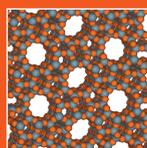


Studies on adsorptive CO₂ removal from nitrogen in variable humidity

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Introduction

Various strategies are being pursued to meet the EU and global climate objectives. In addition to a reduction in fossil fuels, the possibilities of actively removing CO₂ from air or exhaust gases by adsorption are also being investigated /1, 2/. These methods only make sense if acceptable separation rates can be achieved and if they are energy-efficient /3/. Such methods should be less sensitive towards contaminants that may appear with varying concentrations and offer good long-term stability. Water also plays a major role as an interfering component /4/.

This study investigates materials for their suitability in adsorptive systems to separate CO₂ from air. Such porous materials need to have a high sorption capacity, high selectivity for CO₂, fast sorption kinetics, good regenerability and high cycle stability. In addition, this study examines the influence of humidity in sorption capacities in zeolites 4A and 5A and an amine functionalized polymer. In order to obtain results transferable to the application, a dynamic measurement method was used, and the breakthrough curves obtained were evaluated for sorption capacities and sorption kinetics. In addition to the CO₂ breakthrough curves, breakthrough curves of water vapor and their temperature curves at 50 % relative humidity and 313 K at 1 bar were obtained.

Experimental design

Material and sample preparation

Two zeolites with narrow pores, i.e. 4A and 5A, and one amino functionalized macroporous polymer, Lewatit VP OC 1065, were selected. The zeolites have particle sizes of approx. 1.5 up to 2.5 mm; the polymer has smaller particles sized at approx. 0.5 mm. CO₂ with a purity of 99.995 % and N₂ with a purity of 99.999 % were used as fluids. In order to conduct tests in the presence of humidity, the evaporator integrated in the device was used in combination with distilled water. Both zeolites were heated up in situ after they were placed in a N₂ gas flow of 300 ml·min⁻¹. Material was heated with a ramp of 2 K·min⁻¹, and

temperature was kept at a constant level of 673 K for 300 min. The polymer was heated at 10 K·min⁻¹ to 383 K, and temperature was kept at this level for 5 hours. Again, a N₂ gas flow of 300 ml·min⁻¹ was used as carrier gas.

Breakthrough curves

All breakthrough curves were measured in the breakthrough curve analyzer mixSorb L by 3P Instruments. The adsorber has a diameter of 3 cm and a height of 20 cm. It features four temperature sensors and is made of stainless steel. The gas phase composition at the adsorber outlet was analyzed with a thermal conductivity detector and additionally with a mass spectrometer. All evaluations were carried out using the mass spectrometer data set.

After the samples were prepared, the adsorber was fed with the carrier gas and thermostatically controlled at 313 K. When moisture free analysis was desired, nitrogen was used as the carrier gas. For sample runs where moisture was needed, nitrogen with a relative humidity of 50 % was used. Once the conditions were constant (temperature, analyzer signals etc.), carbon dioxide was added. During the measurements, the total gas flow was 5000 ml·min⁻¹ (STP). This corresponds to an empty sample holder (adsorber bed) flow rate of 0.135 m·s⁻¹. Measurements were concluded once a steady-state condition was achieved. This

condition is characterized by constant fixed bed temperatures and a constant gas composition at the adsorber outlet. Once the breakthrough curves were determined with CO₂ from dry carrier gas, samples were re-heated to 523 K in the zeolite setup and 383 K in the polymer setup to desorb CO₂. The progress of the desorption process was analytically monitored. Subsequently, breakthrough curves of water vapor with a relative humidity of 50 %, at 313 K and 1 bar were measured as absolute values. After the equilibrium was achieved, the CO₂ breakthrough curve was again determined for each sample.

Results and discussion

Under dry conditions, zeolites are characterized by good sorption capacity and kinetics. The highest sorption capacity was achieved with zeolite 4A with 0.768 mmol·g⁻¹. The Lewatit sorption capacity is 0.605 mmol·g⁻¹, while a zeolite 5A capacity of 0.341 mmol·g⁻¹ was determined. The lower absorbing capacity of zeolite 5A compared to zeolite 4A at low CO₂ partial pressure can be explained with larger pore width and consequently less interaction. The macroporous polymer's high capacity is not attributable to the pore system, but the amine functionalization of the surface and -accordingly- this group's affinity for CO₂. The breakthrough curves under dry conditions are indicated in Fig. 1. For better clarity, temperature is not included in this figure.

At first sight, a deviation between the load obtained and breakthrough times is obvious. Compared to the high polymer load, the area left of the breakthrough is rather small. This can be explained in regards to the adsorber volume. Due to the low bulk density, the polymer falls behind based on the volume. Zeolite 4A offers the best sorption capacity of all three materials with regard to volume. Such effects need to be considered in the design of industrial-scale systems. Another finding in Fig. 1 is the larger noise in the Lewatit curve. It can be explained with the large volume reduction caused by the drying process, which causes the adsorber not to be filled with the entire volume. Light particles cause a slight movement in the bed, i.e. strictly speaking

it is no longer a fixed bed. Again, this fact needs to be taken into consideration for industrial-scale systems. The breakthrough curves allow conclusions on the sorption kinetics. Zeolite 5A features the best kinetics, as the breakthrough curve shows a sharp increase. The polymer and zeolite 4A produce a wide, slowly increasing breakthrough curve, which is an indicator for the limitations of these materials. In the case of zeolite 4A, slower kinetics are probably attributable to the tighter pore system. In addition, the binder might also have an impact. Zeolites typically involve transport limitations. A transport-limiting effect may be suspected in macroporous polymers in the amino functionalized surface. The kinetics in the polymer are another reason for a reduced load in dynamic experiments compared to equilibrium data described in publications /5/. This limitation needs to be considered in the scaling of industrial systems, as they frequently produce even higher empty flow rates /6/.

Fig. 2 to 4 show the breakthrough curves of water in nitrogen (50% RH) at 313 K and ambient pressure, as well as their temperature profile. These temperature curves are an additional indicator for the affinity of such materials for water. In order to facilitate the comparability of materials, all images are scaled equally.

Considering the breakthrough times and temperature curves, high sorption capacities and affinities for both zeolites can be assumed. Sorption heat produces temperature peaks of approx. 373 K in the bed. In contrast, the polymer produces only little temperature increases combined with rather low sorption capacity. It needs to be assumed that especially the primary amine groups interact with the water.

Breakthrough curves of CO₂ in the presence of humidity are indicated in Fig. 5. In order to increase clarity and because of constant water vapor concentration, lower CO₂ concentration and subsequently a reduced displacement effect during the test, water vapor signals are eliminated from the test. Spontaneous breakthroughs are detected for zeolites. The load is almost zero

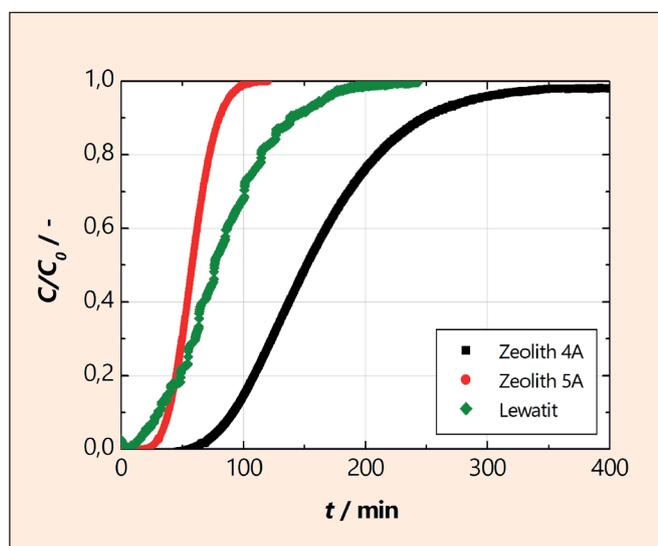


Figure 1 Breakthrough curves of 2000 ppm CO₂ of dry nitrogen in zeolite 4A, 5A and Lewatit VP OC 1065 at 313 K, 1 bar, 5000 cm³·min⁻¹

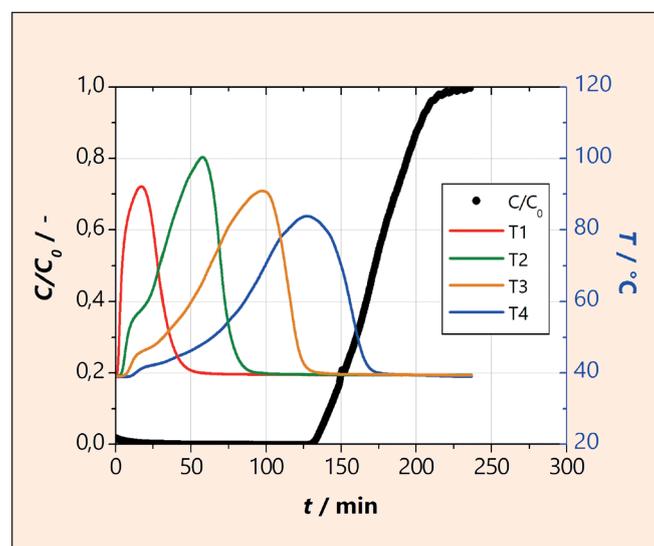


Figure 2 Breakthrough curve of water in zeolite 4A at 313 K, 1 bar, 5000 cm³·min⁻¹, rel. humidity 50 %

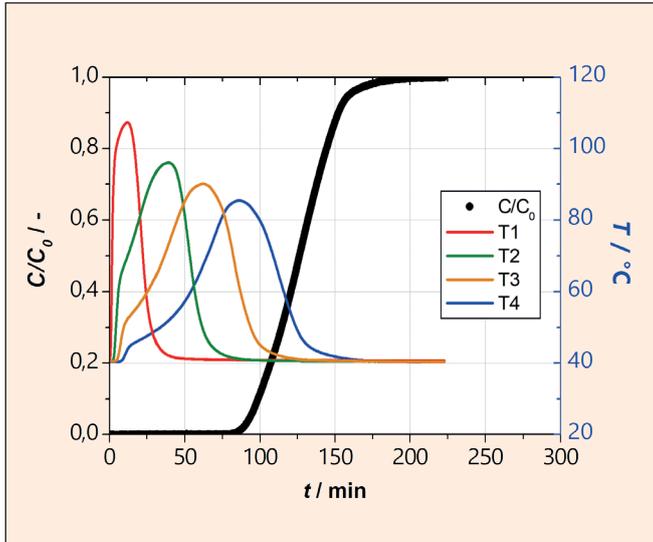


Figure 3 Breakthrough curve of water in zeolite 5A at 313 K, 1 bar, 5000 cm³·min⁻¹, rel. humidity 50 %

in both cases. Water is adsorbed in the zeolite pore system to such an extent that the displacement of CO₂ is insignificant.

Both zeolites are therefore rather unsuitable for CO₂ separation from wet gas flows, as it would be the case in Direct Air Capturing applications. However, there are advantages in the purification of dry gas flows due to improved kinetics. A sorption loading of 0.819 mmol·g⁻¹ was obtained for the polymer. This adsorbent is the most suitable of all materials selected to adsorb CO₂ in low concentrations and with presence of humidity. Accordingly, it is ideal for Direct Air Capturing. All loadings obtained are summarized in Tab. 1.

Due to the slow kinetics, CO₂ was also detected at the adsorber outlet shortly after the start of the experiment using Lewatit. This is reflected in a quickly rising CO₂ concentration. Accordingly, the selected conditions only cause a reduction of CO₂ and not the complete removal from the gas mixture. Material development could focus on the enhancement of polymer kinetics. An interesting observation is the fact that the polymer breakthrough curve in the presence of humidity is less significant than in dry condi-

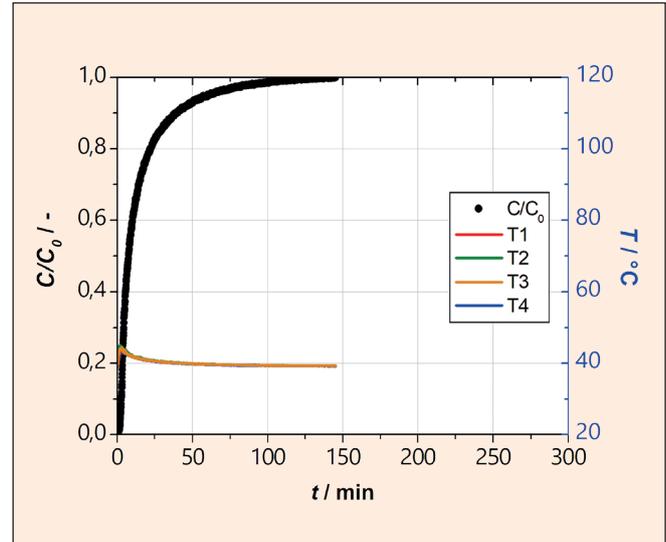
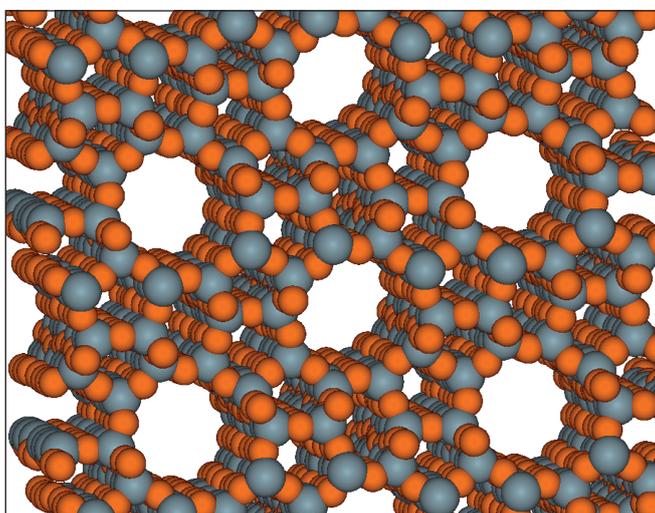


Figure 4 Breakthrough curve of water in Lewatit VP OC 1065 at 313 K, 1 bar, 5000 cm³·min⁻¹, rel. humidity 50 %

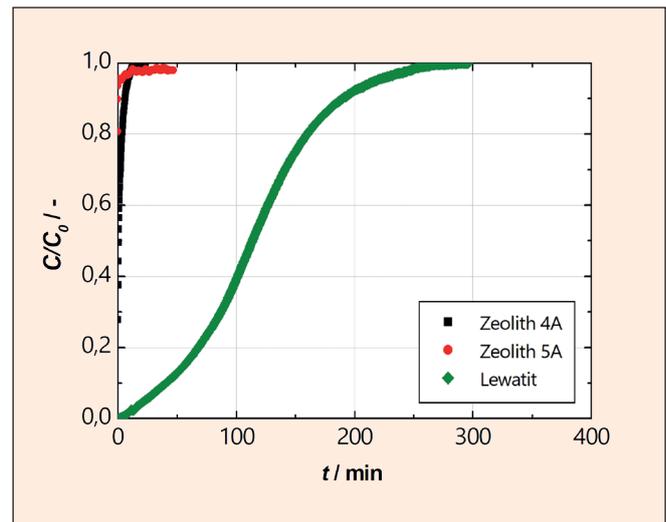


Figure 5 Breakthrough curves 2000 ppm CO₂ from a wet nitrogen flow in zeolite 4A, 5A and Lewatit VP OC 1065 at 313 K, 50 % relative humidity, 1 bar and 5000 cm³·min⁻¹

Table 1 Loadings from breakthrough tests of 2000 ppm CO₂ from dry and wet (50 % RH) nitrogen at 313 K, 1 bar, volume flow 5000 cm³·min⁻¹

Sample	CO ₂ load of dry N ₂	CO ₂ load of moist N ₂
Zeolite 4A	0.768 mmol·g ⁻¹	< 0.010 mmol·g ⁻¹
Zeolite 5A	0.341 mmol·g ⁻¹	< 0.010 mmol·g ⁻¹
Lewatit VP OC 1065	0.605 mmol·g ⁻¹	0.819 mmol·g ⁻¹

Summary

It was shown that zeolite 4A in the presence of humidity produced the best purification efficiency under the specified conditions. This is mainly attributable to the volume-based evaluation of results. Due to the lower bulk density, the Lewatit-filled adsorber achieves a lower purification performance, although the polymer mass loading is similarly high. These effects must be considered in the system design.

As to be expected, breakthrough curves of water vapor show a strong affinity for both zeolites resulting in significant temperature peaks up to approx. 373 K in the adsorber. Although the polymer also has a certain sorption capacity for water, it is connected to a much lower temperature profile. This observation leads to the conclusion that the affinity for water is less for the polymer. In addition, the sorption capacity for water is also lower.

A complete breakdown of sorption capacity for zeolites can be observed for breakthroughs of 2000 ppm CO₂ from a wet carrier gas flow in samples treated with water, while the sorption capacity of amine functionalized polymer even increases. Based on orienting and practice-oriented tests, Lewatit can be recommended for Direct Air Capturing. The experiments are a valuable indicator for the development of material that an improvement of the sorption kinetics of the polymer seems desirable.

Let us personally convince you of the efficiency of our mixSorb systems; larger sample amounts can be tested with mixSorb L, while mixSorb-S series are the recommended choice for very

small sample amounts. Device demonstrations and sample tests in our analysis laboratory are part of our service. We are available at info@3P-instruments.com and +49 8134 93240.

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