

Post-Synthesis Treatment gives Highly Stable Siliceous Zeolites through the Isomorphous Substitution of Silicon for Germanium in Germanosilicates**

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Abstract: Germanosilicates, an important family of zeolites with increasing number of members and attractive porosities, but containing a large quantity of unstable Ge atoms in the framework, meet with great obstacles in terms of limited thermal and hydrothermal stability when it comes to practical use. A facile stabilization method thus has been developed to substitute isomorphously Ge atoms for Si atoms, giving rise to ultrastable siliceous analogues of the pristine germanosilicates.

Zeolites with uniform micropore channels, unique crystal-line structures and high surface areas have achieved great successes in adsorption, separation and catalysis fields.^[1] More than 200 kinds of zeolites with well-defined topologies have been developed up to date,^[2] but novel zeolites with more useful pore structures and higher application values are still desirable. Among various synthetic strategies proposed, introducing germanium into the synthesis gels has proved effective to construct unusual zeolite structures that are difficult to obtain from conventional all-silica or aluminosilicate systems because the Ge atoms have a synergetic structure-directing functionality in cooperation with organic structure-directing agents (OSDA). Successful examples of germanosilicates or Ge zeolites include BEC (FOS-5^[3] and ITQ-17^[4]), ASV (ASU-7),^[5] IWR (ITQ-24),^[6] IWS (ITQ-26),^[7] IWW (ITQ-22),^[8] IRR (ITQ-44),^[9] -ITV (ITQ-37),^[10] ITQ-43,^[11] UTL (IM-12),^[12] ITR (ITQ-34),^[13] STW (SU-32),^[14] UWY (IM-20),^[15] Mesoporous materials with 30-membered ring (MR) pores^[10] and structures with chiral channels^[14] have also been obtained from Ge-zeolite systems. These novel materials have potential uses in processing bulky molecules and asymmetric catalysis. Ge–O (1.860 Å) bonds are beneficial in forming the secondary building units in the framework, for example, double 4-ring (D4R). The formation of D4R requires small T–O–T bond angles. D4R thus is found in almost all germanosilicates.^[16,17] However, the Ge zeolites

are problematic because structural degradation takes place readily owing to the easy hydrolysis of Ge–O bonds, even by moisture under environmental conditions. This problem is one of the most fatal obstacles to applications. To stabilize the Ge-zeolite structures, Al atoms have been introduced into the framework to replace some of the Ge atoms by direct synthesis or post-synthesis treatment.^[6,18] With specially designed OSDA, all-silica HPM-1, the structure analogue of SU-32 germanosilicate, has been synthesized overcoming the expected strains in the D4R units predicted by theoretical calculations.^[19] However, in spite of post-synthesis treatment and direct synthesis, the degree stabilization and the number of examples of stable D4R-containing zeolites are still limited. More recently, the UTL germanosilicate was converted into stable siliceous zeolites by preferential hydrolysis of the D4R units and subsequent reassembly of the layers.^[20–22] This kind of structural transformation, however, decreased the size of the pore windows, and the all-silica analogue with the same topology as UTL could not be obtained.

Herein, we put forward a versatile method to enhance the hydrothermal stability of germanosilicates by increasing their Si/Ge ratios to the high-silica region through an isomorphous substitution process. As described in Scheme 1, the Ge-zeolite structures were stabilized by replacing Ge by Si in the D4R units. For Ge zeolites with a high Si/Ge ratio, such as 4.7, the substitution was realized readily by an acid treatment at elevated temperature, whereas for those with lower Si/Ge ratios, an additional silicon source was needed under carefully handled acid treatment. Through this versatile substitution method, hydrothermally stable siliceous zeolites were obtained from the germanosilicates with the UTL (IM-12), UWY (IM-20), BEC (ITQ-17), and IWR (ITQ-24) topologies.

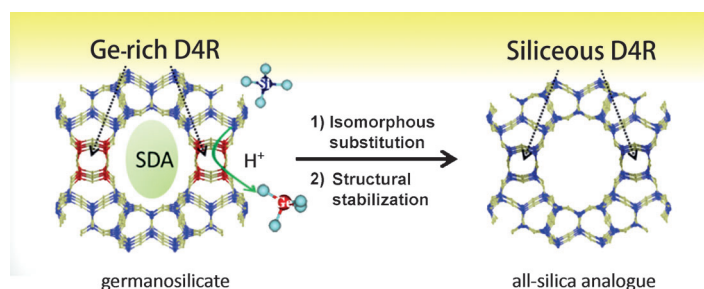
When the calcined IM-20 (Si/Ge = 1.7), ITQ-17 (Si/Ge = 3.1) and ITQ-24 (Si/Ge = 1.8) zeolites were immersed in water at ambient temperature, their crystalline structures were completely degraded to amorphous materials (Supporting Information, Figure S1, B–D). Whereas the calcined IM-12 zeolite with a higher Si/Ge ratio of 4.7 did not collapse totally but was hydrolyzed to a lamellar material with FER layers (Figure S1, A), in agreement to reported results.^[20,21] It is impossible to recover the UTL structure reversibly from this hydrolyzed material. Thus, the calcined Ge zeolites were hydrothermally unstable irrespective of topology and Si/Ge ratio. Nevertheless, when the as-synthesized Ge zeolites were subjected to the stabilization process assisted by isomorphous Si substitution, the four samples all had the characteristic diffraction peaks of the pristine ones (Figure 1). It is worth

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Scheme 1. Strategy for stabilizing the framework of germanosilicates by the isomorphous substitution of Ge (red) with Si (dark blue) in acidic media. The Si sources come from species removed from the crystallites or addition of an external Si source.

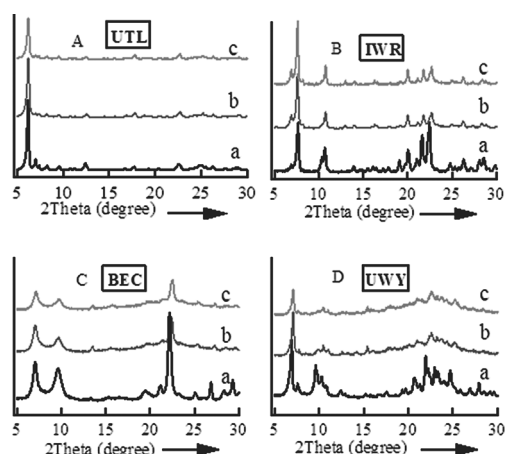


Figure 1. XRD patterns of IM-12 (A), ITQ-24 (B), ITQ-17 (C) and IM-20 (D). As-synthesized (a), stabilized by Si substitution (b), and further autoclaved in 65 % HNO_3 aqueous solution (423 K, 24 h) and calcination (823 K, 6 h) (c).

noting that the structures were highly stable and the porosities were well maintained (Figure S2) even after a harsh treatment in concentrated HNO_3 (65 %) at 423 K and a subsequent calcination at 823 K.

The stabilization treatment removed the Ge species significantly, as the Si/Ge ratio increased to the high-silica region, 233 for IM-12, 15.1 for ITQ-24, 100 for IM-20, and 208 for ITQ-17. According to the X-ray diffraction (XRD) patterns, the stabilized samples preserved the original topologies after an extensive replacement of Si for Ge, although a slight decrease in crystallinity was observed for BEC (ITQ-20) and UWY (IM-20; Figure 1C and D). To clarify the substitution mechanism and to verify the hypothesis, we have traced the substitution process in detail by choosing IM-12 as a representative example.

Recently, Roth et al.^[20,21] and Verheyen et al.^[22] disclosed that when the calcined IM-12 zeolite was heated under reflux in acid solution, a hydrolysis and then a structural reconstruction of the UTL framework occurred, giving rise to IPC-1P, IPC-2, IPC-4, and COK-14 with layered or new crystalline structures. In contrast, we conducted the acid treatment on the as-synthesized IM-12 at a higher temperature (463 K), in which only isomorphous substitution of Ge by Si occurred but

without altering the UTL topology. Thus, the treatment conditions and the choice of the parent are essential to stabilize the framework of Ge zeolites.

Thermogravimetric (TG) analysis indicated that 57.6 % of the structure-directing agents (SDA) species (Figure S3) were removed after the as-synthesized IM-12 was subjected to one treatment in 1M HNO_3 aqueous solution at 463 K, while the Si/Ge ratio increased from 4.7 to 59.4 (Figure S4). The substitution of Ge by Si occurred simultaneously with the removal of the SDA, that is, opening of pores. When the acid treatment was repeated twice, a highly siliceous material IM-12(S) was obtained with a Si/Ge ratio of 233, implying that the Ge species were removed to approximately 97 %. The IM-12(S) thus obtained showed a comparable crystallinity to the pristine IM-12 as demonstrated by XRD patterns.

In the framework of IM-12, the Ge atoms are shown to occupy mainly the T sites in D4R that pillar and connect the up-and-down dense FER-layers.^[9] When most of the Ge atoms were removed by repeated acid treatments, there must be other atoms occupying the Ge positions to preserve the D4R units and then the whole UTL topology. In the acid treatment without an additional Si source, the silica debris dissolved from the dense layer is assumed to substitute the Ge atoms. Then, IR spectra, ^{29}Si MAS NMR spectra, structure refinement, and porosity measurements were carried out to verify whether the newly formed D4R units were constructed of Si atoms and the siliceous material was structurally analogous to original UTL germanosilicate.

Figure 2 shows the IR spectra in the framework-vibration region of pristine IM-12 and its stabilized form IM-12(S). The

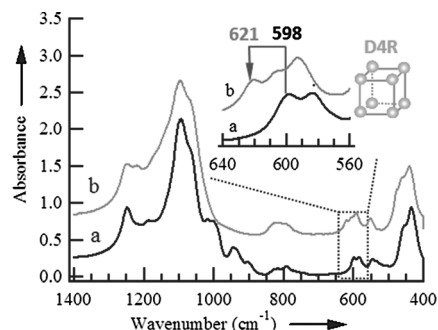


Figure 2. IR spectra in the framework vibration region of a) IM-12 (Si/Ge = 4.7), and b) siliceous analogue IM-12(S) (Si/Ge = 233). Inset: the enlarged region for D4R vibration.

band around 1000 cm^{-1} , attributed to the asymmetric stretching vibration of Si-O-Ge in the framework,^[23] disappeared completely for IM-12(S). This change is reasonable because the Ge content decreased to an extremely low level. On the other hand, the band around 598 cm^{-1} is related to the vibration of D4R units in IM-12.^[24,25] This band still existed but with a blue shift to 621 cm^{-1} after the stabilization treatment. The blue shift of 23 cm^{-1} is in agreement with the theoretical calculation by replacing heavier Ge atoms with Si atoms in D4R units (Figure S5). This result shows that the Si atoms replaced the Ge atoms to reconstruct new siliceous

D4R units. They then pillared the up-and-down FER-layers to make the structure stable against acid treatment and hydrolysis.

The Si atoms in D4R units have ^{29}Si NMR resonance signals that are different from those of ordinary Si in Q^4 groups, appearing mainly in the range of $\delta = -107.7$ – -109.4 ppm.^[19] IM-12(S) showed a resonance signal at $\delta = -107.97$ ppm which is assigned to the Si atoms in D4R units, and accounts for 15.9% of the population of Si atoms (Figure 3a and Table S1). The value was a little smaller than,

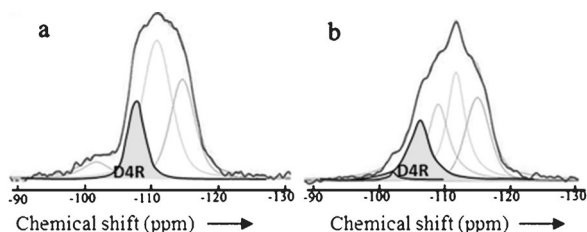


Figure 3. ^{29}Si MAS NMR spectra of a) IM-12(S) and b) IM-12.

but very close to, the theoretical value 21% of UTL topology. This again demonstrated that the D4R units, once rich in Ge for germanosilicate, were still present in the all-silica IM-12(S) but that they were now composed of Si atoms. Pristine IM-12 showed the resonance signals attributed to $n\text{Si}-(4-n)\text{Ge}$ groups in the range $\delta = -102$ ppm to -110 ppm, as well as those signals from $\delta = -112$ ppm to -116 ppm arising from the Q^4 groups.^[26,27] The Si/Ge ratio of IM-12 determined by ^{29}Si NMR spectroscopy was 6.11 (Figure 3b), slightly higher than the Si/Ge ratio of 4.7 determined by ICP analysis (Table S1).

Based on these characterizations, a siliceous structure with the UTL topology was used as the starting geometry for Rietveld refinement of calcined IM-12(S) (Figure 4). According to the refined structure, IM-12(S) had an idealized unit cell composition of $\text{Si}_{76}\text{O}_{152}$ with $\text{C}2/m$ space group (Table S2 and S3). In comparison, the original IM-12 germanosilicate had a chemical formula of $\text{Ge}_{13.8}\text{Si}_{62.2}\text{O}_{152}$ and a same space

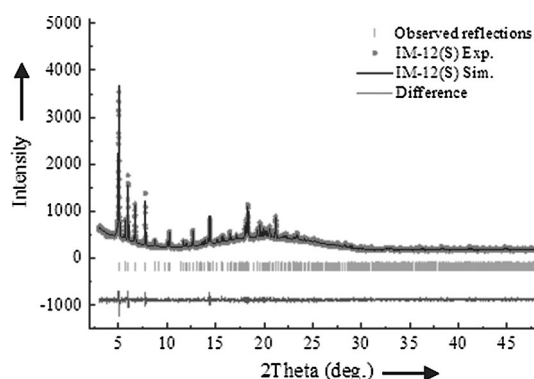


Figure 4. Rietveld refinement of calcined IM-12(S) recorded using synchrotron radiation ($\lambda = 1.2438$ Å). Experimental (top) and calculated XRD patterns as well as their difference profile are shown (bottom). The short tick marks below the patterns give the position of the Bragg reflections. $R_{wp} = 0.0559$, R_{wp} (w/o bck) = 0.239, $R_p = 0.043$.

group of $\text{C}2m$.^[12] Moreover, IM-12(S) and IM-12 have comparable unit-cell parameters, but there is a slight shrinkage along a -axis as a result of the Ge removal. The structure along the a -axis is that attacked under acid aqueous conditions, because the fragile Ge-O-Si and/or Ge-O-Ge bonds can be viewed as the pillars for the FER layers along the a -axis.^[20] Thus, the unit cell parameter a decreased the most by 0.5 Å (Table 1). Meanwhile, the b and c parameters were less

Table 1: Physicochemical properties of IM-12 and IM-12(S).

	IM-12 ^[c]	IM-12(S)
Si/Ge ^[a]	4.7	233
Surface area ^[b]	515	458
Chemical formula	$\text{Ge}_{13.8}\text{Si}_{62.2}\text{O}_{152}$	$\text{Si}_{76}\text{O}_{152}$
Unit Cell [Å]		
a	29.8004	29.3116(35)
b	13.9926	13.9138(56)
c	12.3926	12.3375(45)
Space group	$\text{C}2/m$	$\text{C}2/m$

[a] Determined by ICP. [b] Specific surface area given by N_2 adsorption at 77 K. [c] The chemical formula and unit cell parameters of IM-12 given by Ref. [12].

affected because the Ge content was low within the FER layers.^[12] For the same reason, the XRD pattern of IM-12(S) shifted to a higher 2θ region compared with that of IM-12, with the $[h00]$ reflections varying the most (Figure 1A). The shift could be observed when the XRD patterns were magnified.

N_2 adsorption indicated that siliceous IM-12(S) was of highly porous (Figure S2c), having a specific surface area somewhat lower than IM-12 germanosilicate ($458 \text{ m}^2 \text{ g}^{-1}$ vs. $515 \text{ m}^2 \text{ g}^{-1}$; Table 1). The N_2 sorption isotherm of IM-12(S) showed a hysteresis loop at $P/P_0 > 0.8$, indicating possible presence of mesopores. This would be closely related to a relatively large amount of Q^3 groups in IM-12(S) (Table S1). IM-12 is composed of 12 MR and 14 MR channels.^[12] Ar adsorption evidenced that its pore sizes were 5.6 and 6.8 Å, respectively (Figure S6). After the substitution process, IM-12(S) still had the two different distributions with the same pore sizes as pristine IM-12, which again verified that the leaching of Ge atoms did not change the porosity and topology. In addition, the SEM images showed that the IM-12(S) crystals preserved the platelet morphology of pristine IM-12 (Figure S7), although some voids and holes appeared on the crystal surface as a result of Ge and Si leaching. Those removable Si species may be the source for the substitution of Ge in the absence of additional Si.

The angles of Si-O-Si are bigger than Ge-O-Ge roughly by 15° and the Si-O distance is smaller than Ge-O by around 0.15 Å, which leads to all silica structures analogous to germanosilicates being unfavorable in energy.^[17] In theory, the Ge atoms are more favorable to construct the secondary building units D4R that are of vital importance for germanosilicates. Pure silica zeolites analogous to ITQ-7^[28] and SU-32^[19] have been hydrothermally synthesized with proper OSDAs and the help of F^- ions, which have the ability to stabilize D4R units.^[29,30] Nevertheless, these direct synthesis examples are still few in number. Herein, we have succeeded

in preparing nearly all-silica analogues of parent germanosilicates through an extensive isomorphous substitution by post-synthesis treatment. The whole stabilization process can be described as replacing Ge with Si mainly in the D4R units. In aqueous acid solution, the Ge–O bonds were hydrolyzed and the Si atoms either from the framework or from the additional Si source were inserted into the D4R units, forming more thermally and hydrothermally stable ones. IM-12 with a Si/Ge ratio of 4.7 did not need additional Si source and the dissolvable Si species from the framework were enough to fill the vacancies caused by Ge leaching, leading to 7.5 % Q³ groups in the final stabilized IM-12(S) zeolite (Table S1).

In conclusion, a versatile stabilization process has been proposed to replace the Ge atoms mainly in D4R units of germanosilicates with Si atoms. This further stabilizes the crystalline structures without changing the topologies of the parent germanosilicates. This would solve instability problems encountered in germanosilicates. Considering that introducing catalytically active sites into zeolite frameworks by post-synthesis treatment is practically mature,^[31,32] hydrothermally stable catalysts with promising applications are expected from all-silica analogues of germanosilicates prepared by postsynthesis treatment.^[34]

Experimental Section

IM-12,^[33] ITQ-24,^[6] IM-20,^[15] and ITQ-17^[4] zeolites were synthesized according to the literature methods. IM-12 with a higher Si/Ge ratio was stabilized in 1 M HNO₃ aqueous solution at 463 K for 24 h. The process was repeated to give a highly siliceous structure with a Si/Ge ratio of 233, denoted as IM-12(S). The post-treatment of the germanosilicates (ITQ-24, IM-20, ITQ-17) with lower Si/Ge ratios was carried out in 1 M HCl ethanol solution at 443 K for 24 h. Tetraethyl orthosilicate (TEOS) was needed as additional Si source. This post-treatment procedure was repeated 3–4 times. The stabilized ITQ-24, ITQ-17, IM-20 were denoted as ITQ-24(S), ITQ-17(S), IM-20(S), respectively. The calcined stabilized samples were autoclaved in 65 wt. % HNO₃ solution at 423 K for 24 h and then further calcined in air at 823 K for 6 h.

Powder X-ray diffraction (XRD) was employed to check the structure and crystallinity of the zeolites. Synchrotron radiation XRD measurement was performed to determine the structure of the stabilized material IM-12(S) by Rietveld refinement. The IR spectra were collected on a Nicolet Nexus 670 FT-IR spectrometer using KBr technique (2 wt % wafer). The adsorption isotherms were measured by N₂ adsorption at 77 K on a BELSORP-MAX instrument equipped with a precise sensor for low-pressure measurement. The pore size distribution was calculated with Horvath–Kawazoe method based on the data collected by Ar adsorption at 87 K on a Micromeritics ASAP 2020 instrument. The ²⁹Si MAS NMR spectra were measured on a VARIAN VNMRS 400WB NMR spectrometer. Thermogravimetry (TG) and derivative thermogravimetry (DTG) analyses were carried out on a Mettler TGA/SDTA 851° instrument. The Ge content was determined by inductively coupled plasma emission spectrometry (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer (For details, see Supporting Information).

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- [1] L. Moscou in *Introduction to Zeolite Science and Practice*, Vol. 1 (Eds: H. Van Bekkum, E. M. Flanigen, P. A. Jacobs, J. C. Jansen), Elsevier, Amsterdam, **1991**, p. 58 (Stud. Surf. Sci. Catal.).
- [2] <http://www.iza-online.org>.
- [3] T. Conradsson, M. S. Dadachov, X. D. Zou, *Microporous Mesoporous Mater.* **2000**, *41*, 183–191.
- [4] A. Corma, M. T. Navarro, F. Rey, J. Rius, S. Valencia, *Angew. Chem.* **2001**, *113*, 2337–2340; *Angew. Chem. Int. Ed.* **2001**, *40*, 2277–2280.
- [5] H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 10569–10570.
- [6] R. Castañeda, A. Corma, V. Fornés, F. Rey, J. Rius, *J. Am. Chem. Soc.* **2003**, *125*, 7820–7821.
- [7] D. L. Dorset, K. G. Strohmaier, C. E. Klierer, A. Corma, M. J. Diaz-Cabañas, F. Rey, C. J. Gilmore, *Chem. Mater.* **2008**, *20*, 5325–5331.
- [8] A. Corma, F. Rey, S. Valencia, J. L. Jorda, J. Rius, *Nat. Mater.* **2003**, *2*, 493–497.
- [9] J. Jiang, J. L. Jorda, M. J. Diaz-Cabañas, J. Yu, A. Corma, *Angew. Chem.* **2010**, *122*, 5106–5108; *Angew. Chem. Int. Ed.* **2010**, *49*, 4986–4988.
- [10] J. Sun, C. Bonneau, A. Cantin, A. Corma, M. J. Diaz-Cabañas, M. Moliner, D. Zhang, M. Li, X. Zou, *Nature* **2009**, *458*, 1154–1158.
- [11] J. Jiang, J. L. Jorda, J. Yu, L. A. Baumes, E. Mugnaioli, M. J. Diaz-Cabañas, U. Kolb, A. Corma, *Science* **2011**, *333*, 1131–1134.
- [12] J. Paillaud, B. Harbuzaru, J. Patarin, N. Bats, *Science* **2004**, *304*, 990–992.
- [13] A. Corma, M. J. Diaz-Cabañas, J. L. Jorda, F. Rey, G. Sastre, K. G. Strohmaier, *J. Am. Chem. Soc.* **2008**, *130*, 16482–16483.
- [14] L. Tang, L. Shi, C. Bonneau, J. Sun, H. Yue, A. Ojuva, B. L. Lee, M. Kritikos, R. G. Bell, Z. Bacsik, J. Mink, X. Zou, *Nat. Mater.* **2008**, *7*, 381–385.
- [15] M. Dodin, J. L. Paillaud, Y. Lorgouillous, P. Caullet, E. Elkaim, N. Bats, *J. Am. Chem. Soc.* **2010**, *132*, 10221–10223.
- [16] B. B. Schaaack, W. Schrader, F. Schüth, *Chem. Eur. J.* **2009**, *15*, 5920–5925.
- [17] G. Sastre, A. Corma, *J. Phys. Chem. C* **2010**, *114*, 1667–1673.
- [18] F. Gao, M. Jaber, K. Bozhilov, A. Vicente, C. Fernandez, V. Valtchev, *J. Am. Chem. Soc.* **2009**, *131*, 16580–16586.
- [19] A. Rojas, M. A. Camblor, *Angew. Chem.* **2012**, *124*, 3920–3922; *Angew. Chem. Int. Ed.* **2012**, *51*, 3854–3856.
- [20] W. J. Roth, O. V. Shvets, M. Shamzhy, P. Chlubná, M. Kubů, P. Nachtigall, J. Čejka, *J. Am. Chem. Soc.* **2011**, *133*, 6130–6133.
- [21] W. J. Roth, P. Nachtigall, R. E. Morris, P. S. Wheatley, V. R. Seymour, S. E. Ashbrook, P. Chlubná, L. Grajciar, M. Polozij, A. Zukal, O. Shvets, J. Čejka, *Nat. Chem.* **2013**, *5*, 628–633.
- [22] E. Verheyen, L. Joos, K. Van Havenbergh, E. Breynaert, N. Kasian, E. Gobechiya, K. Houthoofd, C. Martineau, M. Hinterstein, F. Taulelle, V. Van Speybroeck, M. Waroquier, S. Bals, G. Van Tendeloo, C. E. A. Kirschhock, J. A. Martens, *Nat. Mater.* **2012**, *11*, 1059–1064.
- [23] T. Blasco, A. Corma, M. J. Diaz-Cabañas, F. Rey, J. A. Vidal-Moya, C. M. Zicovich-Wilson, *J. Phys. Chem. B* **2002**, *106*, 2634–2642.
- [24] C. S. Blackwell, *J. Phys. Chem.* **1979**, *83*, 3251–3257.
- [25] A. J. M. de Man, R. A. van Santen, *Zeolite* **1992**, *12*, 269–279.
- [26] M. V. Shamzhy, O. V. Shvets, M. V. Opanasenko, P. S. Yaremov, L. G. Sarkisyan, P. Chlubná, A. Zukal, V. R. Marthala, M. Hartmann, J. Čejka, *J. Mater. Chem.* **2012**, *22*, 15793–15803.
- [27] N. Kasian, G. Vanbutsele, K. Houthoofd, T. I. Koranyi, J. A. Martens, C. E. A. Kirschhock, *Catal. Sci. Technol.* **2011**, *1*, 246–254.

- [28] L. A. Villaescusa, P. A. Barrett, M. A. Camblor, *Angew. Chem.* **1999**, *111*, 2164–2167; *Angew. Chem. Int. Ed.* **1999**, *38*, 1997–2000.
- [29] P. Caullet, J.-L. Guth, J. Hazm, J.-M. Lamblin, H. Gies, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 345–361.
- [30] E. Aubert, F. Porcher, M. Souhassou, V. Petricek, C. Lecomte, *J. Phys. Chem. B* **2002**, *106*, 1110–1117.
- [31] H. Xu, Y. T. Zhang, H. H. Wu, Y. M. Liu, X. H. Li, J. G. Jiang, M. Y. He, P. Wu, *J. Catal.* **2011**, *277–284*, 263–272.
- [32] Y. Oumi, R. Mizuno, K. Azuma, S. Nawata, T. Fukushima, T. Uozum, T. Sano, *Microporous Mesoporous Mater.* **2001**, *49*, 103–109.
- [33] O. V. Shvets, N. Kasian, A. Zukal, J. Pinkas, J. Čejka, *Chem. Mater.* **2010**, *22*, 3482–3495.
- [34] After the acceptance of this manuscript we learnt of another very closely related approach, also reported in this issue: L. Burel, N. Kasian, A. Tuel, *Angew. Chem.* **2013**, DOI: 10.1002/ange.20130306744; *Angew. Chem. Int. Ed.* **2013**, DOI: 10.1002/anie.20130306744.