Summary

Research focused on the replacement of natural gas has received increasing attention, with the aim to mitigate anthropogenic greenhouse gas emissions. Biogas, which is obtained through anaerobic digestion of organic waste, such as agricultural waste (e.g. manure) or waste from the food industry, can be used as a direct replacement for natural gas. Biogas contains about 60 vol% CH₄ and 40 vol% CO₂, and in order to be used as a replacement for natural gas, it should be upgraded to > 95% CH₄. (Vacuum) Pressure Swing Adsorption (V)PSA using zeolites as adsorbents is considered an attractive method for upgrading of biogas. Zeolites are considered suitable for this application due to their moderate adsorption capacities (1-7 mmol g⁻¹) at low pressure (1 bar), excellent structural stability, and because they can be produced easily at low cost. In particular, zeolites are of interest for this application due to the possibility to modify their physicochemical properties, and thereby enhance the CO₂ adsorption performance. Though zeolites are typically synthesized in powder format, and subsequently shaped into a macroscopic format by adding about 20 wt% inert binder, in this work we present an attractive alternative. Several macroscopic binderless zeolite beads (0.4-1.2 mm) were synthesized using a hard templating method, resulting in beads displaying an open and accessible hierarchically porous structure which were investigated for their applicability in biogas upgrading.

In Chapter 1, zeolites were thoroughly reviewed for their application in CO₂ adsorption. First, the CO₂ adsorption mechanisms on zeolites with different framework types were discussed. In the most commonly observed adsorption mechanism, one of the oxygens of CO₂ interacts with a single extra-framework cation of the zeolite. Then, the factors affecting CO₂ adsorption in zeolites were evaluated, starting with the physicochemical properties of the zeolite (e.g. framework type, Si/Al ratio and the extra-framework cations), and subsequently the effect of the physicochemical properties on the behaviour of zeolites as CO₂ adsorbents (e.g. enthalpy of adsorption, diffusion of the adsorbate through the zeolite framework and influence of water) was evaluated. An overview of the performance of different types of zeolites for CO₂ adsorption was provided and the most suitable zeolites in terms of high adsorption capacity or high selectivity
were identified. Finally, different shaping methods were discussed – either with or without the use of a binder – which are necessary for the industrial application of zeolites for CO$_2$ adsorption.

A set of four binderless LTA beads with Si/Al ratio 1.2 – 3.9 were synthesized in Chapter 2, by employing a resin template. Though these beads all displayed a spherical macroscopic format, their structural integrity differed, with the LTA-B1 beads displaying the most intact and mechanically stable beads. All synthesized beads displayed a hierarchically porous structure in which the micropores of the zeolite are accessible through the meso- and macropores present within the beads. To evaluate the applicability of the beads for CO$_2$ adsorption in the context of biogas upgrading, their CO$_2$ and CH$_4$ adsorption isotherms were measured and compared with commercial binder-containing beads and zeolite in powder format. The CO$_2$ adsorption capacities of the synthesized beads were comparable to that of the commercial beads, and in the case of the LTA-B2 beads a slightly higher CO$_2$ adsorption capacity was reached compared to the commercial beads.

The CO$_2$/CH$_4$ selectivity at partial pressures mimicking biogas (i.e. 0.6 bar for CH$_4$ and 0.4 bar for CO$_2$) of all synthesized beads was higher (CO$_2$/CH$_4$ = 16-19) than that of the commercial beads and the LTA zeolite in powder format (CO$_2$/CH$_4$ = 14 or 12, respectively). Partial ion-exchange of the LTA-B1 beads with K$^+$ enabled a significant increase in the CO$_2$/CH$_4$ selectivity to 1540, as from approximately 42% K$^+$ essentially no CH$_4$ was adsorbed, while the CO$_2$ adsorption was still substantial (2.4 mmol g$^{-1}$ at 1 bar).

Chapter 3 describes the synthesis of a set of binderless Faujasite beads employing an anion-exchange resin as a hard template. The synthesized beads all presented a hierarchical pore structure in which the zeolitic micropores can be accessed through the meso- and macropores generated by calcination of the polymeric template. The major component in all the beads was the FAU framework, though in all beads also an amorphous silica/silicoaluminate phase was observed. Additionally, for two types of beads, a trace amount of zeolitic LTA phase was present. Among the three beads, also other physicochemical properties differed, which are expected to influence the CO$_2$ adsorption behaviour of the beads, such as the Si/Al ratio, specific surface area, micropore volume and degree of crystallinity. The binderless beads were compared with extrudates made from commercial zeolite Y. The CO$_2$ adsorption capacity of the binderless beads were similar (3.8 – 4.3 mmol g$^{-1}$) and for one material higher than that of the extrudates (4.1 mmol g$^{-1}$). Interestingly, the enthalpy of adsorption of our beads ($\Delta H_{ads}$= -45
kJ mol\(^{-1}\)) was higher than that of the commercial zeolite powder (\(\Delta H_{\text{ads}} = -37\) kJ mol\(^{-1}\)), which indicated that the interaction of our beads with CO\(_2\) was stronger than that of the commercial powder. This is a particularly useful characteristic for CO\(_2\) adsorption from gas streams in which the CO\(_2\) concentration is relatively low, such as flue gas.

In contrast to Chapter 2 and Chapter 3 which describe the synthesis of zeolite beads, in Chapter 4 the synthesis of binderless silicoaluminophosphate (SAPO-34) beads is reported. An advantage of SAPO-34 over zeolites typically used for CO\(_2\) adsorption (i.e. with low Si/Al ratio), is that the electrical field gradient of SAPO-34 is lower. This leads to a less steep adsorption isotherm at low pressure (<0.1 bar) and, therefore, to higher working capacity at relatively mild regeneration conditions in VPSA. The binderless SAPO-34 beads consisted of an interior of small crystals and around the beads a certain degree of large, overgrown crystals was observed. The CO\(_2\) adsorption capacity of the binderless SAPO-34 beads (3.0 mmol g\(^{-1}\)) was slightly lower compared to SAPO-34 in powder format (3.4 mmol g\(^{-1}\)), but higher than that of binder-containing extrudates of SAPO-34 (2.4 mmol g\(^{-1}\)). The beads displayed high CO\(_2\)/CH\(_4\) (8, at 0.4 bar CO\(_2\) and 0.6 bar CH\(_4\)) and CO\(_2\)/N\(_2\) selectivity (33, at 0.15 bar CO\(_2\) and 0.85 bar N\(_2\)), yet these values were lower compared to those of the extrudates. Though the adsorption capacity at 1 bar was lower than that of zeolite LTA, which is often used for CO\(_2\) adsorption, the working capacity of the SAPO-34 beads (1.8 mmol g\(^{-1}\) compared to 0.7 mmol g\(^{-1}\) for zeolite LTA) was significantly higher under relatively mild regeneration conditions (0.2 bar). This working capacity can likely be further increased by increasing the adsorption pressure, as the CO\(_2\) adsorption isotherm did not yet present a plateau at 1 bar. Therefore, the SAPO-34 beads are good candidates for CO\(_2\) separation from biogas in a VPSA application.

In Chapter 5, two different kinds of core-shell beads were synthesized by coating binderless ZSM-5 beads with a silicalite-1 shell in order to decrease the hydrophilicity of the beads while maintaining good CO\(_2\) adsorption capacity. For the Sil-ZSM-A core-shell beads, the binderless ZSM-5 beads were synthesized using an anionic resin as a hard template. The polymeric template was removed by calcination and subsequently a silicalite-1 shell was grown on the external surface of the ZSM-5 beads. Alternatively, the silicalite-1 shell was synthesized without first removing the resin template, resulting in core-shell composite beads that after calcination yielded Sil-ZSM-B core-shell beads. For the Sil-ZSM-B beads, the presence of the resin during the formation of the silicalite-1 shell prevented
growth of silicalite-1 within the pores of the ZSM-5 parent beads and, therefore, the pristine porosity of the beads was largely kept intact. The CO$_2$ adsorption capacity of the Sil-ZSM-B core-shell beads (2.0 mmol g$^{-1}$) was similar to that of the parent ZSM-5 beads (2.1 mmol g$^{-1}$) and a slightly lower H$_2$O adsorption capacity (a decrease of 15% at 20% relative humidity (RH) and of 7% at max RH) was observed. For the Sil-ZSM-A beads, the porosity of the parent ZSM-5 bead was decreased because silicalite-1 formed not only around the beads but the interior was also partially coated by silicalite-1. This resulted in a larger decrease in H$_2$O adsorption capacity (40% at 20% RH and 28% at max RH) for the Sil-ZSM-A beads compared to the parent ZSM-5 beads. At the same time, the CO$_2$ adsorption capacity of the Sil-ZSM-A beads (1.9 mmol g$^{-1}$) was only slightly lower than that of the parent ZSM-5 beads (2.1 mmol g$^{-1}$). For both core-shell beads, defects in the shell were observed and thus a further decrease in hydrophilicity can likely be achieved by reiterating the synthesis step in which the silicalite-1 shell is formed as this is expected to reduce the number of defects in the shell layer. Additionally, the silicalite-1 shell increased the mechanical stability of both the Sil-ZSM-A and Sil-ZSM-B beads compared to that of the parent ZSM-5 beads. This chapter demonstrates an interesting approach of coating zeolite beads by a different zeolite to optimize the properties of the material (e.g. hydrophilicity, mechanical stability).

Finally, in Chapter 6 the application of the beads synthesized in Chapter 2 (zeolite LTA) and Chapter 4 (SAPO-34) in a small scale Vacuum Pressure Swing Adsorption (VPSA) setup was evaluated. Breakthrough experiments were conducted with a gas mixture mimicking biogas (i.e. 60 vol% CH$_4$ and 40 vol% CO$_2$) in a single adsorption column at 4 bar. First, the binderless LTA beads were compared with commercial binder-containing zeolite 4A beads and subsequently they were compared with the binderless SAPO-34 beads. The LTA beads displayed slightly steeper breakthrough and less significant tailing compared to the 4A beads which indicates that the mass transfer rate of the LTA beads was slightly higher than that of the 4A beads. This was attributed to the open and accessible hierarchical pore structure of the LTA beads. The CO$_2$ adsorption capacity of the 4A beads was higher than that of the LTA beads, both for the single component adsorption isotherm as for 5 consecutive cycles of breakthrough experiments. However, for both the LTA and 4A beads the cyclic adsorption capacities at breakthrough were low, indicating that these beads might be more suitable for temperature swing adsorption (TSA) than for VPSA. These low cyclic adsorption capacities were
attributed to the poor regeneration of the LTA and 4A beads as their CO$_2$ adsorption capacity at the desorption pressure was still significant (1.6 mmol g$^{-1}$ and 2.1 mmol g$^{-1}$ for the LTA and 4A beads, respectively). The SAPO-34 beads displayed a less steep CO$_2$ adsorption isotherm and, therefore, the CO$_2$ adsorption capacity at the desorption pressure was very low (0.2 mmol g$^{-1}$). Thus, the SAPO-34 beads were almost fully regenerated during desorption, leading to high cyclic adsorption capacity around 2 mmol g$^{-1}$ and high productivity $>$ 3 mol kg$^{-1}$ h$^{-1}$. Additionally, the SAPO-34 beads showed a similar, yet slightly steeper breakthrough curve with less significant tailing compared to the LTA and 4A beads, indicating that the SAPO-34 beads displayed the highest mass transfer rate. The superior cyclic CO$_2$ adsorption capacity, productivity and mass transfer rate of the SAPO-34 beads indicate that these beads would be suitable for biogas upgrading using VPSA.