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ARTICLE

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This paper is in honour of professor Francois Fajula on the occasion of his 65th birthday.

IWW-type zeolite with Si/Ge of 4.9 is obtained using 5-azonia-spiro[4,4]nonane as template in fluoride-free medium under hydrothermal conditions at 175 °C. In an otherwise identical synthesis, using the related 5-azonia-spiro[4,5]decane as structure directing agent, a mixture of IWW and NON zeolite types was formed. In absence of GeO₂ from the reactant mixture, pure NON formed. The IWW zeolite was characterized by XRD, SEM, and HRTEM. IWW zeolite displayed a unique morphology and could be calcined at 600 °C without loss of crystallinity. The Si/Ge ratio of the IWW zeolite was increased by postsynthesis modification. Part of the germanium could be eliminated from the as-synthesized IWW zeolite by acid leaching using 6 M HCl solution. Also the calcined material could be degermanated. Here the presence of a silicon source in the acidic leaching solution minimized structural damage. This way the Si/Ge ratio of the IWW zeolite was increased from 4.9 up to 10.

Introduction

Zeolites are well established industrial materials implemented in a wide range of applications related to adsorption, ion exchange and catalysis.^{1,2} As inorganic crystalline materials, built up by TO₄ tetrahedra with regular microporous channels, zeolites exhibit well-defined porosity and high surface area, and therewith provide outstanding shape and size selectivity in adsorption and separation processes as well as in catalysis. Since T atoms can be Si, Al, Ge, P, Ga, B, etc., zeolite chemical compositions can be fine-tuned to extend their stability, the dimensions of the pore system or to introduce specific functionality. Especially zeolite frameworks containing a large pore system constructed by 12-membered rings (MR) together with small (8-MR) and medium (10-MR) sized pores are considered of to be of great potential for utilization in industry.³ At present, zeolites successfully implemented as catalysts generally contain medium, large or even extra-large pore openings, and especially those structures having multiple pore sizes in their channel system find considerable interest.^{4,5}

ITQ-22 zeolite having IWW topology was the first synthetic zeolite with a three dimensional interconnected 8-, 10- and 12-MR channel system.⁶ Such a fully interconnected pore system facilitates mass transfer of reagents and products inside zeolite

crystals. ITQ-22 was first synthesized by Corma's group using 1,5-bis-(methylpyrrolidinium)-pentane (MPP) as structure directing agent (SDA) in presence of Ge in fluoride free media.⁶ Later germanium-containing ITQ-22 was also synthesized using hexamethonium (HM) as template.⁷ Both syntheses were performed at 175 °C under agitation for 7 and 15 days, respectively. Here we report the same framework can also be templated by an azonia-spiro compound.

Azoniaspiro compounds are a family of organic templates commonly used for zeolite syntheses. Several zeolites were reported to form in presence of azonia-spiro compounds as structure directing agents. The first azonia-spiro compound templated zeolite synthesis yielded SSZ-19 and dates back to the middle of the 1980s.⁸ Two decades later, Millini *et al.* systematically studied three different azonia-spiro compounds as structure directing agents in a NaO₂-SiO₂-(Al₂O₃)-SDA-H₂O system.^{9,10} Several aluminosilicate zeolites such as MOR, EUO, MTW and intergrowths of NON, EUO and NES were obtained using azonia-spiro[4,5], [5,5], and [5,6] compounds as templates. Literature also reported that azonia-spiro[4,5]decane can lead to formation of several siliceous zeolites such as BEC, *BEA, and MTW in the presence of fluoride.¹¹ The azonia-spiro compound called (6R,10S)-6,10-dimethyl-5-azoniaspiro[4,5]decane was utilized as structure directing agent directing the formation of several germanosilicates such as IM-12 and IM-9.^{11,12} The use of other azonia-spiro compounds for zeolite synthesis in the presence of Ge, however, remains as yet unexplored.

Germanosilicate zeolites receive great attention because a number of extra-large pore systems with ring sizes exceeding 12-membered rings have been reported.¹²⁻¹⁵ Furthermore,

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selective removal of Ge from double four ring (D4R) units in germanosilicate zeolites recently yielded a number of new zeolite topologies. Two different strategies leading to structure transformations based on de-germanation have been described. The inverse sigma-transformation leading to OKO topology was achieved by treating calcined UTL in concentrated hydrochloride acidic solution.¹⁶ In the Assembly-Disassembly-Organization-Reassembly (ADOR) approach, initially layered intermediates are formed by using more dilute acids. Intercalating these layers with an amine followed by calcination leads to the formation of PCR, while the addition of a silicon source also allows to obtain OKO or intergrowths of these structures.¹⁷ This de-germanating process has also been imposed on zeolites with IWW topology.^{18,19} Like UTL, IWW contains D4R units connecting layers. However, unlike UTL zeolite, the IWW structure was maintained rather than being transformed into a different zeolite. During the de-germanation process, the vacancies generated by Ge-removal can be filled with Si or Al, resulting in an almost siliceous or aluminosiliceous IWW.

In this contribution, we report the synthesis of pure germanosilicate zeolite with IWW topology using 5-azoniaspiro[4,4]nonane as structure directing agent in a fluoride free medium. The zeolite can be calcined and leached with acid without compromising its crystallinity. Replacing 5-azoniaspiro[4,4]nonane with 5-azoniaspiro[4,5]decane which has a similar molecular shape and size, yields IWW-type zeolite next to a nonasil phase (NON). Literature reports 5-azoniaspiro[4,5]decane leads to the NON phase in presence of fluoride only, while mixtures of NON and MTW are reported in pure hydroxide media.²⁰ In our work, in absence of GeO₂ this template yields a pure siliceous NON in fluoride free conditions.

Experimental

IWW-type zeolite was synthesized using 5-azoniaspiro[4,4]nonane as structure directing agent. Preparation of this SDA occurred according to literature.²¹⁻²⁴ In short, 11.2 g NaOH was dissolved in 280 mL deionized water, followed by adding 60.45 g 1,4-dibromobutane (Sigma-Aldrich) and 19.91 g pyrrolidine (Sigma-Aldrich) in a round bottom flask, which was heated to boiling and stirred under reflux for 1 hour, which resulted in a homogenous solution. Subsequently, the solution was cooled in an ice bath under vigorous stirring. 140 mL 28.6 wt.% ice cooled sodium hydroxide solution was then added to promote precipitation. The solid was recovered by filtration and dissolved in chloroform twice. The chloroform was evaporated by a rotary evaporator under reduced pressure and the solid was recrystallized from diethyl ether. The obtained white powder of 5-azoniaspiro[4,4]nonane was then converted to its corresponding hydroxide by an anionic exchange resin (Amberlite IRA 402 OH form, Alfa Aesar) for 48 hours. The aqueous SDA solution was further concentrated to 20-30 wt.% by evaporation of water under reduced pressure with a rotary evaporator. Similarly, azonia-spiro[4,5] was synthesized using

1,4-dibromobutane and piperidine. The successful synthesis of templates was confirmed by ¹H NMR and ¹³C NMR.

IWW-type zeolite was synthesized from a reaction mixture with molar oxide ratio of 0.8 SiO₂ : 0.4 GeO₂ : 0.3 SDAOH : 30 H₂O. In a typical synthesis, 1.05 g crystalline GeO₂ (98%, Sigma-Aldrich) and 4.25 g tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich) were added to 5-azoniaspiro[4,4]nonane hydroxide solution and water. The amounts of template solution and water were adjusted to meet the requirement of the above gel composition. The mixture was stirred at room temperature until the silica was fully hydrolysed and then autoclaved at 175 °C under tumbling for 3 days. Subsequently, the crystallized solid was recovered by filtration, extensively washed with deionized water and dried at 60 °C overnight. Calcination was carried out in ambient atmosphere at 600 °C for 6 h with a temperature ramp of 1 °C/min. The same gel composition and hydrothermal conditions were adopted when azonia-spiro[4,5] compound was used as template.

The de-germanation of the obtained IWW-type zeolite was investigated. Calcined and as-made IWW zeolite were suspended in H₂O, 0.1 M HCl, 6 M HCl and 12 M HCl solutions and then treated at 90 °C for 24 h respectively. In addition, TEOS was utilized as silicon source in 6 M HCl solutions to further increase the Si/Ge ratio. 40 µL TEOS was hydrolysed in 50 mL 6 M HCl solution prior to the addition to the solid.¹⁸ The mixture was then heated at 90 °C for 1 day. Afterwards, the solids were recovered by filtration, extensively washed with deionized water and dried at 60 °C overnight. The weight ratio of solid to liquid (s/l) was 50.

High resolution XRD synchrotron data of the calcined IWW and NON samples were measured at room temperature at BM01B (Swiss Norwegian Beam Lines, SNBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France ($\lambda = 0.50493$ Å, sample sealed in a capillary with 0.5 mm diameter). Rietveld refinement on powder diffraction data of calcined IWW- and NON-type zeolite was performed using the GSAS software.^{25,26} Scanning electron microscope images were obtained on a Nova NanoSEM450 electron microscope. High resolution TEM (HRTEM) experiments were carried out on an aberration-corrected FEI Titan microscope operated at 120 kV.

Determination of the Si and Ge content of the samples was done by Inductively Coupled Plasma (ICP) performed on an Optima 4300 DV2 (Perkin Elmer). 50 mg of IWW and 250 mg LiBO₂ were homogenized and transferred in a graphite plate. This was placed for 15 minutes in a muffle furnace at 1000 °C. Subsequently 50 mL of a 0.42 M HNO₃ solution was added and the mixture was stirred for 15 minutes. 10 mL was transferred in a separate bottle. After 24 h, the remaining graphite was precipitated.

Results and discussion

(1). Synthesis and characterization of IWW-type zeolite by using 5-azoniaspiro[4,4]nonane

Phase pure IWW-type zeolite was obtained using 5-azonia-spiro[4,4]nonane hydroxide as structure directing agent after hydrothermal treatment at 175 °C for 3 days. IWW was already formed after 1 day. Prolongation of synthesis time from 3 to 7 days did neither improve crystallinity nor lead to appearance of any other phase next to IWW. Indexing of the high resolution XRD synchrotron data confirmed an orthorhombic unit cell, in space group $Pbam$ with $a = 42.03 \text{ \AA}$, $b = 12.96 \text{ \AA}$ and $c = 12.67 \text{ \AA}$, in accordance with the values for ITQ-22. Rietveld refinement on the calcined sample (Figure 1) confirmed the product to be of IWW topology and that it remained stable after calcination at 600 °C. The azonia-spiro hydroxide used as template was previously employed to prepare SSZ-19 zeolite in alkaline medium.⁸ It can also be used as structure directing agent for zeolites with more open frameworks such as offretite.²⁷ The first zeolite reported to have IWW-topology was ITQ-22, prepared using MPP⁶, a structure directing agent which also supports formation of AFX-type zeolite such as MgAPO-56.²⁸ Similar to 5-azonia-spiro[4,4]nonane, MPP contains two five-membered rings, but these two rings are separated by a carbon chain instead of being directly connected by sharing a spiro nitrogen atom.

Scanning electron microscopy images presented in Figure 2 demonstrate the sample is composed of fragmented sheet-like crystals. These sheets are up to 4 μm in length and 1 μm in width, and consist of several thinner layers with thicknesses varying from 10 nm to 100 nm. Although IWW zeolite framework is known for a considerable time, the presently observed intriguing morphology has not yet been reported in literature.

Chemical analysis by Inductively Coupled Plasma of the as-prepared product confirmed formation of a germanosilicate zeolite with Si/Ge atomic ratio as high as 4.9 (Table 1). For comparison, ITQ-22 zeolite, which possesses the same framework topology and was prepared by using MPP as template, has a Si/Ge atomic ratio of 3.2. High germanium content in zeolite structures usually relates to decreased stability. Depending on their germanium content germanosilicates often degrade in ambient humidity within very short period of times.^{14,29,30} After calcination, the IWW zeolite powder was kept in ambient conditions for a period of 6 months. The XRD pattern shows the structure was well preserved without notable decrease in crystallinity (see supporting information, Figure S1).

The Si/Ge ratio around 4.9 is higher than the composition of the initial synthesis mixture (Si/Ge = 2.0). Consequently the Si/Ge ratio in the synthesis gel was increased to 2.7 by reducing the amount of Ge while amounts of silicon, template and water remained unchanged. Phase-pure IWW zeolite was obtained with a Si/Ge ratio around 4.9, similar to the experiment with the Ge-rich gel. Further increasing the Si/Ge ratio to 4 in the reaction mixtures led to poor crystallinity of the final product, while in absence of germanium, only an X-ray amorphous phase was obtained. The corresponding XRD patterns are shown in the supporting information (Figure S2). This implies presence of Ge is essential for IWW formation under these conditions.

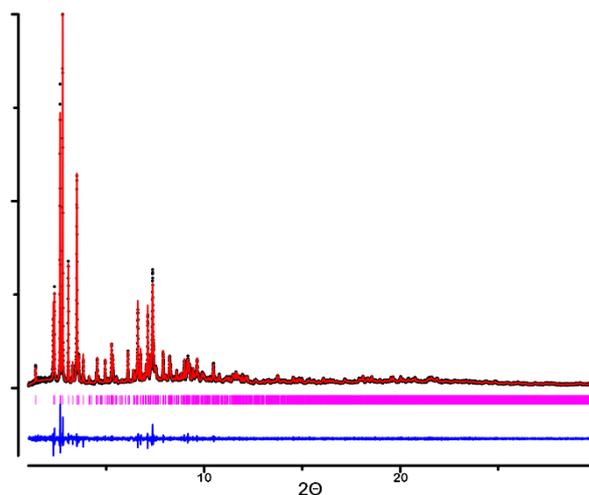


Figure 1. Retrieved refinement on high resolution XRD pattern of calcined IWW sample synthesized using 5-azoniaspiro[4,4]nonane hydroxide as SDA. R-values ($R_p=8.5$ and $R_{wp}=9.8$) and goodness of fit values (GOF) for the refinement are provided in Table S1 in ESI. Listing of atomic coordinates as obtained from Rietveld refinement was shown in Table S2 in ESI.

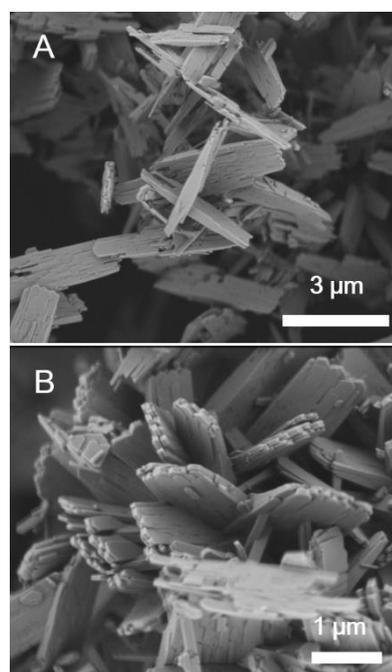


Figure 2. Scanned electronic microscopy (SEM) images on as-prepared IWW product synthesized with azonia-spiro[4,4]nonane hydroxide as SDA.

Table 1. Si/Ge ratios in as-made IWW product, IWW samples treated in 3 M and 6 M HCl solutions, and IWW samples treated in 6 M HCl solutions with additional TEOS.

samples	As-made IWW	As-made IWW treated in 3 M HCl solution	As-made IWW treated in 6 M HCl solution	As-made IWW treated in 6 M HCl and TEOS	Calcined IWW treated in 6 M HCl	Calcined IWW treated in 6 M HCl and TEOS
Si/Ge	4.9	5.1	10.0	11.4	11.8	13.8

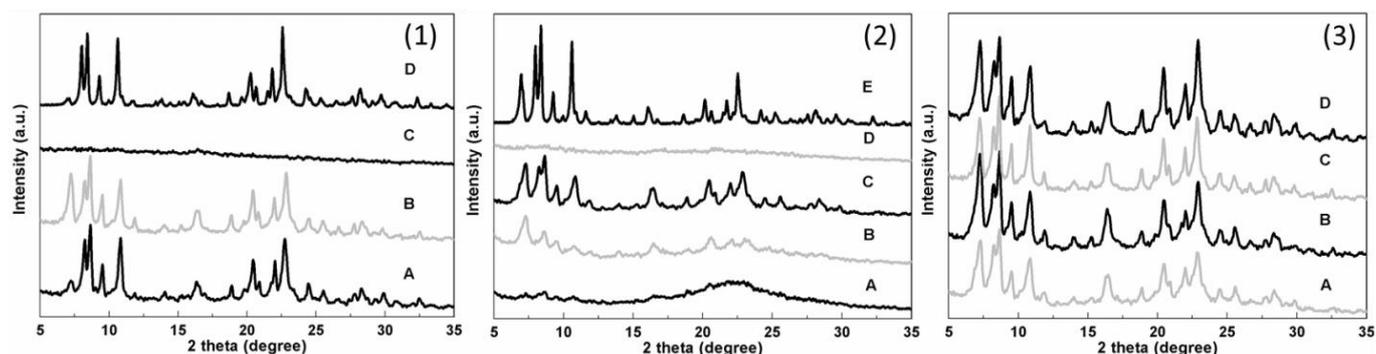


Figure 3. XRD patterns of samples by after acid leaching of IWW zeolite synthesized using azonia-spiro[4,4]nonane as SDA. (1) as-prepared IWW product was used as starting material and treated at 90 °C for 1 day in HCl solutions with different concentrations respectively; A (3M), B(6M), C(12M), D(as-made product as reference). (2) calcined IWW product was utilized as starting material and treated at 90 °C for 1 day using water and different concentrated HCl solutions; A (water), B (0.1M), C (6M), D (12M), E (calcined product as reference); (3) A (calcined) and C (as-made) IWW samples treated in 6 M HCl solutions at 90 °C for 1 day; B (calcined) and D (as-made) IWW samples treated in 6 M HCl and TEOS solutions (50 µL TEOS/50 mL 6 M HCl solution).

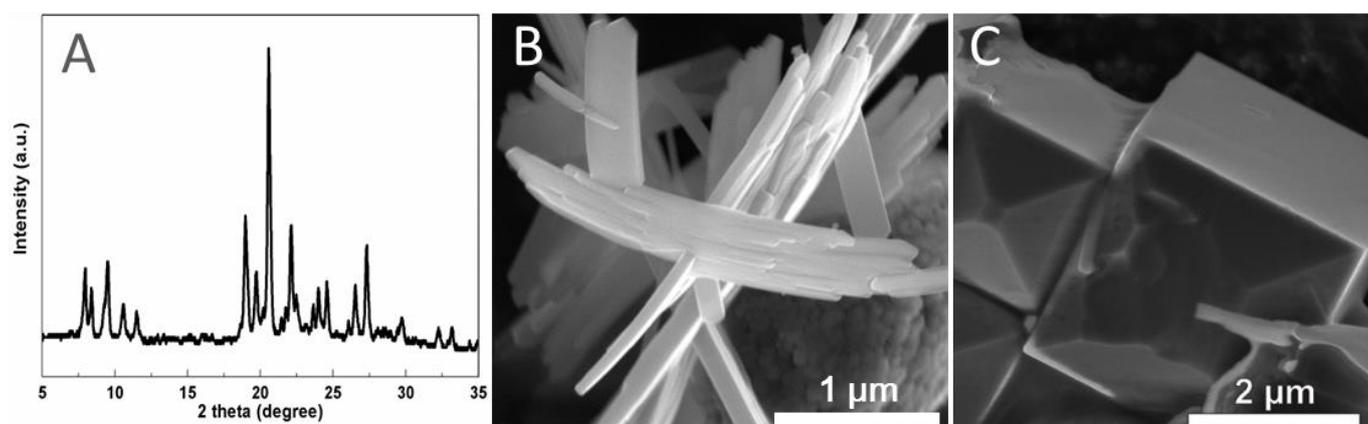


Figure 4. XRD pattern and SEM images of as-prepared sample synthesized with azonia-spiro[4,5]decane hydroxide as SDA in the presence of GeO₂. Thin sheets are observed superimposed on top of spheres in the SEM image (B). At only several positions, the pyramids were detected and enlarged image of this phase is shown in (C).

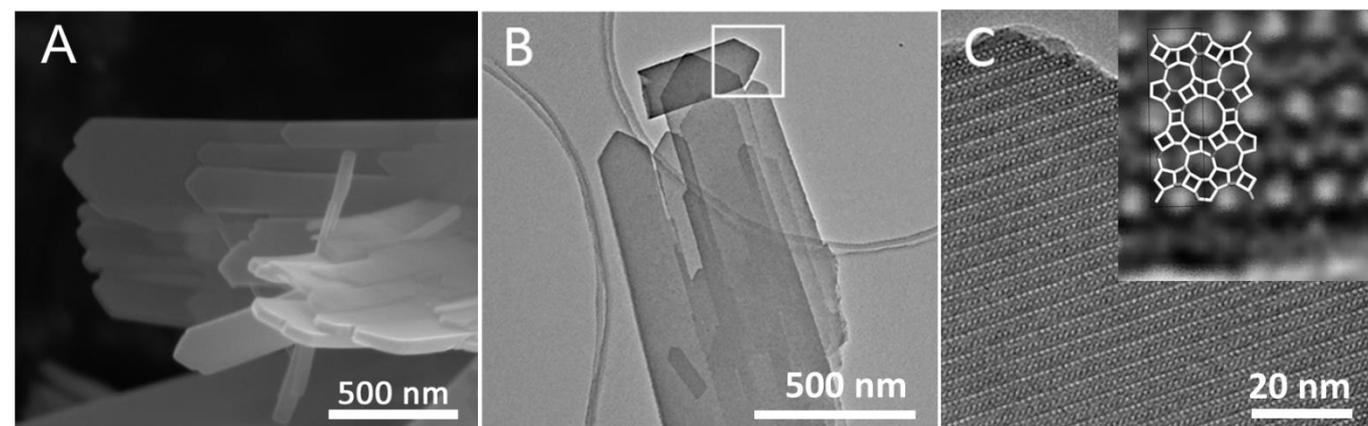


Figure 5. SEM (A) and (HR)TEM (B,C) of IWW phase obtained with using azonia-spiro[4,5] decane as SDA. IWW was observed as thin films. Figure C shows the magnified area of the region indicated by the white square in image B. Inset in image C shows the IWW structure on top of the HRTEM.

(2). Post modifications on IWW-type zeolite by acid leaching

To further improve hydrothermal stability and test the potential for zeolite transformation, post-synthesis by acid leaching was performed. Literature reports this treatment on IWW zeolite prepared with MPP as structure directing agent led to substantial de-germanation,^{18,19} and the resultant ITQ-22

materials contained only trace amounts of Ge in the framework.¹⁸ Also an attempt to transform the IWW structure by the ADOR approach using various HCl concentrations led to decreased Ge-content, but in an otherwise unchanged IWW-type zeolite.¹⁹ The now reported IWW-type zeolite, prepared with 5-azonia-sprio[4,4]nonane, in as-prepared and calcined

form was suspended in water, 0.1 M, 3 M, 6 M and 12 M HCl solutions at 90 °C for 1 day. XRD patterns of the resulting materials are shown in Figure 3. Calcined IWW zeolite became amorphous after one day treatment in 12 M HCl solution (Figure 3, 2D). Similarly, after treatment in water (2A) or mildly acidic conditions (2B), crystallinity of the calcined IWW-type zeolite decreased. Though the relative intensities decreased, the main diffraction peaks in the pattern were well retained after treatment in 6 M HCl solution, indicating that at least part of the IWW topology was preserved. The as-made IWW zeolite, still containing the structure directing agent, was more stable towards acidic solutions compared to the calcined sample, as demonstrated by XRD patterns in Figure 3.1. The reflections of the as-made IWW products after treatment in 3 M (1A) and 6 M HCl (1B) solutions remained intense and well resolved. However, the as-synthesized zeolite also degraded in 12 M HCl solution (1C). The increased stability of as-prepared IWW compared to the calcined form is in full agreement with similar observations on ITQ-22.^{18,19}

The Si/Ge ratio increased from 4.9 to 5.1 and 10 for the as-made sample treated in 3 M and 6 M HCl solutions respectively. The Si/Ge ratio of as-prepared sample treated with 3 M HCl remains almost unchanged, while 6 M HCl removed significant amounts of germanium (Table 1). Calcined IWW sample exhibited more obvious germanium elimination upon acid leaching comparing to the as-made sample and the Si/Ge ratio was increased from 5 to 11.8 (Table 1). In the XRD patterns (Figure 3.1), the intensity of the reflection at 7° remarkably increased for the sample treated in 6 M HCl solution (1B), while this reflection for the sample treated in 3 M HCl solution does not significantly increase in intensity (1A). An explanation for this observation could be that a considerable amount of organic template was removed prior or simultaneously to de-germanation in 6 M HCl facilitating Ge dissolution. The 3 M HCl solution did not remove significant amounts of template from pores which protected the germanium from dissolving in the framework. Additionally, TEOS was utilized as silicon source to fill vacancies created by leaching of Ge in 6 M HCl solutions. As shown in Figure 3.3, compared with samples treated in HCl solutions without TEOS, the crystallinity increased significantly by incorporating Si during leaching of calcined samples, whilst no obvious improvement was observed for the as-prepared set of samples, indicating that Si was successfully incorporated and improved IWW stability. This has also been approved by ICP measurement, as shown in Table 1. Comparing to the IWW samples treated in 6 M HCl solutions without TEOS, the Si/Ge ratios of as-prepared IWW and calcined IWW have been further increased to 11.4 and 13.8 respectively by acid leaching in HCl solutions with TEOS (Table 1). As also reported by others³¹, this strategy appears promising to prepare high silica zeolites, using germanosilicate frameworks as starting materials, but further work is needed to reveal the mechanistic details.

(3). Investigation on zeolite synthesis by using 5-azonia-spiro [4,5]decane in the presence of germanium

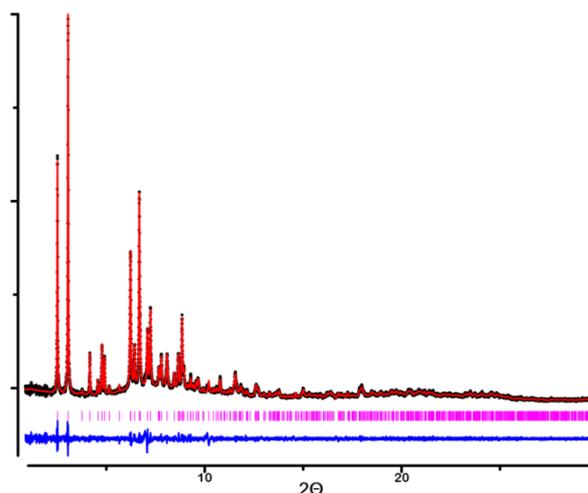


Figure 6. Retrieved refinement on high resolution XRD pattern of calcined NON product prepared using 5-azoniaspiro[4,5]decane hydroxide as SDA. R-values ($R_p=6.1$ and $R_{wp}=9.1$) and goodness of fit values (GOF) for the refinement are provided in Table S1 in ESI. Listing of atomic coordinates as obtained from Rietveld refinement was shown in Table S3 in ESI.

An azonia-spiro[4,5] compound, with a similar molecular shape and size as the up to now discussed [4,4] compound was also explored as structure directing agent for synthesis of germanosilicate zeolites. XRD pattern and SEM images are shown in Figure 4. Three phases were observed in the SEM images where sphere and sheet morphologies were dominant, while pyramid-like shapes were detected only as traces. Electron diffraction allowed identification of the structures.

According to the electron diffraction patterns, the spheres, sheets and pyramids were identified as NON zeolite, IWW zeolite and $\text{Na}_4\text{Ge}_9\text{O}_{20}$ respectively (see supporting information, Figure S3-S6). The thin platelets, with an average thickness of around 0.12 μm , exhibits an orthorhombic unit cell in the space group $Pbam$ with cell parameters $a = 41.57 \text{ \AA}$, $b = 13.42 \text{ \AA}$ and $c = 12.46 \text{ \AA}$, corresponding to the IWW topology. NON appeared as spheres in the SEM images, possessing an orthorhombic unit cell in the space group $Fmmm$ with $a = 22.11 \text{ \AA}$, $b = 15.02 \text{ \AA}$ and $c = 13.62 \text{ \AA}$. The identification of the pyramid-like crystallites as sodium germanate with tetragonal unit cell ($a = b = 14.98 \text{ \AA}$, $c = 7.38 \text{ \AA}$) in the space group $I41/a$, clearly indicates that a trace amount of sodium hydroxide remained from the structure directing agent purification process.

During the synthesis itself, no extra sodium was added to the reaction mixtures, leaving the template solution as the only possible source for this element. The sodium contents, determined by atomic absorption spectroscopy (AAS) for azonia-spiro[4,4]nonane and azonia-spiro[4,5]decane hydroxides solutions, was found to be $0.006 \text{ mol} \cdot \text{L}^{-1}$ and $0.038 \text{ mol} \cdot \text{L}^{-1}$ respectively. The latter contains about 6 times more residual sodium than the [4,4] compound, which explains the formation of the sodium germanate phase, which apparently has only very low solubility in these conditions. When GeO_2 was eliminated from the synthesis mixture with azonia-spiro [4,5]decane as structure directing agent, pure NON was formed whilst both sodium germanate and IWW phase disappeared. The high

quality and crystallinity of the NON phase was confirmed by Rietveld refinement on the diffraction patterns, as shown in Figure 6.

Conclusions

In summary, synthesis of IWW-type zeolite was performed using 5-azonia-spiro[4,4]nonane compound as structure directing agent in the presence of Ge in fluoride-free medium for the first time. This crystalline phase was already observed after one day of hydrothermal treatment. Germanosilicate zeolites generally degrade after template removal. However, the obtained product was stable in ambient for more than 6 months after calcination. This observation implies that this IWW zeolite possesses good hydrothermal stability. In addition, Si/Ge was increased from 4 to 10 by acid leaching without significant loss of crystallinity. By introducing TEOS during acid leaching, recrystallization of the IWW structure was observed. A similar azonia-spiro[4,5] compound was also utilized as structure directing agent leading to the formation of the three phases IWW, NON and sodium germanate. Furthermore, in absence of GeO₂ but with the same structure directing agent, pure NON-type zeolite was obtained.

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IWW-type zeolite was formed using azonia-spiro[4,4]nonane as template. The material shows low Ge-content and can be further degermanated.