Synthesis and Crystal Structure of Zeolite RUB-41 Obtained as Calcination Product of a Layered Precursor: a Systematic Approach to a New Synthesis Route

Y. X. Wang,† H. Gies,* and B. Marler

Institute für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, 44780 Bochum, Germany

U. Müller

BASF AG, GCC/Z M 301, 67056 Ludwigshafen, Germany

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Zeolite RUB-41, framework type code RRO, having a new framework structure has been synthesized as a calcination product using a layered silicate, RUB-39, as precursor. The precursor was obtained from hydrothermal synthesis using dimethyldipropylammonium hydroxide as structure directing agent. RUB-41, $18SiO_2$ per unit cell, crystallizes in the monoclinic space group $P2/c$ with $a = 7.345(1)$ Å, $b = 8.724(1)$ Å, $c = 17.125(1)$ Å, and $\beta = 114.2(1)°$. The material has a 2-dimensional channel system with intersecting 8- and 10-membered ring pores. The pore openings determined from structure analysis are 5.8 Å × 4.1 Å (8MR) and 5.9 Å × 4.1 Å (10MR). The surface area determined from nitrogen adsorption experiments is 510 m^2/g and the pore space is accessible for linear molecules. The material shows high sorption interaction for C4 alkenes and excludes i-butane from the pore system.

Introduction

The synthesis of new microporous silicates has had a very successful period over the past decade. In particular, the development of the synthesis route based on fluoride as mineralizer and the substitution of Si by Ge has had a major impact on the extension of the existing synthesis field for high-silica and all-silica microporous zeolites.[1−5] The development was assisted by the discovery of new and tailor-made structure-directing agents (SDA) as templates for the channel void space that yielded a number of new materials.[4−7] Developments such as modern high-throughput synthesis techniques and more efficient and innovative synthesis concepts also have been realized.[8,9] Finally, the mathematical proof that there is an infinite number of 3-dimensional 4-connected networks, the topological descriptor of silicate zeolite frameworks,[10] represented a new challenge for the synthesis community and also created the demand from the application-oriented scientist for particular zeolite framework structures. And indeed, there seems to be no limit for new framework structures.

In the past 10−20 years the focus of zeolite research was directed mainly toward the synthesis of new ultra-large pore materials exceeding 12-membered rings in the silicate framework. In the case of silicate zeolites the synthesis of large-pore materials required complicated and expensive SDA and/or the replacement of cheap silica by GeO_2. However, there was little innovative research initiative in the field of small- and medium-pore zeolites. Although the group of high-silica zeolites with pores limited by 10 or 12 $[TO_4]$-units, 10- or 12-membered ring (MR) zeolites, is most researched in catalysis and shows the highest commercial value, there was little innovation in this field. The synthesis studies of new 8- to 10-MR silicate zeolites, where the zeolite-specific properties in catalysis and sorption, i.e., shape and form selectivity, are most pronounced,[11] have almost been neglected. The few examples of new silicate zeolites with pores smaller than 10 MR discovered over the past 10 years are ITQ-3[12] (framework type code ITE), SSZ-23 (STT),[13,14] with intersecting 7- and 9-MR, MCM-35[15] (MTF),

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* Corresponding author. E-mail: hermann.gies@rub.de.

† On leave from College of Chemistry and Molecular Engineering, Peking University, Beijing, PR China.

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ITQ-12[16] (ITW), and UZM-5[17] (UFI). Still, the demand for this type of zeolite catalysts and molecular sieves with pores in the range of 8−10 MR and with properties selective for the separation and catalysis involving small molecules is very high and requires fine-tuning of the structural properties through innovative chemical processes.

In the past 10 years several reports were published on layered silicate materials which have been converted into zeolite framework structures upon calcination. The first example reported was a material coined PREFER,[18] which condensed to Ferrierite. Also MWW-framework type materials can be obtained as layered precurser. MCM-22,[19] ITQ-1,[20] ERB-1,[21] and SSZ-25[22] are examples which had also been studied intensively by several groups in its delaminated state.[23−25] Again, calcination transforms these material into a perfect 3-dimensional silicate framework structure. However, all materials in the literature were examples of layered precursors leading to known zeolite frameworks after calcination, i.e., they could be thought of reaction intermediates in the formation of the framework type structure. In addition, the framework structures can also be obtained in a one-step synthesis process. The interesting observation in these experiments is the fact that layered precursors of framework silicates exist and that they can be transformed in a topotactic condensation reaction into 3-dimensional porous silicate frameworks through simple calcination procedures. Based on this observation we systematically studied the synthesis of hydrous layered silicates which should be transformed into porous framework structures upon calcination. Since none of the well-known layered sodium silicates has been transformed into a porous framework structure so far, we studied hydrous layer silicates charge balanced with organic cations. As SDA we chose small tetraalkylammonium cations substituted with mixed alkyl chains R1 to R4.

Here we report on the synthesis of the new high-silica zeolite RUB-41 with a 2D pore system of 8MR and 10MR channels obtained by calcination of a so-far unknown layered silicate RUB-39. This is the first time this concept has led to the synthesis of a so-far unknown framework structure (see Note Added in Proof). The new material shows promising separation and sorption properties for C3−C6 alkanes.

Experimental

Synthesis. In the course of a systematic study using asymmetrically substituted tetraalkylammonium salts as templates, a series of SDAs has been investigated. Dimethydipropylammonium hydroxide was one of the new template cations sucessfully employed for the synthesis of new crystalline layered silicate materials. The SDA dimethyldipropylammonium hydroxide was synthesized using dimethlyamine (alcoholic solution) and propylbromide in ethanol as solvent at 40−50 °C under continuous stirring. The solid product was filtered, washed with ethanol, and characterized by chemical analysis and solid-state NMR spectroscopy. Using Amberlyst, an ion-exchange resin, the hyroxide form was obtained.

Appropriate amounts of amorphous SiO_2 and dimethyldipropylammonium hydroxide solution were mixed and stirred until a uniform gel was obtained. Then the water content was controlled by evaporation at 70 °C in an oven. The typical composition of the starting gel is 1:0.5:8−12 SiO_2/SDA/H_2O. The mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 150 °C with a 15 rpm rotating speed for 15−45 days. After quenching in cold water, a thick suspension was recovered in the container. The solid product, lab-code RUB-39, was separated by filtration, washed with distilled water, and dried at 75 °C.

The as-synthesized RUB-39 was heated in air from room temperature to 600 °C. Calcination of larger quantities of sample and annealing procedures of the silica framework sample were done at 520 °C for 12 h before heating the sample to 560 °C for another 2 h until the white color of the sample indicated that the organic SDA was removed completely. The calcined product has the lab-code RUB-41.

Analyses. TG- and DT-analysis experiments were carried out on a Bähr STA 503 thermal analyzer with 10 °C heating rate.

Powder X-ray diffraction (XRD) was performed on a Siemens D-5000 with monochromatized Cu Kα_1 radiation and a capillary sample holder to prevent preferred orientation. The diffraction data were collected with a Braun position sensitive detector in the range from 5 to 95° 2θ and step width of 0.00778°. Indexing of the powder diagram was carried out with the program Treor-90 implemented in powder-X.[26] The structure was solved from model building and subsequently refined with FULLPROF 2k.[27] The details of data collection and the results of the structure refinement are summarized in Tables 1 and 2.

Solid-state MAS NMR spectroscopy was performed on a Bruker ASX 400 using conventional 7-mm Bruker probes. The samples were spun at RT about the magic angle with ~5 kHz spinning speed. For quantitative spectra the HP DEC pulse program was used.

For sorption measurements the freshly calcined powdered sample was kept in vacuo at 10^{-6} MPa at 120 °C overnight. Nitrogen sorption measurements were carried at out 77 K with a volumetric sorption analyzer Autosorb AS-6 (Quantachrome). The sorption measurements with alkanes were conducted gravimetrically at 296 K using a Sartorius 4003 microbalance in the pressure range up to 800 mbar.

Results and Discussion

SEM micrographs and the TG-, NMR-, and XRD-analyses of the synthesis product clearly showed that a layer silicate

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Table 1. Results of the Rietveld Analysis of the Powder XRD Diagram of RUB-41

sample holder	capillary
wavelength	1.54059 Å
2θ range	5−95°
number of points	11569
total no. of reflections	1016
temp. of data collection	20 °C
fwhm (15.68°)	0.099°
peak profile	Thompson−Cox−Hastings pseudo-Voigt
number of parameters	41
number of restraints	56
chemical composition per unit cell	18 SiO_2
space group	*P*2/*c*
lattice parameters:	
a	7.345(1) Å
b	8.724(1) Å
c	17.152(1) Å
β	114.2(1) deg
unit cell volume	1002.5
framework density	18 T-atoms/1000 Å^3
R-factors (background corrected)	
R_p	8.9
R_{wp}	8.9
R_{exp}	5.9
χ^2	2.3
R_{Bragg}	2.8

Table 2. Atomic Coordinates of RUB-41 Obtained from Rietveld Analysis Considering Durbin−Watson Statistics

	x	*x*	*z*	*B*
Si1	−0.0620(4)	0.8238(3)	−0.0084(2)	1.61(8)
Si2	0.6912(5)	0.3973(4)	0.9447(2)	1.61(8)
Si3	0.2873(5)	0.6479(4)	0.6786(2)	1.61(8)
Si4	0.2730(5)	0.3470(4)	0.9209(2)	1.61(8)
Si5	0.0	0.4969(5)	0.25	1.61(8)
O1	0.1315(8)	0.7211(7)	0.0296(5)	1.80(16)
O2	0.0	0.0	0.0	1.80(16)
O3	0.8079(10)	0.7985(5)	0.0468(4)	1.80(16)
O4	0.8077(10)	0.7770(6)	0.8939(2)	1.80(16)
O5	0.7255(11)	0.5097(6)	0.0222(4)	1.80(16)
O6	0.4877(51)	0.3072(6)	0.9240(5)	1.80(16)
O7	0.6798(11)	0.4931(6)	0.8640(32)	1.80(16)
O8	0.1420(9)	0.6127(7)	0.7243(5)	1.80(16)
O9	0.5	0.7013(9)	0.75	1.80(16)
O10	0.1281(10)	0.3913(6)	0.8263(2)	1.80(16)

(lab-code RUB-39) intercalated with an organic tetraalkylammonium cation has been obtained.

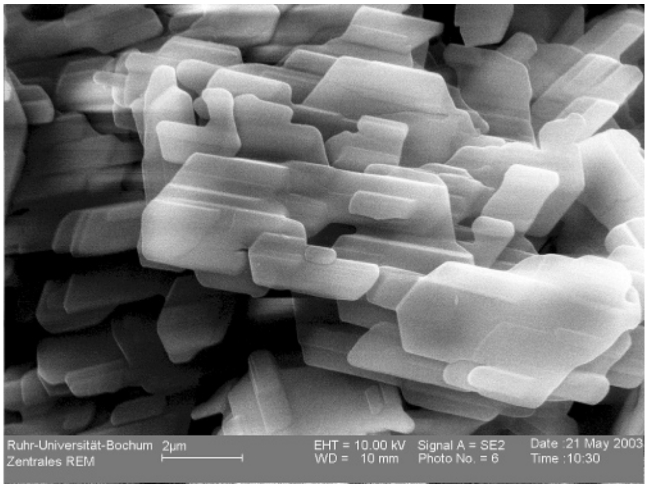

Figure 1. SEM photograph of the layered silicate RUB-39 obtained in the synthesis run.

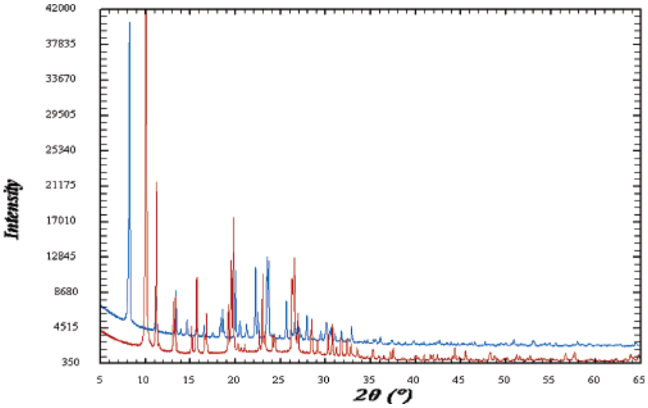

Figure 2. Powder XRD of RUB-39 (top) and RUB-41 (bottom). The shift of the diffraction peaks is due to the condensation reaction.

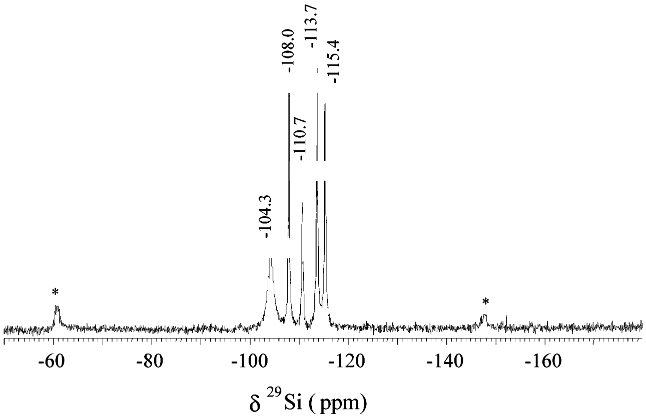

Figure 3. ^{29}Si MAS NMR spectrum of RUB-39. The low field signal at 104.3 ppm has been assigned to Si carrying one silanol group, Q^3(3Si1OH), typical for layered silicates. The narrow signals at higher field all belong to 4-connected Q^4(4Si)-silicate units. The asterisks mark spinning sidebands.

RUB-39 crystallizes in aggregates of colorless crystals with platy morphology (Figure 1). The size of the thin disks is about 5 μm in diameter and submicrometer in thickness. The symmetry of the crystal is monoclinic and the powder XRD pattern (Figure 2) was indexed in space group *P*2/*c* with the unit cell parameters $a = 7.331(5)$ Å, $b = 10.724(1)$ Å, $c = 17.514(1)$ Å, and $\beta = 115.7(1)°$. In the ^{29}Si MAS NMR spectra of the as-made sample the signals have been grouped in two sets (Figure 3). There is a broad signal centered at approximately −104 ppm relative to TMS as standard representing the layer terminating Q^3-silicate group carrying one hydroxyl functionality. The chemical shift of the Q^3 signal is shifted to a rather high field value, however, it shows the typical feature for silanol groups. In$^1H-^{29}Si$ cross polarization (CP) experiments, the intensity of the signal of the OH-carrying Q^3-group is greatly enhanced for short contact times, supporting the interpretation of the spectrum as characteristic for a layered silicate structure. The other 4 signals show constant intensity ratios and are at chemical shift values typical for 4-connected Q^4-groups characteristic for framework silicates. $^1H-^{13}C$ CP MAS NMR confirms the integrity of the dimethyldipropylammonium cation used as SDA. From XRD and NMR data it is concluded that the SDA cation is intercalated between neighboring silicate layers. From ^1H NMR spectroscopy (Figure 4) the SDA protons give a broad signal centered at 1.5 ppm with another maximum at 3.5 ppm which indicate the intercalated organic SDA. An interesting additional feature is the isolated proton signal at 16.4 ppm typical for a very short hydrogen bond.[28]

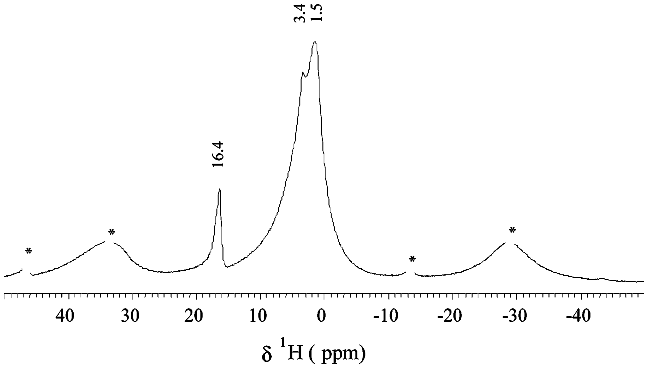

Figure 4. ^{1}H MAS NMR spectrum of RUB-39. The low field signal at 16.4 ppm indicates strongly H-bonded Si−OH-groups involving the silicate layer.

The correlation between hydrogen bond length as determined from diffraction studies and ^{1}H chemical shifts[28] predicts a bridging H···O bond length in the range of ca. 1.5−1.6 Å for RUB-39. Similar low field shifted ^{1}H NMR signals already have been observed in a number of other layer silicates such as RUB-18[29] and MCM-47.[30] Neutron-structure analyses[31] and detailed NMR[32] studies of RUB-18 revealed that two neighboring silanol groups in the silicate layer share one hydrogen atom and carry a negative charge. This structural feature gives rise to the isolated, high field shifted ^{1}H signal. It is likely that a similar structural unit exists in the silicate layer of RUB-39 compensating partially the residual Coulomb charge of the silicate layer.

The calcination of the as-synthesized RUB-39 at 520 °C under atmospheric conditions leads to the new, highly crystalline, colorless solid silica−RUB-41. The lattice parameters of the calcined product obtained from the indexed powder pattern revealed that the *a*- and *c*-lattice parameters including the β-angle remained almost unchanged, however, *b* decreased by ca. 2 Å (Figure 2). The lattice parameters of RUB-41 for the monoclinic unit cell are $a = 7.345(1)$ Å, $b = 8.724(1)$ Å, $c = 17.152(1)$ Å, $\beta = 114.2(1)°$. Also the crystal morphology is conserved. This signifies that the neighboring layers reacted in a topotactic condensation to a 3-dimensional silica framework. Indeed, the ^{29}Si MAS NMR spectrum clearly shows that the low field Q^{3}-signal disappeared and a much simpler spectrum with 3 signals at chemical shifts for Q^{4} silicon of −107.9, −112.9, and −115.2 ppm (Figure 5) with an intensity ratio of 2:2:5 is obtained. No evidence for residual Q^{3}-signals has been detected in the spectrum. The signals are rather broad, indicating structural distortion. In thermogravimetry, a total weight loss of ca. 18% is realized in the temperature range from RT to 600 °C due to the decomposition and removal of the organic SDA and the subsequent condensation of neighboring silicate layers (Figure 6). The fact that there is no weight loss below 250 °C indicates that there is no crystal water intercalated in the structure of the original RUB-39. The first exothermic maximum at 350 °C accompanied with a 13% weight loss indicates the breakdown and removal of the SDA, and is followed by a second thermal signal for the condensation reaction centered at 450 °C.

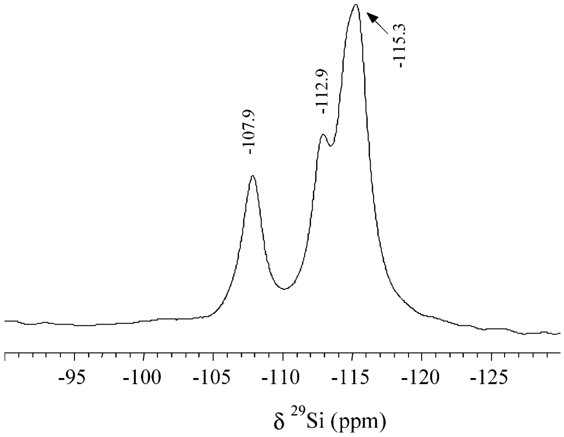

Figure 5. ^{29}Si MAS NMR spectrum of the calcined material. RUB-41 shows a typical spectrum for framework silicas with 3 Q^{4} signals indicating, at least, 3 symmetrically nonequivalent Si-sites for the all silica porous framework. There is no intensity for Q^{3}-silicate units indicating structure defects.

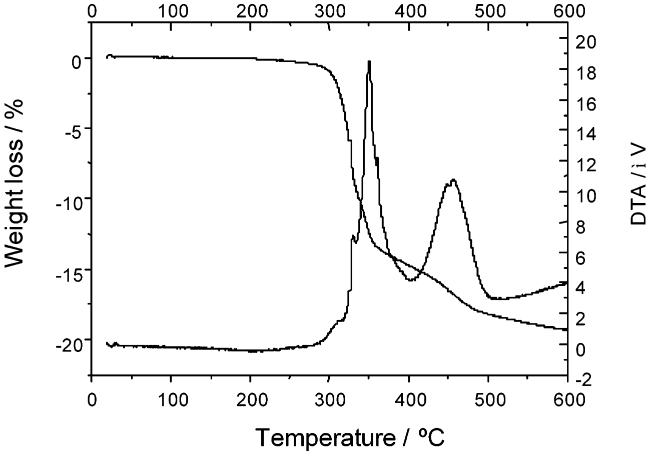

Figure 6. TG and DTA curves of RUB-39 leading to RUB-41 after calcination. The weight loss at 300 °C indicates the breakdown and removal of the SDA followed by the condensation of the silicate layers.

The crystal structure of the all-silica condensation product was solved from powder XRD data. For the solution of the crystal structure it was important to realize that the layered building block is monoclinic with a 7.34 Å × 17.17 Å and $\beta = 114°$ repeat unit and stacks in 8.7 Å periodicity along *b*. The metric of the layer resembles the one known from the HEU-family of zeolite framework structures, however, with slightly reduced cell parameters due to the Al-free composition of the RUB-41 framework. The *b*-repeat unit of Heulandite is 17.9 Å which is about twice the *b*-parameter of RUB-41. In Heulandite sets of layers stack in an $\overline{AB}AB$ sequence where A- and B-layer are related by a 180° rotation about the layer normal. Model building with the HEU-layer as building block and using an $\bar{A}A$ stacking sequence yielded a 3-dimensional model of a new microporous framework structure which fits all symmetry and geometry requirements of the experimental data obtained for silica-RUB-41, i.e., the space group symmetry and the lattice parameters. A

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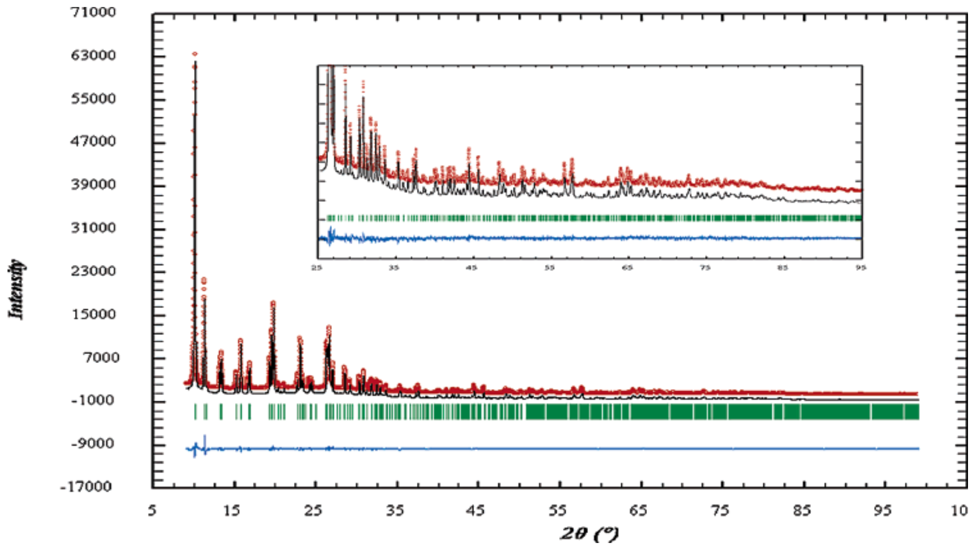

Figure 7. Experimental (red), calculated (black), and difference (blue) powder XRD diagram of RUB-41 as obtained after Rietveld analysis. The insert shows an enlarged section of the Rietveld fit.

distance-least-squares minimization of the model using d(Si−O) = 1.6 Å and d(O−O) = 2.5 Å leads to an optimized geometry and refined to residuals of 0.3%. The refinement shows that the structure model is plausible and might exist. The simulation of the X-ray powder pattern of the geometrically optimized structure model revealed strong similarities with the experimental powder XRD diagram, further supporting the structure model. Finally, a full pattern Rietveld structure refinement of the high-resolution powder XRD diagram was performed, which led to residuals $\chi^2 = 2.3$, confirming experimentally the structure model beyond any doubt. RUB-41 crystallizes in the monoclinic space group $P2/c$ with $a = 7.345(1)$ Å, $b = 8.724(1)$ Å, $c = 17.125(1)$ Å, and $\beta = 114.2(1)°$. The result of the final Rietveld fit is shown in Figure 7; all relevant data concerning the structure solution and refinement are summarized in Table 2 and provided as Supporting Information.

The structure of silica−RUB-41, with composition of $18SiO_2$ per unit cell, consists of [4^25^4]-cages as a basic unit linked to chains parallel to z. Neighboring chains connect via oxygen bridges yielding sequences of 4-, 5-, 5-MR. The layer characteristic for the heulandite− and silica−RUB-41 framework type structures is shown in Figure 8 in $\bar{A}A$ stacking via oxygen bridges leading to the 3-D silica framework. For the new framework type the code **RRO** was assigned. This creates 2 sets of intersecting channels between neighboring layers. The 8MR channels run parallel to z, and the 10MR channels run parallel to x. The interlayer pore space is partitioned by linear, pillar-like Si−O−Si-bridges with an experimentally determined Si−O−Si-angle ∠(Si−O−Si) = 180°. As known for many porous and nonporous silicas, the oxygen atoms involved in 180°-angles are often dynamically disordered which cannot be revealed in single-temperature powder X-ray diffraction experiments. However, from the correlation of Si−O−Si-angles and ^{29}Si chemical shifts[33,34] the signal at −115 ppm indicates that the true angle in the layer-connecting bond is significantly lower than 180°. Therefore, static or dynamic disorder of the oxygen atom around the Si−Si-axis is postulated. These bridging oxygen atoms are particularly exposed to the void space between neighboring layers and, thus, interact preferentially with sorbate molecules. Their specific chemistry, therefore, might be responsible for the unusual sorption and catalytic properties of RUB-41 materials. The pore diameters are 5.8 Å × 4.1 Å for the 8MR and 5.9 Å × 4.1 Å for the 10MR indicating an almost uniform pore structure in 2 dimensions. Here, the 8MR is distorted, however, quite open, whereas the 10MR, also distorted, is rather narrow. The fact that both pores show almost the same pore diameter and pore distortion should lead to pronounced selectivity in sorption experiments. The framework density FD is 18; the nitrogen isotherm measured at 77 K gives a surface area of 510 m^2/g which is expected for microporous zeolitic materials. Considering the fact that heulandite, $K_9[Si_{27}Al_9O_{72}]\cdot 20H_2O$, and clinoptilolite, $Na_2K_2Ca[Si_{30}Al_6O_{72}]\cdot 21H_2O$, possess highly specific sorption properties for small amines, all silica−RUB-41 which is structurally closely related should show similar specificity for small molecules, however, enhanced for more hydrophobic ones as typical for all-silica zeolites. Measurements of the sorption of pure n- and i-isomers of small molecules strongly support the expectation for RUB-41. Pressure-dependent adsorption experiments of C1 to C4 hydrocarbons showed enhanced uptake of the linear chain over the branched isomers. Whereas methane, ethane, propane, and butane enter the pore system easily and occupy the pore void with, e.g., ca. 20 mg/g sorbate at 750 mbar pressure and 290 K for ethane, isobutane is excluded from the void space (Figure 8). Using similar experimental conditions, alkenes become adsorbed much more strongly than alkanes. As examples, 1-buten and *trans*-2-buten are given with ca. 70 mg/g and 92 mg/g sorbate uptake, respectively. The isotherms also reveal interesting properties for the various sorbate/zeolite systems which might be important for application-oriented research. The remarkable differences of uptake at lower pressures for 1-butene and *trans*-2-butene, e.g., make RUB-41 a promising candidate in the field of

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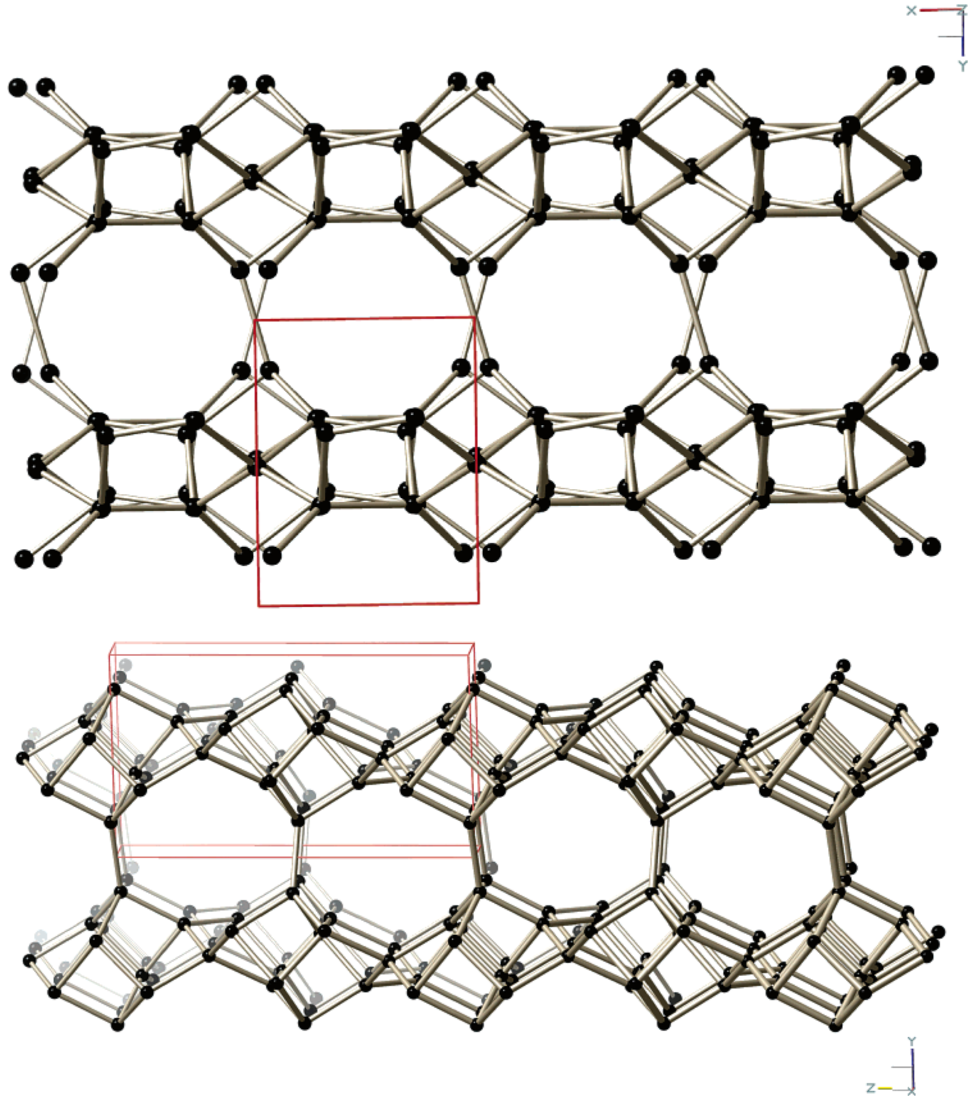

Figure 8. (a) Skeletal model of the structure of RUB-41 showing a projection along the 8MR channels. The box marks the unit cell. From the skeletal model it is clear that the tetrahederal density within the layers is high, however, the gallery between is very open and provides good access to the pores system. (b) Skeletal model of the structure of RUB-41 viewed along the 10MR-channel. Because of the tilted 10MR the pore diameter is almost the same as that for the spherical 8MR running perpendicular. This is the structural feature which yields the highly selective sorption properties of the zeolite.

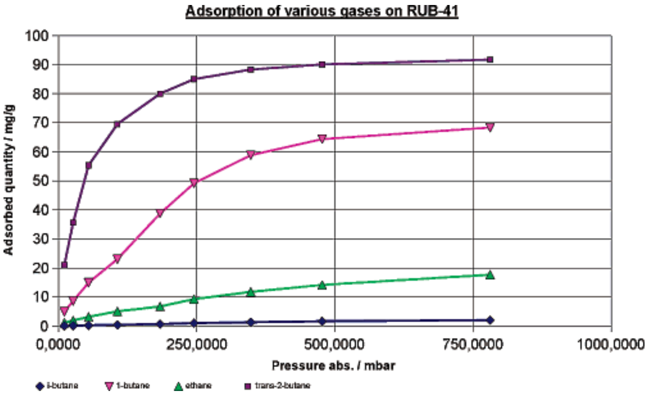

Figure 9. Adsorption isotherms of pure gases for RUB-41 as a function of pressure. There is almost no uptake of i-butane, however, 1-butene and *trans*-2-butene are strongly adsorbed. The striking difference in uptake at low pressure between 1-butene and *trans*-2-butene is remarkable.

molecular sieving and separation of small molecules. Further detailed studies are required to fully exploit and understand these unexpected properties of the zeolite.

Conclusion

Zeolite RUB-41 is one of the few, new high-silica materials with small to medium pore size. It had been synthesized by topotactic condensation of silicate layers during the calcination process of the layer silicate RUB-39. The all-silica zeolite has a 2-dimensional pore system with selective sorption properties for small, linear, or branched molecules. Its almost uniform pore size, its hydrophobic character, and its high thermal stability makes it suitable for various gas-phase sorption and separation processes, in particular as a function of pressure. Light carbon separation using the sorption properties has become an interesting field of research recently, mainly due to the availability of new hydrophobic silica molecular sieves.[35,36] With the current technology, using cryogenic distillation, this separation is one of the most energy-intensive separation processes in the

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petrochemical industries. A kinetic-based process such as pressure swing adsorption could clearly have large economic and environmental benefits. In this respect RUB-41 is an interesting new material with promising separation properties.

The fact that the heulandite-type layer has been obtained as a structural subunit of a new silica framework shows that the templating effect of small, asymmetric SDA used at lower synthesis temperatures leads to new structure units which crystallize as layered materials. In an extension of this study several other, new layer silicates have been obtained which also condense to silica frameworks upon calcination. The approach to use layered silicates as precursor for new zeolite framework structures, therefore, seems to open a new synthesis route to porous materials.

Heulandite and RUB-41 have the same layerlike building unit and thus belong to the same family of structures. Because of the different layer orientations and stacking sequences in the 3-dimensional framework structure, they constitute simple, ordered end-member structures of which more variants might be realized with appropriate template molecules and synthesis conditions.

A very challenging field of further research will be the substitution of Si by other, trivalent T-atoms such as Al, B, and Fe or tetravalent Ti and Sn. This would lead to the most important catalytic functionalities in the zeolite framework interesting for the fine chemical industries.

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Note Added in Proof: A new microporous framework silicate was obtained by topotactic condensation simultaneously. For further information see framework code CDO on http://www.iza-structure.org/databases/ and Ikeda, T., Akiyama, Y.; Oumi, Y.; Kawai, A.; Mizukami, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4892.

Supporting Information Available: Table of bond lengths, figure of layer building unit of RUB-41, ^{13}C CP MAS NMR spectrum, nitrogen adsorption isotherm for RUB-41, and adsorption isotherm for n-butane and i-butane. This material is available free of charge via the Internet at http://pubs.acs.org.

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