Binderless zeolite LTA beads with hierarchical porosity for selective CO$_2$ adsorption in biogas upgrading

This chapter is based on a publication:

Abstract
In the context of CO$_2$ removal from biogas, a series of binderless zeolite LTA adsorbents with a macroscopic bead format (0.5–1.0 mm) and with hierarchical porosity (i.e. with the zeolitic micropores being accessible through meso- and macropores mainly in the 10–100 nm range) was synthesized with a variety of Si/Al ratios (1.2–3.9) using Amberlite IRA-900 anion-exchange resin beads as a hard template. The CO$_2$ and CH$_4$ adsorption capacity of the beads in Na-form with different Si/Al ratios were measured, reaching higher CO$_2$/CH$_4$ selectivity and similar, yet slightly higher CO$_2$ adsorption compared to commercial zeolite LTA pellets containing a binder. Subsequently, one the zeolitic beads was subjected to different degrees of ion-exchange (0–96%) with KCl and then tested in the adsorption of CO$_2$ and CH$_4$. The best performance among all the ion-exchanged beads was achieved with Na$_{58}$K$_{42}$-LTA beads, which gave very high CO$_2$/CH$_4$ selectivity (1540). Although essentially no CH$_4$ was adsorbed on these beads, the CO$_2$ adsorption capacity was still substantial (1.9 mmol g$^{-1}$ at 0.4 bar CO$_2$, i.e. the partial pressure of CO$_2$ in biogas).
2.1. Introduction

Biogas is produced through the anaerobic digestion of organic matter and consists of approximately 60 vol% CH₄ and 40 vol% CO₂ as main components [1]. The energy content of biogas is directly related to the CH₄ content. The energy content of methane, described by the Lower Calorific Value (LCV), is 36 MJ/m³ CH₄ compared to 20 MJ/m³ biogas (60 vol% CH₄) at STP conditions [2]. By upgrading biogas through selective separation of carbon dioxide, a substitute for natural gas is obtained that can be used as a renewable fuel, for example in combined heat and power plants, or as a vehicle fuel [1]. An additional benefit of biogas upgrading and utilization is the prevention of emission of methane into the atmosphere, as methane has a global warming potential 28 times larger than carbon dioxide [3].

Among the approaches for biogas upgrading, adsorption using solid sorbents is considered an attractive separation technology because it is a straightforward process in which no liquid waste is generated. Additionally, regeneration of solid adsorbents is easier than that of liquid absorbents, because CO₂ is mainly physisorbed on solid adsorbents, whilst it is chemisorbed on liquid absorbents. Therefore, solid adsorbents typically require lower energy for regeneration [4,5].

The development of suitable materials for the selective CO₂ adsorption from biogas is thus a strategically important field of research. Some of the most promising and widely-studied adsorbents for CO₂ adsorption are carbon-based materials, zeolites, and metal-organic frameworks (MOFs). The assets of carbon-based materials are that they have high thermal stability, are insensitive to moisture due to their hydrophobic nature, and are available at low cost [6–8]. However, they generally have a relatively weak interaction with CO₂ and, therefore, low CO₂ adsorption capacity and selectivity towards CO₂ at low pressure [9,10]. This limitation can be mitigated by nitrogen-doping of the carbon surface, thus enhancing the interaction with CO₂ molecules [11]. MOFs are highly porous materials with specific surface areas of 1000-10000 m²/g, and have demonstrated remarkably high CO₂ adsorption capacities, with reported values up to 33.5 mmol g⁻¹ (at 35 bar) [12,13]. However, such high pressures (35 bar) are not desired in biogas upgrading applications due to the high equipment cost and energy requirements [14]. These MOFs with exceptional adsorption capacity at high pressures are less suitable for application in lower pressure ranges (< 5 bar), due to their weak interaction with CO₂ [13,15,16]. Additional limitations for MOFs are the high synthesis costs and the relatively low hydrothermal stability, which
poses difficulties for regeneration [17,18]. Zeolites possess moderate adsorption capacities (1-7 mmol g⁻¹) at low pressure (1 bar), and can reach extremely high selectivity towards CO₂ (CO₂/CH₄ > 100) [19–22]. Furthermore, they possess excellent structural stability and can be produced easily and at low costs [15,23]. One of the biggest challenges for the application of zeolites as adsorbents is the presence of water in the gas mixture, because H₂O and CO₂ compete for the same adsorption sites and zeolites with low Si/Al ratios are susceptible to hydrolysis [24–27]. However, this limitation can be overcome, also at industrial scale, by including a pre-treatment step to remove water before the gas mixture is brought in contact with the zeolite adsorbent [28]. Zeolites typically have a relatively stronger interaction with CO₂ than carbon-based materials and MOFs and, therefore, the energy required for their regeneration can be relatively high. Although each adsorbent has specific assets and shortcomings, zeolites are of particular interest for the adsorption of CO₂ from biogas due to their high stability, low cost, and the possibility to tune their physicochemical properties (e.g. pore size and organization, composition) to optimize their adsorption behaviour.

Among the zeolite framework types, zeolite A and zeolite ZK-4 have shown promising performance for biogas upgrading. Both zeolites are characterized by the LTA framework type, with the difference being the Si/Al ratio (1 for zeolite A; > 1 for zeolite ZK-4). The LTA framework possesses a supercage which is accessible through 8 membered rings (8MRs) with apertures of 0.3 to 0.5 nm, depending on the size and charge of the extra-framework cations [29]. The synthesis of zeolite A and ZK-4 yields the material in the Na-form, with apertures of about 0.4 nm, and these can be adjusted by post-synthesis ion-exchange. This means that the adsorption behaviour can be optimized by tuning the type and degree of ion-exchange [30]. Particularly, high CO₂ selectivity can be achieved by choosing the extra-framework cations such that the size of the pore aperture is in between the kinetic diameter of CO₂ (3.3 Å) and CH₄ (3.8 Å). Bacsik et al. [22] partially exchanged zeolite NaA with K⁺, and through this pore size reduction, nearly no CH₄ was adsorbed whilst the CO₂ adsorption was only slightly reduced (in %). This led to a CO₂/CH₄ selectivity of >100 at 1 bar. Cheung et al. [21] not only incorporated K⁺, but also Cs⁺, which even further reduced the CH₄ adsorption resulting in a CO₂/CH₄ selectivity of >1500 at 0.5 bar CO₂ and 0.5 bar CH₄. The same principle was shown for CO₂/N₂ separation, with N₂ having a kinetic diameter of 3.64 Å. Cheung et al. partially exchanged zeolite Na-ZK-4 with 26 at%
K⁺, and reached a CO₂/N₂ selectivity > 800 at 0.15 bar CO₂ and 0.85 bar N₂ and 273K, indicating that essentially no N₂ was adsorbed whilst the CO₂ adsorption was still high (4.4 mmol g⁻¹) [31]. Zeolites are normally synthesized in the form of powders. This means that in order to use them in an adsorption processes, they first must be shaped into macroscopic pellets (typical size: 2-6 mm) to minimize the pressure drop over the adsorption column [32]. Typically, an inert binder material is added to the zeolite powder to form pellets with cylindrical shape or bead format. However, this decreases the adsorption capacity per gram, and there is a trade-off between high mechanical stability and facile diffusion of CO₂ through the pellets [33]. In this work, we overcome the limitations caused by the use of a binder by introducing and investigating an attractive alternative: binderless zeolite LTA beads with a macroscopic format and with hierarchical porosity. The synthesis of these zeolite beads was achieved using an anion-exchange resin as hard template with the double role of shaping the material into a bead format and, upon removal by calcination, to generate a network of meso- and macropores providing access to the micropores of the zeolite LTA framework. This method was inspired by the work of Tosheva et al., who reported the synthesis of Silicalite-1, ZSM-5 and zeolite Beta beads [34–36], and by more recent reports on titanosilicate beads for application as oxidation catalysts [37–40], and zeolite ZK-4 beads for n-hexane adsorption [41]. This is the first time that a hard template method employing resin beads is employed for preparing LTA beads with different Si/Al ratios and that such class of materials is investigated as CO₂ adsorbents in the context of biogas upgrading, achieving promising results in terms of CO₂/CH₄ selectivity. Our method differs significantly from emulsion-based sol-gel processing method that have been reported for preparing SiO₂ [42–44] or zeolitic [45] microspheres and from a method that uses metakaolin as a temporary binder, which after granulation to form beads is hydrothermally converted into a zeolite LTA phase [46,47]. Additionally, the resin beads employed as hard template in our work are commercially available and inexpensive (ca. 8 €/kg for bulk orders in 2020), which represents an asset in view of a potential upscaled production of these novel CO₂ adsorbents.
2.2. Experimental

2.2.1. Materials

Amberlite IRA-900 in chloride form (particle size 650-820 μm), Ludox HS-40 colloidal silica (40 wt% in H₂O), potassium chloride (KCl, ≥ 99%), silica gel (SiO₂, high purity grade, 230-400 mesh particle size), sodium aluminate (NaAlO₂), sodium metasilicate (Na₂SiO₃, 50-53% SiO₂), and tetramethylammonium hydroxide (TMAOH, 25 wt% in H₂O) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 98%) was purchased from Boom. Zeolite 4A beads were obtained from Luoyang Jalon Micro-Nano New Materials Co. Ltd. H₂O used in this work was always MilliQ grade.

2.2.2. Synthesis of the zeolite beads

In Table 1, an overview is given of the synthesis parameters used in the preparation of the four zeolite bead samples. The amount of chemicals used and the aging and crystallization times differ between the zeolites, but the general procedure is the same in all cases. The method is based on an original ZK-4 synthesis protocol from the IZA database of verified zeolite synthesis methods [48]. The synthesis of zeolite LTA-B1 (with bead format) is described in detail below.

14.65 g of deionized H₂O was added to a 100 ml beaker, after which 0.30 g NaOH and 2.15 g NaAlO₂ were added subsequently. The resulting solution was stirred using a magnetic bar at 500 rpm for 2h. 29.20 g TMAOH (25 wt%) and 1.71 g H₂O were added to the Teflon liner of a 100 ml stainless steel autoclave. 2.28 g SiO₂ (silica gel) was subsequently added to the Teflon liner and the suspension was

| Table 1: Overview of synthesis parameters for zeolite LTA-B1 to LTA-B4. |
|:------------------|---|---|---|---|---|---|---|---|---|---|
|                  | H₂O  | NaOH | NaAlO₂  | + TMAOH (25 wt%)  | H₂O  | SiO₂  | Amber- | Aging  | Crystallization time (h) | Si/Al ratio in the reaction mixture | Yield |
| LTA-B1            | 14.7 | 0.3  | 2.2    | 29.2          | 1.7  | 2.3   | 2.2    | 72    | 72                         | 1.45                          | 0.68  |
| LTA-B1b           | 61.5 | 1.3  | 9.0    | 122.6         | 7.2  | 9.5   | 9.2    | 96    | 96                         | 1.45                          | 2.08  |
| LTA-B2            | 29.3 | 0.6  | 2.2    | 25.0          | 3.4  | 5.1   | 2.2    | 72    | 72                         | 3.26                          | 0.47  |
| LTA-B3            | 29.3 | 0.6  | 2.2    | 20.0          | 3.4  | 5.1   | 2.0    | 72    | 72                         | 3.26                          | 0.41  |
| LTA-B4            | 12.5 | 3.2  | 2.4    | -             | 27.7 | 2.4   | 2.4    | 24    | 72                         | 1.39                          | 0.44  |
stirred at 500 rpm for 2 h. After both mixtures had been stirred for 2h, the aluminate solution was added to the silicate suspension, and the resulting silicoaluminate mixture was stirred at 500 rpm for 1 h. 2.20 g Amberlite IRA-900 was added to the silicoaluminate mixture. After mixing for 1 min, the autoclave was closed and the reaction mixture was aged statically at room temperature for 72 h. The autoclave was then placed into an oven for the static hydrothermal crystallization at 100°C for 72 h. After cooling down to room temperature, the product was filtered over a Büchner funnel and washed with 1 L of deionized H₂O. This procedure yielded the desired beads and a powder-fraction side-product. After drying overnight at room temperature, the beads were separated from the powder fraction by sieving. The beads and the powders were calcined using the following programme: heating 3 °C/min to 200 °C, 6 h at 200 °C, heating 2 °C/min to 600 °C, 6 h at 600 °C. The yield of the beads is given in Table 1. The synthesis of zeolite LTA-B1 was repeated on a larger scale (LTA-B1b), by employing a 500 ml stainless steel autoclave with a Teflon liner insert. For the washing step, 3 L of deionized H₂O was used. The yield of the beads is given in Table 1. The molar composition in the reaction mixtures was:

LTA-B1  \[ \text{1 Al}_2\text{O}_3 : 2.9 \text{ SiO}_2 : 1.3 \text{ Na}_2\text{O} : 6.1 \text{ TMAOH} : 162 \text{ H}_2\text{O} \]
LTA-B1b \[ \text{1 Al}_2\text{O}_3 : 2.9 \text{ SiO}_2 : 1.3 \text{ Na}_2\text{O} : 6.1 \text{ TMAOH} : 162 \text{ H}_2\text{O} \]
LTA-B2 \[ \text{1 Al}_2\text{O}_3 : 6.5 \text{ SiO}_2 : 1.6 \text{ Na}_2\text{O} : 5.2 \text{ TMAOH} : 218 \text{ H}_2\text{O} \]
LTA-B3 \[ \text{1 Al}_2\text{O}_3 : 6.5 \text{ SiO}_2 : 1.6 \text{ Na}_2\text{O} : 4.2 \text{ TMAOH} : 203 \text{ H}_2\text{O} \]
LTA-B4 \[ \text{1 Al}_2\text{O}_3 : 2.8 \text{ SiO}_2 : 3.8 \text{ Na}_2\text{O} : 158 \text{ H}_2\text{O} \]

A mass ratio in the range 20:1 to 30:1 between the reaction mixture and the Amberlite resin beads used as hard template was found to be optimal in the synthesis of the zeolite beads (data for mass ratios outside the optimum interval are not shown). In this optimum range, nearly all Amberlite beads are filled and covered by a shell of zeolitic matter (Figure 1 for microscopy images of LTA-B1; Figure S1 for those of the pristine Amberlite beads and Figure S2 for those of all other beads) and good crystallinity in the beads can be obtained. Increasing the amount of template beads in the reaction mixture can lead to partially or completely empty Amberlite beads or to a decrease in crystallinity.
Figure 1: Digital microscopy image of the LTA-B1 beads before calcination (left) and after calcination (right). For most uncalcined beads, a shell of zeolitic matter (white) is formed around the resin bead (yellow/orange). See Figure S1 for a digital microscopy image of the Amberlite resin used as a hard template.

2.2.3. Synthesis of zeolite powder

Zeolite A in powder format (LTA-P1) was synthesized following a method from the IZA database of verified zeolite synthesis procedures [49], by employing half of the amounts compared to the original synthesis method. The synthesis was performed in a 100 ml polypropylene bottle. Na₂SiO₃ and NaAlO₂ were used as Si and Al source, respectively. NaOH was used as a base. The molar composition in the reaction mixture was 1 Al₂O₃ : 1.4 SiO₂ : 2.6 Na₂O : 88 H₂O. The final yield was 2.9 g.

2.2.4. Ion-exchange of the zeolite beads

The zeolite LTA-B1b beads (in their original Na-form) were partially ion-exchanged, which gave a series of beads with potassium content (determined by XRF and reported as K⁺/(Na⁺ + K⁺)) ranging from 0 to 96% (Table 2). For each ion-exchange procedure, zeolite LTA-B1b was added to a solution of deionized H₂O and KCl and the mixture was stirred for 30 min, 400 rpm at room temperature (see Table 2 for the detailed reaction conditions). The stirring was performed by means of an overhead stirrer because agitation with a stirring bar may damage the zeolite beads. After stirring for 30 min, the sample was washed with deionized H₂O and dried overnight at room temperature. For the LTA-B1b-96 sample, a second cycle of ion-exchange with the same reaction conditions was performed.
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Table 2: Reaction conditions for the ion-exchange of zeolite LTA-B1b beads.

<table>
<thead>
<tr>
<th></th>
<th>LTA-B1b (g)</th>
<th>H$_2$O (g)</th>
<th>KCl (g)</th>
<th>[KCl] (M)</th>
<th>%K$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-B1b</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>LTA-B1b-13</td>
<td>0.25</td>
<td>12.5</td>
<td>0.0074</td>
<td>0.008</td>
<td>13</td>
</tr>
<tr>
<td>LTA-B1b-21</td>
<td>0.25</td>
<td>12.5</td>
<td>0.015</td>
<td>0.016</td>
<td>21</td>
</tr>
<tr>
<td>LTA-B1b-28</td>
<td>0.25</td>
<td>12.5</td>
<td>0.027</td>
<td>0.029</td>
<td>28</td>
</tr>
<tr>
<td>LTA-B1b-42</td>
<td>0.5</td>
<td>25</td>
<td>0.10</td>
<td>0.053</td>
<td>42</td>
</tr>
<tr>
<td>LTA-B1b-55</td>
<td>0.5</td>
<td>25</td>
<td>0.19</td>
<td>0.10</td>
<td>55</td>
</tr>
<tr>
<td>LTA-B1b-64</td>
<td>0.25</td>
<td>12.5</td>
<td>0.19</td>
<td>0.20</td>
<td>64</td>
</tr>
<tr>
<td>LTA-B1b-74</td>
<td>0.25</td>
<td>12.5</td>
<td>0.38</td>
<td>0.41</td>
<td>74</td>
</tr>
<tr>
<td>LTA-B1b-88</td>
<td>0.25$^a$</td>
<td>12.5</td>
<td>0.75</td>
<td>0.81</td>
<td>88</td>
</tr>
<tr>
<td>LTA-B1b-96</td>
<td>0.25$^b$</td>
<td>12.5</td>
<td>0.75</td>
<td>0.81</td>
<td>96</td>
</tr>
</tbody>
</table>

$^a$ The starting material was LTA-B1b-55 instead of LTA-B1b

$^b$ The starting material was LTA-B1b-42 instead of LTA-B1b; for this sample, two ion-exchange cycles at the provided conditions were carried out.

2.2.5. Characterization

Powder X-ray diffraction (PXRD) measurements were carried out on a Bruker D8 Advance diffractometer with Cu Kα1 radiation ($\lambda = 1.5418$ Å) under 40 kV and 40 mA in the range 5-60° with a step size of 0.02°. Prior to the PXRD measurements, the beads were ground to a powder using a mortar and pestle. The slit-width was 2 mm. Elemental analysis was performed using X-ray fluorescence (XRF) measurements on an Epsilon 3$^{xLE}$ spectrometer from PANalytical. The samples (powders or beads) were placed in a plastic cup with 6 μm mylar film. Quantification was done using the fundamental parameters method. The elements were determined assuming that they were in their oxide form and the sum of the obtained concentrations was normalized to 100%. Nitrogen physisorption measurements were performed on a Micromeritics ASAP 2420 machine at -196°C. The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) method. The pore size distribution and the meso- and macropore volume were calculated using the Barrett-Joyner-Halenda (BJH) model (from the desorption branch). The micropore volume was calculated using the t-Plot method. It should be noted that the Na$^+$ cations in the unit cell of zeolite LTA have been reported to limit the accessibility of the zeolite micropores to N$_2$, which means that for zeolite A (i.e. LTA with Si/Al = 1) the specific surface area and micropore volume assessed by N$_2$ physisorption are expected to be very low,
whereas for zeolite ZK-4 (Si/Al > 1, and thus lower Na-content), larger values have been observed [50]. A VHX-7000 Keyence digital microscope was used to determine the average bead size, by measuring a random set of 40 beads. The obtained bead size was reported as average diameter (mm) ± standard deviation (mm). The surface morphology of the beads was determined using scanning electron microscopy (SEM) on a FEI NovaNano SEM 650 apparatus. Mechanical strength measurements of selected beads were carried out on an Instron 4301 compression tester with a maximum load of 1 kN (for the LTA-B1b and the commercial 4A beads) and an Instron 4301 compression tester with a maximum load of 5 kN (for the commercial 4A beads). For each test, a stainless steel holder (in which the piston exerting the force fits exactly) was filled with a small bed of adsorbent. The piston crushes the bed (speed 2 mm min\(^{-1}\)) until it reaches the maximum load (1 kN or 5 kN). The mechanical strength of the bed is determined by dividing the load at breakage by the surface area of the bed (see Appendix for further details). CO\(_2\) and CH\(_4\) adsorption tests were carried out at room temperature (24°C) on a Micromeritics ASAP 2020 apparatus. Prior to the tests, the samples were degassed under vacuum at 350 °C for 10 h to eliminate H\(_2\)O and other possible adsorbates.

2.3. Results and discussion

With the purpose of developing novel, binderless zeolitic adsorbents with hierarchical porosity, a set of zeolite beads (LTA-B1 – LTA-B4) was synthesized using a new hard templating method developed by adapting previously reported protocols for the synthesis of LTA zeolites in powder format [48]. The obtained zeolite beads were characterized by a combination of techniques (XRD, SEM, XRF, N\(_2\) physisorption) and compared with a zeolite LTA powder (LTA-P1). Their applicability for CO\(_2\) adsorption in the context of biogas upgrading was investigated and the most promising beads were ion-exchanged in order to improve their performance in terms of CO\(_2\)/CH\(_4\) selectivity.

2.3.1. Synthesis and characterization of the zeolite beads

The zeolite beads were synthesized utilizing Amberlite IRA-900, a meso- and macroporous anion-exchange resin with a bead format [51], as hard template with two roles: (i) shaping the zeolitic material into macroscopic bead format and (ii) generating a network of meso- and macropores connecting the zeolite crystallites that constitute the beads (Figure 2). It is proposed that negatively
charged zeolite oligomers are formed in the basic reaction solution [39]. After adding the resin beads to the reaction mixture, the anions in the resin beads are exchanged with these oligomers. Hydrothermal crystallization of these oligomers yields polymer beads filled with interconnected zeolite particles. Not all the oligomers present in the reaction mixture enter the beads: the hydrothermal crystallization of the oligomers that remain in solution yields zeolite particles in powder form as side product. The bead fraction was then calcined to remove the polymer template, yielding binderless zeolite beads, which are expected to present an interconnected hierarchical porous structure in which the meso- and macropores generated by burning off the polymer provide access to the micropores of the zeolite crystals (Figure 2).

A set of four different binderless zeolite beads was prepared according to this methodology, by varying the parameters that were expected to exert a significant influence on the formation of the zeolites, i.e. the amount of chemicals that were used in the synthesis, as well as the aging and crystallization times (Table 1). All syntheses yielded zeolite LTA beads, but the physicochemical properties of the beads differed, which in turn is anticipated to influence their performance as adsorbents. Although a bead format with a size in the range 0.49-0.97 mm was obtained in all syntheses (Table 3), SEM analysis indicates a different degree of structural integrity, with the LTA-B1 materials displaying a well-defined, intact

Figure 2: Proposed synthesis route of binderless zeolite beads using an anion resin template.
bead format (Figure 3A), whereas the LTA-B2 and LTA-B3 beads were more fragile and some of them would get damaged (Figure 3D, Figure 3F) by pressing them with a spatula against the carbon tape used as support for SEM measurements. The LTA-B4 beads were the most fragile of the set, and a significant fraction of them were found to present a less well defined, deformed spherical shape and to display imperfections or damages (Figure 3I and Figure S2). Despite these differences at the macroscopic level, XRD analysis demonstrated that all the beads displayed crystallinity, showing the characteristic peaks corresponding to the LTA framework (Figure 4). Additionally, all the diffractograms presented a broad peak with relatively low intensity centred at ~23°, which indicates the presence of amorphous silica or aluminosilicate in the beads (see also Figures S3–S6). Deconvolution of the XRD patterns allowed us to estimate the degree of crystallinity of the zeolite beads (Table 3, Figure S7 and S8, explanation of the applied method in SI). The ratio of the peaks originating from the LTA framework to the broad peak corresponding to amorphous silica/aluminosilicates is highest in the LTA-B4 beads, which thus possess superior degree of crystallinity (79%) compared to the other beads. In agreement with the XRD results, SEM images with higher magnification clearly showed the presence of the zeolite crystals that constitute the beads, with LTA-B4 displaying the most defined cubic crystals with size up to 10 μm (Figure 3K). In line with expectations, all the beads contain a large amount of mesopores and macropores in the form of structural voids between the zeolite crystals, as it can clearly be seen in Figure 3C, Figure 3E, Figure 3H, Figure 3K. An additional feature that was observed by SEM is the presence of a shell that can completely or only partly cover the surface of the beads (Figure 3A, Figure 3B). This shell is most likely amorphous and is present in

Table 3: Yields of the zeolite beads and the crystalline phase of the beads and the corresponding side product.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield beads (g)</th>
<th>Yield powder (g)</th>
<th>Bead size (mm)</th>
<th>Reaction mixture: hard template mass ratio</th>
<th>Crystalline phase of the beads</th>
<th>Degree of crystallinity (%)</th>
<th>Crystalline phase of the powder side product</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-B1</td>
<td>0.68</td>
<td>2.3</td>
<td>0.77 ± 0.13</td>
<td>23:1</td>
<td>LTA</td>
<td>75</td>
<td>LTA + trace FAU</td>
</tr>
<tr>
<td>LTA-B2</td>
<td>0.47</td>
<td>2.5</td>
<td>0.73 ± 0.11</td>
<td>30:1</td>
<td>LTA</td>
<td>64</td>
<td>SOD + trace LTA</td>
</tr>
<tr>
<td>LTA-B3</td>
<td>0.41</td>
<td>3.8</td>
<td>0.60 ± 0.11</td>
<td>30:1</td>
<td>LTA</td>
<td>52</td>
<td>CHA + LTA + SOD</td>
</tr>
<tr>
<td>LTA-B4</td>
<td>0.44</td>
<td>3.3</td>
<td>0.81 ± 0.16</td>
<td>20:1</td>
<td>LTA</td>
<td>79</td>
<td>LTA + FAU</td>
</tr>
<tr>
<td>LTA-B1b</td>
<td>2.08</td>
<td>11.5</td>
<td>0.82 ± 0.12</td>
<td>23:1</td>
<td>LTA</td>
<td>75</td>
<td>LTA</td>
</tr>
</tbody>
</table>
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beads LTA-B1–LTA-B3, whereas it is only observed in a few LTA-B4 beads (Figure 3I). We hypothesize that the lack of such an amorphous shell could be the reason of the observed lower structural stability of the LTA-B4 beads.

The Si/Al ratio is an important feature in determining the CO$_2$ adsorption behaviour of a zeolite. The presence of Al (oxidation state +3) instead of Si (+4) in an aluminosilicate zeolite leads to a negatively charged framework, which needs to be balanced by extra-framework cations (typically Na$^+$. In zeolites with a lower

Figure 3: SEM images of the zeolitic beads LTA-B1, LTA-B2, LTA-B3, and LTA-B4.
Si/Al ratio (i.e. with a higher content of Al in the framework), a higher number of Na\(^+\) cations is present per gram of material (and thus a lower Si/Na, see Table 4). These Na\(^+\) cations are the active sites for the adsorption of CO\(_2\) in LTA zeolites [52,53]. Therefore, a lower Si/Al ratio is expected to give a higher CO\(_2\) adsorption capacity. The different syntheses yielded beads with a range of Si/Al ratios, as determined by XRF (full chemical composition in Table S1). Zeolite A has Si/Al = 1, whereas for higher Si/Al ratios the material should be referred to as zeolite ZK-4.

### Table 4: Physicochemical properties of the zeolitic beads LTA-B1 to LTA-B4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m(^2)g(^{-1}))</th>
<th>Micropore volume (cm(^3)g(^{-1}))</th>
<th>Meso- and macropore volume (cm(^3)g(^{-1})) (^a)</th>
<th>Si/Al (^b)</th>
<th>Si/Na (^b)</th>
<th>Na/Al (^b)</th>
<th>Na(^+) (mol g(_{\text{bead}})(^{-1})) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-B1</td>
<td>186</td>
<td>0.08</td>
<td>0.11</td>
<td>1.45</td>
<td>1.69</td>
<td>0.86</td>
<td>0.25</td>
</tr>
<tr>
<td>LTA-B2</td>
<td>253</td>
<td>0.09</td>
<td>0.29</td>
<td>2.31</td>
<td>3.05</td>
<td>0.76</td>
<td>0.17</td>
</tr>
<tr>
<td>LTA-B3</td>
<td>563</td>
<td>0.19</td>
<td>0.40</td>
<td>3.91</td>
<td>4.58</td>
<td>0.85</td>
<td>0.13</td>
</tr>
<tr>
<td>LTA-B4</td>
<td>24</td>
<td>&lt;0.01</td>
<td>0.09</td>
<td>1.21</td>
<td>1.35</td>
<td>0.90</td>
<td>0.28</td>
</tr>
<tr>
<td>LTA-P1</td>
<td>3</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>1.05</td>
<td>1.18</td>
<td>0.85</td>
<td>0.31</td>
</tr>
</tbody>
</table>

\(^a\) Determined with the BJH method.

\(^b\) Determined by XRF analysis.
Based on the XRF analysis (Table 4), it was found that the zeolitic beads have a Si/Al ratio between 1.2 (LTA-B4) and 3.9 (LTA-B3) and, therefore, it can be inferred that all the beads (LTA-B1 – LTA-B4) consist of zeolite ZK-4. However, it must be noted that the measured Si/Al ratio is the value of the whole beads and because these also contain an amorphous phase, the zeolitic domains do not necessarily have the same Si/Al ratio as the whole material. The fact that the synthesis of the LTA-B2 and LTA-B3 beads only differ in the amount of TMAOH used (higher for LTA-B2) and that the obtained materials have similar morphology but significantly different Si/Al (2.31 for LTA-B2 vs. 3.91 for LTA-B3) suggests that the higher concentration of OH\(^-\) in solution facilitated the incorporation of Al in the material. It is worth noting that a correlation was observed between the degree of crystallinity and the Si/Al ratio of the beads (Figure S9), with higher crystallinity being associated with a lower Si/Al, which might indicate that the amorphous phase is richer in Si compared to the zeolitic domains.

The pore volume and specific surface area of the prepared materials were investigated by \(\text{N}_2\) physisorption (Table 4). The \(\text{N}_2\) adsorption isotherms of the beads (LTA-B1 - LTA-B4, see Figure 5) all show a hysteresis at higher relative pressure (\(p/p^0 = 0.6-1\)), which indicates the presence of meso- and/or macropores. The pore size distribution is broad (10-100 nm, see Figure S10) and

\[\text{Figure 5: } \text{N}_2\text{ physisorption isotherms of LTA-B1, LTA-B2, LTA-B3, and LTA-B4.}\]
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covers both the mesopore and macropore range. Combining the pore size
distribution obtained from the N\textsubscript{2} physisorption results with the SEM images, we
can conclude that the desired hierarchically porous structure was obtained for
the LTA-B1 – LTA-B4 beads, in which the micropores in the zeolite crystals are
accessible through the network of meso- and macropores present within the
beads. This hierarchical configuration of the pores is expected to facilitate the
diffusion of CO\textsubscript{2} into the beads.

The meso- and macropore volume differs significantly among the beads (Table 4),
showing an increasing trend in meso- and macropore volume with decreasing
crystallinity of the beads. This suggests that the amorphous phase contributes in
generating and/or preserving the meso- and macropores.

While the N\textsubscript{2} physisorption data are useful to estimate the mesopores present in
our beads, care should be taken in the analysis of the zeolitic micropores and of
the specific surface area. The reason for this is that N\textsubscript{2} has been reported to
experience diffusion limitations through the narrow pore mouth of zeolite A (i.e.
LTA with Si/Al = 1) in Na-form, leading to extremely low BET surface area and
micropore volume [50]. This effect is correlated to the amount of Na\textsuperscript{+} cations
present in the framework, which cause a decrease in the available micropore
volume. Zeolite ZK-4 (i.e. LTA with Si/Al > 1) contains less Na\textsuperscript{+} cations in the pores
per unit cell compared to zeolite A, making the effective pore size comparatively
larger. Therefore, it has been shown that for LTA zeolites with lower Na-content
(Si/Al $\geq$ 1.9) the surface area and micropore volume assessed by N\textsubscript{2}
physisorption are much higher than for zeolite A [50] and are in the typical range
observed for zeolite frameworks.

In line with these previous findings, we observed a decreasing trend in specific
surface area and micropore volume with increasing Na-content in our beads
(Figure 6). An analogous trend is observed with increasing Al-content, and thus
with decreasing Si/Al. The adsorption isotherms for LTA-B1, LTA-B2 and LTA-B3
show a sharp increase below $p/p^0 = 0.05$ (Figure 5), indicative of the presence of
micropores, whereas the adsorption isotherms for LTA-B4, which are the beads
with the highest Na-content and lowest Si/Al ratio, does not show such
behaviour, leading to a very low micropore volume (Table 4). The remarkably low
surface area and pore volume of LTA-B4 are probably not only caused by the
higher number of Na\textsuperscript{+} cations per unit cell, but also by the larger size of the zeolite
crystals that constitute this material (as shown by SEM, *vide supra*), which implies
that a larger fraction of the microporous structure will experience the diffusion
Binderless zeolite LTA beads with hierarchical porosity for selective CO₂ adsorption in biogas upgrading

Figure 6: BET surface area and micropore volume as a function of the amount of Na⁺-sites for the zeolite LTA beads (LTA-B1, LTA-B1b, LTA-B2, LTA-B3, and LTA-B4) and for the LTA zeolite in powder form (LTA-P1).

Limitations caused by the large amount of Na⁺ cations in the material. The beads with the lowest Na-content and highest Si/Al ratio (LTA-B3), displayed the largest surface area (563 m² g⁻¹) and micropore volume (0.19 cm³ g⁻¹), with the former being very similar and the latter being lower compared to those reported in the literature for ZK-4 zeolites with Si/Al ≥ 1.9 [50].

It is worth noting that the surface area and micropore volume of LTA-B2 (Si/Al = 2.31) are markedly lower than those of a zeolite ZK-4 (in powder form) with Si/Al = 1.9 reported in the literature [50]. This is in line with our above-mentioned hypothesis that the zeolitic domains of our beads have a higher Al content and thus a lower Si/Al compared to that of the whole material, and that the amorphous phase is richer in Si compared to the zeolitic phase.

The yield of the beads and of the zeolites in powder form that were obtained as side product are shown in Table 3 (see Table S2 for the chemical composition of these powders and Table S3 for their Si/Al ratio). The yield of the beads varies between 10-23% of the total yield. The powder product formed during the synthesis of the LTA-B1 beads consist of LTA zeolite with small amounts of FAU zeolite (Figure S11). On the other hand, the powder product that was formed during the synthesis of LTA-B4 consisted mainly of FAU zeolite with small amounts of LTA zeolite (Figure S12). The powder product obtained during the preparation
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of the LTA-B2 beads consists mainly of SOD zeolite mixed with trace amounts of LTA zeolite (Figure S13). Finally, the powder obtained together with the LTA-B3 beads is less valuable because it consists of a mixture of zeolites (CHA + LTA + SOD + other unknown peaks) (Figure S14).

The synthesis of zeolite beads LTA-B1 was repeated at a larger scale (LTA-B1b), leading to a comparable material in terms of features of the bead (see SEM images, XRD pattern and N₂ physiosorption data, Figures S15-S17, Table S4), and thus proving the upscalability (by a factor 4) of our synthesis method. The powder product obtained together with the LTA-B1b beads is pure LTA zeolite powder and is therefore also a valuable product (Figure S18). Yet, future work should aim at optimizing the yield of the beads fraction compared to the powder one, particularly in the perspective of a potential large-scale application. Additionally, we prepared LTA in powder form (LTA-P1) as reference material, following a verified literature procedure [49]. The highly crystalline powder (see XRD pattern in Figure S19 and SEM image in Figure S20) possessed a Si/Al ratio of 1.05 and, therefore, can be considered to be zeolite A (whilst the beads all possess Si/Al > 1). Due to its low Si/Al ratio and, therefore, high amount of Na⁺ cations, N₂ is not able to access most of the micropores resulting in a very low BET surface area and almost no available micropore volume for LTA-P1 (Figure S21, Table 4).

Since the LTA-B1 and LTA-B1b beads displayed the most intact bead format, the mechanical strength of a bed of LTA-B1b beads was determined by means of a compression test and compared to that of the commercial zeolite 4A beads. As anticipated, the measurements show that the mechanical strength of the beads (0.14-0.82 MPa, see Table S5 and Figures S22-S24 for further information) is lower than that of commercial binder-containing beads (1.6-18.4 MPa). Yet, based on a calculation of the pressure exerted by a bed of beads in an industrial-scale adsorption column (height: 3 m, diameter, 1m, see Appendix for details), we estimated that the mechanical strength of beads should be sufficient for being used for this application without significant structural deterioration.

2.3.2. Application of the zeolite beads as adsorbents for CO₂

In order to estimate the potential of the prepared zeolite LTA beads in biogas upgrading, we measured the CO₂ and CH₄ adsorption capacities for all the binderless zeolite bead samples and for commercial zeolite 4A beads (containing a binder) at room temperature in the 0-1 bar range (Figure 7 and Table 5). The
CO₂ adsorption capacities of all the synthesized zeolite beads are comparable to that of the commercial beads, and in the case of the LTA-B2 beads a slightly higher CO₂ adsorption was achieved (3.8 mmol\textsubscript{CO₂} g\textsubscript{bead}\textsuperscript{-1} at 1.0 bar CO₂, 3.4 mmol\textsubscript{CO₂} g\textsubscript{bead}\textsuperscript{-1} at 0.4 bar CO₂, i.e. the partial pressure of carbon dioxide in biogas, see Table 5). The observed trend for the CO₂ adsorption capacity (LTA-P1 > LTA-B2 > 4A...
Table 5: CO$_2$ and CH$_4$ adsorption capacity at 1.0 bar and CO$_2$/CH$_4$ selectivity for LTA-B1 to LTA-B4 beads, LTA-P1, and the commercial 4A beads.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO$_2$ adsorption capacity (mmol g$^{-1}$) at 1.0 bar</th>
<th>CO$_2$ adsorption capacity (mmol g$^{-1}$) at 0.4 bar</th>
<th>CH$_4$ adsorption capacity (mmol g$^{-1}$) at 1.0 bar</th>
<th>CH$_4$ adsorption capacity (mmol g$^{-1}$) at 0.6 bar</th>
<th>CO$_2$/CH$_4$ selectivity$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-B1</td>
<td>3.36</td>
<td>2.95</td>
<td>0.45</td>
<td>0.29</td>
<td>15.5</td>
</tr>
<tr>
<td>LTA-B1b</td>
<td>3.39</td>
<td>3.01</td>
<td>0.38</td>
<td>0.25</td>
<td>18.4</td>
</tr>
<tr>
<td>LTA-B2</td>
<td>3.85</td>
<td>3.43</td>
<td>0.48</td>
<td>0.30</td>
<td>17.0</td>
</tr>
<tr>
<td>LTA-B3</td>
<td>3.34</td>
<td>2.94</td>
<td>0.36</td>
<td>0.23</td>
<td>18.8</td>
</tr>
<tr>
<td>LTA-B4</td>
<td>3.16</td>
<td>2.82</td>
<td>0.37</td>
<td>0.22</td>
<td>19.4</td>
</tr>
<tr>
<td>LTA-P1</td>
<td>4.48</td>
<td>4.02</td>
<td>0.75</td>
<td>0.49</td>
<td>12.4</td>
</tr>
<tr>
<td>4A beads</td>
<td>3.63</td>
<td>3.25</td>
<td>0.55</td>
<td>0.35</td>
<td>14.0</td>
</tr>
<tr>
<td>(commercial)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ CO$_2$/CH$_4$ selectivity calculated as Sel. = ($q_{CO_2}$/$q_{CH_4}$)/($p_{CO_2}$/$p_{CH_4}$), in which $q_x$ is the adsorbed amount measured at the partial pressure $p_x$ in the hypothetical gas mixture. To mimic biogas, the following partial pressures were used: 0.6 bar for CH$_4$ and 0.4 bar for CO$_2$.

commercial > LTA-B1b ~ LTAB1 ~ LTA-B3 > LTA-B4) is the same at 1.0 bar and at 0.4 bar.

Although the adsorption capacities of all the binderless zeolite beads are in a similar range, they do display clear differences as it is expected considering their differences in terms of degree of crystallinity, Na-content, and of accessible micropore volume and specific surface area (Table 4). Since LTA-B2 and LTA-B3 exhibit a higher Si/Al and Si/Na ratio and a lower degree of crystallinity than LTA-B1, their amount of Na$^+$/g$_{bead}$ in the zeolitic microporous structure acting as adsorption sites for CO$_2$ is lower. However, our results indicate that the number of adsorption sites is not the only important factor in determining the CO$_2$ adsorption capacity. Indeed, LTA-B3, with the lowest Na-content (0.13 mol g$_{bead}^{-1}$) and the lowest degree of crystallinity (52%), had a similar adsorption capacity to LTA-B1, which has the second highest Na-content (0.25 mol g$_{bead}^{-1}$) and the second highest degree of crystallinity (75%). The highest adsorption capacity was achieved with LTA-B2, which has an intermediate Na-content (0.17 mol g$_{bead}^{-1}$) and degree of crystallinity (64 %) among our beads. The LTA-B4 beads displayed the highest degree of crystallinity (79%) and the largest Na-content (0.28 mol g$_{bead}^{-1}$), and yet had the lowest CO$_2$ adsorption capacity. This is ascribed to the
much lower accessible micropore volume and surface area displayed by this material (Table 4).

It should be noted that these textural properties were measured by N\textsubscript{2} adsorption, and that the kinetic diameter of CO\textsubscript{2} (3.3 Å) is only slightly smaller than that of N\textsubscript{2} (3.6 Å). This implies that CO\textsubscript{2} is also expected to experience diffusion limitations in the micropores of this material, though to a lower extent than N\textsubscript{2}. Therefore, the trends in accessible micropore volume and surface area measured by N\textsubscript{2} physisorption are expected to be useful for interpreting the CO\textsubscript{2} adsorption behavior.

This set of results shows that there is a trade-off between the Na-content and the degree of crystallinity, and thus the number of adsorption sites of the zeolitic beads, which increase with decreasing Si/Al ratio in the material, and the available micropore volume and surface area, which follow the opposite trend as a function of the Si/Al ratio (vide supra). It is thus not surprising that the best CO\textsubscript{2} adsorption capacity was obtained for a material with intermediate Na-content, intermediate degree of crystallinity and intermediate micropore volume and surface area (i.e. LTA-B2).

The complex interplay between these different factors is further demonstrated by the results obtained with the powder sample LTA-P1, which had the highest Na-content (0.31 mol g\textsubscript{bead}\textsuperscript{-1}) but also the lowest accessible micropore volume, and yet the highest adsorption capacity (Table 4, Table 5). This can be ascribed to its higher degree of crystallinity compared to the beads, which implies well-defined adsorption sites. Although XRD analysis showed that the beads are largely crystalline, a fraction of amorphous material was present in all our samples (vide supra). On the other hand, the powder LTA-P1 was highly crystalline and did not show the presence of a detectable amount of amorphous silica/aluminosilicates (Figure S19).

In order to evaluate further the effect of the degree of crystallinity of the beads on their CO\textsubscript{2} adsorption capacity, we chose a systematic approach and synthesized a new set of zeolite LTA beads (LTA-B5, LTA-B6 and LTA-B7, chemical composition in Table S6) using exactly the same synthesis method and amounts of chemicals, with the only difference being the aging and crystallization times (synthesis methods in SI). These three beads were compared in terms of crystallinity (XRD, Figures S25-27 and Table S7), Na-content, surface area and micropore volume (Table S7) and CO\textsubscript{2} adsorption capacity (Figure 8) with a
powder (LTA-P2, XRD in Figure S28) that was synthesized with the same method, but without adding the Amberlite beads (synthesis method in SI).

The LTA-B5 beads are partly crystalline (LTA) and partly amorphous, as indicated by the presence of the large, broad peak stemming from amorphous silica/aluminosilicates from about 10 to 40°, with an estimated degree of crystallinity of 31%. The LTA-B6 beads are mostly crystalline and only show a small, broad peak corresponding to the presence of amorphous material (more clearly seen in Figure S26), leading to an estimated degree of crystallinity of 62%. The LTA-B7 beads show a further but much less marked increase in crystallinity (65%, see also Figure S27). The observed increase in crystallinity upon increasing the aging and crystallization times (Figures S25-S28) was correlated with a decrease in the Si/Al ratio of the beads (Table S7), similarly to what observed with LTA-B1-LTA-B4 beads (*vide supra*).

The fact that this trend was clearly observed with beads prepared with the same method provides insights in the synthesis mechanism. In the relatively crystalline LTA-B6 and LTA-B7 beads, a Si/Al = 1.3 was observed, while the partly crystalline and partly amorphous LTA-B5 beads had a Si/Al = 4.3. This suggests that a Si-rich amorphous phase is initially formed within the Amberlite beads while the Al species tend to remain in solution, and that the latter are incorporated in the material only at longer synthesis times.

Within this new set of zeolitic beads, LTA-B5 displayed by far the lowest CO₂ adsorption capacity (Figure 8). This is attributed to its low degree of crystallinity, combined with the low Na-content (Table 7). LTA-B6 and LTA-B7 presented

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*Figure 8: XRD patterns (left) and CO₂ adsorption isotherms (right) of LTA-B5, LTA-B6, LTA-B7, and LTA-P2.*
similar features to each other in terms of degree of crystallinity, Na-content, accessible micropore volume and surface area (Table 7) and, accordingly, displayed very similar CO$_2$ adsorption capacity (Figure 8). The most notable result of this systematic study is the comparison between LTA-B6 and the highly crystalline LTA-P2 powder (84%, see also Figure S28). These two materials were prepared with the same synthesis method and are very similar in terms of Na-content, accessible micropore volume and surface area but differ significantly in the degree of crystallinity (Table 7). The higher CO$_2$ adsorption capacity shown by LTA-P2 compared to LTA-B6 (Figure 8) clearly indicates that a high degree of zeolite crystallinity is favourable for the CO$_2$ adsorption capacity of the material. The hierarchical structure of the beads is expected to facilitate the diffusion of CO$_2$ into the adsorbing material. Therefore, in the comparison between materials in bead and powder format discussed above, we assumed that the meso- and macropores of the beads are able to provide access to the microporous zeolitic structures without causing any significant mass transfer limitation. In order to check whether this was actually the case, we ground LTA-B1 and LTA-B1b into powders and measured again the CO$_2$ adsorption capacity (Figure S29). The fact that the two measurements took approximately the same time and that the CO$_2$ adsorption curves of the beads overlapped with those of the corresponding ground samples (in which the hierarchical structure is not anymore present) demonstrates that the meso- and macropores of the beads indeed allow the unhindered diffusion of CO$_2$.

Our zeolite beads (LTA-B1 to B4), the commercial bead (4A) and the LTA-P1 powder sample were tested also for their CH$_4$ adsorption capacity (Figure 7). There was only a small difference in CH$_4$ adsorption capacity between our binderless zeolite beads. The lowest CH$_4$ adsorption capacity (0.22 mmol g$^{-1}$ at $p = 0.6$ bar, i.e. the partial pressure of methane in biogas) was found with LTA-B4 and led to the highest CO$_2$/CH$_4$ selectivity (Table 5). On the other hand, the commercial beads and particularly the powder LTA zeolite displayed higher CH$_4$ adsorption capacity than the beads (0.35 and 0.49 mmol g$^{-1}$ at $p = 0.6$ bar, respectively). As a consequence of their lower CH$_4$ adsorption capacity, our binderless beads display enhanced CO$_2$/CH$_4$ selectivity compared to the commercial zeolite LTA pellets prepared using a binder and to the LTA zeolite in powder form (Table 5).
2.3.3. Ion-exchange of the zeolite beads

Partial ion-exchange of LTA zeolites in Na-form with K\(^+\) cations causes a decrease in the pore size that has been reported to significantly limit the adsorption of CH\(_4\) while still allowing the adsorption of a significant amount of CO\(_2\) [22]. Therefore, we selected one of our binderless zeolite beads and subjected it to various degrees of ion-exchange with K\(^+\), with the purpose of enhancing the CO\(_2\)/CH\(_4\) selectivity. Among the prepared materials, the LTA-B1 beads consisted of the most intact spherical beads and have the highest mechanical stability (upon pressing them manually with a spatula) compared to LTA-B2, LTA-B3 or LTA-B4. Therefore, the synthesis of LTA-B1 was repeated at a larger scale with the aim of performing ion-exchange on one single batch of zeolite beads. The obtained LTA-B1b sample has analogous physicochemical properties to LTA-B1 (see SEM images, XRD pattern and N\(_2\) physisorption data, Figures S15-S17, Table S4), demonstrating the robustness of our synthesis protocol. Also the CO\(_2\) and CH\(_4\) adsorption capacity of the Na-form of LTA-B1b is similar to that of LTA-B1 (compare Figure 7 and Figure S30). Then, the LTA-B1b beads were divided into 10 batches and each was subjected to a different degree of ion-exchange in the range from 0 to 96\% K\(^+\) (and thus from 100 to 4\% Na\(^+\)). The ion-exchange procedure we adopted was efficient in achieving a library of zeolite LTA beads with gradually increasing K-content, as demonstrated by XRF analysis (Table 2, full chemical composition in Table S8). This library of zeolite beads was tested for their CO\(_2\) and CH\(_4\) adsorption capacity.

At low K-content (up to 13\%), the CH\(_4\) adsorption capacity of the beads is unaffected compared to their counterpart in Na-form (Figure 9). Above 13\% K\(^+\), the CH\(_4\) adsorption capacity starts to decrease (Figure 9), which is attributed to an increased diffusion limitation of CH\(_4\) as a consequence of the decrease in the micropore size caused by the larger size of K\(^+\) compared to Na\(^+\). More specifically, it has been shown that K\(^+\) is preferentially located in the 8MR windows and its presence hinders the diffusion of CH\(_4\) and CO\(_2\) through these windows [21]. From an ion-exchange degree of 42\% K\(^+\), the diffusion of CH\(_4\) through the 8MRs is hindered to such a degree that essentially no CH\(_4\) is adsorbed (Figure 9). These results confirm the anticipated decrease in CH\(_4\) adsorption as a function of the K-content. The ion-exchange with K\(^+\) also caused a noticeable decrease in CO\(_2\) adsorption capacity, already at a K-content as low as 13\% (Figure 9). This effect can also partly be attributed to a decrease in diffusion through the 8MR windows. Additionally, because K\(^+\) is significantly larger than Na\(^+\), the CO\(_2\) adsorption
Binderless zeolite LTA beads with hierarchical porosity for selective CO$_2$ adsorption in biogas upgrading

Figure 9: CO$_2$ and CH$_4$ adsorption capacity of ion-exchanged zeolite LTA-B1b samples at the partial pressures mimicking biogas (i.e. 0.4 bar CO$_2$ and 0.6 bar CH$_4$), as a function of K-content.

capacity decreased due to the decreasing available micropore volume. Yet, a significant CO$_2$ adsorption capacity was preserved even at very high degree of ion-exchange of Na$^+$ with K$^+$. In terms of CO$_2$/CH$_4$ selectivity, an optimum was found with the zeolite beads with a K-content of around 42%, which lead to a virtually full CO$_2$/CH$_4$ selectivity of 1540 (at the partial pressures that mimic biogas, i.e. 0.6 bar CH$_4$ and 0.4 bar CO$_2$; it should be noted that at such low degree of adsorption the quantification of CH$_4$ might become less accurate). At this K-content, essentially no CH$_4$ was adsorbed (< 0.01 mmol g$^{-1}$ at 1.0 bar CH$_4$) whilst the CO$_2$ adsorption capacity was still substantial (2.4 mmol g$^{-1}$ at 1.0 bar CO$_2$). The observed trends are in agreement with previous reports on other NaK-zeolite-LTA powders [22,31]. However, in the literature the optimal K-content for maximizing the CO$_2$/CH$_4$ selectivity was found to be 27% [22]. At this K-content, the CH$_4$ adsorption capacity of our zeolite beads was still 0.2 mmol g$^{-1}$. We propose that this difference is related to the lower Si/Al ratio of the zeolite in the literature (A type), which implies a larger population of cations (Na$^+$ or K$^+$) per unit cell and thus a general lower accessibility of the micropores of the zeolite at each K-exchange degree.
2.4. Conclusions

Novel hierarchically porous zeolitic beads with LTA framework and a range of Si/Al ratios (1.2-3.9) were synthesized by a hard templating method using an inexpensive, commercially available anion-exchange resin, thoroughly characterized with a combination of techniques and then tested as adsorbents for CO₂ and CH₄. These binderless zeolite beads in Na-form possess CO₂ adsorption capacities comparable to that of commercial zeolite 4A beads but with increased CO₂/CH₄ selectivity (up to 19.4 compared to 14.0 with the commercial 4A beads). The degree of crystallinity, the Na-content, the accessible micropore volume and specific surface area were shown to play a role in determining the CO₂ adsorption capacity of these zeolite beads. Intermediate values of these physicochemical features were found to lead to the highest CO₂ adsorption capacity (3.85 mmol g⁻¹ at 1.0 bar CO₂) as a consequence of a trade-off between the number of adsorption sites and their accessibility. Ion-exchange was used to tune the counter-cation composition of the zeolite beads and thus enhance their CO₂/CH₄ selectivity. The optimal K⁺/(Na⁺+K⁺) composition was 42%, which resulted in a significantly increased CO₂/CH₄ selectivity of 1540. At this composition, essentially no CH₄ was adsorbed whilst the CO₂ adsorption selectivity was still considerable (1.9 mmol g⁻¹ at 0.4 bar CO₂, i.e. the partial pressure of CO₂ in biogas, 2.4 mmol g⁻¹ at 1.0 bar CO₂). In conclusion, we introduced a new class of hierarchically porous zeolite beads that possess a favourable pore structure, which in combination with their high CO₂/CH₄ selectivity makes them attractive adsorbents for CO₂ separation from biogas. The macroscopic format of the beads and their binder-free nature are additional assets that will enable to employ them as such in an adsorption column for biogas upgrading. This work opens new perspectives for the development of selective adsorbents as the strategy of using binderless zeolite beads for this application can be extended to other zeolite frameworks and to the separation of other gas mixtures.

2.5. References

Binderless zeolite LTA beads with hierarchical porosity for selective CO$_2$ adsorption in biogas upgrading


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Appendix chapter 2

*Figure S1*: Digital microscopy image of the Amberlite IRA-900 beads.
Figure S2: Digital microscopy images of LTA-B1-LTA-B4 beads.
Binderless zeolite LTA beads with hierarchical porosity for selective CO$_2$ adsorption in biogas upgrading

**Figure S3:** XRD pattern of LTA-B1 beads.

**Figure S4:** XRD pattern of LTA-B2 beads.
**Figure S5:** XRD pattern of LTA-B3 beads.

**Figure S6:** XRD pattern of LTA-B4 beads.
Estimation of the degree of crystallinity of the LTA beads

The degree of crystallinity of the LTA beads was estimated by deconvolution of the XRD patterns. It should be noted that the values obtained through this approach provide a qualitative evaluation of the degree of crystallinity, which means that the order in degree of crystallinity among the different beads is reliable, while the individual values should be considered as an estimate. Deconvolution of XRD patterns was performed using the Fit Peaks function in OriginPro. For the peaks corresponding to the crystalline phase, Lorentzians were selected as the peak type to account for peak broadening. For the peaks corresponding to the amorphous phase, Gaussians were selected as the peak type. Parameters were optimized until a good fit was reached ($R^2 \geq 0.96$), see for example Figure S28 and Figure S29. The degree of crystallinity was estimated by dividing the area of all peaks corresponding to the crystalline phase by the total area of all peaks. The degree of crystallinity was normalized to the highly crystalline LTA-P1 (to which a 100% degree of crystallinity was assigned) to account for background noise from the sample holder.

**Figure S7**: Deconvolution of the XRD pattern of LTA-P1.
Figure S8: Deconvolution of the XRD pattern of LTA-B4.

Table S1: Chemical composition (mol%) of LTA-B1, LTA-B1b, LTA-B2, LTA-B3, LTA-B4 and LTA-P1 as determined by XRF.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LTA-B1</th>
<th>LTA-B1b</th>
<th>LTA-B2</th>
<th>LTA-B3</th>
<th>LTA-B4</th>
<th>LTA-P1</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>57.2</td>
<td>53.4</td>
<td>70.2</td>
<td>79.0</td>
<td>51.5</td>
<td>52.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.6</td>
<td>20.9</td>
<td>15.2</td>
<td>10.1</td>
<td>21.3</td>
<td>24.9</td>
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<tr>
<td>Na₂O</td>
<td>17.0</td>
<td>19.4</td>
<td>11.5</td>
<td>8.6</td>
<td>19.1</td>
<td>22.1</td>
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<tr>
<td>Cl</td>
<td>4.7</td>
<td>4.9</td>
<td>1.6</td>
<td>0.8</td>
<td>6.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure S9: Correlation between the degree of crystallinity and the Si/Al ratio of the synthesized materials.
Figure S10: BJH pore size distribution (from the desorption branch) of all synthesized beads and commercial zeolite 4A beads.
Binderless zeolite LTA beads with hierarchical porosity for selective CO$_2$ adsorption in biogas upgrading

Table S2: Chemical composition (mol%) of the powder side products of LTA-B1, LTA-B1b, LTA-B2, LTA B3 and LTA-B4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LTA-B1 powder</th>
<th>LTA-B1b powder</th>
<th>LTA-B2 powder</th>
<th>LTA-B3 powder</th>
<th>LTA-B4 powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>64.0</td>
<td>64.5</td>
<td>76.2</td>
<td>74.4</td>
<td>56.2</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>19.1</td>
<td>18.9</td>
<td>13.6</td>
<td>14.7</td>
<td>20.0</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>15.1</td>
<td>15.1</td>
<td>9.0</td>
<td>9.5</td>
<td>22.3</td>
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<tr>
<td>Cl</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table S3: Si/Al ratio of powder side products, as determined by XRF.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-B1 powder</td>
<td>1.7</td>
</tr>
<tr>
<td>LTA-B1b powder</td>
<td>1.7</td>
</tr>
<tr>
<td>LTA-B2 powder</td>
<td>2.8</td>
</tr>
<tr>
<td>LTA-B3 powder</td>
<td>2.5</td>
</tr>
<tr>
<td>LTA-B4 powder</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure S11: XRD pattern of the LTA-B1 powder side product. Peaks indicated with an F correspond to [FAU], all other peaks correspond to [LTA].
Figure S12: XRD pattern of the LTA-B4 powder side product. Peaks indicated with an L correspond to [LTA], all other peaks correspond to [FAU].

Figure S13: XRD pattern of the LTA-B2 powder side product. Peaks indicated with an S correspond to [SOD], peaks indicated with an L correspond to [LTA].
Binderless zeolite LTA beads with hierarchical porosity for selective CO$_2$ adsorption in biogas upgrading

**Figure S14**: XRD pattern of the LTA-B3 powder side product. Peaks indicated with an L correspond to [LTA], peaks indicated with a C correspond to [CHA], peaks indicated with an S correspond to [SOD], other peaks are unknown.

**Figure S15**: XRD pattern of LTA-B1b beads.
**Figure S16:** \( N_2 \) physisorption isotherms of LTA-B1b.

**Figure S17:** SEM images of LTA-B1b beads.
Binderless zeolite LTA beads with hierarchical porosity for selective CO$_2$ adsorption in biogas upgrading

Table S4: Physicochemical properties of LTA-B1b and LTA-P1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$ g$^{-1}$)$^a$</th>
<th>Meso- and macropore volume (cm$^3$ g$^{-1}$)$^a$</th>
<th>Micropore volume (cm$^3$ g$^{-1}$)$^a$</th>
<th>Si/Al ratio $^b$</th>
<th>Na/Al ratio $^b$</th>
<th>Na$^+$ (mol g$_{bead}^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-B1b</td>
<td>121</td>
<td>0.16</td>
<td>0.05</td>
<td>1.28</td>
<td>0.93</td>
<td>0.28</td>
</tr>
</tbody>
</table>

$^a$ Based on N$_2$ physisorption analysis. $^b$ Based on XRF analysis.

Figure S18: XRD pattern of the LTA-B1b powder side product.
Figure S19: XRD pattern of LTA-P1.

Figure S20: SEM image of LTA-P1.
Binderless zeolite LTA beads with hierarchical porosity for selective CO₂ adsorption in biogas upgrading

Figure S21: N₂ physisorption isotherms of LTA-P1. Note that due to the large amount of Na-cations, N₂ cannot access the micropores of the zeolite and the machine cannot accurately measure the isotherm.

Mechanical strength

In order to determine whether the binderless beads possess sufficient mechanical strength to be used in an industrial adsorption process, compression tests of a bed of LTA-B1b beads in a stainless steel sample holder were performed. For each test, a small stepwise increase in load (to 4 N and 9 N) is observed which does not relate to the mechanical strength since this occurs before the piston touches the sample (vertical line in Figure S24 and S25). When the piston compresses the sample, the load increases rapidly, and when the beads break, bumps in the line are observed. These bumps in the line are formed when one or multiple bead(s) break(s) as this is accompanied with the generation of free space in the bed. As a consequence, the beads can rearrange in a more favourable position in the bed and thus a lower load is measured by the machine. This effect is more pronounced for larger beads, as the free space generated by breaking such a bead is larger. In an adsorbtent bed, not all beads break at the same time, thus the bed strength for a material is given by a range (first break – last break, see Table S5).
Table S5: Mechanical strength of a bed of LTA-B1 and of a bed of 4A commercial beads.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mechanical strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-B1b</td>
<td>0.14 – 0.82</td>
</tr>
<tr>
<td>4A commercial beads</td>
<td>1.60 – 18.43</td>
</tr>
</tbody>
</table>

The mechanical strength of our beads is significantly lower than that of the commercial beads, thus to determine if the mechanical strength of our beads is high enough to use them in an industrial process, the pressure exerted on the beads in such an adsorption column was calculated. A fast switching Pressure-Swing Adsorption (PSA) system for 500 Nm³/h of biogas is generally around 3 m high and 1 m in diameter. A cylindrical column with such dimensions would contain about 916 kg of our beads. The force that is exerted by the adsorbent bed (9.0 kN) can be calculated using \( \vec{F} = m \cdot \vec{g} \), in which \( \vec{F} \) is the force, \( m \) is the mass of adsorbent (kg), and \( \vec{g} \) is the gravitational acceleration (\( g = 9.81 \text{ m s}^{-2} \)). The estimated pressure exerted by the adsorbent bed is 0.02 MPa, which was calculated using \( p = \frac{F}{A} \), in which \( p \) is the pressure per unit area (MPa), \( F \) is the magnitude of the normal force (expressed in N), and \( A \) is the area of the surface on contact (in m²). The contact surface in the adsorbent bed is actually lower than the total surface area of the column due to the void volume in between the beads. However, this assumption is applied for both the calculation of the mechanical strength as for the pressure that is exerted by the adsorbent bed. Since the estimated pressure that is generated by the adsorbent bed (0.02 MPa) is significantly lower than the mechanical strength of our beads (0.14 – 0.82 MPa), it is expected that our binderless beads could be used in an industrial process without suffering significant deterioration.
Binderless zeolite LTA beads with hierarchical porosity for selective CO\textsubscript{2} adsorption in biogas upgrading

Figure S22: Mechanical strength measurement for LTA-B1b beads. The vertical lines indicate the point where the piston starts to touch the adsorbent bed. The green circles correspond to the first and last breakage of the zeolite beads.

Figure S23: Mechanical strength measurements for 4A commercial beads. The vertical lines indicate the point where the piston starts to touch the adsorbent bed. Note that for LTA-B1b beads in this region the lines were bumpy and thus indicate breakage of beads, but for these commercial beads the first breakage does not occur in this range of pressures. Therefore, a test at higher pressures was carried out (see Figure S26).
Figure S24: Mechanical strength measurements for 4A commercial beads up to a load of 5 kN. The green circles correspond to the first and last breakage of the commercial zeolite beads.

Synthesis of LTA-P2

29.3 g of H₂O was added to a 100 ml beaker, after which 0.30 g NaOH and 2.15 g NaAlO₂ were added subsequently. The resulting solution was stirred at 500 rpm for 2h. 29.20 g TMAOH (25 wt%) and 5.7g Ludox HS-40 were added to the Teflon liner of a 100 ml stainless steel autoclave and the solution was stirred at 500 rpm for 2h. After both solutions had been stirred for 2h, the aluminate solution was added to the silicate solution, and the resultant silicoaluminate solution was stirred at 500 rpm for 1h. The autoclave was closed and placed into an oven for the hydrothermal crystallisation at 100°C for 48h. After cooling down to RT, the product was filtered over a Büchner funnel and washed with 1L of H₂O. After drying overnight at RT, the beads were calcined using the following programme: heating 3°C/min to 200°C, 6h at 200°C, heating 2°C/min to 600°C, 6h at 600°C.
Syncthesis of LTA-B5, LTA-B6 and LTA-B beads

29.3 g of H$_2$O was added to a 100 ml beaker, after which 0.30 g NaOH and 2.15 g NaAlO$_2$ were added subsequently. The resulting solution was stirred at 500 rpm for 2h. 29.20 g TMAOH (25 wt%) and 3.42 g H$_2$O were added to the Teflon liner of a 100 ml stainless steel autoclave. 2.28g SiO$_2$ was subsequently added to the Teflon liner and the solution was stirred at 500 rpm for 2h. After both solutions had been stirred for 2h, the aluminate solution was added to the silicate solution, and the resultant silicoaluminate solution was stirred at 500 rpm for 1h. 2.22 g Amberlite IRA-900 was added to the silicoaluminate solution. After mixing for 1 minute, the autoclave was closed and the reaction mixture was aged statically at RT for 24 (LTA-B5), 48 (LTA-B6), or 72h (LTA-B7). The autoclave was then placed into an oven for the hydrothermal crystallisation at 100°C for 24 (LTA-B5), 48 (LTA-B6), or 72h (LTA-B7). After cooling down to RT, the product was filtered over a Büchner funnel and washed with 1L of H$_2$O. This yielded the desired beads and a powder-fraction side-product. After drying overnight at RT, the beads were separated from the powder fraction by sieving. The beads were calcined using the following programme: heating 3°C/min to 200°C, 6h at 200°C, heating 2°C/min to 600°C, 6h at 600°C.

SiO$_2$ is used as silica source for the synthesis of LTA-B5, LTA-B6 and LTA-B7 beads. For the synthesis of LTA-P2 Ludox HS-40 is used as a silica source. The molar composition in the reaction mixture for the beads and the powder synthesis was kept at 1 NaAlO$_2$ : 1.4 SiO$_2$ : 0.3 NaOH : 3.1 TMAOH : 115.6 H$_2$O.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LTA-B5</th>
<th>LTA-B6</th>
<th>LTA-B7</th>
<th>LTA-P2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>81.0</td>
<td>55.8</td>
<td>56.8</td>
<td>58.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>9.5</td>
<td>21.6</td>
<td>21.5</td>
<td>22.3</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>7.1</td>
<td>18.7</td>
<td>18.0</td>
<td>18.6</td>
</tr>
<tr>
<td>Cl</td>
<td>0.6</td>
<td>2.6</td>
<td>2.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Table S6: Chemical composition (mol%) of LTA-B5, LTA-B6, LTA-B7 and LTA-P2 as determined by XRF.*
Table 57: Si/Al ratio of LTA-B5, LTA-B6, LTA-B7 and LTA-P2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al ratio a</th>
<th>Na⁺ (mol g⁻¹ bead) a</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Micropore volume (cm³ g⁻¹)</th>
<th>Degree of crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-B5</td>
<td>4.26</td>
<td>0.11</td>
<td>264</td>
<td>0.06</td>
<td>31</td>
</tr>
<tr>
<td>LTA-B6</td>
<td>1.29</td>
<td>0.27</td>
<td>216</td>
<td>0.09</td>
<td>62</td>
</tr>
<tr>
<td>LTA-B7</td>
<td>1.27</td>
<td>0.27</td>
<td>124</td>
<td>0.05</td>
<td>65</td>
</tr>
<tr>
<td>LTA-P2</td>
<td>1.32</td>
<td>0.27</td>
<td>180</td>
<td>0.08</td>
<td>84</td>
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</tbody>
</table>

a Determined by XRF analysis.

Figure 25: XRD pattern of LTA-B5.
Binderless zeolite LTA beads with hierarchical porosity for selective CO$_2$ adsorption in biogas upgrading

Figure S26: XRD pattern of LTA-B6.

Figure S27: XRD pattern of LTA-B7.
Figure 28: XRD pattern of LTA-P2.

Figure S29: CO$_2$ adsorption isotherms of pristine beads and of beads ground to a powder for LTA-B1 and LTA-B1b.
Binderless zeolite LTA beads with hierarchical porosity for selective CO$_2$ adsorption in biogas upgrading

**Figure S30:** CO$_2$ (black) and CO$_3$ (red) adsorption isotherm measured at room temperature for LTA-B1b.

**Table S8:** Chemical composition (mol%) of ion-exchanged LTA-B1b beads as determined by XRF.

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>53.9</td>
<td>53.0</td>
<td>51.9</td>
<td>50.6</td>
<td>50.1</td>
<td>49.5</td>
<td>48.2</td>
<td>47.7</td>
<td>47.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>20.5</td>
<td>20.8</td>
<td>20.3</td>
<td>20.1</td>
<td>19.3</td>
<td>19.6</td>
<td>19.3</td>
<td>19.1</td>
<td>18.2</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>17.1</td>
<td>16.1</td>
<td>16.0</td>
<td>13.9</td>
<td>11.4</td>
<td>9.1</td>
<td>7.1</td>
<td>3.3</td>
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<tr>
<td>K$_2$O</td>
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<td>16.4</td>
<td>20.2</td>
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<tr>
<td>Cl</td>
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<td>4.7</td>
<td>4.5</td>
<td>4.2</td>
<td>4.4</td>
<td>4.6</td>
<td>4.2</td>
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