Transformation of porous glass beads into MFI-type containing beads

F. Scheffler a,*, W. Schwieger a, D. Freude b, H. Liu b, W. Heyer c, F. Janowski c

a Lehrstuhl für Technische Chemie I, Universität Erlangen, D-91058 Erlangen, Germany
b Fakultät für Physik und Geowissenschaften, Universität Leipzig, D-04103 Leipzig, Germany
c Institut für Technische und Makromolekulare Chemie, Martin-Luther-Universität Halle-Wittenberg, D-06108 Halle/Saale, Germany

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Dedicated to Professor Sergey Petrovich Zhdanov on the occasion of his 90th birthday

Abstract

Macroporous glass beads (Na₂O–B₂O₃–SiO₂) with a particle diameter of ~300 μm and an average pore diameter of 92 nm, obtained by the VYCOR-process, were transformed into MFI-type containing beads, that retained the original shape. The conversion was achieved through a hydrothermal treatment with an aqueous mixture of an Al-source (sodium aluminate or aluminum sulfate) and a template (tetrapropylammonium bromide (TPABr) or dipropylamine (DPA)). The resulting products were characterized by X-ray diffraction, ²⁷Al MAS NMR, N₂-adsorption and SEM. The filtrates were analyzed by ICP-OES. Using two different templates and two kinds of Al-source MFI-type beads with varying properties were obtained. The boron atoms, which are constituents of the glass material, were used as probe atoms for the characterization of the synthesis procedure. With DPA the crystallization took place inside and on the outer surface of the spheres, while TPABr led to a shell-like crystallization starting from the outer surface of the glass particles. The type of Al-source influences the pH value of the reaction mixture and varies the Si/Al ratio in the obtained products.

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1. Introduction

Methods for obtaining shaped zeolite materials in a single step synthesis are of special interest for a lot of new and to some extend also for established applications. Composites, which are generated without an additional shaping step, can substitute conventional binder-shaped zeolite bodies for catalytic use and initiate new fields of applications, e.g. for sensors and light weight adsorbents [1,2]. Such materials can be obtained by crystallization on the inert surface of dense substrates [3,4] or by transformation of meso and macroporous substrates [5,6]. Depending on the support material used and on the composition of the synthesis mixture, there are three approaches to form a zeolite coating: (i) nutrient sources are only in the
liquid phase, (ii) nutrient sources are provided by the liquid phase and support and (iii) nutrient sources are present within the support [7]. According to principle (i) Tosheva et al. [8,9] reported the preparation of silicalite-1 and beta spheres using anion exchange resin beads as shape directing macrotemplates. Our work, described in the following, corresponds to principle (ii). Porous glass acts as a reactive SiO2 source with high surface area and is available in many different shapes (spheres, rods, sheets...). The second zeolite framework builder (aluminum) is provided by the reaction mixture. Recently, we have reported the transformation of macroporous boron–silicate glass fragments into zeolite particles maintaining the original shape [10]. The zeolite structures ferrierite (FER) and ZSM-5 (MFI) were obtained by varying the Al-concentration in the aqueous reaction mixture and the products were characterized by several methods, including 11B MAS NMR [10], since boron atoms are constituents of the porous glass material. Dong et al. [11] used the vapor phase method, in order to obtain a B–Al–ZSM-5 zeolite with a composition similar to the starting glass material. The concentration of boron in the zeolite was even higher (up to 6.8 boron atoms per unit cell) than in the starting material, if only a partial transformation of glass to zeolite took place [12]. Tuan et al. [13] described the synthesis of boron containing membranes even with a Si/B ratio of 12. Jansen et al. [14] found in a conventional hydrothermal synthesis a maximum of only 5 boron atoms in the unit cell of the ZSM-5 framework. It should be noted that the framework boron in MFI zeolites has a lower thermal and chemical stability than the framework aluminum [15–17]. Catalytic applications usually require a higher thermal stability.

In the present work the partial transformation of macroporous glass beads into zeolite containing beads was investigated. It could be demonstrated that the choice of the template and aluminum source drastically influences the pathway of crystallization and the properties of the obtained material remaining in the original shape of the glass particles. Two different templates and two different Al sources were used and the transformation mechanism was investigated with respect to the role of the template and of the aluminum source.

Furthermore, the present work uses the boron nuclei as probe atoms for the characterization of the crystallization process.

2. Experimental

Starting material for the zeolite crystallization was porous glass V6 (beads) with a particle diameter of 300 µm and an average pore diameter of 92 nm, obtained by the Vycor-process [18]. A specification of making the macroporous glass (MaPG) V6 is given in [19]. The chemical composition of V6 is 93.7 wt.% SiO2, 0.2 wt.% Na2O, 0.1 wt.% Al2O3, 6.0 wt.% B2O3, the surface area is 38.0 m2 g⁻¹ (BET) and the pore volume averages 0.32 cm³ g⁻¹. The synthesis procedure is based on a hydrothermal reaction of a synthesis mixture with the following batch composition:

\[
a\text{Na}_2\text{O}:b\text{SDA}:17.6\text{SiO}_2:0.57\text{B}_2\text{O}_3: c\text{Al}_2\text{O}_3:d\text{H}_2\text{O}
\]

with \(a = 1.1–3.1, b = 0.5–5.5, c = 0.3–1, \) and \(d = 616–638\). SDA denotes the structure directing agent (also called template).

Porous glass beads provided the SiO2 and B2O3 constituents, sodium aluminate or Al2(SO4)3·16H2O were used as Al-sources and sodium hydroxide (NaOH) was the alkali source. Al-source, NaOH and the template were dissolved in distilled water and 1 g of the porous glass was added to 10 g of the above solution. When TPABr was used as template, it was dissolved in the reaction mixture before the addition of glass. Dipropylamine (DPA) was simply added to the glass–solution-mixture, since DPA is not soluble in the aqueous solution. After stirring the whole mixture for 15 min, degassing was carried out under vacuum for 15 min, in order to fill the total pore volume.

The particular reaction mixtures (10 g solution plus 1 g solid) were shared into Teflon lined stainless steel autoclaves (nominal volume 50 ml). The synthesis was carried out at 175 °C. All autoclaves were rotated in a conventional oven around a horizontal axis with 20 rpm. The autoclaves were...
removed at the chosen crystallization time and quenched with cold water to interrupt the crystallization process. After filtering and multiple washing steps the products were dried at 100 °C for 16 h, calcined at 500 °C and rehydrated in open atmosphere. The sample nomenclature is X–Y and is used in all figures. According to Table 1 the letter X describes the run number of the synthesis and Y the reaction time.

Phase composition and crystallinity were characterized by X-ray diffraction (XRD) (Xpert Philips, Netherlands) from 2 to 30° 2θ with CuKα radiation. In order to retain the spherical shape, the samples were not ground. In order to compare the products amongst themselves and to determine a relation with respect to conventional powder samples, the \( Q_{Al} \)-method was used. A relative measure of the yield of the crystallization process can be obtained from the intensity \( I \) (height of the reflection peaks in counts/s) of the main X-ray reflection of MFI-type zeolite in relation to the intensities of two reflections of an external standard (corundum). The value \( Q_{Al} \) is defined as

\[
Q_{Al} = \frac{2 \times I(\text{MFI}, 2\theta \approx 23.1)}{I(\text{Cor}, 2\theta = 35.2) + I(\text{Cor}, 2\theta = 43.1)},
\]

where MFI denotes the reflection of zeolite MFI and Cor denotes the reflections of corundum as reference sample, which has the same volume and is measured under the same conditions as the zeolite sample.

The changes of the coordination of the boron atoms during the reaction were studied by \(^{11}\text{B}\) MAS NMR spectroscopy at room temperature on a Bruker MSL-300 spectrometer at a Larmor frequency of 96.3 MHz and a rotation frequency of 4 kHz. The chemical shift is related to BF\(_3\)·Et\(_2\)O in CDCl\(_3\). The relative concentration of boron in the solid material is related to the same mass of the porous glass V6 (100% total intensity). The micropore volume was determined by adsorption of nitrogen (Carlo Erba, ASAP 2010). The samples were degassed for 2 h at 260 °C. The micropore volumes were calculated by the \( t \)-method from statistical thickness values between 3.5 and 5 Å (\( p/p_0 \) from 0.03 to 0.3). The morphology was investigated by scanning electron microscopy (SEM).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis time (h)</th>
<th>( Q_{Al} )-value</th>
<th>Boron three-coordinated (glass) 12.9 ppm</th>
<th>Boron four-coordinated (glass) 2 ppm</th>
<th>Boron four-coordinated (zeolite) –0.33 ppm</th>
<th>Total content of boron*</th>
<th>Micropore volume (cm(^3)g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>V6</td>
<td></td>
<td>90.9%</td>
<td>9.1%</td>
<td>0%</td>
<td>100%</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Synthesis 1: 1.1Na(_2)O:5.5DPA:17.6SiO(_2):0.3Al(_2)O(_3):1B(_2)O(_3):638 H(_2)O:0.45H(_2)SO(_4)(^b)</td>
<td>1–8</td>
<td>8 0 12.7%</td>
<td>33.4%</td>
<td>0%</td>
<td>46.1%</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1–15</td>
<td>15 0.28 0%</td>
<td>50.1%</td>
<td>3.2%</td>
<td>53.3%</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1–90</td>
<td>90 0.73 0%</td>
<td>1.2%</td>
<td>57.8%</td>
<td>59.0%</td>
<td>0.089</td>
<td></td>
</tr>
<tr>
<td>Synthesis 2: 3.1Na(_2)O:5.5DPA:17.6SiO(_2):1Al(_2)O(_3):12O(_3):616H(_2)O(^c)</td>
<td>2–24</td>
<td>24 0.63 0%</td>
<td>18.5%</td>
<td>3.0%</td>
<td>21.5%</td>
<td>0.085</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2–48</td>
<td>48 0.82 0%</td>
<td>4.4%</td>
<td>9.3%</td>
<td>13.7%</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2–72</td>
<td>72 0.78 0%</td>
<td>2.8%</td>
<td>9.4%</td>
<td>12.2%</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Synthesis 3: 3.1Na(_2)O:0.5TPABr:17.6SiO(_2):1Al(_2)O(_3):1B(_2)O(_3):616H(_2)O(^d)</td>
<td>3–12</td>
<td>12 0 0%</td>
<td>50.8%</td>
<td>0%</td>
<td>50.8%</td>
<td>0.0005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3–24</td>
<td>24 0.32 0%</td>
<td>8.1%</td>
<td>14.5%</td>
<td>22.6%</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3–48</td>
<td>48 0.66 0%</td>
<td>0%</td>
<td>19.0%</td>
<td>19.0%</td>
<td>0.082</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3–72</td>
<td>72 0.68 0%</td>
<td>0%</td>
<td>13.1%</td>
<td>13.1%</td>
<td>0.085</td>
<td></td>
</tr>
</tbody>
</table>

* Percentage of the boron from the starting material.
\(^b\) Al-source Al\(_2\)(SO\(_4\))\(_3\):16 H\(_2\)O.
\(^c\) Al-source Na-aluminate.
with a Stereoscann MK II (Cambridge Instruments, UK). The concentrations of Al and B in the filtrates were determined by ICP-OES analysis (Plasma 400 Perkin–Elmer).

3. Results and discussion

3.1. Synthesis with DPA and aluminum sulfate

DPA is a template that broadens the synthesis field compared to template-free synthesis [20]. It accelerates the MFI crystallization, although it does not belong to the so-called genuine templates in this synthesis, since its molecular dimensions are much smaller than those of the resulting zeolite channel network. DPA was used in combination with Al$_2$(SO$_4$)$_3$·16H$_2$O as the Al source. It can be assumed that the sulfate ion has no influence on the synthesis. The composition of the reaction mixture is given in Table 1 as synthesis 1. The pH value of the reaction mixture was 11.2 before the template addition and after the template addition the pH value increased to 11.7. Samples were taken after a crystallization time of 8, 15 and 90 h, respectively.

From the XRD-plots shown in Fig. 1, it can be seen that the crystal growth starts between 8 and 15 h. While the XRD-plot of the product after 8 h hydrothermal treatment has the same profile like the amorphous starting material, the product after 15 h reaction time shows the typical reflections of MFI-type zeolite at 8.0°/9.0° and 23.2°/23.9°/24.5° (2Θ). From aluminum concentrations of the reaction mixture and filtrates, given in Table 2 it can be concluded, that a considerable amount of aluminum is adsorbed on the surface of the glass beads in the first part of the reaction. During the further crystallization process (from 8 to 90 h) only a small decrease of the aluminum concentration was found. The $^{11}$B MAS NMR spectra are shown in Fig. 2. Only two coordination states of boron exist in the porous glass after 8 h crystallization time. A weak signal shows strong second-order quadrupole broadening, has an isotropic chemical shift of $\delta = 12.9$ ppm and can be assigned to the three-coordinated boron in glass. The intense line at about $-2.0$ ppm originates from the tetrahedrally coordinated boron in the starting glass, cf. [16,21]. Tetrahedrally coordinated boron atoms are exposed to a weaker electrical field gradient, which reduces the quadrupole broadening. The line can be fit by a Gaussian curve.

Threefold coordinated boron disappeared after 15 h synthesis time, and a narrow line at about $-3.7$ ppm appeared, which can be assigned to tetrahedrally coordinated boron in the zeolite framework [16,21]. The small intensity of the narrow line at $-3.7$ ppm points towards a very

![Fig. 1. XRD-plots of samples of synthesis 1 and a high crystalline powder sample (HZSM-5, Süd-Chemie Si/Al = 15).](image)

Table 2

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration aluminum/g1$^{-1}$</th>
<th>Concentration boron/g1$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction mixture 1</td>
<td>1.1</td>
<td>0</td>
</tr>
<tr>
<td>Filtrate 1–8</td>
<td>0.45</td>
<td>3.2</td>
</tr>
<tr>
<td>Filtrate 1–15</td>
<td>0.43</td>
<td>3.0</td>
</tr>
<tr>
<td>Filtrate 1–90</td>
<td>0.40</td>
<td>2.7</td>
</tr>
<tr>
<td>Reaction mixture 2</td>
<td>2.4</td>
<td>0</td>
</tr>
<tr>
<td>Filtrate 2–24</td>
<td>1.75</td>
<td>4.8</td>
</tr>
<tr>
<td>Filtrate 2–48</td>
<td>1.73</td>
<td>5.1</td>
</tr>
<tr>
<td>Filtrate 2–72</td>
<td>1.73</td>
<td>5.1</td>
</tr>
<tr>
<td>Reaction mixture 3</td>
<td>2.4</td>
<td>0</td>
</tr>
<tr>
<td>Filtrate 3–12</td>
<td>1.70</td>
<td>3.0</td>
</tr>
<tr>
<td>Filtrate 3–24</td>
<td>1.68</td>
<td>4.4</td>
</tr>
<tr>
<td>Filtrate 3–48</td>
<td>1.60</td>
<td>4.7</td>
</tr>
<tr>
<td>Filtrate 3–72</td>
<td>1.54</td>
<td>5.3</td>
</tr>
</tbody>
</table>

lower degree of crystallization. This corresponds to the low $Q_{\text{Al}}$-value (0.28). The amount of zeolite-incorporated boron increased from 3.2% to 57.8% of the boron present in the starting glass when the crystallization time was prolonged from 15 to 90 h. This is accompanied by a further increase of the $Q_{\text{Al}}$-value up to 0.73.

A remarkable loss of 54% of the boron in the porous glass (6 wt.%) was observed during the first 8 h of synthesis. This correlates to an increase of boron concentration in the filtrates measured by ICP-OES, cf. Table 2. The amount of threefold coordinated boron decreased from 90.9% in the starting material to 12.7%, while the fourfold coordinated boron in the glass matrix increased from 9.1% to 33.4%.

Fig. 3 shows SEM images of the starting material V6 (Fig. 3a) and of the samples 1–8 (Fig. 3b and c) and 1–90 (Fig. 3d–f) in different magnifications. Even after 90 h hydrothermal treatment and after the transformation of more than two-thirds of the glass material into MFI-structure the original size and shape of the beads have not changed. The detailed image of sample 1–8 (Fig. 3c) shows small particles on the surface of the glass beads even though there is no indication of a crystalline phase in the XRD pattern. Longer crystallization times lead to a complete covering of the outer surface with nonorientated oblong crystals (3e). A cross-section in order to have a view into a “zeolite bead” is shown in Fig. 3f. Inside the beads, the primary crystals have similar shape and dimension like the crystals on the outer surface but they are ordered to larger cubic units. Since no reflections of an extraneous crystalline phase can be seen in the XRD plot, both types of crystals should be of MFI-type. The micropore volume, which was determined by nitrogen adsorption, increases from ~0 (sample 1–8) to 0.089 cm$^3$g$^{-1}$ (sample 1–90). This correlates to the increase of the crystallinity, which is given as the $Q_{\text{Al}}$-value. The micropore volume of a MFI-powder (100% crystalline) obtained by a conventional hydrothermal synthesis is 0.17 cm$^3$g$^{-1}$. The decreased BET-surface area of sample 1–8 (18.7 m$^2$g$^{-1}$) compared to the starting material V6 (38.0 m$^2$g$^{-1}$) indicates an adsorption of Al-species in the glass pores. This is confirmed by the significantly smaller Al-concentration in the filtrate, which was measured by ICP-OES, cf. Table 2.

3.2. Synthesis with DPA and Na-aluminate

Na-aluminate is also a common Al-source for zeolite synthesis. In reaction mixture 2 (given in Table 1 as synthesis 2) it was used in combination with DPA, in order to test its applicability for the preparation of MFI-type containing beads. Apart from this it leads to a higher alkalinity compared to the use of aluminum sulfate, since the composition is 10.3 wt.% Al$_2$O$_3$, 20.6 wt.% Na$_2$O and 69.1 wt.% H$_2$O. The pH value of the reaction mixture before and after template addition was about 14. Samples were taken after 24, 48 and 72 h crystallization time. The XRD-plots of the samples, shown in Fig. 4 evidence well crystallized MFI-type zeolites. Already after 24 h the $Q_{\text{Al}}$-value reached 0.63 and increased to 0.82 after 48 h. Further hydrothermal treatment lead to a slight decrease of the $Q_{\text{Al}}$-value.

The $^{11}$B MAS NMR spectra in Fig. 5 and the values in Table 1 show that boron atoms are less
incorporated into the zeolite framework, when Na-aluminate is used as Al-source instead of aluminum sulfate. Of the boron content of the porous glass (6 wt.% B$_2$O$_3$) 58% was incorporated into the framework of zeolite using aluminum sulfate as Al-source, while only about 9% boron was incorporated into the framework using Na-aluminate as Al-source. The amount of boron in the solid material obtained after 72 h is 12% of the boron in the starting material V6. SEM images (Fig. 6) show that the original shape and size (~300 µm) of the porous glass beads remained even at higher degree of transformation into the MFI-type structure. The $Q_{\text{Al}}$-value of sample 2–48 is 0.82 which represents a high crystallinity. From the details shown in Fig. 6b, d, and f it can be concluded that a thin layer of crystals were formed on the outer surface of the beads. But a considerable part of the transformation took place inside the beads and produced hollow spheres with layers of MFI.
crystals in a cubic shape. This implies that the template DPA is able to penetrate the glass pores. The estimated volumes of micropores correlate with the crystallinity, cf. Table 1.

3.3. Synthesis with TPABr and Na-aluminate

In this synthesis the template DPA was replaced by TPABr. This ionic template is counted among the “genuine” templates [20] and is soluble in water. An influence on the pH value of the starting reaction mixture (~14) was not detectable. Samples were also taken after 12, 24, 48 and 72 h. The hydrothermal treatment of porous glass V6 with the TPABr and aluminate containing reaction mixture lead to materials with MFI-type structure as well. Fig. 7 shows the XRD patterns of the synthesized materials. The XRD plot of sample 3–12 did not change compared to the starting material V6, although after this time a considerable part of aluminum disappeared out of the filtrate (Table 2). Furthermore, the $^{11}$B MAS NMR spectra in Fig. 8 show a drastic decrease of the boron content in the solid phases. The remaining boron is fourfold coordinated in the glass. A crystalline phase with the characteristic reflections of MFI was found after 24 h crystallization time. The increase of the $Q_{Al}$ values from 0.32 after 24 h reaction time to 0.68 at 72 h reaction time demonstrates the increasing crystallinity. The total boron content decreased to 19% (48 h) and 13% (72 h) of the boron present in the starting glass, and it is solely fourfold coordinated zeolitic boron.

The SEM images in Fig. 9 show that the composite spheres lost their original shape after 24 h crystallization time in mixture 3. Small particles beside and on the surface of the spheres can be observed already after 12 h. After 24 h crystallization time large particles with the shape of broken glass can be seen in the SEM images (Fig. 9c). The large particles are covered by uniform cubic crystals smaller than 1 μm. Hollow spheres could not be found, but beads with reduced sizes (<200 μm) were present.

It can be concluded that the crystallization with TPABr is initiated on the surface of the spheres. This leads to the formation of zeolite shells with decreased mechanical stability. During further crystallization the shells crack and separate from the spheres. Subsequently the crystallization starts again on the outer surface of the resulting smaller beads. From this behaviour it can be concluded, that in contrast to DPA the TPA cations can not infiltrate the glass pores or that the adsorption on the pore surface is inhibited. The different diameters should not be the reason, since both molecules
(TPABr and DPA) are more than ten times smaller than the glass pores. Rather the charge of TPA$^+$ could play an important role.

The $^{11}$B MAS NMR spectra (Figs. 2, 5, and 8) demonstrate that the change from three-coordinated to four-coordinated boron in glass is one of the first steps of the conversion. After that the tetrahedrally coordinated boron can be incorporated into the MFI-crystals via the solution. The higher alkalinity of the reaction mixtures 2 and 3

Fig. 6. SEM pictures of sample 2–24 ((a) overview, (b) details of the surface) sample 2-48 ((c) overview, (d) details of the surface) and sample 2–72 ((e) overview, (f) view into a bead/cross-section).
compared to 1 gives rise to a higher relative concentration of threefold coordinated boron in the solution, cf. [22,23]. This is one of the reasons for lower incorporation of boron into the zeolitic framework.

4. Conclusions

Macroporous glass beads can be transformed into material with a high content of the MFI-type structure without destroying the original shape of the glass particles. The synthesis can be carried out in a liquid/solid phase reaction comparable to a conventional zeolite synthesis.

Depending on the kind of template and on the pH value of the reaction mixture (changed by the type of Al-source) MFI-beads with varying properties were obtained. The type of template influences the path of crystallization. While TPABr initiates the crystallization on the outer surface of the spheres, DPA accelerates the crystallization uniformly in the whole volume. The first step of the transformation is a fast adsorption of aluminum in the porous glass. This is independent of the Al-source and the pH value of the reaction mixture.

The intensity and coordination of boron atoms, which are constituents of the glass matrix and can be incorporated into the MFI-crystals, was monitored by $^{11}$B MAS NMR spectroscopy. It could be shown that the concentration of boron in the zeolite framework depends on the pH value of the reaction mixture. The smaller incorporation at a higher pH value can be explained by the increase of trigonal boron relative to fourfold coordinated boron in the solution for increasing basicity of the reaction mixture.

Although the amount of boron in the MFI framework is influenced by the basicity of the reaction mixture, in certain circumstances (lower pH value, synthesis 1) the intensity of the narrow signal at $-3.7$ ppm in the $^{11}$B MAS NMR spectra can be used as qualitative measure of the material conversion from the glass to the MFI-type structure.
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References


