

Framework Stabilization of Ge-Rich Zeolites via Postsynthesis Alumination

Feifei Gao,[†] Maguy Jaber,[‡] Krassimir Bozhilov,[§] Aurelie Vicente,^{||}
Christian Fernandez,^{||} and Valentin Valtchev*^{||}

Laboratoire de Chimie, UMR 5182 CNRS, Ecole Normale Supérieure de Lyon,
46 allée d'Italie, 69364 Lyon, France, Laboratoire de Réactivité de Surface, Université de
Pierre et Marie Curie, 4 place Jussieu, Tour 54-55, 75252 Paris, France, Central Facility for
Advanced Microscopy and Microanalysis, University of California, Riverside, California 92521,
and Laboratoire Catalyse et Spectrochimie, ENSICAEN - Université de Caen - CNRS,
6 bd du Maréchal Juin, 14050 Caen, France

Received June 2, 2009; E-mail: valtchev@ensicaen.fr

Abstract: The use of organic structure directing agents in zeolite syntheses has dramatically extended the number of zeolite structure types during the past decades. However, for about 20% of all known zeolite structure types, the necessary postsynthesis elimination of organic templates by high-temperature combustion leads to structure collapse, where the particularly strongly affected are Ge-rich zeolites. Here, we present a treatment approach that leads to zeolite structure stabilization by postsynthetic isomorphous substitution of Al for Ge. An important advantage of this new method is that no preliminary elimination of the organic structure directing agent from zeolite pores is required; thus it can be applied to microporous materials that cannot withstand the high temperature combustion of organic templates. The experimental data unambiguously show that besides framework stabilization the postsynthesis treatment facilitates incorporation of active sites in the zeolite framework. The feasibility of this new approach is corroborated by alumination of a BEC-type material. The presented method is expected to broaden the practical utilization of many microporous materials by improving their thermal stability.

Introduction

Zeolites are a class of microporous solids, which are extensively used in the chemical process industry. Lately their application has been extended far beyond the traditional uses. The crystal structure and the physicochemical properties of zeolites are strongly dependent on the chemical composition of their framework. In general, the framework composition is controlled by the ratio of the components in the initial gel, which comprises the “intelligence” required for the successful synthesis of a desired material.¹ However, the variation of the framework composition is often limited by the structure type of zeolite or the conditions of crystallization. Thus, in order to obtain the composition desired for a specific application postsynthesis treatments have to be employed sometimes. For instance, the catalytic properties of zeolites are function of their aluminum content. Hence it is desirable to be able to vary the latter while retaining high crystallinity of the material. Methods have already been developed where the desired characteristics are achieved by postsynthesis dealumination² or alumination³ and even consecutive dealumination and alumination of the same material.⁴ The postsynthesis reaction leading to successful replacement of framework cations requires free access of the substituting ions or molecules to the entire volume of the zeolite

crystal. Therefore, materials synthesized with organic structure directing agents (SDAs) are first subjected to calcination in order to combust the organic species and then they are treated to replace the framework cations. Such approach, however, is not applicable to a significant number of potentially useful microporous materials, which cannot withstand high temperature treatment in as-synthesized forms. Partial wet chemistry extraction of the organic SDA could be applied to stable microporous silicates,⁵ but it is not appropriate for materials with limited framework stability, such as Ge-rich microporous solids.

On the basis of the different stability of cations in tetrahedral coordination, the objective of the present study is to develop a wet chemistry approach for postsynthesis framework substitution

- (2) (a) Li, S.; Huang, S.-J.; Shen, W.; Zhang, H.; Fang, H.; Zheng, A.; Liu, S.-B.; Deng, F. *J. Phys. Chem. C* **2008**, *112*, 14486–14494. (b) Wouters, B. H.; Chen, T.; Grobet, P. J. *J. Phys. Chem. B* **2001**, *105*, 1135–1139. (c) Martens, J. A.; Geerts, H.; Grobet, P. J.; Jacobs, P. A. *J. Chem. Soc., Chem. Commun.* **1990**, 1418–1419. (d) Zanjanchi, M. A.; Ebrahimi, A. *Mater. Chem. Phys.* **2008**, *110*, 228–233. (e) Triantafyllidis, C. S.; Vlessidis, A. G.; Nalbandian, L.; Evmiridis, N. P. *Microporous Mesoporous Mater.* **2001**, *47*, 369–388.
- (3) (a) Yang, C.; Xu, Q. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1675–1680. (b) Yang, C.; Wang, J.; Xu, Q. *Micropor. Mater.* **1997**, *11*, 261–268. (c) Omegna, A.; Haouas, M.; Pirngruber, G.; Prins, R. *Stud. Surf. Sci. Catal.* **2001**, *135*, 215. (d) Anderson, M. W.; Klinowski, J.; Xinsheng, L. *J. Chem. Soc., Chem. Commun.* **1984**, 1596–1597. (e) Namba, S.; Yamagishi, K.; Yashima, T. *Chem. Lett.* **1987**, *6*, 1109–1112.
- (4) (a) Omegna, A.; Prins, R.; van Bokhoven, J. A. *J. Phys. Chem. B* **2005**, *109*, 9280–9283. (b) Omegna, A.; van Bokhoven, J. A.; Prins, R. *J. Phys. Chem. B* **2003**, *107*, 8854–8860. (c) Zhang, J.; Zhou, L.; Li, X. *Stud. Surf. Sci. Catal.* **2001**, *135*, 213–220.

[†] Ecole Normale Supérieure de Lyon.

[‡] Université de Pierre et Marie Curie.

[§] University of California, Riverside.

^{||} Université de Caen.

(1) Corma, A.; Davis, M. E. *ChemPhysChem* **2004**, *5*, 304–313.

of microporous materials with limited framework stability. For instance, Si and Al show much higher lattice stability in tectosilicate structures in respect to B, Ga, and Ge. The different stability of these cations in tetrahedral coordination has already been employed by Chen and Zones to replace B with Al in zeolites SSZ-33 and UTD-1.⁶ On the grounds of such experimental evidence, and the close crystal-chemical similarity between Al and Ge in tetrahedral coordination, one may expect that Ge in zeolite frameworks could be readily substituted by Al. The major obstacle to the above goal is the presence of an organic SDA in zeolite channels that blocks the access of active species to the zeolite framework. As a consequence, framework substitution can be successful only if the process can overcome the presence of organic SDA.

In the present work, a Ge-rich microporous zeolite-type material was employed to study the possibility for one-pot template extraction and framework substitution in zeolite frameworks. During the past decade, Corma and co-workers have introduced germanium as a costructure directing agent in zeolite synthesis.⁷ Many new exciting structure types have been synthesized using the fluoride route and germanium as a costructuring agent.⁸ The same team has just published in *Nature* the synthesis and structural determination of the largest pore zeolite (ITQ-37) that closes the gap between micro- and mesoporous materials.⁹ This family of microporous materials is interesting from both academic and industrial point of view. However, the members with high Ge content are not thermally stable, which is an obstacle for their practical uses. In addition, the high price of germanium limits the broad application of Ge-containing catalysts. Hence, a method that could enable at least partial replacement and recycling of germanium cations is highly desirable.

We chose a Ge-rich zeolite, in particular BEC-type, in order to exemplify the feasibility of the approach proposed here. BEC-type zeolite is polymorph C (denoted ITQ-17) of zeolite Beta.^{7a} It could be generated from polymorph A by recurrent application to the building layers of a shear operation along both *a* and *b* axes. BEC-type zeolite contains three-dimensional (3D) twelve-membered ring (12MR) channels that are linear and intersect perpendicularly. Large pore opening ($6.3 \times 7.5 \text{ \AA}$ and $6.0 \times 6.9 \text{ \AA}$) favors the diffusion of guest species and thus the processing of bulky molecules. Furthermore, it contains double 4-membered ring (D4MR) cages as secondary building units

(two D4MR cages per unit cell), which do not exist in the structures of polymorph A or B of zeolite Beta.

Experimental Section

Synthesis of BEC-Type Material. The initial gel was prepared by dissolving colloidal silica (Ludox, AS-40, Aldrich) in hexamethonium hydroxide (Hex(OH)_2 , 0.1 M, Fluka). Then, hexamethonium bromide (HexBr_2 , Fluka) and germanium dioxide (GeO_2 , Aldrich) were added and the solution was stirred until their complete dissolution, followed by the addition of ammonium fluoride (NH_4F 98%, Aldrich). The gel was stirred at room temperature for 2 h then freeze-dried. Appropriate amount of water was added so as to obtain a gel with the following composition $0.85 \text{ SiO}_2:0.33 \text{ GeO}_2:0.15 \text{ Hex(OH)}_2:0.1 \text{ HexBr}_2:0.5 \text{ NH}_4\text{F}:2.0 \text{ H}_2\text{O}$. The hydrothermal crystallization was performed at $180 \text{ }^\circ\text{C}$ for 6 days.

Alumination Procedure. Postsynthesis alumination was carried out with polyaluminum hydroxide chloride solution (Ekoflock 70, Akzo Nobel) at solid:liquid ratio of 1:50. The mixture was stirred in a round-bottom flask under reflux system at $80 \text{ }^\circ\text{C}$. The obtained sample was purified by a series of high speed centrifugation decanting of the supernatant and redispersion in distilled water under ultrasonic treatment. Extra framework aluminum was extracted with 0.01 M HCl at room temperature for 24 h. After the treatment the sample was thoroughly washed with distilled water and dried at $70 \text{ }^\circ\text{C}$. The initial material was denoted as BEC, while the aluminated and subjected to acid extraction samples were denoted as BEC+Al and BEC+Al-HCl, respectively.

Characterization. Powder samples were studied using a conventional X-ray diffractometer (PANanalytical, X'Pert Pro MPD). Morphological features of zeolite crystals were investigated with a scanning (SEM, Philips XL30 FEG) and a transmission (TEM, FEI-Philips CM300, LaB₆ cathode) electron microscope. The latter was operated in a low-dose mode at 300 kV accelerating voltage. The TEM instrument was equipped with EDAX energy dispersive X-ray spectrometer (EDS). The zeolite composition was determined by flame atomic absorption (Varian, AA240FS) and X-ray Fluorescence (Philips, MagiX). Thermogravimetric (TG) analysis was performed with a Setaram TG-ATD Labsys thermal analyzer at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ in air. Prior to the TG experiment the sample was exposed to 77% humidity at room temperature for three days. Nitrogen adsorption/desorption measurements were performed with an ASAP 2040 MP instrument after degassing of the sample at $300 \text{ }^\circ\text{C}$ overnight. The specific surface area was calculated with the BET equation while the microporous volume was distinguished from the mesoporous one by the *t*-plot method. Water adsorption isotherm was recorded at $25 \text{ }^\circ\text{C}$ using a SARTORIOUS 7012 vacuum microbalance. Prior to the analysis, the sample was activated at $300 \text{ }^\circ\text{C}$ for 1 h.

Temperature programmed desorption of ammonium (NH_3 -TPD) was carried out by using BEL-CAT-48 (BEL Japan, Inc.). A sample of 50 mg was heated at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $500 \text{ }^\circ\text{C}$ and kept at $500 \text{ }^\circ\text{C}$ for 1 h, under the He flow of $50 \text{ cm}^3 \text{ min}^{-1}$. After cooling down to $100 \text{ }^\circ\text{C}$, ammonia (with 5% in He) was passed over the sample for 30 min. To remove weakly adsorbed NH_3 , He flow was performed for another 30 min. Then NH_3 -TPD curve was recorded from 100 to $610 \text{ }^\circ\text{C}$ at the heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ with He flow of $30 \text{ cm}^3 \text{ min}^{-1}$.

¹H, ¹³C, and ²⁷Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) were all performed on a Bruker Avance DSX400 spectrometer (9.4 T) using a 4-mm rotor and a double-resonance probehead. MAS rates were adjusted to 14.5 kHz for all samples. Recycling time was generally adjusted to 1 s, except for ²⁷Al NMR for which it was 500 ms. Supplementary experimental parameters are given in the figure captions. Quantification of the various carbon atoms in the [¹H]-¹³C CPMAS spectra was achieved using a series of spectra acquired with different contact times, in order to correct possible variations in the polarization and relaxation times of the

- (5) (a) Jones, C. W.; Hwang, S.; Okubo, T.; Davis, M. E. *Chem. Mater.* **2001**, *13*, 1041–1050. (b) Jones, C. W.; Tsuji, K.; Takewaki, T.; Beck, L. W.; Davis, M. E. *Microporous Mesoporous Mater.* **2001**, *48*, 57–64.
- (6) Chen, C. Y.; Zones, S. I. *Stud. Surf. Sci. Catal.* **2001**, *135*, 211–218.
- (7) (a) Corma, A.; Navarro, M. T.; Rey, F.; Rius, J.; Valencia, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2277–2280. (b) Sastre, G.; Vidal-Moya, J. A.; Blasco, T.; Rius, J.; Jorda, J. L.; Navarro, M. T.; Fey, F.; Corma, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4722–4726.
- (8) (a) Alvaro, M.; Atienzar, P.; Corma, A.; Ferrer, B.; Garcia, H.; Navarro, M. T. *J. Phys. Chem. B* **2005**, *109*, 3696–3700. (b) Corma, A.; Diaz-Cabanas, M. J.; Martinez-Triguero, J.; Rey, F.; Rius, J. *Nature* **2002**, *418*, 514–517. (c) Castaneda, R.; Corma, A.; Fornes, V.; Rey, F.; Rius, J. *J. Am. Chem. Soc.* **2003**, *125*, 7820–7821. (d) Corma, A.; Diaz-Cabanas, M. J.; Rey, F. US Patent 6797254, 2003. (e) Corma, A.; Diaz-Cabanas, M. J.; Jorda, J. L.; Martinez, C.; Moliner, M. *Nature* **2006**, *443*, 842–845.
- (9) Sun, J.; Bonneau, Ch.; Cantín, A.; Corma, A.; Díaz-Cabañas, M. J.; Moliner, M.; Zhang, D.; Li, M.; Zou, X. *Nature* **2009**, *458*, 1154–1157.

Table 1. Chemical Analysis and Nitrogen Adsorption Data for the Parent BEC-Type Sample and the Materials Subjected to Postsynthesis Treatments

samples	Si:Al	Si:Ge	Ge:Al	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)
BEC	—	3.6	—	89	0.002
BEC+Al	14.6	5.2	2.8	93	0.003
BEC+Al-HCl	138.9	6.2	22.6	239	0.047
BEC+Al-HCl-Al	8.3	6.7	1.2	251	0.045
BEC+Al-HCl-Al-HCl	30.8	6.7	4.6	303	0.064
BEC+Al-HCl-Al-HCl ^a	30.8	6.7	4.6	609	0.174

^a Sample is calcined at 600 °C for 5 h.

different species. The 2D heteronuclear correlation experiment (HETCOR) was acquired using cross-polarization (CPMAS) transfer.

Results and Discussion

In a previous investigation we employed a micrometer-sized BEC-type material synthesized with tetraethylammonium hydroxide.¹⁰ The post synthesis alumination of the material was performed in order to replace Ge with Al. The analysis of the obtained products and their intermediates revealed that partial substitution of Al for Ge is possible. However, the stabilization of BEC-type material was not achieved, which was attributed to the large crystals and thus limited penetration of aluminum species in the depth of zeolite crystals. Consequently, we employed nanosized zeolite crystals in the present study. BEC-type material was synthesized using hexamethonium as a SDA. Physicochemical characterization showed that the as-synthesized material is highly crystalline with Si/Ge ratio of 3.6. The crystallites were smaller than 50 nm in size (Supplementary Figure 1, Supporting Information) building complex aggregates, which could be resolved clearly in the SEM. After calcination at 450 °C for 7 h almost total lost of crystallinity was observed in its X-ray diffraction (XRD) pattern (Supplementary Figure 2, Supporting Information).

The as-synthesized material was subjected to hydrothermal treatment (80 °C for 6 h) in a polyaluminum hydroxide chloride solution. The choice of the reactant was inspired by the fact that acidic solutions have already been used for the partial extraction of organic template species from BEA-type zeolite,⁵ as well as for grafting aluminum in ordered mesoporous all-silica materials.¹¹

After purification the aluminated sample (BEC+Al) was subjected to chemical analysis, which revealed a substantial amount of aluminum (Table 1). The incorporation of the aluminum in the solid was accompanied by a decrease in the Si/Ge ratio.

The aluminum coordination in the modified BEC-type sample was studied by MAS NMR. The ²⁷Al MAS NMR investigation revealed that after the first alumination step the BEC-type material contained both tetrahedral and octahedral aluminum (Figure 1a). The intensity ratio between the peaks centered at about -50 and 0 ppm indicates that the main part of the aluminum is in tetrahedral coordination. Since the presence of extra framework species in the channel system is not favorable for practical application, the material was consequently subjected to a mild acid treatment (BEC+Al-HCl). The ²⁷Al NMR inspection showed that all extra framework species were eliminated, while tetrahedral aluminum was still present in the sample (Figure 1b). It is worth mentioning that together with Al a part of Ge was also removed and the Si/Ge ratio increased to 6.2 (Table 1). Although a limited amount of Al

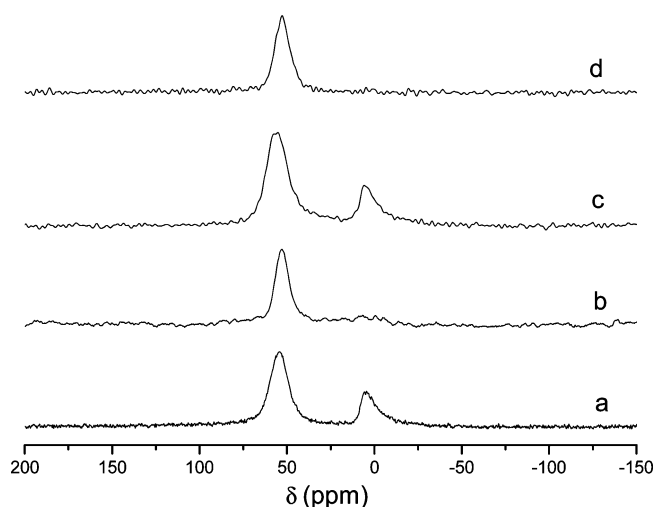


Figure 1. ²⁷Al MAS NMR spectra of the aluminated BEC-type materials. The products obtained after (a) the first step alumination (BEC+Al), (b) the acid extraction of extra framework species (BEC+Al-HCl), (c) the second step aluminated (BEC+Al-HCl-Al), and (d) the second step acid extraction of extra framework species (BEC+Al-HCl-Al-HCl).

was incorporated in the framework, the material showed high thermal stability since the structure resisted calcination at 600 °C for 5 h.

The above experiments confirmed the feasibility of the synthetic approach without reaching, however, substantial incorporation of aluminum in the zeolite framework. The hydrothermal treatment procedure was repeated at extended duration of 16 h (BEC+Al-HCl-Al), which led to incorporation of the largest amount of Al in the present study. After another acid extraction of extra framework species (BEC+Al-HCl-Al-HCl) the Al content was reduced again (Table 1). The presence of extra framework species (Figure 1c) and their complete removal (Figure 1d) were proved by the ²⁷Al MAS NMR analysis. Utilizing the described treatment procedure, a BEC-type zeolite was obtained with the Si/Al ratio of 30.8 in the process the amount of Ge was reduced almost twice from its original concentration. Thus, the unit cell composition of BEC-type material changed from Si₂₀₁Ge₅₅O₅₁₂ to Si₂₁₇Ge₃₂-Al₇O₅₁₂.

As known in a tectosilicate framework the replacement of Si⁴⁺ (or Ge⁴⁺) with Al³⁺ introduce a negative charge in the framework which is balanced by a cation. Under the employed conditions, namely treatment in acidic media, the counteraction of framework Al is expected to be a proton. Thus, the protons of the initial and subjected to consecutive aluminations-acid extraction steps samples were studied by ¹H MAS NMR (Supplementary Figure 3, Supporting Information). Besides the protons attributed to organic template a new resonance at 4.8 ppm attributed to water molecule appeared in the aluminated material. This relatively strong peak suggests large amount of water in the aluminated material. Further BEC-type material subjected to aluminations-acid extraction steps (BEC+Al-HCl-Al-HCl) was dehydrated and studied by ¹H MAS NMR analysis (Supplementary Figure 4, Supporting Information). The broad peak, around 2.0 ppm, corresponding to the two methylene groups of the template chain, was better resolved due to the decrease of hydrogen bound with water molecules. The template was eliminated by high temperature calcinations. ¹³C MAS NMR study (not shown here) did not find residual carbon confirming complete elimination of the organic structure directing agent, which allowed to study on the protons incorporated

(10) Tosheva, L.; Mahe, N.; Valtchev, V. *Stud. Surf. Sci. Catal.* **2007**, *170*, 616–621.

(11) Mokaya, R.; Jones, W. J. *Mater. Chem.* **1999**, *9*, 555–561.

into the zeolite framework. Thus, the presence of Bronsted acid sites (SiOHAl) with resonance at 6.8 and 8.5 ppm was clearly distinguished.¹² In addition, peaks at 2.1 and 2.8 ppm were found that correspond to silanol nests (SiOH) and protons connected to extra framework aluminum (EF-AlOH), respectively.

NH₃-TPD experiments were in full agreement with ¹H MAS NMR analysis. Two distinct maxima were observed in the TPD curve (Supplementary Figure 5, Supporting Information). The first peak, centered at about 170 °C, is attributed to NH₃ desorption from defect sites and weak Bronsted and Lewis sites. The second one, typical of strong Bronsted acid sites, has a maximum at about 310 °C. A conventional BEA-type material was employed as a reference and the TPD analysis performed under similar conditions. Again two peaks with maxima overlapping those of BEC-type material were observed, which shows the similar nature of the active sites in BEA-type and aluminated BEC-type material. On the other hand the low temperature peak, corresponding to weak NH₃ attraction, was much more intense in the BEC-type material. This larger presence of weak sites was attributed to more abundant presence of defect sites in aluminated and acid treated material. This larger presence of oxygen vacancies is most probably due to the post aluminated procedure, where extra framework aluminum was extracted by mild acid treatment. We anticipate that a part of framework aluminum is also extracted during this treatment giving rise to a number of defects in zeolite framework. Future experiments will show whether this extraction can be minimized which will decrease the number of weak sites in the zeolite framework.

The presence of cation exchange sites created by incorporation of aluminum in the zeolite framework was further confirmed by potassium ion-exchange. Aluminated materials prior to and after calcination steps were subjected to ion-exchange under mild conditions. Less than 10% of the available aluminum sites were counterbalanced by K⁺ in the noncalcined material modified via multistep aluminated and chemical treatment in acidic media. This result shows that prior to the calcination step only a negligible part of AlO₄⁻ tetrahedral are accessible for the K⁺ cations, while the remaining charges are compensated by the charged organic structure directing agent or protons. This statement is supported by {¹H}-²⁷Al HETCOR experiments, where a single correlation peak between the methyl protons of the hexamethonium head (-N⁺(CH₃)₃) and the tetrahedral aluminum was detected (Figure 2). The presence of such a correlation is due to the short distance between the positively charged head of the template and the negatively charged tetrahedral aluminum in the framework. The HETCOR experiment provided also important clues about the mechanism of framework substitution. The close proximity between the charged part of the molecule and the aluminum tetrahedron suggests specific interactions that assist the isomorphous substitution. The most plausible explanations are: (i) the presence of framework defects; or (ii) destabilization of the tetrahedron at the vicinity of charged cationic head. After calcination and ion exchange 94% of Al was counterbalanced by potassium cations. The presence of minor amount of extra

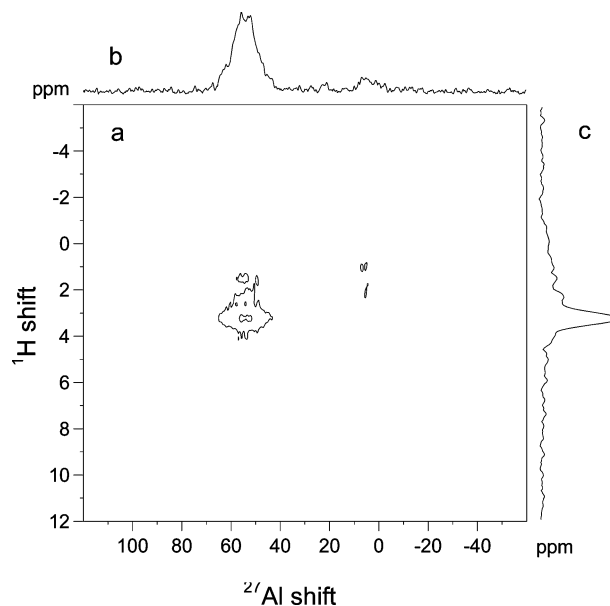


Figure 2. ¹H-²⁷Al CPMAS HETCOR spectrum of the two-step aluminated BEC-type material dehydrated. $\nu_R = 14.5$ kHz, $B_0 = 9.4$ T. $\nu_{Al} = 10.0$ kHz, $\nu_H = 4.5$ kHz, and $\tau_{CP} = 700$ μ s.

framework aluminum species is most probably the reason that the K:Al ratio slightly deviated from 1:1. These data fully support the results of ²⁷Al MAS NMR analysis, namely the incorporation of aluminum in tetrahedral positions in the zeolite framework and thus providing ion exchange sites. It is worth mentioning that no changes related to potassium ion-exchange in the XRD crystallinity of BEC-type material were observed.

The effect of consecutive aluminated - acid extraction steps on the specific surface area and micropore volume of the samples were studied by N₂ adsorption/desorption measurement (Table 1). As can be seen the initial noncalcined material exhibits a relatively large external surface area (89 m² g⁻¹), which is indicative of the small crystal size. For the sake of comparison a conventional micron-sized material exhibits external surface area of a few m² g⁻¹. The term external surface area is employed to distinguish the surface of crystallites from total surface area, which includes also the pores of microporous crystals. In order to obtain the external surface area material was degassed at relatively low temperature (130 °C) so as to keep intact organic structure directing agent that filled up micropore volume. After the first aluminated - acid extraction step the S_{BET} increased almost three times and reached 239 m² g⁻¹. Further increase of the specific surface area (303 m² g⁻¹) was observed after the second-step treatment. The augmentation of the specific surface area was coupled with the increase of the pore volume of the material. The latter suggests that the acid treatment leads to partial extraction and probably perturbs the close packing of hexamethonium in zeolite channels so the N₂ molecule can penetrate in the intercrystalline voids.

The above interpretations were verified by thermogravimetric analysis of the sample subjected to consecutive wet chemical treatments. The mass loss attributed to the organic species in the chemically treated sample was ca. 50 wt. % in respect to the initial material. The decrease in the organic content was coupled with increase of the water amount from 3 wt. % in the as-synthesized BEC-type zeolite to 10.5 wt. % in the modified sample (Figure 3). Besides the larger amount of water adsorbed into aluminated material a high temperature shift of the peak corresponding to the water desorption was observed. Thus, the

(12) (a) Li, S.; Huang, S. J.; Shen, W.; Zhang, H.; Fang, H.; Zheng, A.; Liu, S. B.; Deng, F. *J. Phys. Chem. C* **2008**, *112*, 14486. (b) Müller, M.; Harvey, G.; Prins, R. *Microporous Mesoporous Mater.* **2000**, *34*, 281. (c) Freude, D.; Hunger, M.; Pfeifer, H.; Schwieger, W. *Chem. Phys. Lett.* **1986**, *128*, 62. (d) Karge, H. G.; Hunger, M.; Beyer, H. K. *Catalysis and Zeolites Fundamentals and Applications*; Weitkamp, J., Puppe, L., Eds.; Springer: Berlin, 1999; p 267. (e) Feng, M. H.; Chao, K. J. *J. Mol. Struct.* **1996**, *364*, 51.

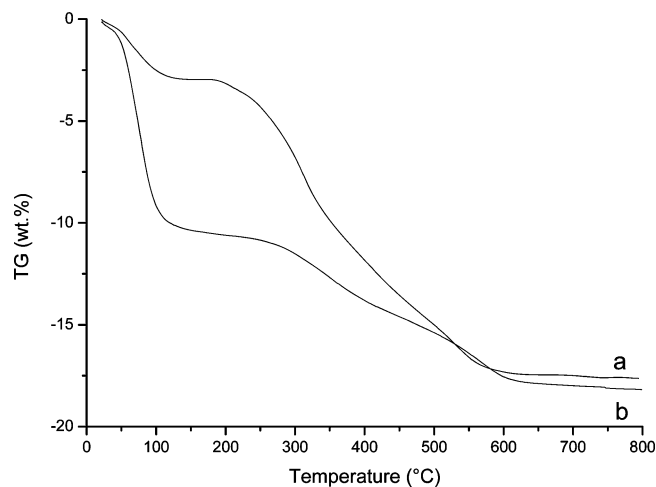


Figure 3. TG analyses of the (a) as-synthesized and (b) two-step modified BEC-type materials.

initial material desorbed the water in the temperature range 100–200 °C, whereas the water release in the aluminated material was extended to 300 °C. The latter suggests that the water in the aluminated material is more strongly bound to the framework or/and the diffusion of the molecules is partially blocked by the other guest species, namely the remains from the template and some extra framework aluminum. The presence of such species is most probably the reason for the observed slow saturation of the material. The water adsorption isotherm is somewhat different from a classical one, where full saturation is achieved at relatively low partial pressure. The aluminated noncalcined sample showed a more pronounced take up at high relative pressure ($P/P_0 > 0.5$) suggesting the presence of barriers that limit the water diffusion (Supplementary Figure 6, Supporting Information). Nevertheless, a substantially larger amount of water was adsorbed in respect to the initial BEC-type material. The increased water capacity is a consequence of wet chemical treatment that led to partial extraction and rearrangement of the templating species, thus opening a part of the micropore volume. The large external surface area of zeolite nanocrystallites also contributes to the water adsorption, especially after the consecutive chemical treatments that increase the number of oxygen vacancies. It should be added that extra framework aluminum species also comprise water as revealed by ^1H MAS NMR study. Thus, the cumulative amount of water in the aluminated material is relatively high, although the pore volume of the sample is $0.064\text{ cm}^3\text{g}^{-1}$ according to the N_2 adsorption measurements (Table 1).

The consequence of chemical treatment of the species occupying the zeolite channels and the mechanism of template extraction was further studied by quantitative $\{^1\text{H}\}$ - ^{13}C cross-polarization MAS NMR of the series of samples (Figure 4). The signals from different carbons of the template molecule were found at 67.5, 57.5, 26.5, and 23.6 ppm that correspond to $\text{N}-\text{CH}_2$, $\text{N}-\text{CH}_3$ and the second and third CH_2 groups of the hexamethonium chain, respectively. The quantification of carbons showed a substantial decrease of template content (ca. 50%) in the treated material. A closer look at the ratio between different species revealed a more significant decrease (ca. 65%) of $\text{N}-\text{CH}_2$ groups. The latter suggests breaking of $\text{C}-\text{N}$ bond between the $\text{N}-(\text{CH}_3)_3$ headgroup and the first carbon in the hydrocarbon chain. Thus, the decrease of template content in zeolite channels is a consequence of partial destruction and extraction of hexamethonium cation.

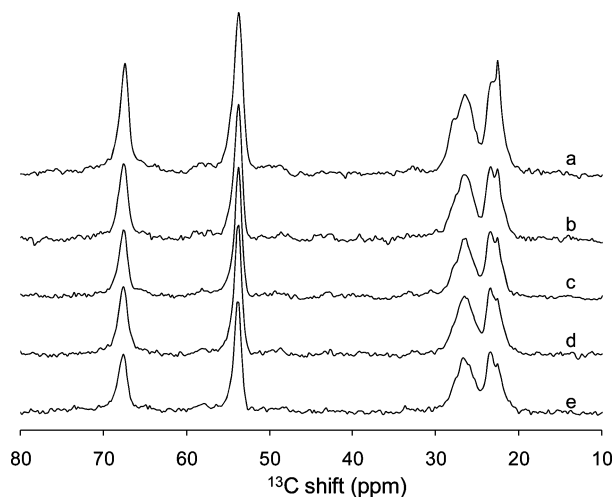


Figure 4. $\{^1\text{H}\}$ - ^{13}C CPMAS NMR spectra of (a) the initial BEC-type material (BEC), and (b) the products obtained after the first alumination step (BEC+Al), (c) one aluminations-acid extraction step (BEC+Al-HCl), (d) two aluminations steps (BEC+Al-HCl-Al), and (e) two aluminations-acid extraction steps (BEC+Al-HCl-Al-HCl).

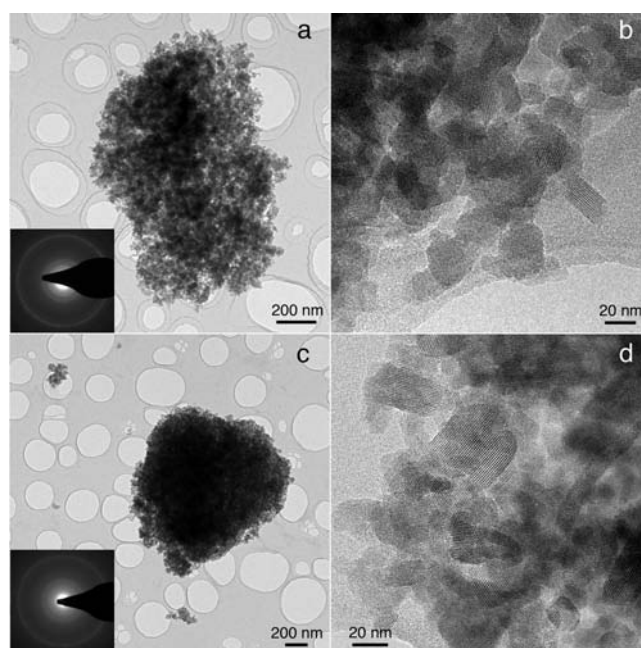


Figure 5. TEM micrographs of initial BEC-type material and the product obtained after two aluminations-acid extraction steps (BEC+Al-HCl-Al-HCl). (a) Low magnification images of the aggregates in the initial BEC-type material. (b) High magnification images of the initial BEC-type zeolite. (c) Low magnification images of the modified material BEC+Al-HCl-Al-HCl. (d) High magnification images of the modified material BEC+Al-HCl-Al-HCl. As an inset in (a) and (c) are given the SAEDs obtained from the corresponding samples. The reflection rings in (a) and (c) correspond to the $\{200\}$, $\{202\}$ and $\{602\}$ of the BEC-type structure.

The effects of the wet chemical treatment on the morphological features of BEC-type crystals and aggregates were studied by TEM. The inspection of the initial material showed that the individual crystallites range between 10 and 40 nm in size and form complex aggregates (Figure 5a, b). The major part of crystallites are short prismatic particles with aspect ratio between 3 and 2. After the wet chemical treatment no changes in the size of the aggregates and morphology of the nanocrystallites were observed (Figure 5c, d), which pointed out that no chemical reaction of recrystallization or dissolution of the zeolite crystals

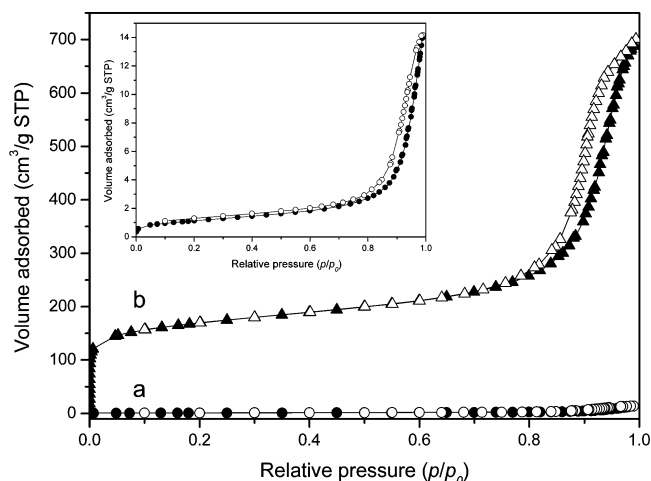


Figure 6. N_2 adsorption/desorption isotherms of the (a) initial and (b) thermally stable BEC-type material obtained by two aluminations—acid extraction steps and calcination at 600 °C for 5 h. (Inset) Enlarged isotherm of as-synthesized BEC-type material.

took place. The microanalyses performed on isolated single crystals show an average ratio between Si:Ge:Al of 20:3:1. This ratio corresponds to higher framework aluminum content than that obtained from the bulk analysis. We attribute the disagreement between bulk and local analysis to nonhomogeneous distribution of aluminum in different nanocrystals. In other words, the aluminum concentration in nanocrystals is variable and most probably it depends on the spatial location of each nanocrystal in the aggregate and the level of intergrowth between individual crystals during the process of treatment.

Improvement in the porosity of the BEC-type material after the postsynthesis treatment was verified by N_2 adsorption/desorption measurement. A mesoporous type adsorption/desorption isotherms with hysteresis loop suggesting large textural porosity was recorded for the as-synthesized BEC-type material (Figure 6, inset). Type I adsorption/desorption isotherm characteristic of microporous solids was obtained after two aluminations - acid extraction steps followed by calcination at 600 °C for 5 h (Figure 6). A step rise in the uptake at low relative pressure corresponds to the filling of micropores with N_2 . In contrast to conventional micrometer-sized microporous materials, the steep uptake at low relative pressures is not followed by a flat curve, instead an inclination of the curve with the increase of pressure can be observed. At high relative pressure the upward turn with a hysteresis loop is indicative of the intercrystalline mesoporosity. The latter is a consequence of the aggregation of nanoparticles into complex aggregates. The specific surface area of the material is 609 $m^2 g^{-1}$ (Table 1), which corresponds to a highly crystalline material. On the other hand, the micropore volume is slightly below the expected one for a highly crystalline zeolite Beta. Lower micropore volume indicates that the conversion of the initial BEC-type material into stable Al-containing counterpart is not accomplished. It is probably a consequence of nonuniform incorporation of aluminum in individual zeolite crystals as revealed in the combined bulk and local analysis.

To investigate the framework stability, the product obtained after two aluminations - acid extraction steps was subjected to an *in situ* high temperature XRD study in air atmosphere. A stepwise heating was carried out from ambient temperature to 600 °C, where the heating rate between individual steps was 1 °C min^{-1} . After each 100 °C segment the temperature was kept

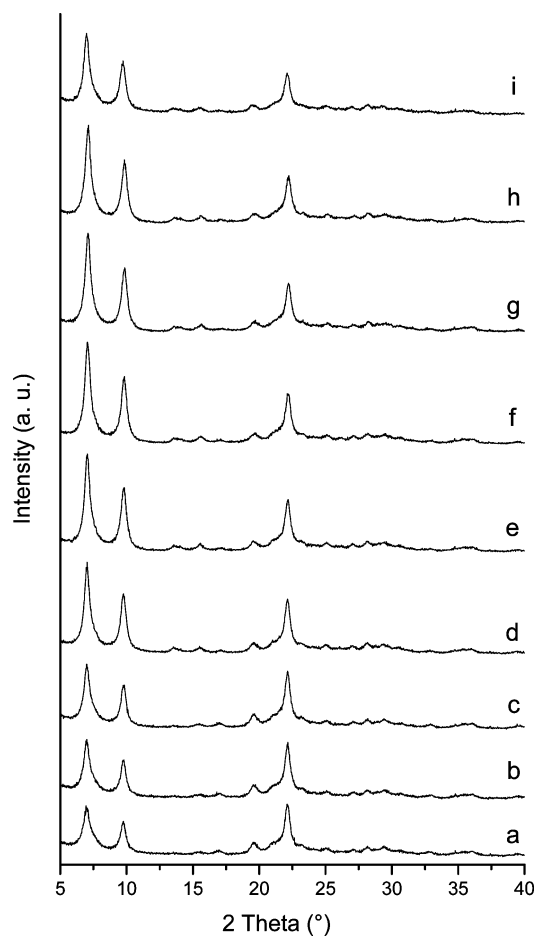


Figure 7. XRD patterns of (a) the initial BEC-type material and the modified product after heated at a rate of 1 °C min^{-1} to (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C, (g) 600 °C, and (h) calcined at 600 °C for 3 h and (i) then cooled down to ambient temperature.

constant for 30 min and an XRD pattern was recorded. The material was then held at 600 °C for 3 h and subsequently cooled down to room temperature. The results of this experiment are presented in Figure 7. There is no difference between the crystallinity of the Al-substituted BEC-type material and the initial nonheated Al-free Ge-silicate zeolite. Further, the calcined material was exposed to 77% humidity at room temperature and subjected to XRD measurements after 18, 24, and 30 days. No difference among the XRD patterns of parent and moisture-exposed materials was observed (Supplementary Figure 7, Supporting Information), which further confirms the framework stability of modified microporous material.

The above physicochemical analyses of aluminated BEC-type material show that aluminum ions are incorporated into the zeolite framework. It is clear that the incorporation occurs namely as isomorphous substitution of aluminum for germanium since the increase of the aluminum content in the zeolite is accompanied by decrease in the germanium content. It is worth mentioning that after the postsynthesis isomorphous substitution the crystal structure and crystallinity of BEC-type material are not affected, and the thermal stability increased. Most probably the substitution of Ge^{4+} by Al^{3+} is favored by the virtual identity of the ionic radii of Ge^{4+} and Al^{3+} in tetrahedral coordination (0.49 Å versus 0.5 Å) whereas substitution of Si^{4+} would be energetically less favorable due to the larger difference in ionic radii between Si and Al. The partial replacement of Ge^{4+} by Al^{3+} is probably accompanied by creation of oxygen vacancies

or protonation to maintain the electroneutrality of the framework. Minor amounts F (less than 0.4 at. %) were detected in some of BEC-type batches, but its concentration did not correlate with Al substitution.¹³ As discussed above, the incorporation of some aluminum in defect sites of zeolite framework or replacement of some of the silicon atoms cannot be excluded. However, the major part of aluminum replaces Ge as unambiguously proved by the chemical analysis. The above assumptions about the mechanism of substitution would need more rigorous analysis in order to be verified.

The chemical analyses of the solid after the first alumination step showed relatively high aluminum concentration. According to the ²⁷Al MAS NMR investigation aluminum is predominantly in tetrahedral coordination. Nevertheless, the mild acid treatment performed to eliminate the octahedral aluminum resulted in extraction of a part of framework Al, which was revealed by the ¹H MAS NMR (Supplementary Figure 4, Supporting Information) and NH₃-TPD analysis (Supplementary Figure 5, Supporting Information). Thus, the aluminum content decreased dramatically, after the first acid treatment step. Our interpretation of these observations is that initially a substantial part of the aluminum is relatively loosely attached to the external surface of the zeolite crystals. It is worth noting that the zeolite nanocrystals exhibit large external surface area (Table 1), where the reactive aluminum species could be anchored. Consequently, these species did not withstand the acid treatment and the following washing steps. The second alumination step was more efficient in incorporating Al in the zeolite framework. The latter is most probably due to: (i) partial decomposition and extraction of closely packed template molecules during the first alumination–acid extraction step; (ii) longer alumination procedure which allowed deeper penetration of aluminum species in zeolite nanocrystals; (iii) possible partial protonation by the acid treatment which in turn could make Al³⁺ substitution for Ge⁴⁺ more electrostatically favorable. Further optimization of the alumination process will allow identifying the most appropriate conditions for effective isomorphous substitution of Al for Ge in Ge-rich zeolites.

Replacement of Ge with Al could take place by two potential mechanisms. First is so-called T-jump mechanism, where defect sites migrate from the volume to the surface of a crystal.¹⁴ This mechanism is usually observed at high temperature in the presence of steam and takes place without dissolution and transport of discrete soluble species. Neither the experimental conditions nor the set of experimental data support the existence of such a mechanism in the present case. Second possible mechanism passes via hydrolysis, transport through the channels system and thus expelling of germanium atoms from zeolite structure. The hydrolyzing ability of aqueous acidic solutions that leads to removal of framework cations as boron and aluminum from zeolite framework is well-known.^{6,15} In previous investigations this ability was employed to extract aluminum and boron from zeolite frameworks leaving behind silanol nests and then in a second step incorporation of other tetrahedral species such as titanium or silicon. In the present study this ability was used to extract germanium from the framework of BEC-type zeolite. Another important difference between present and previous investigation is the simultaneity of

the reactions. Namely, the alumination of as-synthesized Ge-silicate molecular sieves includes the following parallel reactions: (i) partial decomposition and extraction of closely packed template molecules during alumination–acid extraction step; (ii) hydrolysis of a part of framework Ge⁴⁺ cations leaving behind silanol nests with Si–O(H) groups positioned for the incorporation of other tetrahedral species; and (iii) incorporation of Al³⁺ in framework position. Among these reactions the extraction and reorganization of template molecules is of primary importance for the access of hydrolyzing species to the Ge positions in the framework. In other words, the key factor is the vulnerability of the template to undergo decomposition in acidic media into species small enough to circulate through the channels and leave the microporous space. Simultaneous extraction of Ge and replacement by Al is also a reaction whose efficiency is controlled by the diffusion of the species in and out of the channel system. The analysis of the results of the present study and previous investigation performed on micrometer-sized crystals¹⁰ revealed the importance of the pathway length that aluminum and germanium species should cross for the efficient replacement of Ge in the depth of zeolite crystals. Summarizing the above discussion one can say that the successful application of the present approach depends on two main factors, that are, successful degradation of the template in acidic media and the size of zeolite crystals. Future studies will show the impact of the type of the channel system on the isomorphous substitution of Al for Ge in microporous zeolite-type frameworks.

Conclusion

The present study has unambiguously proved that Ge in the framework of BEC-type zeolite was partially substituted by Al. The isomorphous substitution was achieved by a postsynthesis wet chemistry method. An important advantage of this approach is that the preliminary elimination of the organic structure directing agent from zeolite pores is not required. Thus, the method is applicable to those microporous materials that cannot withstand the high temperature combustion of the organic template. The developed postsynthetic approach opens up routes for: (i) stabilizing of Ge-rich zeolitic materials; (ii) fine-tuning of acidic properties of thermally stable Ge-containing zeolites via isomorphous substitution of Al for Ge; (iii) incorporating other cations in zeolite frameworks; and (iv) investigating advancement in wet chemical framework stabilization of related materials such as microporous GaPO₄. The presented synthesis approach is expected to lead to practical utilization of many materials with interesting framework topologies, which have not been available up to now because of their low thermal stability.

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Supporting Information Available: SEM images of as-synthesized and alluminated BEC-type material; XRD patterns of as-synthesized and calcined initial BEC-type zeolite; ¹H MAS NMR of modified and calcined samples; NH₃-TPD analysis; H₂O adsorption isotherm; and XRD patterns of aluminated BEC-type material exposed to atmosphere of 77% humidity for different periods of time. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) Villaescusa, L. A.; Barrett, P. A.; Cambor, M. A. *Chem. Mater.* **1998**, *10*, 3966–3973.

(14) Kornatowski, J.; Bauer, W. H.; Pieper, G.; Rozwadowski, M.; Schmitz, W.; Cielowlas, A. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 1339–1348.

(15) Lee, E. F. T.; Rees, L. V. C. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 1531–1540.