15-17,19,20,42] Nevertheless, the Al atoms of the Al pairs in the individual T sites of the 6-MR can be exactly located only for the α-site of ferrierite, which exhibits high symmetry.[34] In other cases, combination of Vis spectroscopy and $^{27}$Al MAS NMR must be employed. Knowledge of the location of the Al pairs in 6-MRs enables a decrease in the number of Al pairs for which the $^{27}$Al isotropic chemical shift has to be calculated to an acceptable number.[34]

## 2.4.    Distribution of Al atoms and siting of Al pairs in zeolites

The Al-O-Si-O-Al sequences are not present in Si-rich zeolites.[21] The majority of Al atoms in the framework of Si-rich zeolites represent Al pairs and single Al atoms, which are complementary Al species, while unpaired Al corresponds to only a minor part of the Al.[21]

***ZSM-5 MCM-22***,f***errierite, mordenite and the beta zeolite*** with the same content of framework Al for the individual zeolites dramatically differ in the concentration of Al pairs and single Al atoms for a wide range of Si/Al compositions.[21,24-29,44]

**Table 1**. Maximum concentrations of Al in Al-O-(Si-O)$_2$-Al sequences in one ring (Al$_{2Al}$) and single Al atoms (Al$_{1Al}$) for selected zeolites and Si/Al molar ratios.

| zeolite | Si/Al | max. Al$_{2Al}$ | | max. Al$_{1Al}$ | |
|---|---|---|---|---|---|
| | | Al$_{2Al}$ (rel. %) | Al$_{1Al}$ (rel. %) | Al$_{2Al}$ (rel. %) | Al$_{1Al}$ (rel. %) |
| ZSM-5 | 12 | 84 | 16 | 10 | 90 |
| | 30 | 60 | 40 | 6 | 94 |
| Ferrierite | 10 | 66 | 34 | 20 | 80 |
| Beta | 15 | 65 | 35 | 39 | 61 |
| MCM-22 | 40 | 68 | 32 | 18 | 82 |

The maximum populations of Al pairs and single Al atoms for various Si/Al compositions and zeolites are given in Table 1.

Although higher concentrations of Al might be expected to result in higher concentrations of Al pairs, zeolites with Si/Al from 12 to 15 can contain a predominant population of single Al atoms, up to 96 %, and those with a low concentration of Al (Si/Al 30 – 40) can exhibit predominant concentrations of Al pairs. Typically, for one synthesis procedure (composition and conditions), the concentration of Al pairs increases, but not proportionally, to increasing Al concentration in the zeolite; nevertheless, quite the opposite effect of the concentration of Al on the formation of Al-O-(Si-O)$_2$-Al sequences has also been observed. Such dramatic differences in the distribution of Al atoms in the framework again clearly indicate that the Al siting in the zeolite is not random and not controlled by statistical rules. The reactivity of the synthesis mixtures is responsible for the observed distribution of Al atoms between Al pairs and single Al atoms, as discussed in Par. 2.5.

In contrast to ZSM-5, ferrierite and MCM-22 with, at the most, a negligible amount (< 4 %) of unpaired Al atoms in the framework, reflected in the formation of bridging Co-oxo species, unpaired Al atoms represent a significant fraction (> 20 %) of the Al in some beta zeolites. Co-oxo species balancing these unpaired Al atoms cannot be detected by any spectroscopic method and their presence is indicated only from the difference between the Co loading and the concentration of bare Co$^{2+}$ ions monitored by Vis and FTIR spectroscopy.[8,28,67] These unpaired Al atoms easily dealuminate, yielding beta zeolites with Si/Al$_{FR}$ of 20 – 24, and a negligible population of close Al atoms.

The above results provide clear evidence that the distribution of Al atoms in Si-rich zeolites is not random or controlled by some simple rules but that zeolites with the same framework Al content can exhibit different distributions of Al atoms. Moreover, as follows from the variability in the Al distribution observed for ZSM-5, practically monomodal presence of Al pairs or single Al atoms

A
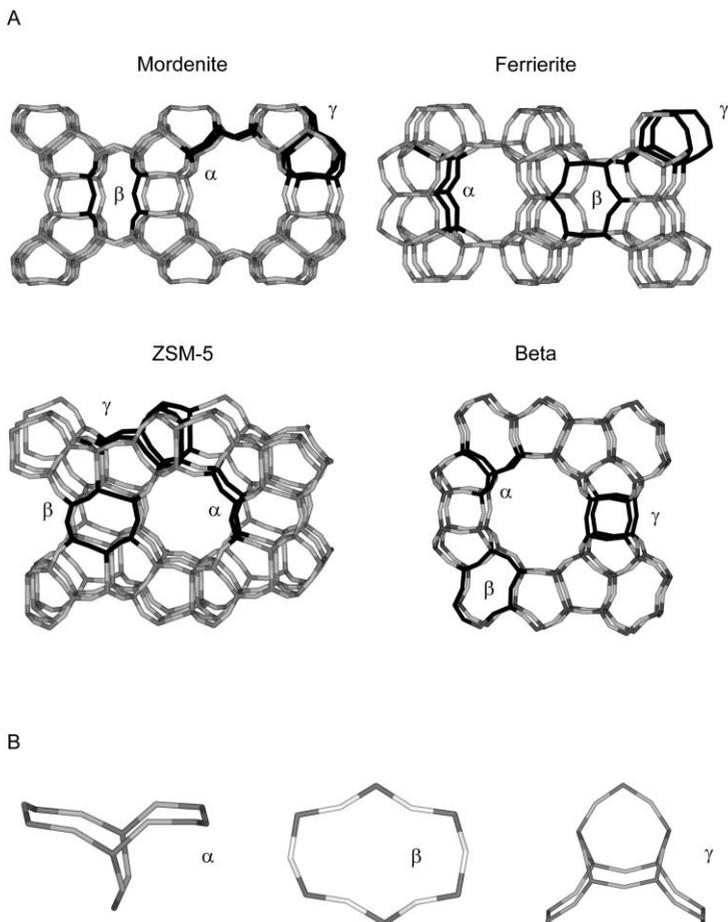


Figure 2. The rings of the α-, β- and γ-type sites in the framework of mordenite, ferrierite, ZSM-5 and beta zeolites (A), and detail of the α-type site in mordenite , β-type site in the beta zeolite, and γ-type site in ferrierite (B).

(resulting in dramatically different properties of these zeolites, see below) can be attained even for zeolites with Si/Al ratio close to the limiting value of 12.[21]

**_Three cationic sites of the α-, β- and γ-types_** containing Al pairs were suggested for mordenite, ferrierite, ZSM-5 and beta zeolites,[15-18,21] Figure 2.

The α-type 6-MR is twisted and composed of two 5-MRs and is located in the main channels of mordenite, ferrierite, and ZSM-5 and in the beta cage of the BEA framework. The twisted 8-MR of the mordenite pocket is arranged so as to form a planar β-type ring of six oxygen atoms. Al can then also be located in the

Al-O-(Si-O)$_3$-Al sequence in one ring, which cannot be distinguished by its properties from the Al pairs and will be described here for simplicity as an Al pair. In ferrierite, a planar 6-MR of the β-type is located in the ferrierite cavity while, in ZSM-5 and beta zeolites, this planar 6-MR is located at the channel intersections of ZSM-5 and forms the beta cage in the beta zeolite. The γ-type site corresponds to a complex boat-shaped structure, composed of several 5- and 6-MRs. It is located in the mordenite pocket, in the ferrierite cavity, in the sinusoidal channel of ZSM-5 and in the beta cage of the BEA structure. The location of the Al atoms has not yet been elucidated in detail in the γ-type rings.

In **ZSM-5, ferrierite, mordenite, and beta zeolit**es, depending on the conditions of the hydrothermal synthesis, the Al-O-(Si-O)$_2$-Al sequences in the β-type 6-MR (8-MR in mordenite) predominate in these structural types and represent 60 – 85 % of the Al pairs in these zeolites. The α-type 6-MR contains a substantially lower concentration of Al pairs, but with significant variability from 10 to 38 % of the Al pairs. The concentration of the Al pairs in the γ-type rings is low and varies from 2 - 12 % of the Al pairs.[21,24-26,28] The distribution of the Al pairs among the α-, β- and γ-rings does not reflect the population of the corresponding rings in frameworks with different topologies. While two β-type 6-MRs correspond to one α-type 6-MR in ZSM-5, this relationship is the opposite in ferrierite.[21] It is thus suggested that the mechanism of synthesis and the composition of the synthesis gel control the distribution of the Al-O-(Si-O)$_2$-Al sequences in the individual rings of the cationic sites in Si-rich zeolites.

## 2.5.    Control of the distribution of Al atoms in the framework by the zeolite synthesis

The distribution of framework Al atoms in zeolites is a result of the interplay of Si-Al/structure directing agents (SDA)/inorganic cations/anionic species/pH present in the synthesis gel. Their mutual interactions already occur in the initial gels and are further developed during crystallization under hydrothermal conditions. We found for ZSM-5 that practically all the parameters of the zeolite synthesis (Al and Si source, presence of inorganic co-cations, anions, sequence of mixing of components of the synthesis gel and gel ageing, presence of co-solvent) affect the distribution of Al in the framework and the distribution of Al atoms can be tailored in a wide population range of Al pairs and single Al atoms in the framework,[21,26,28] see Table 2.

The preferential formation of single Al atoms in the framework is a result of the use of Al nitrate and Na silicate as Si and Al sources, the additional presence of Na$^+$ cations and minimized aging of the synthesis gel. The formation of Al pairs is connected with Al chloride and tetraethyl orthosilicate as Si and Al sources, aging of the synthesis mixture and addition of an Al source in the final stage of preparation of the mixture instead of prior to the addition of SDA. The analysis

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**Table 2.** Synthesis of ZSM-5 of various distribution of framework Al atoms depending on the synthesis gel composition.

| gel | Si/Al$_{gel}$ | Si/Al$_{prod}$ | Al$_{2Al}$ | Al$_{1Al}$ | Al$_{UNPAIR}$ | Al$_{2Al}$ in | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | α | β | γ |
| | | | (%) | (%) | (%) | (%) | (%) | (%) |
| Al(NO$_3$)$_3$+TEOS | 30 | 27 | 6 | 94 | 0 | | n.a. | |
| Al(OH)$_3$+TEOS | 22 | 43 | 37 | 62 | 1 | 22 | 72 | 6 |
| AlCl$_3$+TEOS | 30 | 21 | 40 | 58 | 2 | 28 | 60 | 3 |
| AlCl$_3$+TEOS+NaCl | 30 | 23 | 15 | 84 | 1 | 13 | 78 | 9 |
| AlCl$_3$+TEOS+NaOH | 30 | 22 | 46 | 54 | 0 | 17 | 72 | 11 |
| Al(NO$_3$)$_3$+Na-SIL | 30 | 14.5 | 8 | 92 | 0 | | n.a. | |
| AlCl$_3$+Na-SIL | 30 | 16.5 | 4 | 96 | 0 | | n.a. | |

Al$_{1Al}$ – single Al atoms, Al$_{2Al}$ – Al in Al-O-(Si-O)$_2$-Al in one ring, Al$_{UNPAIR}$ – unpaired Al atoms accommodating [Co$^{2+}$(H$_2$O)$_6$]$^{2+}$.

of the synthesis mixtures by multinuclear MAS NMR combined with the distribution of Al atoms in the resulting zeolites enabled us to describe mechanisms leading to the different distribution of Al atoms. We suggested two parameters/mechanisms which lead to variability of the Al atom distribution: (i) the reactivity of the synthesis gel or its components resulting from the pre-organized organic-inorganic composite around SDA formed in the initial stage and (ii) interaction of SDA and the inorganic co-cation with Si-Al species during crystallization, which leads to different distribution of Al atoms even in zeolites prepared from the same organic-inorganic composite around SDA.

Ad (i) The presence of highly reactive Al species not fully networked in the Si-Al gel in the synthesis mixture allows incorporation of single Al atoms in the Si(Al)/SDA protozeolitic unit. For full Si-Al networking in the synthesis mixture, typically reflected in the formation of a dense gel, larger building blocks take part in the formation of the Si(Al)/SDA protozeolitic unit and the Al arrangement in the Si-Al amorphous network is decisive for the distribution of Al in the zeolite. A high concentration of close Al atoms in the synthesis gel leading to a high concentration of Al pairs can be obtained by addition of an Al source to the Si/SDA mixture when the number of Si atoms available for Si-Al networking is limited or by ageing the gel, leading to a greater degree of networking, stabilizing entities with close Al atoms against their dissolution during the formation of the Si(Al)/SDA protozeolitic unit.

Ad (ii) Polarization of the SDA was reported to be essential for the formation of a zeolite protozeolitic unit. We suggested that the degree of polarization of the SDA (TPA$^+$ in our case) represents a decisive parameter for the

incorporation of a single Al atom or Al pair into the protozeolitic unit. A high degree of polarization, resulting in a higher partial positive charge of the N atom of TPA$^+$ enables accommodation of the Al pair in the vicinity of the N atom in the Si(Al)/SDA protozeolitic unit, while a low degree of polarization promotes accommodation of a single Al atom. Our results showed that the different polarization abilities of inorganic anions (NO$_3^-$ and Cl$^-$) controls the polarization of the SDA and thus the incorporation of Al pairs (high polarization by Cl$^-$) and single Al atoms (low polarization by NO$_3^-$). The presence of an inorganic co-cation (Na$^+$) is an additional parameter related to the interaction of Si-Al species and SDA. In contrast to the above interaction of Si-Al species and SDA, the Na$^+$ cation can balance the negative charge of the Al-Si species and allows location of Al in other positions than in the vicinity of the N atom of the SDA. A dramatic increase in the number of single Al atoms in the zeolite can be achieved by preferential accommodation of Al-Si species with one Al atom in the protozeolitic unit in the vicinity of the Na$^+$ cation or by incorporation of an Al pair with one Al atom balanced by SDA and another one by the Na$^+$ cation at a position separating the Al atoms of the Al pair by the ZSM-5 wall.[28]

These conclusions were also confirmed for other Si-rich zeolites such as ferrierite and the beta zeolite. Understanding of the mechanisms governing the arrangement of Al atoms in the framework enabled us to develop the syntheses of zeolites with controlled distribution of framework Al atoms suitable for larger scale syntheses.[29] This opens the way for tuning the properties of zeolite catalysts leading to their higher activity and selectivity.

## 2.6.  Relationship of the distribution of Al atoms and the properties of zeolites

The presence and distribution of Al atoms in the zeolite framework can be more or less directly connected with all the zeolite properties, starting from the framework stability up to the transport properties. Studies have been centered on the structural stability and catalytic properties of zeolites that are unambiguously attributable to the distribution of Al atoms in their frameworks.

The isomorphous substitution of the Al atom into the Td coordinated silicate framework can be regarded as a perturbation of the T-O-T bonds owing to the longer Al-O bonds in AlO$_4$ tetrahedra compared to the SiO$_4$ tetrahedra. This perturbation is largest when AlO$_4^-$ is charge-balanced by a proton, and mostly or completely suppressed by the presence of monovalent or divalent counter cations. Accordingly, the high-temperature treatment of Si-rich zeolites in an H-form, in contrast to metal-zeolites, can result in substantial perturbation leading to opening of the Al-O bonds during zeolite dehydroxylation. If the dehydroxylation is reversible, "framework" electron-acceptor Al$_{FR}$-Lewis sites are considered to be formed, while the irreversible effect is connected with release of the Al atom from

the framework T site, i.e. zeolite dealumination.[68-71] Both perturbations can exhibit a dramatic impact on the properties of zeolite catalysts. The concentration of proton sites is decreased and the formed $Al_{FR}$-Lewis sites enhance olefin oligomerization and hydrogen-transfer aromatization reactions, which usually lead to the undesirable formation of polyaromatic coke deposits. The instability of the Al atoms in the framework of Si-rich zeolites was generally suggested to be a result of the proximity of Al atoms in the framework. Nevertheless, the results for the dealumination of beta zeolites during SDA removal clearly showed that preferentially single Al atoms are released from their framework.[8,67] Moreover, reversible perturbation of the framework cannot be connected with the Al distances in zeolites.[21] In addition, the release of Al atoms from the framework as a result of chemical treatment was shown to be affected by the siting of the Al atoms in the T sites and not by the distribution of the Al atoms.[72,73]

The balance of the framework negative charge, originating from the individual T(Al) atoms, by protons results in the formation of structural bridging SiOHAl groups. The substantial difference in the acid strength between Al- and Si-rich zeolites is attributed to the mutual interactions of SiOHAl groups in Al-rich zeolites. This suggestion was supported by the calculated similar deprotonation energies of OH groups in the siliceous faujasite, ZSM-5, mordenite and ferrierite,[74] and by the increase in the acid strength of protons in Al-rich zeolites after their dealumination.[75] Contrary to this assumption, our results showed that the effect of the proximity of Al atoms in the Al-O-(Si-O)$_2$-Al sequence on the strength of the acid site is negligible, as there is no difference in the properties of adsorbed $H_2$ (77 K) in ZSM-5 between the protonic sites adjacent to single Al atoms and the Al-O-(Si-O)$_2$-Al sequences.[30]

Understanding the role of the distribution of Al atoms in the accommodation and formation of metal ion species in zeolites as well as its effect on the properties of these metal ion species is essential for understanding the catalytic properties of metallo-zeolites. In general, oxygen atoms of the zeolite framework neighboring the isomorphously substituted Al atom represent negatively charged ligands to counter–metal ion species exhibiting open coordination spheres (bare cations).[60] The individual framework rings bearing the Al atom(s) and their spatial distribution through the three-dimensional zeolite network determine the structure and coordination of the counter-ion species and their spatial arrangement. While, with Al-rich zeolites (Si/Al 1 − 3), the high local density of the framework Al atoms provides stabilization of up to trivalent bare cations and the Si-rich zeolites (Si/Al > 8) contain a high predominance both of Al-O-(Si-O)$_2$-Al sequences in 6-MRs and of distant single Al atoms, whose population governs the coordination of divalent or monovalent cation complexes. These complexes could correspond to bare cations as well as polyvalent cation-oxo complexes.[21] The formal ion-exchange capacity refers to the framework Al

content; nevertheless, the real capacity for divalent cation exchange in Si-rich zeolites depends on the distribution of Al atoms in the framework. In dehydrated zeolites, only rings with Al pairs accommodate bare divalent cations, while single Al atoms can be exclusively balanced by the monovalent cations (or protons) and formally monovalent complexes. Therefore, the structure of the resulting metal-ion species is determined by both these factors, the distribution of Al atoms in the framework and the metal-ion complexes formed during the ion exchange.[21] Evidence has been found for quite well-described species in metallo-zeolites, including bare divalent cations, charged metal-ligand complexes or metal-oxo species, including metal-oxo bridged species, depending on the conditions of their incorporation and calcination. The majority of the enormous volume of literature data analyzing the structure of metal-ion species by various spectral and diffraction methods deals only with the Si/Al ratio of the parent zeolite and the M(II)/Al composition of the product. Nonetheless, information on the distribution of Al atoms was absent and the possible occurrence of Al atoms in Al pairs and single Al atoms was a subject of speculation, without any experimental analysis. The broad spectrum of metal-ion species (analyzed for Cu, Co and Fe species) and diversity of the results did not provide straightforward elucidation of the structure of metallo-zeolites.

Thus, our results taking into account the parameter of the distribution of Al atoms in zeolites represent a breakthrough in the analysis of Si-rich metallo-zeolites. We provided evidence for the formation of quite well-described species including bare divalent cations, charged metal-ligand complexes or metal-oxo (bridged) species, depending on the Al distribution and conditions of metal ion incorporation into the zeolite. The relationship between the distribution of Al atoms, which controls the local charges of the framework rings decisive for the coordination of bare ions or various metal-oxo complexes, and the formation of metal ion species of various structures can be briefly described as follows: [21,27,41]

(i) Monovalent cations balance all the Al atoms, regardless of their location as Al pairs or single or unpaired Al atoms. The only restriction lies in the sizes of the cation and of the Al-containing ring. 6-MRs are too small to accommodate monovalent cations. Considerable stabilization of their valence state is a general feature of cations coordinated in sites with a single Al atom. For metals with mono- or polyalent cations, this results in significant preference for their monovalent state in sites with single Al atoms.[21,60]

(ii) In all Si-rich zeolites, bare divalent cations with significantly smaller diameters prefer siting in the 6-MRs but the key parameter for their location is the presence of an Al pair in the ring. A bare divalent cation in a ring containing a single Al atom is highly reactive and unstable. Bare trivalent cations do not occur in Si-rich zeolites (SiAl > 8), as the absence of Al-O-Si-O-Al sequences excludes the presence of three Al atoms in the 6- or 8-MRs. The Al distribution in the ring,

in combination with the ring geometry, results in unexpected coordination arrangements not known from the coordination chemistry of either liquids or solids.[15-20] In the α-site, the cation exhibits an extremely open coordination sphere on one side, coordinated to four framework oxygen atoms and located at the top of a pyramid with an oblong base. For the β-site, the cations exhibit an open coordination sphere with planar coordination available from both sides. The cations are coordinated to three or four framework oxygens forming a highly irregular only approximately planar geometric shape. Only cations in the γ-site can be attributed to the pseudo-octahedral coordination with close coordination sphere, described in the literature. Nevertheless, the concentration of cations in the γ-site is usually low. The high flexibility of the T-O-T angle in the zeolite framework enables optimization of the geometry of the framework rings of the cationic sites to preserve the preferred metal-oxygen distance of the metal ion coordinated to the framework oxygen atoms, as follows from the $Co^{2+}$-framework oxygen distance of approx. 0.2 nm in different cationic sites of mordenite, ferrierite and ZSM-5.[19,20] The perturbation of the T-O-T angles and thus of the geometry of the zeolite rings by coordination of the divalent cation is reflected in the characteristic perturbation of the anti-symmetric T-O-T vibration.[76-78] As the cations are coordinated to $AlO_4$ tetrahedra, preservation of the metal-oxygen distance can result in the perturbation of the framework rings of the cationic sites.[50,79] A typical feature of bare divalent cations coordinated in the site with an Al pair is their high resistance to reduction. The reduction of bare divalent cations not exhibiting a monovalent state ($Co^{2+}$, $Fe^{2+}$) takes place only at high temperatures (~ 900 $^{o}C$) connected with the degradation of the zeolite framework.[21]

(iii) Monovalent complexes of divalent metal-oxo species can be balanced by single Al atoms. Decisive parameters for the formation of these species consist in the concentration of the metal ions in the zeolite and the conditions of their incorporation into the zeolite. Monovalent metal-oxo species of divalent cations are formed only at metal loadings at which all sites with Al pairs are occupied. In this case, the formally monovalent species were proposed to be coordinated to different rings containing single Al atoms or to one ring containing an Al pair. These species are readily reducible to the monovalent state balanced by a single Al atom and exhibit oxidation activity for various redox processes.[27,41,80] The trivalent cations could be stabilized as formally mono- and divalent complexes balanced by single Al atoms or Al pairs, respectively.[21]

(iv) Divalent metal-oxo species can also occur as balanced by an Al pair. Decisive parameters for their formation consist in the concentration of Al pairs and the conditions for their incorporation into the zeolite.[21] It is speculated that the oxygen atoms of these stable metal-oxo species exhibit unique activity in selective incorporation of an oxygen atom into hydrocarbons.[21,81,82]

(v) The bridged metal-oxo or metal-hydroxo species require the presence of at least two Al atoms at an optimum distance in the zeolite channel. Three types of the formed bridging structures can be suggested. The bridge can be formed from two originally bare divalent cations, by monovalent cations or monovalent complexes or directly from the binuclear charged complex. Accommodation of such species in the zeolite requires the cooperation of two Al pairs, two single Al atoms or one Al pair and one single Al atom in a proper arrangement/distance in dependence on the structure of the bridging species.[8,21,67] The bridging metal-oxo species, similarly to non-bridged metal-oxo species, are much more readily reduced than bare cations. It is evident that the distribution of the Al atoms is a decisive parameter for the formation of bridging oxo-species in zeolites which is, however still poorly understood.[83,84]

## 2.7.     Distribution of Al atoms and catalytic activity of zeolites

The location of two Al atoms in the 6-MR (Al pair) leads to the presence of *two close protonic sites* in one ring. It is evident that cooperation of two acid sites in acid-catalyzed reactions might result in a different reaction pathway compared to the isolated proton of a single Al atom reflected in different activity/selectivity/stability of the zeolite catalyst. Demonstration of this effect requires that the other zeolite parameters (concentration of Lewis acid sites and acid sites on the external surface, crystal size and morphology) be kept constant. Our achievements in controlling the distribution of Al atoms in zeolites led to a pioneering work in demonstration of the significance of the distribution of Al atoms for acid catalysis over zeolites. We have shown that olefin cracking is preferentially connected with protons of single Al atoms, and the vicinity of two protonic sites of the Al pair supports oligomerization and hydrogen transfer reactions.[30] The significance of Al distribution for acid-catalyzed reactions has recently been adopted in the field of complex acid-catalyzed reactions of hydrocarbons, an important part of industrial catalytic processes.[85,86]

The distribution of the negative charge in the zeolite framework is strictly local and thus the distribution of Al atoms between *Al pairs and single Al atoms* representing the most important framework Si-Al arrangement is essential in relation to metallo-zeolite catalysts. The 6-MRs containing Al pairs are essential for the accommodation of bare divalent cations in Si-rich zeolites and a predominant sequence with two close Al atoms in Si-rich zeolites controlling the incorporation of polyvalent cations into the zeolite and their redox and catalytic behavior. Compared to cations supported on inorganic carriers, the divalence of bare cations (Cu and Co) in zeolites is highly stabilized when compensated by two framework negative charges of Al pairs in the ring.
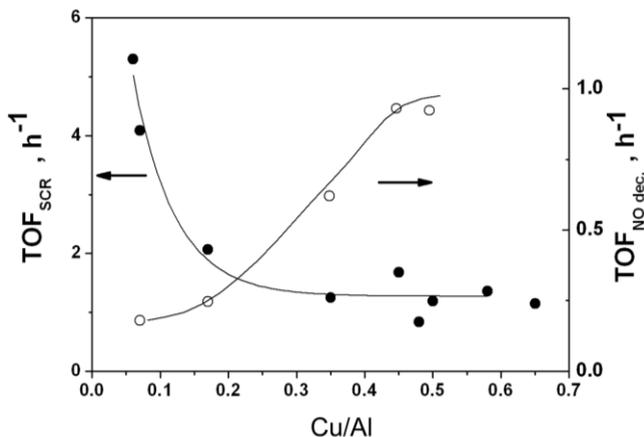
**Figure 3.** Dependence of NO conversion in $C_{10}H_{22}$-SCR-NO and NO decomposition on Cu loading in Cu-ZSM-5. Reaction conditions: $C_{10}H_{22}$-SCR-NO - 1000 ppm NO, 450 ppm $C_{10}H_{22}$, 6% $O_2$, 12 % $H_2O$, 250 °C and GHSV 30000 h$^{-1}$; NO decomposition – 4000 ppm NO, 400 °C and GHSV 15000 h$^{-1}$.

The $Cu^{2+}$ ions coordinated to 6-MRs containing ***Al pairs*** are the most active sites in the $C_{10}H_{22}$-SCR-NO$_x$ reaction over Cu-ZSM-5. This follows from the superior activity of Cu-ZSM-5 with predominant Al pairs in the framework compared to those with the same composition but with predominant single Al atoms, see Figure 3. This complex reaction consists of oxidation of NO to $NO_2$ and of a hydrocarbon with NO$_x$. The high activity of $Cu^{2+}$ ions stabilized in the 6-MRs with two Al atoms even in the presence of a large excess of water vapor at low (280 $^o$C) temperature is attributed to the strong adsorption of an oxygenated intermediate of long hydrocarbon products on the $Cu^{2+}$ sites protecting them against water adsorption.[27,43] The $Co^{2+}$ ions in Co-ZSM-5 and Co-ferrierite containing highly predominant Co ions coordinated to 6-MRs with Al pairs behave as Lewis sites. As strong electron acceptor sites, they activate methane, the crucial step in CH$_4$-SCR-NO$_x$ reaction, as indicated by the increasing conversion of CH$_4$-SCR-NO$_x$ with an increasing degree of Co ion exchange. High catalytic activity was connected with $Co^{2+}$ ions in the β-site of ZSM-5 and α-site of ferrierite. This indicates the cooperation of the $Co^{2+}$ Lewis centers with another catalytic/sorption center. The distance between the $Co^{2+}$ Lewis center and the other site is controlled by the arrangement of the surroundings of the individual sites, which is different in ferrierite and ZSM-5.[87,88] Similarly to CH$_4$-SCR-NO$_x$ over Co-zeolites, bare $Co^{2+}$ ions in 6-MRs with Al pairs in the beta zeolite exhibited high activity in $C_3H_8$-SCR-NO$_x$. The activity of Co-beta zeolite in $C_3H_8$-SCR-NO$_x$ in the absence of water vapor can be attributed to $Co^{2+}$ ions in the β-site. $Co^{2+}$ ions exhibit an open

coordination sphere exposed to crossing of the 12-MR channel of the beta zeolite. The negligible activity of the $Co^{2+}$ ions in the $\alpha$-site can be explained by their limited accessibility.[8] However, as bare $Co^{2+}$ ions are strong Lewis sites, the presence of water vapor in the $NO_x$ stream completely suppresses the activity in both the $CH_4$- and $C_3H_8$-SCR-$NO_x$ reactions,[8,67] see Table 3. Bare $Fe^{2+}$ ions located in 6-MRs with Al pairs are undoubtedly responsible for $N_2O$ decomposition over Fe-zeolites. These $Fe^{2+}$ ions predominate in Fe-zeolites at low Fe loadings (Fe/Al < 0.1) when introduced by a procedure preferring the accommodation of Fe ions in rings with Al pairs and resulting in comparable activity in $N_2O$ decomposition over Fe-BEA and Fe-ZSM-5.[27,50,51,54,55,89]

**Table 3.** $CH_4$-SCR-NOx and $C_3H_8$-SCR-NOx in the absence and presence of water over Co-zeolites.

| Paraffin | Zeolite | $M/Al_{FR}$ | $c_{NOx}$ | $C_{paraffin}$ | $C_{H2O}$ | $Yield_{N2}$ |
|----------|---------|-------------|-----------|-----------------|-----------|--------------|
| | | | (ppm) | (ppm) | (vol. %) | (%) |
| $CH_4$ | Co-ZSM-5 | 0.46 | 900 | 1200 | 0 | 78 |
| | | | | | 10 | 0 |
| $CH_4$ | Co-ferrierite | 0.42 | 900 | 1200 | 0 | 92 |
| | | | | | 10 | 0 |
| $C_3H_8$ | Co-beta | 0.46 | 1000 | 1000 | 0 | 48 |
| | | | | | 10 | 11 |
| $C_3H_8$ | Co-beta* | 0.42 | 1000 | 1000 | 0 | 90 |
| | | | | | 10 | 91 |

In contrast to rings with two Al atoms stabilizing the divalent state of the metal ions, cations located in the vicinity of ***single Al atoms*** can be assumed to be readily reducible when the monovalent state of the cation is able to exist. The preferred monovalent state of Cu ions in zeolites with a single Al atom facilitating the $Cu^{2+}/Cu^+$ redox cycle can be reflected in a much higher activity in NO decomposition of the Cu ions in ZSM-5 with predominating single Al atoms compared to those with similar Cu/Al/Si composition, but with highly predominant Al pairs, see Fig. 3. The negligible activity of $Cu^{2+}$ ions stabilized in the 6-MRs with two Al atoms in Si-rich zeolites further follows from the low activity of Cu-ZSM-5 with low Cu loadings, where rings with Al pairs are preferentially occupied by $Cu^{2+}$ ions. The $Cu^{2+}$ ions are increasingly exchanged into the vicinity of single Al atoms in the form of monovalent $[Cu^{2+}(H_2O)_5X^-]^+$ complexes, mainly at higher Cu loadings. It can be assumed that they are auto-reduced to $Cu^+$ during the catalyst dehydration. This assumption is in sound agreement with the practically inactive Cu ions in the Al-rich faujasites in NO decomposition in which

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reduction of $Cu^{2+}$ ions does not occur, as they are balanced by close Al atoms.[12,13,27,35,41,42,49,90]

The Si-rich zeolites could also accommodate monovalent Co-oxo species coordinated to rings with single Al atoms. In contrast to the bare $Co^{2+}$ ions, the Co-oxo species do not represent Lewis centers, which are highly sensitive to adsorption of water vapor at the reaction. The resistance of the active Co-oxo-species against water vapor has been manifested for $C_3H_8$-SCR-$NO_x$ over the Co-beta zeolite. While the activity of bare $Co^{2+}$ ions in CoH-BEA is high only in the absence of water in the reactant stream and disappears under conditions close to real $NO_x$ streams (10 % water vapor in the presence of 1000 ppm of $NO_x$), the Co-beta zeolites with Co-oxo species balanced by single Al atoms exhibit high and stable activity. The crucial role of single Al atoms for the formation of Co-oxo species has been demonstrated by synthesis of the beta zeolite containing predominantly single Al atoms in the framework. The obtained high concentration of Co-oxo species bonded to rings containing single Al atoms provided the Co-beta catalyst with high activity preserved even in the presence of a large excess of 10 % water vapor.[8,27,67]

It can be summarized that the results for the distribution of Al atoms in the framework demonstrate the potential for its manipulation by varying the conditions of zeolite hydrothermal synthesis and its decisive effect on the activity of metallo-zeolites.[21] This encourages us to suggest the crucial effect of the distribution of framework Al atoms on the activity and selectivity of zeolite catalysts and the necessity of inclusion of the analysis of the distribution of Al atoms in the rings coordinating the counter-ion species to complete the description of the structure of extra-framework counter-ion species accommodated in Si-rich zeolites. Control of the distribution of Al atoms in a wide range of framework Al concentrations and concentrations of Al pairs and single Al atoms supported by the knowledge of the related structure and properties of extra-framework species opens new possibilities for designing highly active, selective and stable catalysts.

## 3.     Siting of Al atoms in the framework of Si-rich zeolites
## 3.1.     Outline of the problem and strategy for its solution

In contrast to the distribution of Al atoms in zeolites, the siting of Al atoms in the zeolite framework attracted attention from the first syntheses of Si-rich zeolites, they all exhibit a larger number (> 4) of T sites of $Si(Al)O_4$ tetrahedra forming the unit cell of the zeolite. The idea of preferential, non-random siting of Al atoms was intuitively accepted by many researchers. However, the question of whether the Al atoms are distributed in the framework T sites randomly or according to some rules has remained unanswered for years. This was because of the absence of unambiguous methods for analysis of the siting of Al atoms. Although calculations of the stabilization energies of Al atoms in the framework T

sites exhibited differences between individual Al atoms, these differences were too low to confirm thermodynamic control of the Al siting.[91-94] The aspect of random or preferred siting of Al atoms in the framework has become even more important with the development of quantum chemical methods (QM/MM and periodic DFT), enabling realistic calculations of zeolite catalysts and providing insight into the properties of counter-ion species and catalytic processes over zeolites. Theoretical modeling confirmed that counter metal ions at different cationic sites, controlled by the siting and distribution of framework Al atoms, can result in quite different structures of the metal species and thus different pathways of catalytic reactions.

Developments in high resolution solid state NMR have brought a new, powerful method for analysis of Al atoms in zeolites – $^{27}$Al multiple quantum (MQ) MAS NMR, which permits minimization of difficulties in analysis of the Al environment caused by quadrupolar interactions.[95] However, even application of this highly sophisticated method has not elucidated the aspect of the siting of Al atoms, as interpretation of the experimental results was lacking.[72,73,96,97] The $^{27}$Al isotropic chemical shifts and experimental linear correlation between the average T-O-T angle of a T atom in the framework reported for Al-rich zeolites[98] could not be employed for interpretation of the $^{27}$Al MAS NMR spectra of Si-rich zeolites, not only because of their inexactness, but for fundamental reasons, see Paragraph 3.3. X-ray diffraction experiments also do not allow us to distinguish between Al and Si atoms, as the crystallographic data for Si-rich materials describe only the geometry of the $SiO_4$ tetrahedra and that of the $AlO_4$ tetrahedra is not known. In addition, the reported linear correlation between the geometric parameters of the $AlO_4$ tetrahedra and the $^{27}$Al NMR parameters seems rather improbable.[21]

The results indicating an unambiguously non-random, synthesis-driven distribution of Al atoms in Si-rich zeolites following from our previous studies (see Par. 2.3.), together with our results showing non-random location of Al pairs in zeolite rings (see par 3.3), led us to suppose that the siting of Al atoms in the framework T sites is also not random, but probably controlled by the kinetics of the synthesis process. To confirm this hypothesis, we directed our efforts in analysis of the siting of Al atoms in ZSM-5, the most important Si-rich zeolite, in two directions: (i) acquisition of a sufficient experimental data set for the synthesized zeolites and, (ii) development of an approach for highly accurate calculation of the $^{27}$Al NMR parameters for Al atoms located in the individual framework T sites in cooperation with Dr. Štěpán Sklenák of the Department of Theoretical Chemistry.

Ad (i) Only a large experimental data set of results on zeolites synthesized under different conditions can clearly provide evidence for the type of Al siting (random, controlled by thermodynamics, controlled by synthesis). To attain high accuracy of the analysis of the $^{27}$Al 3Q MAS NMR spectra, we improved the methods used for the 2D $^{27}$Al 3Q MAS NMR spectral analysis.[32,33]

Moreover, we focused only on zeolites not containing Al pairs because of our assumption that the vicinity of a second Al atom in the zeolite ring might affect the geometry of the framework Al site. This essential assumption was later confirmed by both the theoretical study and by experiments.[34,99,100]

Ad (ii) As the NMR spectroscopy is extremely sensitive to the local environment of the investigated nuclei, very precise prediction of the ^{27}Al NMR parameters is required for interpretation of the ^{27}Al 3Q MAS NMR spectra. Calculation of the NMR parameters represented a challenge because of the enormously large number of atoms in the unit cell of ZSM-5. As NMR parameters are a standard part of quantum chemical software, we exploited the advantages of cooperation with the group of Professor Sauer (Humboldt University, Berlin) in precise calculation of the Al environment in the zeolite. An essential problem lay in overcoming the gap between the conditions of the experiment and the calculations. While ^{27}Al 3Q MAS NMR spectra can be collected exclusively for fully hydrated samples, the presence of a large number of water molecules and solvated cations balancing the framework negative charge cannot be included into the calculated structure. We coped with this problem by the development and verification of the "bare framework" model, which gave realistic values of [27]Al isotropic chemical shifts in Si-rich zeolites.[32-34,99-101]

The application of the above approach provided the first and unambiguous evidence that the siting of Al atoms in Si-rich zeolites is not random and depends on the synthesis conditions. Moreover, the siting of framework Al atoms in ZSM-5 (with 24 different T sites) was partly solved and the occupation of 7 T sites by Al atoms was suggested for the first time.[32,33] The developed methodology was also applied to other zeolite structures.[34,101] With ferrierite, we provided the first and so far the only complete analysis of the siting of framework Al atoms in Si-rich zeolites.[34]

The siting of Al atoms in framework T sites governs the location of monovalent extra-framework species (like protons) in zeolites, which is reflected in their local arrangement/coordination, accessibility and size and arrangement of the reaction space around these counter species. Our finding that the siting of Al atoms in the framework is not random and depends on the conditions of the zeolite synthesis thus represents a breakthrough in the field of zeolites, particularly in light of the recently reported unique activity of protons of a zeolite catalyst attributable to the location of an Al atom in a distinct site surrounded by a specific free space. This opens a new approach for tailoring the activity and especially the selectivity of zeolite catalysts.

In the field of the siting of framework Al atoms in Si-rich zeolites, it can be concluded that we have developed methods for the analysis of the siting of single Al atoms. Our results clearly demonstrate non-random, hydrothermal synthesis-controlled Al siting and provide new opportunities for the development

of highly active and selective catalysts. We demonstrated the significant effect of the location of the Al pairs on the catalytic activity of zeolites, which can be exploited up to technical applications. Our knowledge and experience in this area were recently summarized in a review paper by Ref..[21]

## 3.2. Definition of the siting of Al atoms in the framework

The siting of Al atoms in the framework of Si-rich zeolites can be regarded as well-defined. The high number of crystallographically different $T(Si,Al)O_4$ tetrahedra units forming the frameworks in Si-rich zeolites consist of as few as 4 units in mordenite across 24 units in monoclinic ZSM-5 up to as many as 48 units in TNU-9. Together with the low Al content (Si/Al > 8), this fact leads to high variability in the siting of Al atoms, i.e. occupation of the individual framework T sites, and different populations of Al atoms in these sites. The parameters describing the Al siting can be suggested as:

(i) *Siting of Al atoms in the individual framework T sites* which represents a basic parameter governing the derived distribution of Al atoms.

(ii) *Siting of Al atoms in the individual framework rings,* essential for the location of protons and location and coordination of metal ions

(iii) *Siting of Al atoms with respect to the structural channel/cavity system,* which thereafter controls the accessibility of charge-balancing metal ions or protons for reactants or guest molecules, and the formation of various types of reaction intermediates in the void volume surrounding the counter ions.[21] Note that siting of Al pairs in the rings and channel system of zeolite is discussed in Section 2.

## 3.3. Analysis of the siting of Al atoms in the framework

The two-dimensional (2D) MQ MAS NMR experiment allows suppression of quadrupolar broadening in one projection and careful analysis of the spectrum yields identification of the resonances of Al atoms in the individual T sites. Moreover, the isotropic chemical shift of the quadrupolar nucleus, analogous to the chemical shift of non-quadrupolar nuclei, which characterizes the geometry of the $AlO_4$ tetrahedron, can be calculated. On this basis, we developed a methodology for analysis of the siting of Al atoms in Si-rich zeolites. However, there are three crucial aspects which must be taken into account for successful analysis of the Al siting in Si-rich zeolites:

(i) There is no simple correlation between the Al siting and the [27]Al isotropic chemical shift in Si-rich zeolites. The Lippmaa correlation,[98] which has been suggested for determination of the relationship between the [27]Al isotropic chemical shift and average T-O-T angle of the $T(Al,Si)O_4$ tetrahedra in Al-rich zeolites, cannot be used for two reasons: (i) there is no linear correlation between the $AlO_4$ geometry and [27]Al isotropic chemical shift,[32,33,99] (ii) the geometry of the

T(Al,Si)O$_4$ tetrahedra obtained from the diffraction experiment does not reflect the geometry of the AlO$_4$ tetrahedra.[21] The Al atoms in the Si-rich zeolites typically represent less than 10 % of the T atoms and the deformation of the AlO$_4$ tetrahedron due to the longer Al-O distance is thus not reflected in the T and O coordinates.

(ii) A significant effect of the closeness of the second Al atom in the Al-O-(Si-O)$_{1,2}$-Al sequence, as well as of the defective Al-O-Si-OH site on the $^{27}$Al isotropic chemical shift, have been reported. The change in the $^{27}$Al isotropic chemical shift due to this close Al atom is as much as 5 ppm while, e.g., chemical shifts in the T sites in ZSM-5 range within 12 ppm. Thus, the $^{27}$Al NMR experiment, without analysis of the Al-O-(Si-O)$_{1,2}$-Al sequences by $^{29}$Si MAS NMR and Vis spectroscopy of the Co$^{2+}$ ions (see par. 2.3), does not even allow estimation of whether the location of the Al atoms is or is not the same in the samples. Different $^{27}$Al resonances can reflect single Al atoms and Al of the Al-O-(Si-O)$_{1,2}$-Al sequences in the same T site.[34,99,100]

(iii) The dependence of the $^{27}$Al isotropic chemical shift in hydrated zeolites on the type of charge-balancing cations was reported for ferrierite containing Al pairs in the framework.[102] This effect can be attributed to the interaction of the framework with solvated cations located in channels/cavities with a limited space for the accommodation of a larger number of solvated monovalent cations. This interaction can be minimized by transformation of the zeolite into a form where close Al atoms are balanced by small divalent cations, such as Mg$^{2+}$ or Ca$^{2+}$.[21,34]

The isotropic chemical shifts of $^{27}$Al atoms in the individual T sites ad (i) can be predicted by quantum chemical calculations. The local arrangement of the AlO$_4$ tetrahedra in the silicate framework must first be calculated. The $^{27}$Al isotropic chemical shift is highly sensitive to the Al geometry and high accuracy in prediction of the arrangement of the Al atoms in the framework is essential. Periodic DFT and embedding approaches were reported to be sufficiently accurate for this purpose. The $^{27}$Al shielding of the Al atom in the cluster with the predicted geometry is then calculated. Finally, the $^{27}$Al shielding must be converted to the $^{27}$Al isotropic chemical shift. Calculation of the $^{27}$Al shielding in the Si-rich chabasite or Al(NO$_3$)$_2$ was successfully employed for the calibration.[32-34,99,101]

## 3.4.     Siting of Al atoms in the framework T sites

*Ferrierite* is the only zeolite for which the siting of the Al atoms was completely elucidated for a set of samples with Si/Al 8.5 – 30 and for Al pairs ranging from 0 to 66 % of the Al atoms. Quantum-chemical calculations showed that the Al atoms in the T1 site can exhibit two different geometries and thus the Al atom can occupy five different T sites in the ferrierite structure. In ferrierites containing exclusively single Al atoms, the T1$_a$ site is not occupied, while the T3
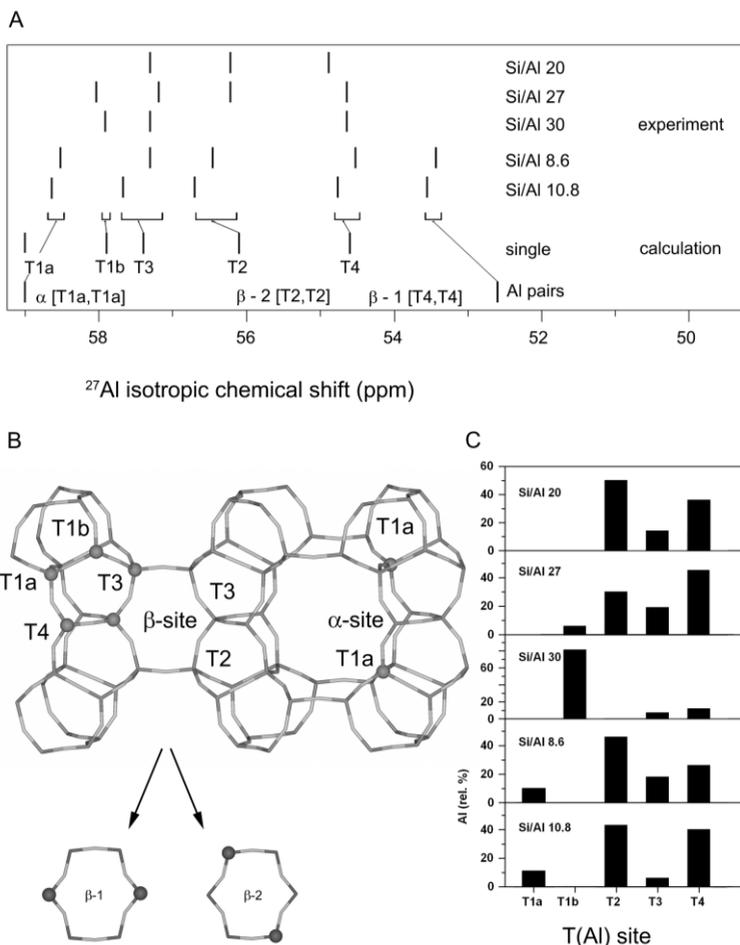
**Figure 4.** Al siting in ferrierite. Notation of individual framework T sites and α- and β-type 6-MRs (A), attribution of the observed [27]Al isotropic chemical shifts to those predicted for single Al atoms in the framework T sites and for Al atoms in the Al-O-(Si-O)$_2$-Al sequences in the α- and β-type 6-MRs (B), and quantitative analysis of the Al siting in framework T sites (C).

and T4 sites are occupied in all the analyzed zeolites. The T1$_b$ and T2 sites are occupied in two samples. These observations provide clear evidence that the Al siting in the framework T sites is not random and is not controlled by simple statistical rules or by the stabilization energy in the template-free zeolite

framework. Quantitative analysis of the occupancy of the individual T sites by Al atoms shows that ferrierite with Al located predominantly in one T site can be prepared. $Al(T1_a)$-O-$(Si$-$O)_2$-$Al(T1_a)$ and $Al(T2)$-O-$(Si$-$O)_2$-$Al(T2)$ sequences in one 6-MR are present in ferrierites with Si/Al 8.5 and 10.5 synthesized in the Na,K-form. The $T1_a$ site is not occupied and single Al atoms are located at the T2, T3 and T4 sites. The $Al(T4)$-O-$(Si$-$O)_2$-$Al(T4)$ sequence is not present in the 6-MR. It should be pointed out that, while the same T sites are occupied in both the analyzed ferrierites, there are significant differences in the concentrations of the Al atoms at the individual T sites.[34] The results and their interpretation are graphically depicted in Figure 4.

*ZSM-22 and theta-1* are iso-structural TON topologies prepared under different conditions and representing monodimensional counterparts to ZSM-5. Comparison of these two zeolites is very often used to analyze the role of channel dimensionality in hydrocarbon transformations. Derewinski et al. reported two resonances with isotropic chemical shifts at 55.1 and 57.6 ppm for ZSM-22, while three resonances at 55.5 and 57.6 and 58.7 ppm were reported for theta-1, but attribution of these resonances to Al atoms in the T sites used the Lipmaa correlation. We recently refined interpretation of these experimental data. Splitting of the T1 and T2 eight-fold sites into two four-fold sites ($T1_a$ and $T1_b$, and $T2_a$ and $T2_b$) was observed. The resonance at 55.1 ppm corresponds to the Al atoms in the T4 sites, which predominate in both zeolites (55 - 60 % of Al). The T4 site is located in the pockets at the wall of the channel and thus a significant part of the Al atoms in the zeolite exhibits limited accessibility. The T1 ($T1_a$ and $T1_b$) sites are not occupied by Al atoms. Resonance at 58.7 ppm reflecting 10 % of the Al atoms in the theta-1 zeolite can be attributed to the T3 site, while the resonance at 57.6 ppm (30 -40 % of Al) could correspond to Al atoms in the $T2_a$ and $T2_b$ sites.[101]

*ZSM-5.* Our results on the Al siting in ZSM-5 can be summarized as follows: (i) all twelve T sites differ from the aspect of the $AlO_4^-$ geometry and orthorhombic ZSM-5 exhibits 24 T sites available for Al atoms; (ii) Al siting in the ZSM-5 framework is neither random nor controlled by the stabilization energy of the Al atoms in the framework, but depends mainly on the conditions of the zeolite synthesis; (iii) from three to five T sites are occupied by Al atoms in the ZSM-5 sample; (iv) seven resonances reported for ZSM-5 were attributed to the T(Al) sites. The remaining five resonances cannot be attributed to the T(Al) sites due to the large number of T(Al) sites with similar $^{27}Al$ isotropic shift values; (v) the presence of the second Al atom in the Al-O-$(Si$-$O)_{1,2}$-Al sequences can result in a significant change in the predicted $^{27}Al$ isotropic shift, by up to 5 ppm, (vi) from the point of view of control of the Al siting, it can be tuned without changing the SDA by the presence of an inorganic co-cation and employing the type of anion species present in the synthesis mixture.[32,33,100] The observed resonances and their

attribution to the T(Al) sites and the quantitative analysis of the siting of Al atoms are is given in Figure 5.
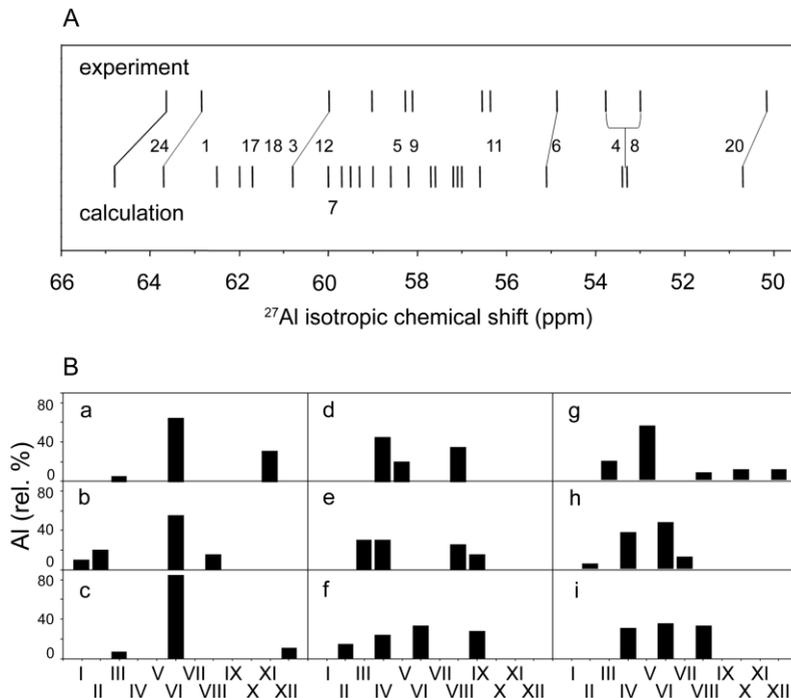


**Figure 5.** Observed and predicted $^{27}$Al isotropic chemical shifts in ZSM-5 with single Al atoms (A), and the effect of synthesis conditions on Al siting reflected in $^{27}$Al resonances I – XII (B). ZSM-5 synthesized using TPA-OH, Al(NO$_3$)$_3$ and TEOS (a), TPA-OH, Al-isopropoxide and TEOS (b), TPA-OH, AlCl$_3$ and TEOS (c), TPA-OH, AlCl$_3$, TEOS and Na$_2$CO$_3$ (d), TPA-Br, Al(NO$_3$)$_3$ and TEOS (e), commercial sample (f), (g), TPA-OH, Al(NO$_3$)$_3$ and TEOS (h), and TPA-OH, AlCl$_3$, TEOS and NaCl (i).

## 3.5.    Siting of Al atoms and catalytic activity of zeolites

The siting of single Al atoms has recently been resolved. So far we have no experimental data on the relationship between the siting of single Al atoms and zeolite properties. A dramatic effect of the siting of framework Al atoms on the catalytic activity of mordenite and ferrierite in selective carbonylation of methanol or dimethyl ether, was suggested, as the location of the Al atoms controls the location of the protons in pores of different dimensions.[103,104] For mordenite, unique enzyme-like activity was attributed to the proton bound to oxygen O33 neighbouring the Al atom of the mordenite pocket. However, these suggestions

stem from theoretical modelling and have not yet been supported by experiments; the synthesis of mordenite with this siting of an Al atom has not been performed yet.[105,106]

It can be summarized that our results clearly demonstrate the potential for manipulation of the siting of framework Al atoms in Si-rich zeolites by the conditions of their hydrothermal synthesis, and its decisive effect on the activity of zeolites. These results, together with those obtained by other research groups, encourage us to suggest the crucial effect of the siting of framework Al atoms on the activity and selectivity of zeolite catalysts, and the necessity of analysis of the siting of Al atoms to complete the description of the structure of extra-framework counter-ion species accommodated in Si-rich zeolites.

## 4.    Conclusions

Our work lead to acceptance of the siting and distribution of Al atoms in the framework as new and decisive parameters of Si-rich zeolites with an impact on the structure and siting of counter-ion species and their properties/activity, comparable in importance with the zeolite topology and Al content of the zeolite framework. Variability in the Al siting in Si-rich zeolites follows from the low content of isomorphously substituted Al atoms in the silicate framework and large number of distinct crystallographic framework T sites in these zeolites.

We showed that the siting of the Al atoms in the framework is not random or controlled by simple rules and depends on the zeolite hydrothermal synthesis. Thus, Si-rich zeolites can be prepared with the same topology and chemical composition but different positions of the Al atoms in the framework, as we demonstrated for ZSM-5 and ferrierite in unique studies analyzing the Al siting in the framework of these zeolites. The method developed by our group and combining $^{27}Al$ MQ MAS NMR with quantum chemical calculations of $^{27}Al$ isotropic chemical shifts represents a powerful and as yet the only tool for analysis of the Al atoms in the framework T sites. We suggested that governing of the catalytic behavior of the zeolite-based catalyst by controlling the siting of the Al atoms in the framework can be used as a general tool for tuning the zeolite activity/selectivity for a range of catalytic reactions.

Our studies provided the first evidence that the distribution of the Al atoms between single Al atoms and Al pairs in one ring is not random or controlled by simple rules, but depends on the conditions of the zeolite synthesis. Procedures were successfully developed by our team for synthesis of the MFI, FER and BEA topologies with a predominance of either Al pairs in one ring or single Al atoms in a wide range of framework Al contents. We have introduced bare $Co^{2+}$ ions in dehydrated zeolites exchanged to a maximum degree, followed by Vis spectroscopy, in combination with other spectroscopic methods (e.g. $^{29}Si$ MAS NMR), as a powerful tool for analysis of the distribution of Al atoms in the

zeolite framework. According our studies, the distribution of Al atoms in the framework is an essential parameter controlling the accommodation and structure of metal-ion species in Si-rich zeolites and the dramatic impact of the framework Al distribution on a number of redox- and Lewis-catalyzed reactions carried out over metallo-zeolites, as well as in acid-catalyzed hydrocarbon transformations over H-zeolites, was clearly demonstrated.

Variability of the siting and distribution of Al atoms in the framework represents a general feature of Si-rich zeolites, resulting in zeolites of the same chemical Si/Al composition, but significantly different siting and distribution of Al atoms and thus different zeolite properties controlled by these parameters. As we have successfully developed both methods for control of the Al siting and distribution of the Al atoms in the zeolite framework and their monitoring, this knowledge suggests the possibility of designing a new generation of highly selective zeolite-based catalysts and catalytic processes. Our findings significantly affected zeolite science in general in connection with known Si-rich zeolite topologies and also newly discovered topologies with tuned siting and distribution of Al atoms in their framework.

# 5. References

(1)     Barrer, R. M. *Hydrothermal Chemistry of Zeolites*; Academic press: London, 1982.

(2)     *Introduction to zeolite science and practice*; Bekkum, H. v.; Flanigen, E. M.; Jansen, J. C., Eds.; Elsewier: Amsterdam, 1991; Vol. 58.

(3)     www.iza-structure.org/databases/.

(4)     Weitkamp, J.; Puppe, L. *Catalysis and Zeolites: Fundamentals and Applications*; Springer: Berlin, 1999.

(5)     Iwamoto, M.; Furukawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S. I.; Kagawa, S. *Journal of the Chemical Society-Chemical Communications* **1986**, 1272.

(6)     Iwamoto, M.; Yahiro, H.; Tanda, K.; Mizuno, N.; Mine, Y.; Kagawa, S. *Journal of Physical Chemistry* **1991**, *95*, 3727.

(7)     Sato, S.; Yoshihiro, Y.; Yahiro, H.; Mizuno, N.; Iwamoto, M. *Applied Catalysis* **1991**, *70*, L1.

(8)     Capek, L.; Dedecek, J.; Wichterlova, B. *Journal of Catalysis* **2004**, *227*, 352.

(9)     Capek, L.; Kreibich, V.; Dedecek, J.; Grygar, T.; Wichterlova, B.; Sobalik, Z.; Martens, J. A.; Brosius, R.; Tokarova, V. *Microporous and Mesoporous Materials* **2005**, *80*, 279.

(10)    Dedecek, J.; Sobalik, Z.; Tvaruzkova, Z.; Kaucky, D.; Wichterlova, B. *Journal of Physical Chemistry* **1995**, *99*, 16327.

(11)    Dedecek, J.; Wichterlova, B. *Journal of Physical Chemistry* **1994**, *98*, 5721.

(12)    Wichterlova, B.; Dedecek, J.; Sobalik, Z.; Vondrova, A.; Klier, K. *Journal of Catalysis* **1997**, *169*, 194.

(13)    Wichterlova, B.; Dedecek, J.; Vondrova, A. *Journal of Physical Chemistry* **1995**, *99*, 1065.

(14)    Wichterlova, B.; Sobalik, Z.; Dedecek, J. *Catalysis Today* **1997**, *38*, 199.

(15)    Dedecek, J.; Wichterlova, B. *Journal of Physical Chemistry B* **1999**, *103*, 1462.

(16)    Kaucky, D.; Dedecek, J. I.; Wichterlova, B. *Microporous and Mesoporous Materials* **1999**, *31*, 75.

(17)     Dedecek, J.; Kaucky, D.; Wichterlova, B. *Microporous and Mesoporous Materials* **2000**, *35-6*, 483.

(18)     Dedecek, J.; Capek, L.; Kaucky, D.; Sobalik, Z.; Wichterlova, B. *Journal of Catalysis* **2002**, *211*, 198.

(19)     Sobalik, Z.; Dedecek, J.; Kaucky, D.; Wichterlova, B.; Drozdova, L.; Prins, R. *Journal of Catalysis* **2000**, *194*, 330.

(20)     Drozdova, L.; Prins, R.; Dedecek, J.; Sobalik, Z.; Wichterlova, B. *Journal of Physical Chemistry B* **2002**, *106*, 2240.

(21)     Dedecek, J.; Sobalik, Z.; Wichterlova, B. *Catalysis Reviews-Science and Engineering* **2012**, *54*, 135.

(22)     Kucherov, A. V.; Shelef, M. *Journal of Catalysis* **2000**, *195*, 106.

(23)     Kucherov, A. V.; Slinkin, A. A. *Zeolites* **1986**, *6*, 175.

(24)     Dedecek, J.; Kaucky, D.; Wichterlova, B. *Chemical Communications* **2001**, 970.

(25)     Dedecek, J.; Kaucky, D.; Wichterlova, B.; Gonsiorova, O. *Physical Chemistry Chemical Physics* **2002**, *4*, 5406.

(26)     Gabova, V.; Dedecek, J.; Cejka, J. *Chemical Communications* **2003**, 1196.

(27)     Dedecek, J.; Capek, L.; Sazama, P.; Sobalik, Z.; Wichterlova, B. *Applied Catalysis a-General* **2011**, *391*, 244.

(28)     Dedecek, J.; Balgova, V.; Pashkova, V.; Klein, P.; Wichterlova, B. *Chemistry of Materials* **2012**, *24*, 3231.

(29)     Bortnovsky, O.; Tokarova, V.; Wichterlova, B.; Dedecek, J.; Sobalik, Z.; Gonsiorova, O.; Balgova, V., WO/2011/095140

(30)     Sazama, P.; Dedecek, J.; Gabova, V.; Wichterlova, B.; Spoto, G.; Bordiga, S. *Journal of Catalysis* **2008**, *254*, 180.

(31)     Wichterlova, B. *Topics in Catalysis* **2004**, *28*, 131.

(32)     Sklenak, S.; Dedecek, J.; Li, C. B.; Wichterlova, B.; Gabova, V.; Sierka, M.; Sauer, J. *Angewandte Chemie-International Edition* **2007**, *46*, 7286.

(33)     Sklenak, S.; Dedecek, J.; Li, C.; Wichterlova, B.; Gabova, V.; Sierka, M.; Sauer, J. *Physical Chemistry Chemical Physics* **2009**, *11*, 1237.

(34)     Dedecek, J.; Lucero, M. J.; Li, C. B.; Gao, F.; Klein, P.; Urbanova, M.; Tvaruzkova, Z.; Sazama, P.; Sklenak, S. *Journal of Physical Chemistry C* **2011**, *115*, 11056.

(35)     Dedecek, J.; Wichterlova, B. *Journal of Physical Chemistry B* **1997**, *101*, 10233.

(36)     Biscardi, J. A.; Meitzner, G. D.; Iglesia, E. *Journal of Catalysis* **1998**, *179*, 192.

(37)     Gonzales, N. O.; Chakraborty, A. K.; Bell, A. T. *Catalysis Letters* **1998**, *50*, 135.

(38)     Rice, M. J.; Chakraborty, A. K.; Bell, A. T. *Journal of Catalysis* **1999**, *186*, 222.

(39)     Rice, M. J.; Chakraborty, A. K.; Bell, A. T. *Journal of Catalysis* **2000**, *194*, 278.

(40)     Rice, M. J.; Chakraborty, A. K.; Bell, A. T. *Journal of Physical Chemistry B* **2000**, *104*, 9987.

(41)     Wichtelova, B.; Sobalik, Z.; Dedecek, J. *Applied Catalysis B-Environmental* **2003**, *41*, 97.

(42)     Dedecek, J.; Bortnovsky, O.; Vondrova, A.; Wichterlova, B. *Journal of Catalysis* **2001**, *200*, 160.

(43)     Capek, L.; Dedecek, J.; Wichterlova, B.; Cider, L.; Jobson, E.; Tokarova, V. *Applied Catalysis B-Environmental* **2005**, *60*, 147.

(44)     Dedecek, J.; Cejka, J.; Oberlinger, M.; Ernst, S. In *Impact of Zeolites and Other Porous Materials on the New Technologies at the Beginning of the New Millennium, Pts a and B*; Aiello, R., Giordano, G., Testa, F., Eds. 2002; Vol. 142, p 23.

(45)     Dalconi, M. C.; Alberti, A.; Cruciani, G. *Journal of Physical Chemistry B* **2003**, *107*, 12973.

(46)     Dalconi, M. C.; Alberti, A.; Cruciani, G.; Ciambelli, P.; Fonda, E. *Microporous and Mesoporous Materials* **2003**, *62*, 191.

(47)     Dalconi, M. C.; Cruciani, G.; Alberti, A.; Ciambelli, P. *Catalysis Today* **2005**, *110*, 345.

(48)     Dalconi, M. C.; Cruciani, G.; Alberti, A.; Ciambelli, P.; Rapacciuolo, M. T. *Microporous and Mesoporous Materials* **2000**, *39*, 423.

(49)     Dedecek, J.; Capek, L.; Wichterlova, B. *Applied Catalysis a-General* **2006**, *307*, 156.

(50)     Sklenak, S.; Andrikopoulos, P. C.; Boekfa, B.; Jansang, B.; Novakova, J.; Benco, L.; Bucko, T.; Hafner, J.; Dedecek, J.; Sobalik, Z. *Journal of Catalysis* **2010**, *272*, 262.

(51)     Sobalik, Z.; Novakova, J.; Dedecek, J.; Sathu, N. K.; Tabor, E.; Sazama, P.; Stastny, P.; Wichterlova, B. *Microporous and Mesoporous Materials* **2011**, *146*, 172.

(52)     Benco, L.; Bucko, T.; Grybos, R.; Hafner, J.; Sobalik, Z.; Dedecek, J.; Hrusak, J. *Journal of Physical Chemistry C* **2007**, *111*, 586.

(53)     Benco, L.; Bucko, T.; Grybos, R.; Hafner, J.; Sobalik, Z.; Dedecek, J.; Sklenak, S.; Hrusak, J. *Journal of Physical Chemistry C* **2007**, *111*, 9393.

(54)     Jisa, K.; Novakova, J.; Schwarze, M.; Vondrova, A.; Sklenak, S.; Sobalik, Z. *Journal of Catalysis* **2009**, *262*, 27.

(55)     Kaucky, D.; Sobalik, Z.; Schwarze, M.; Vondrova, A.; Wichterlova, B. *Journal of Catalysis* **2006**, *238*, 293.

(56)     Tabor, E.; Zaveta, K.; Sathu, N. K.; Tvaruzkova, Z.; Sobalik, Z. *Catalysis Today* **2011**, *169*, 16.

(57)     Loewenstein, W. *American Mineralogist* **1954**, *39*, 92.

(58)     Attfield, M. P.; Weigel, S. J.; Cheetham, A. K. *Journal of Catalysis* **1997**, *170*, 227.

(59)     Mortier, W. J.; Pluth, J. J.; Smith, J. V. *Materials Research Bulletin* **1975**, *10*, 1037.

(60)     *Extraframework cationic positions in zeolites*; Mortier, W. J., Ed.; Elsevier: Amsterdam, 1982.

(61)     Schlenker, J. L.; Pluth, J. J.; Smith, J. V. *Materials Research Bulletin* **1978**, *13*, 901.

(62)     Schlenker, J. L.; Pluth, J. J.; Smith, J. V. *Materials Research Bulletin* **1978**, *13*, 169.

(63)     Schlenker, J. L.; Pluth, J. J.; Smith, J. V. *Materials Research Bulletin* **1978**, *13*, 77.

(64)     Schlenker, J. L.; Pluth, J. J.; Smith, J. V. *Materials Research Bulletin* **1979**, *14*, 751.

(65)     Schlenker, J. L.; Pluth, J. J.; Smith, J. V. *Materials Research Bulletin* **1979**, *14*, 961.

(66)     Benco, L.; Bucko, T.; Hafner, J.; Toulhoat, H. *Journal of Physical Chemistry B* **2005**, *109*, 20361.

(67)     Capek, L.; Dedecek, J.; Sazama, P.; Wichterlova, B. *Journal of Catalysis* **2010**, *272*, 44.

(68)     Do, T. O.; Nossov, A.; Springuel-Huet, M. A.; Schneider, C.; Bretherton, J. L.; Fyfe, C. A.; Kaliaguine, S. *Journal of the American Chemical Society* **2004**, *126*, 14324.

(69)     Kiricsi, I.; Flego, C.; Pazzuconi, G.; Parker, W. O.; Millini, R.; Perego, C.; Bellussi, G. *Journal of Physical Chemistry* **1994**, *98*, 4627.

(70)     van Bokhoven, J. A.; Danilina, N. In *Zeolites and Catalysis*; Wiley-VCH Verlag GmbH & Co. KGaA: 2010, p 283.

(71)     Bortnovsky, O.; Sobalik, Z.; Wichterlova, B.; Bastl, Z. *Journal of Catalysis* **2002**, *210*, 171.

(72)     van Bokhoven, J. A.; Koningsberger, D. C.; Kunkeler, P.; van Bekkum, H.; Kentgens, A. P. M. *Journal of the American Chemical Society* **2000**, *122*, 12842.

(73)     Abraham, A.; Lee, S. H.; Shin, C. H.; Hong, S. B.; Prins, R.; van Bokhoven, J. A. *Physical Chemistry Chemical Physics* **2004**, *6*, 3031.

(74)     Brandle, M.; Sauer, J. *Journal of the American Chemical Society* **1998**, *120*, 1556.

(75)     Sonnemans, M. H. W.; Denheijer, C.; Crocker, M. *Journal of Physical Chemistry* **1993**, *97*, 440.

(76)     Sobalik, Z.; Tvaruzkova, Z.; Wichterlova, B. *Microporous and Mesoporous Materials* **1998**, *25*, 225.

(77)     Sobalik, Z.; Tvaruzkova, Z.; Wichterlova, B. *Journal of Physical Chemistry B* **1998**, *102*, 1077.

(78)     Sponer, J. E.; Sobalik, Z.; Leszczynski, J.; Wichterlova, B. *Journal of Physical Chemistry B* **2001**, *105*, 8285.

(79)     Georgieva, I.; Benco, L.; Tunega, D.; Trendafilova, N.; Hafner, J.; Lischka, H. *Journal of Chemical Physics* **2009**, *131*.

(80)     Wichterlova, B.; Dedecek, J.; Sobalik, Z. In *Catalysis by Unique Metal Ion Structures in Solid Matrices: From Science to Application*; Centi, G., Wichterlova, B., Bell, A. T., Eds. 2001; Vol. 13, p 31.

(81)     Garten, R. L.; Delgass, W. N.; Boudart, M. *Journal of Catalysis* **1970**, *18*, 90.

(82)     Lobree, L. J.; Hwang, I. C.; Reimer, J. A.; Bell, A. T. *Journal of Catalysis* **1999**, *186*, 242.

(83)     Smeets, P. J.; Woertink, J. S.; Sels, B. F.; Solomon, E. I.; Schoonheydt, R. A. *Inorganic Chemistry* **2010**, *49*, 3573.

(84)     Woertink, J. S.; Smeets, P. J.; Groothaert, M. H.; Vance, M. A.; Sels, B. F.; Schoonheydt, R. A.; Solomon, E. I. *Proceedings of the National Academy of Sciences of the United States of America* **2009**, *106*, 18908.

(85)     Gomes, J.; Zimmerman, P. M.; Head-Gordon, M.; Bell, A. T. *Journal of Physical Chemistry C* **2012**, *116*, 15406.

(86)     Mlinar, A. N.; Zimmerman, P. M.; Celik, F. E.; Head-Gordon, M.; Bell, A. T. *Journal of Catalysis* **2012**, *288*, 65.

(87)     Dedecek, J.; Kaucky, D.; Wichterlova, B. *Topics in Catalysis* **2002**, *18*, 283.

(88)     Kaucky, D.; Vondrova, A.; Dedecek, J.; Wichterlova, B. *Journal of Catalysis* **2000**, *194*, 318.

(89)     Kubanek, P.; Wichterlova, B.; Sobalik, Z. *Journal of Catalysis* **2002**, *211*, 109.

(90)     Wichterlova, B.; Dedecek, J.; Sobalik, Z. In *Catalysis by Microporous Materials*; Beyer, H. K., Karge, H. G., Kiricsi, I., Nagy, J. B., Eds. 1995; Vol. 94, p 641.

(91)     Derouane, E. G.; Fripiat, J. G. *Zeolites* **1985**, *5*, 165.

(92)     Alvaradoswaisgood, A. E.; Barr, M. K.; Hay, P. J.; Redondo, A. *Journal of Physical Chemistry* **1991**, *95*, 10031.

(93)     Blanco, F.; Urbinavillalba, G.; Deagudelo, M. M. R. *Molecular Simulation* **1995**, *14*, 165.

(94)     Lonsinger, S. R.; Chakraborty, A. K.; Theodorou, D. N.; Bell, A. T. *Catalysis Letters* **1991**, *11*, 209.

(95)     Mackenzie, K. J. D.; Smith, M. E. *Multinuclear Solid State NMR of Inorganic Materials*; Elsevier, 2002.

(96)     Sarv, P.; Fernandez, C.; Amoureux, J. P.; Keskinen, K. *Journal of Physical Chemistry* **1996**, *100*, 19223.

(97)     Han, O. H.; Kim, C. S.; Hong, S. B. *Angewandte Chemie-International Edition* **2002**, *41*, 469.

(98)     Lippmaa, E.; Samoson, A.; Magi, M. *Journal of the American Chemical Society* **1986**, *108*, 1730.

(99)     Dedecek, J.; Sklenak, S.; Li, C.; Wichterlova, B.; Gabova, V.; Brus, J.; Sierka, M.; Sauer, J. *Journal of Physical Chemistry C* **2009**, *113*, 1447.

36

(100)     Dedecek, J.; Sklenak, S.; Li, C. B.; Gao, F.; Brus, J.; Zhu, Q. J.; Tatsumi, T. *Journal of Physical Chemistry C* **2009**, *113*, 14454.

(101)     Sklenak, S.; Dedecek, J.; Li, C. B.; Gao, F.; Jansang, B.; Boekfa, B.; Wichterlova, B.; Sauer, J. *Collection of Czechoslovak Chemical Communications* **2008**, *73*, 909.

(102)     Sarv, P.; Wichterlova, B.; Cejka, J. *Journal of Physical Chemistry B* **1998**, *102*, 1372.

(103)     Bhan, A.; Allian, A. D.; Sunley, G. J.; Law, D. J.; Iglesia, E. *Journal of the American Chemical Society* **2007**, *129*, 4919.

(104)     Roman-Leshkov, Y.; Moliner, M.; Davis, M. E. *Journal of Physical Chemistry C* **2011**, *115*, 1096.

(105)     Boronat, M.; Martinez, C.; Corma, A. *Physical Chemistry Chemical Physics* **2011**, *13*, 2603.

(106)     Boronat, M.; Martinez-Sanchez, C.; Law, D.; Corma, A. *Journal of the American Chemical Society* **2008**, *130*, 16316.

## Appendix A – List of thesis publications

### Distribution of Al atoms

1. Role of Hydrated Cu Ion Complexes and Aluminium Distribution in the Framework on the Cu Ion Siting in ZSM-5.
   *J. Dedecek, B. Wichterlova*, **J. Phys. Chem. B** 101 (1997) 10233-10240.
   **44 – 32 – 4.80**
2. Co$^{2+}$ Ion Siting in Pentasil-Containing Zeolites. I. Co$^{2+}$ Ion Sites and their Occupation in Morednite. A Vis-NIR Diffuse Reflectance Spectroscopy Study.
   *J. Dedecek, B. Wichterlová*, **J. Phys. Chem. B** 103, (1999) 1462-1476.
   **99 – 70 – 4.80**
3. Co$^{2+}$ ion siting in pentasil-containing zeolites II. Co$^{2+}$ ion sites and their occupation in ferrierite. A VIS diffuse reflectance spectroscopy study.
   *D. Kaucky, J. Dedecek, B. Wichterlova*, **Micropor. Mesopor. Mater**. 31 (1999) 75-87.
   **86 – 60 - 3.28**
4. Co$^{2+}$ ion siting in pentasil-containing zeolites, part 3. Co$^{2+}$ ion sites and their occupation in ZSM-5: a VIS difuse reflectance spectroscopy study.
   *J. Dedecek, D. Kaucky, B. Wichterlova*, **Micropor. Mesopor. Mat**. 35-36 (2000) 483-494.
   **110 – 84 – 3.28**
5. Al distribution in ZSM-5. An experimental study.
   *J. Dedecek, D. Kaucky, B. Wichterlova*, **Chem. Commun**. 11 (2001) 970-971.
   **33 – 18 – 6.16**
6. Catalytic Activity of Cu-Beta Zeolite in NO Decomposition: Effect of Copper and Aluminium Distribution
   *J. Dedecek, O. Bortnovsky, A. Vondrova, B. Wichterlova*, **J. Catal**. 200 (2001) 160-170.
   **16 – 11 – 6.00**
7. Does Density of Cationic Sites Affect Catalytic Activity of Co Zeolites in Selective Catalytic Reduction of NO with Methane?
   *J. Dedecek, D. Kaucky, A. Vondrova, Z. Sobalik, B. Wichterlova*, ***Top. Catal***. 18 (2002) 283-290.
   **22 – 17 – 2.62**
8. Co$^{2+}$ Ions as Probes of Al Distribution in the Framework of Silicon Rich Molecular Sieves. The ZSM-5 study.
   *J. Dedecek, D. Kaucky, O. Gonsiorova, B. Wichterlova,* **Phys. Chem. Chem.**

**Phys**. 4 (2002) 5406-5413.
**42 – 26 – 3.57**

9.  Siting and Distribution of the Co ions in Beta Zeolite. A UV-Vis-NIR and FTIR Study.
    *J. Dedecek, L. Capek, D. Kaucky, Z. Sobalik, B. Wichterlova*, **J. Catal**. 211 (2002) 198-207.
    **39 – 26 – 6.00**

10. Control of Al distribution in ZSM-5 by conditions of zeolite synthesis
    *V. Gabova, J. Dedecek, J. Cejka,* **Chem. Commun**. 10 (2003), 1196-1197.
    **28 – 19 – 6.16**

11. Redox catalysis over metallo-zeolites. Contribution to environmental catalysis
    *B. Wichterlova, Z. Sobalik, J. Dedecek*, **Appl. Catal. B - Environ.** 41 (2003) 97-114.
    **65 – 55 – 5.62**

12. Co-beta zeolite highly active in propane–SCR-NO$_x$ in the presence of water vapor: effect of zeolite preparation and Al distribution in the framework
    *L. Capek, J. Dedecek, B. Wichterlova*, **J. Catal**. 227(2004) 352-366**.**
    **33 – 27 – 6.00**

13. Cu-ZSM-5 zeolite highly active in the reduction of NO with decane. Effect of zeolite structural parameters on the catalyst performance
    *L. Capek, J. Dedecek, B. Wichterlova, L. Cider, E. Jobson, V. Tokarova*, **Appl. Catal. B - Environ**. 60 (2005) 147-153.
    **15 – 11 – 5.62**

14. Nature of active sites in decane-SCR-NO$_x$ and NO decomposition over Cu-ZSM-5 zeolites
    *J. Děděček, L. Čapek, B. Wichterlová*, **Appl. Catal. A – Gen**. 307 (2006) 156-164.
    **12 – 8 – 3.90**

15. Effect of aluminium distribution in the framework of ZSM-5 on hydrocarbon transformation. Cracking of 1-butene
    *V. Gabová, P Sazama, J. Dedecek, B. Wichterlova, G. Spoto, A. Bordiga,* **J. Catal**. 254 (2008) 180-189.
    **25 – 19 – 6.00**

16. The decisive role of distribution of Al in the framework of BEA zeolites on the activity of counter Co ion species in propane-SCR-NOx under water vapor presence
    *B. Wichterlova, J. Dedecek, P. Sazama, L. Capek*, **J. Catal**. 272 (2010) 44-54.
    **6 – 2 – 6.00**

17. Control of metal ion species in zeolites by distribution of aluminium in the framework: From structural analysis to performance under real conditions of SCR-NO$x$ and NO, N$_2$O decomposition
    *J. Dedecek, L. Capek, P. Sazama, Z. Sobalik*, *B. Wichterlova,* **Appl. Catal. A –**

**Gen.** 391 (2011) 244-253.

    **7 – 3 – 3.90**

18. Synthesis of ZSM-5 zeolites with defined distribution of Al atoms in the framework and multinuclear MAS NMR analysis of the control of Al distribution J. Dedecek, V. Balgová, V. Pashkova, P. Klein, B. Wichterlová, **Chem. Mat.** 24 (2012) 3231-3239.

    **0 – 0 – 7.28**

## Siting of Al atoms

19. Aluminum Siting in Silicon-rich Zeolite Frameworks. A Combined High Resolution ^{27}Al NMR and Quantum Mechanics / Molecular Mechanics Study of ZSM-5
*S. Sklenak, J. Dedecek, Ch. Li, B. Wichterlova, V. Gabova, M. Sierka, J. Sauer*, **Angew. Chem. Int. Edit.** 46 (2007) 7286-7289**.**

    **38 – 26 – 13.45**

20. Aluminum Siting in the ZSM-22 and Theta-1 Zeolites Revisited: A QM/MM study
*S. Sklenak, J. Dedecek, C. Li, F. Gao, B. Boekfa, B. Wichterlova, J. Sauer*, **Collect. Czech. Chem. C.** 73 (2008) 909-920.

    **4 – 1 – 1.28**

21. Aluminum Siting in the Frameworks of Silicon-rich Zeolites. A Combined High Resolution ^{27}Al NMR and QM/MM Study of ZSM-5
*J. Dedecek, S. Sklenak, C. Li, B. Wichterlova, V. Gabova, M. Sierka, J. Sauer*, **Phys. Chem. Chem. Phys**. 11 (2009) 1237-1247.

    **29 - 22 - 3.57**

22. Effect of Al-Si-Al and Al-Si-Si-Al Pairs in the ZSM-5 Zeolite Framework on the Al-27 NMR Spectra. A Combined High-Resolution Al-27 NMR and DFT/MM Study
*J. Dedecek, S. Sklenak, C. Li, B. Wichterlova, V. Gabova, J. Brus, M. Sierka, J. Sauer*, **J. Phys. Chem. C** 113 (2009) 1447-1458.

    **18 – 11 – 4.80**

23. Effect of Al/Si Substitutions and Silanol Nests on the Local Geometry of Si and Al Framework Sites in Silicone-Rich Zeolites: A Combined High Resolution Al-27 and Si-29 NMR and Density Functional Theory/Molecular Mechanics Study
*J. Dedecek, S. Sklenak, C. Li F. Gao, J. Brus, Q. Zhu, T. Tatsumi*, **J. Phys. Chem. C** 113 (2009) 14454-14466.

    **10 – 7 – 4.80**

24. Complex Analysis of the Aluminum Siting in the Framework of Silicon-Rich Zeolites. A Case Study on Ferrierites
*J. Dedecek, M. J. Lucero, C. B. Li, F. Gao, P. Klein, M. Urbanova, Z. Tvaruzkova,*

*P. Sazama, S. Sklenak,* **J. Phys. Chem. C**. 115 (2011) 11056-11064.
**6 – 4 – 4.80**

25. Siting and Distribution of Framework Aluminium Atoms in Silicon-Rich Zeolites and Impact on Catalysis
*J. Dedecek, Z. Sobalik, B. Wichterlova*, **Catal. Rev.** 54 (2012), 135-223.
**1 – 0 – 7.50**

## Patents

26. Způsob výroby zeolitů pentasilové struktury s řízenou distribucí hliníkových atomů ve skeletu
*O Bortnovsky, V Tokarova, B Wichterlova, J Dedecek, Z Sobalik, O Gonsiorova, V Balgova,* CZ301937 (2010).
27. Method of manufacture of zeolites with pentasil structure with controlled distribution of aluminium atoms in the skeleton
*O Bortnovsky, V Tokarova, B Wichterlova, J Dedecek, Z Sobalik, O Gonsiorova, V Balgova,* WO/2011/095140 (2011).

### Statement about authorship of the presented publications
The research covered in this Thesis represents a very complex, demanding and complicated experimental work. Analysis of siting of Al atoms moreover requires interpretation based on state-of-the art quantum chemical calculations. Therefore the presented publications resulted from the collaboration of several co-authors and a theoretical group was involved. However, the contribution of the author of this Thesis was pivotal. In most cases the author was responsible for the experimental proposal, measuring and evaluating of experimental data, proposal of the model for calculations, interpretation of experimental data and finally writing the publications. This is reflected by the fact that he was the corresponding author of 16 publications and the corresponding author of further one from the 25 publications covered in this Thesis.

## Appendix B – List of publications not relevant for Thesis

(Citations – Citations without self-citations – Impact Factor, According WoS, October 1$^{st}$ 2012)

28. Siting and Redox Behaviour of Cu ions in CuH-ZSM-5 Zeolites. Cu$^+$ Photoluminescence study.
    *J. Dedecek, B. Wichterlova*, **J. Phys. Chem**. 98 (1994) 5721-5427.
    **106 – 90 – 4.80**
29. Identification of Cu sites in ZSM-5 Active in NO Decomposition.
    *B. Wichterlova, J. Dedecek, A. Vondrova,* **J. Phys. Chem**. 99 (1995) 1065-1067.
    **96 – 84 – 4.80**
30. Coordination of Cu Ions in High Silica Zeolite Matrices. Cu$^+$ Photoluminescence, IR of NO Adsorbed on Cu$^{2+}$, and Cu$^{2+}$ ESR study.
    *J. Dedecek, Z. Sobalik, Z. Tvaruzkova, D. Kaucky, B. Wichterlova*, **J. Phys. Chem**. 99 (1995) 16327-16337.
    **185 – 169 – 4.80**
31. On the Cu Site in ZSM-5 Active in Decomposition of NO. Luminescence, FTIR Study and Redox Properties.
    *B. Wichterlova, J. Dedecek, Z. Sobalik, A. Vondrova, K. Klier,* **J. Catal**. 169, (1997) 194-202.
    **109 – 90 – 6.00**
32. Cu Ion Siting in High Silica Zeolites. Spectroscopy and Redox Properties.
    *B. Wichterlova, Z. Sobalik, J. Dedecek,* **Catal. Today** 38, (1997) 199-203.
    **29 – 23 – 3.40**
33. Catalytic Activity of Cu-MeAlPO-11 in NO Decomposition.
    *J. Dedecek, J. Cejka, B. Wichterlova*, **Appl. Catal. B – Environ**. 15, 233-240 (1998).
    **31 – 26 – 5.62**
34. State and Coordination of Metal Ions in High Silica Zeolites. Incorporation, Development and Rearrangement during Preparation and Catalysis.
    *Z. Sobalik, J. Dedecek, I. Ikonnikov, B. Wichterlova*, **Micropor. Mesopor. Mat**. 21 (1998) 525-532.
    **73 – 63 – 3.28**
35. Catalytic Activity of Cu ion exchanged metaloalumophosphates in NO Decomposition.
    *J. Dedecek, A. Vondrova, J. Cejka*, **Collect. Czech. Chem. C.** 63, 1755-1768 (1998).
    **4 – 1 – 1.28**

36. Siting and Reactivity of the Cobalt Ions in Ferrierite in Selective Catalytic Reduction of NO with $CH_4$.

    *D. Kaucky, J. Dedecek, A. Vondrova, Z. Sobalik, B. Wichterlova*, **Collect. Czech Chem. C.** 63, 1781-1792 (1998).

    **12 – 8 - 1.28**

37. Geometry of the $Cu^+$ 540 nm luminescence centres in zeolites.

    *J. Dedecek, B. Wichterlova*, **Phys. Chem. Chem. Phys**. 1 (1999) 629-637.

    **52 – 46 - 3.57**

38. Siting of the $Cu^+$ ions in dehydrated ion exchanged synthetic and natural chabasites. A $Cu^+$ photoluminescence study.

    *J. Dedecek, P. Kubat, B. Wichterlova*, **Micropor. Mesopor. Mat.** 32 (1999) 63-74.

    **17 – 16 – 3.28**

39. Effect of Framework Charge Density on Catalytic Activity of Copper Loaded Molecular Sieves of Chabasite Structure in Nitrogen(II) Oxide Decomposition.

    *J. Dedecek, A. Vondrova, J. Cejka,* **Collect. Czech Chem. C.** 65 (2000) 343-351.

    **3 – 1 - 1.28**

40. Coordination and properties of cobalt in the CoAlPO-5 and –11 molecular sieves.

    *J. Sponer, J. Cejka, J. Dedecek, B. Wichterlova*, **Micropor. Mesopor. Mat**. 37 (2000) 117-127.

    **42 – 39 - 3.28**

41. Structure, Distribution and Properties of Co Ions in Ferrierite Revealed by FTIR, UV-Vis and EXAFS.

    *Z. Sobalik, J. Dedecek, D. Kaucky, B. Wichterlova, L. Drozdova, R. Prins*, **J. Catal.** 194 (2000) 330-342.

    **55 – 43 – 6.00**

42. Activity of Co Ion Sites in ZSM-5, Ferrierite and Mordenite in Selective Catalytic Reduction of NO with Methane.

    *D. Kaucky, A. Vondrova, J. Dedecek, B. Wichterlova,* **J. Catal**. 194 (2000) 318-329.

    **111 – 101 – 6.00**

43. Uniformity and ordering of inner walls of the (Al)MCM-41.

    *J. Dedecek, N. Zilkova, J. Cejka,* **Collect. Czech. Chem. C**. 66 (2001) 567-574.

    **6 - 4 -1.28**

44. Alkylation and disproportionation of aromatic hydrocarbons over mesoporous molecular sieves.

    *J. Cejka, A. Krejci, N. Zilkova, J. Dedecek, J. Hanika*, **Micropor. Mesopor.**

**Mat**. 44-45 (2001) 499-507.

**29 – 28 – 3.28**

45. Experimental Study of the Effect of Si/Al Composition on the Aluminium Distribution in (Al)MCM-41.

    *J. Dedecek, N. Zilkova, J. Cejka,* **Micropor. Mesopor. Mat**. 44-45 (2001) 259-266.

    **28 – 25 – 3.28**

46. Bonding of Co Ions in ZSM-5, Ferrierite and Mordenite. An X-ray Absorption, UV-Vis and IR Study.

    *L. Drozdova, R. Prins, J. Dedecek, Z. Sobalik, B. Wichterlova*, **J. Phys. Chem. B** 106 (2002) 2240-2248.

    **47 – 39 – 4.80**

47. Analysis of Low Concentration of Free Ferric Oxides in Clays by Vis Diffuse Reflectance Spectroscopy and Voltametry

    *T. Grygar, J. Dedecek, D. Hradil*, **Geol. Carpath.** 53 (2002) 71-77.

    **5 – 3 – 0.78**

48. Synthesis and characterisation of CoSBA-1 cubic mesoporous molecular sieves.

    A. *Vinu, J. Dedecek, V. Murugesan, M. Hartmann*, **Chem. Mater**. 14 (2002) 2433-2435.

    **49 – 48 – 7.28**

49. (Al)MCM-41. Aluminium Distribution and Uniformity and Structure of Inner Surface.

    *J. Dedecek, N. Zilková, J. Kotrla, J. Cejka*, **Collect. Czech. Chem. C.** 68 (2003) 1998-2018.

    **5 – 5 – 1.28**

50. $Fe_2O_3$-$Cr_2O_3$ system revised

    *T. Grygar, P. Bezdicka, J. Dedecek, E. Petrovsky, O. Schneeweiss*, **Ceram-Silikaty** 47 (2003) 32-39.

    **19 – 18 – 0.38**

51. Iron oxide mineralogy in late Miocene red beds from La Gloria, Spain: Rock-magnetic, voltammetric and Vis spectroscopy analyses

    *T. Grygar, J. Dedecek, P.P. Kruive and M.J. Dekkers*, **Catena** 53 (2003) 115-132.

    **35 – 34 – 1.88**

52. [6]Li MAS NMR study of lithium insertion into solvothermally prepared Li-Ti-O spinel

    *P. Krtil, J. Dedecek, T. Kostlanova, J. Brus*, **Electrochem. Solid. St.** 7 (2004) A163-A166.

    **9 – 7 – 1.99**

53. NO Oxidation Kinetics on Iron Zeolites: Influence of Framework Type and Iron Speciation
*R. Brosius, D. Habermacher, J.A. Martens, L. Vradman, M. Herskowitz, L. Capek, Z. Sobalik, J. Dedecek, B. Wichterlova, V. Tokarova, O. Gonsiorova,* **Top. Catal**. *30-31 (2004) 333-339.*
**16 – 16 - 2.62**

54. Preparation and Characterisation of Ag/Alumina Catalysts for the Removal of $NO_x$ Emissions Under Oxygen Rich Conditions
*K. Arve, L. Capek, F. Klingstedt, K. Eränen, L. -E. Lindfors, D. Yu. Murzin, J. Dedecek, Z. Sobalik, B. Wichterlova,* **Top. Catal**. *30-31 (2004) 91-95*.
**26 – 26 – 2.62**

55. Analysis of Fe species in zeolites by UV–VIS–NIR, IR spectra and voltammetry. Effect of preparation, Fe loading and zeolite type
*L. Capek, V. Kreibich, J. Dedecek, T. Grygar, B. Wichterlova, Z. Sobalik, J.A. Martens, R. Brosius, V. Tokarova,* **Micropor. Mesopor. Mat**. 80 (2005) 279-289.
**56 – 53 - 6.00**

56. Enhancement of decane-SCR-$NO_x$ over Ag/alumina by hydrogen. Reaction kinetics and in situ FTIR and UV–Vis study
*P. Sazama, L. Capek, H. Drobna, Z. Sobalik, J. Dedecek, K. Arve, B. Wichterlova,* **J. Catal**. 232 (2005) 302-317.
**89 – 86 – 6.00**

57. Solvothermal synthesis and electrochemical behavior of nanocrystalline cubic Li-Ti-O oxides with cationic disorder
*D. Fattakhova, V. Petrykin, J. Brus T. Kostlanova, J. Dedecek, P. Krtil,* **Solid State Ionics**, 176 (2005) 1877-1885.
**23 – 22 – 2.64**

58. Analysis of the state and size of silver on alumina in effective removal of NOx from oxygen rich exhaust gas
*K. Arve, F. Klingstedt, K. Eränen, D. Yu. Murzin, L. Capek, J. Dedecek, Z. Sobalik, B. Wichterlova, K. Svenneberg, L. R. Vallenberg, J. O. Bovin,* **J. Nanosci. Nanotechno**. *6 (2006) 1076*.
**2 – 2 – 1.56**

59. The effect of the inner particle structure on the electronic structure of the nanocrystalline Li-Ti-O spinels
*T. Kostlanova, J. Dedecek , P. Krtil,* **Electrochim. Acta** 52 (2007) 1847-1856.
**14 – 14 - 3.83**

60. Adsorption of NO in $Fe^{2+}$-exchanged ferrierite. A Density Functional Theory Study
*L. Benco, T. Bucko, R. Grybos, J. Hafner, Z. Sobalik, J. Dedecek, J. Hrušák*, **J.**

**Phys. Chem. C** 111 (2007) 576.
**23 - 18 - 4.80**

61. Multiple Adsorption of NO on $Fe^{2+}$ Cations in the α- and β-Positions of Ferrierite: An Experimental and Density Functional Study
*L. Benco, T. Bucko, R. Grybos, J. Hafner, Z. Sobalik, J. Dedecek, S. Sklenak, J. Hrusak, J.*, **J. Phys. Chem. C** 111 (2007) 9393.
**23 - 20 - 4.80**

62. Discoloration of Fired Kaolinitic Clays (Study of $Fe^{3+}$ Coordination by Mössbauer and UV-ViS-NIR Spectroscopy)
*T. Hanzlicek, D. Niznansky, J. Dedecek, M. Steinerova, P. Straka, J. Triskova*, **J. Am. Ceram. Soc.** 90 (2007) 2843.
**1 – 1 – 2.27**

63. Metal ions as probes for characterization of geopolymer materials
*O. Bortnovsky, J. Dedecek, Z. Tvaruzkova, Z. Sobalik, J. Subrt*, **J. Amer. Ceram. Soc**. 91 (2008) 3052-3057.
**8 – 5 – 2.27**

64. Ag-ZSM-5 zeolite as high-temperature water-vapor sensor material
*P. Sazama, H. Jirglova, J. Dedecek*, **Mater. Lett.** 62 (2008) 4239-4241.
**3 – 3 – 2.30**

65. SBA-15 Immobilized Ruthenium Carbenes as Catalysts for Ring Closing Metathesis and Ring Opening Metathesis Polymerization
*D. Bek, N. Zilkova, J. Dedecek, J. Sedlacek, H. Balcar*, ***Top. Catal.*** 53 (2010) 200 – 209.
**11 – 11 – 2.62**

66. Ru(*p*-cymene)Cl$_2$PCy$_3$ immobilized on mesoporous molecular sieves as catalyst for ROMP of norbornene
*H. Balcar, D. Bek, J. Sedlacek, J. Dedecek, M. Lamac*, **J. Mol. Catal. A Chem.** 332 (2010) 19-24.
**4 – 4 – 2.94**

67. Role of the morphology and the dehydroxylation of metakaolins on geopolymerization
*V. Medri, S. Fabbri, J. Dedecek, Z. Sobalik, Z. Tvaruzkova, A. Vaccari*, **Appl. Clay Sci.** 50 (2010) 538-545.
**4 – 4 – 2.47**

68. N$_2$O decomposition over Fe-zeolites: Structure of the active sites and the origin of the distinct reactivity of Fe-ferrierite, Fe-ZSM-5, and Fe-beta. A combined periodic DFT and multispectral study
*S. Sklenak, P. Andrikopoulos, B. Boekfa, B. Jansang, J. Novakova, L. Benco, T. Bucko, J. Hafner, J. Dedecek, Z. Sobalik*, **J. Catal**. 272 (2010) 262-274.
**17 – 13 – 6.00**

69. Effect of the particle size and surface area of tungstated zirconia on the WOx nuclearity and n-heptane isomerization over Pt/WO3-ZrO2
*D. Kaucky, B. Wichterlovy, J. Dedecek, Z. Sobalik, I. Jakubec*, **Appl. Catal. A-Gen.** 397 (2011) 82-93.
**3 – 3 – 3.90**
70. Geopolymer based catalyst – new group of catalytic materials
*Z. Sobalik, J. Dedecek, P. Sazama, O. Bortnovsky*, **Catal. Today** 164 (2011) 92-99.
**1 – 1 – 3.40**
71. FTIR and (27)Al MAS NMR analysis of the effect of framework Al- and Si-defects in micro- and micro-mesoporous H-ZSM-5 on conversion of methanol to hydrocarbons
*P. Sazama, B. Wichterlova, J. Dedecek, Z. Tvaruzkova, Z. Musilova, L. Palumbo, S. Sklenak, O. Gonsiorova*, **Micropor. Mesopor. Mat. 143 (2011)** 87-96.
**11 – 9 - 3.28**
72. Tailoring of Fe-ferrierite for N(2)O decomposition: On the decisive role of framework Al distribution for catalytic activity of Fe species in Fe-ferrierite
*Z. Sobalik, J. Novakova, J. Dedecek, N. K. Sathu, E. Tabor, P. Sazama, P. Stastny, B. Wichterlova,* **Micropor. Mesopor. Mat.** 146 (2011) 172-183.
**2 – 0 – 3.28**
73. SiC-based refractory paints prepared with alkali aluminosilicate binders
*V. Medri, S. Fabbri, A. Ruffini, J. Dedecek, A Vaccari,* **J. Eur. Ceram. Soc**. 31 (2011) 2155-2165.
**2 – 0 – 2.35**

**Patents and patent application**

74. Katalyzátor pro úplnou oxidaci těkavých organických látek na bázi geopolymeru a způsob jeho výroby
*O. Bortnovsky, K. Dvořáková, Z. Sobalík , P. Sazama, J. Dědeček, Z. Tvarůžková,* CZ301936 (2010).
75. Antibakteriální anorganické pokrytí na bázi geopolymeru a způsob jeho výroby
*O. Bortnovsky, K. Dvořáková, Z. Sobalík , J. Dědeček, Z. Tvarůžková,* CZ302987 (2012).
76. Katalyzátor pro selektivní redukci oxidů dusíku na bázi geopolymeru a způsob jeho výroby
*O. Bortnovsky, W. Poslední, Z. Sobalík , P. Sazama, J. Dědeček, Z. Tvarůžková,* CZ2009-240.