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Influence of material composition on the CO\textsubscript{2} and H\textsubscript{2}O adsorption capacities and kinetics of potassium-promoted sorbents

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GRAPHICAL ABSTRACT

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ABSTRACT

Two different potassium-promoted hydrotalcite (HTC)-based adsorbents and a potassium-promoted alumina sorbent were investigated using thermogravimetric analysis (TGA) and different characterization methods in order to study CO\textsubscript{2} and H\textsubscript{2}O adsorption capacity and kinetics. A higher Mg content improves the cyclic working capacity for CO\textsubscript{2} due to the higher basicity of the material. The initial adsorption rate for CO\textsubscript{2} is very fast for all sorbents, but for sorbents with higher MgO content, this fast-initial adsorption is followed by a slower CO\textsubscript{2} uptake probably caused by the slow formation of bulk carbonates. A longer half-cycle time can therefore increase the CO\textsubscript{2} cyclic working capacity for sorbents with a higher MgO content. Potassium-promoted alumina has a very stable CO\textsubscript{2} cyclic working capacity at different operating temperatures compared to the potassium-promoted HTC's. Usually a higher operating temperature increases the desorption kinetics for a HTC-based adsorbent, but not for potassium-promoted alumina. HTC-based adsorbents show the highest cyclic working capacity for H\textsubscript{2}O. The adsorption kinetics for H\textsubscript{2}O are not influenced by the material composition, indicating that the mechanism behind the adsorption of H\textsubscript{2}O is different compared to CO\textsubscript{2}. Depending on the material composition, adsorption of steam at high operating temperatures (> 500 °C) results in an irreversible decomposition of carbonate species. Steam can reduce the temperature where usually K\textsubscript{2}CO\textsubscript{3} is irreversibly decomposed resulting in a significantly reduced cyclic working capacity, which is very important concerning the use of these sorbents for sorption-enhanced water-gas shift processes.

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1. Introduction

Layered double hydroxides (LDHs), also often called hydrotalcite-like materials (HTCs), belong to a large group of anionic or basic clays. These materials showed a wide range of applications as catalysts, precursors and adsorbents [1]. Several thousands of tons of HTCs are produced annually by several chemical companies, such as BASF, SASOL, Clariant, Kisuwa Chemicals, Sakai Chemical, etc. [2]. A general formula for this type of materials is \[ \text{LDH} = \left[ \text{M}^{2+}_{\text{a}} \right] \cdot \left[ \text{M}^{2+}_{\text{b}} \right] \left( \text{OH} \right)_{\text{x}} \cdot \left( \text{A}^{-} \cdot \text{nH}_{2}\text{O} \right)^{+} \] Here \( \text{M}^{2+} \) is a divalent cation like \( \text{Mg}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+} \) and \( \text{M}^{3+} \) is a trivalent cation like \( \text{Al}^{3+}, \text{Fe}^{3+} \) or \( \text{Cr}^{3+} \). \( \text{A}^{-} \) is an interlayer anion such as \( \text{CO}_{3}^{2-}, \text{SO}_{4}^{2-}, \text{NO}_{3}^{-}, \text{Cl}^{-} \) or \( \text{OH}^{-} \). A schematic representation of a LDH can be seen in Fig. 1.

More recently hydrotalcite-based adsorbents have been investigated for the use in sorption-enhanced water-gas shift (SEWGS) processes. SEWGS is a promising concept for pre-combustion CO2 capture, which combines the water-gas shift (WGS) reaction with in situ CO2 removal. In situ CO2 removal increases the CO conversion attainable at elevated temperatures (300–500 °C) due to the shift of the WGS equilibrium (Le Chatelier’s principle). Additionally, the operational costs in comparison to alternative processes, like the conventional Sxelox process, can be reduced due to a lower steam/CO2 ratio [4,5]. To deal with the periodic behavior of the adsorption/desorption cycles usually multiple columns are operated in parallel to obtain a continuous process.

In addition to their high stability [6,7] and fast adsorption/desorption kinetics, hydrotalcites show a high selectivity towards CO2 compared to CO and H2 [8,9]. At elevated temperatures, the typical layered structure is lost and the LDH is converted into a mixed metal oxide (LDO) with a high surface area and basicity [10]. To increase the basicity and the reversible adsorption capacity of hydrotalcite-based adsorbents, they are promoted with alkaline cations [7]. K2CO3 promotion has been reported to be very beneficial in terms of CO2 adsorption capacity [8,9,11–15]. In addition, promotion with also other alkaline cations, like Sr and Cs, and their effect on the CO2 adsorption capacity were investigated [13]. Not only hydrotalcite-based adsorbents with different Mg/Al ratios and promotion with different alkali-metals were investigated, but also potassium-promoted alumina and MgO were studied as a possible adsorbent for their use in a SEWGS process [3,12,16]. However, the formation of MgCO3 can lead to mechanical instability for some HTC-based adsorbents and MgO, which can cause major problems for the operation in packed-bed reactors [17]. Usually, the cyclic working capacity of CO2 is reported for the different adsorbents at various operating conditions. Since the sorbents will be exposed to high partial pressures of CO2 and H2O, not only the CO2 adsorption capacity, but also the capacity for H2O and the influence of H2O on the sorption of CO2 are important, especially for a more accurate process optimization and cost analysis of SEWGS processes with these sorbents. Capacity and adsorption kinetics of a potassium-promoted hydrotalcite with a Mg/Al ratio of 0.54 for both CO2 and H2O were investigated in an earlier work. It has been shown that the adsorption capacity of CO2 and H2O are highly dependent on the desorption time due to the relatively slow desorption kinetics [18].

In order to study the influence of the material composition on the adsorption and desorption kinetics of CO2 and H2O, a hydrotalcite-based adsorbent with a higher MgO content and a potassium-promoted alumina were compared in this study at the same operating conditions. In the first part of this paper we will show how the MgO content can influence the adsorption kinetics of CO2 and we will demonstrate the positive effect of a higher MgO content on the CO2 cyclic working capacity, while the adsorption kinetics of H2O are not significantly affected by the material composition. Finally, to explain the decomposition of potassium carbonate on the sorbents due to exposure to H2O at high temperature TGA-MS and TGA-TPD experiments were conducted. XRD and BET analysis were used to characterize the sorbent before and after steam treatment.

2. Materials and methods

Two different calcined potassium-promoted hydrotalcite-based sorbents (SASOL), with different Mg/Al ratio were used in the experiments and compared to a potassium-promoted alumina (BASF). The names and compositions have been summarized in Table 1. The materials were pre-calcined by the manufacturer at 250 °C and 450 °C for 24 h [19].

KMG30 and KMG70 adsorbent pellets (4.7 × 4.7 mm) and KSORB (spheres with a diameter of 2 mm) were crushed to powders with similar particle size, which have subsequently been used in TGA-measurements.

The materials were characterized using a helium Pycnometer (Quantachrome Upyc 1200e), BET (Thermo Fischer Surfer), XRD (Rigaku Minillex 600) and SEM-EDX (FEI-Quanta) to study the morphology of the used material. Particle size distribution was measured in a Fritsch Analysette 22 laser diffraction Particle Size measurement. The

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller method for surface area determination</td>
</tr>
<tr>
<td>BHJ</td>
<td>B.C. Lippens, B.G. Linsen, J.H. de Boer for mesoporous materials</td>
</tr>
<tr>
<td>CWC</td>
<td>cyclic working capacity</td>
</tr>
<tr>
<td>HTC</td>
<td>hydrotalcite</td>
</tr>
<tr>
<td>LDHs</td>
<td>layered double hydroxides</td>
</tr>
<tr>
<td>LDO</td>
<td>mixed metal oxide (hydrotalcite based material after thermal treatment)</td>
</tr>
<tr>
<td>PBR</td>
<td>packed bed reactor</td>
</tr>
<tr>
<td>PCO2</td>
<td>partial pressure of CO2 [bar]</td>
</tr>
<tr>
<td>PH2O</td>
<td>partial pressure of H2O [bar]</td>
</tr>
<tr>
<td>TGA</td>
<td>thermo-gravimetric analysis</td>
</tr>
<tr>
<td>TGA-MS</td>
<td>thermo-gravimetric analysis couples with a mass spectrometer</td>
</tr>
<tr>
<td>TGA-TPD</td>
<td>thermo-gravimetric analysis with temperature programmed desorption</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray crystallography</td>
</tr>
</tbody>
</table>

**Fig. 1.** General structure for a layered double hydroxide [3].
samples used for XRD measured after TGA experiments were transported in N2 to a glovebox and prepared on air sensitive sample holder to avoid exposure to CO2 and H2O from the atmosphere during the XRD measurements.

A screening experiment in a Mettler Toledo TGA was carried out to determine the decomposition of the material during heat treatment. A Pfeiffer vacuum mass spectrometer connected to the outlet of the TGA was used to determine the release of H2O and CO2. A total volumetric flow rate of 40 ml/min containing 50% N2 and 50%. He was used during the experiments. The samples were heated to 900 °C at a rate of 20 °C/min.

Sorption experiments were carried out in two similar in-house developed TGA setups, which were already described elsewhere [18]. Prior to the adsorption experiments all materials were pretreated in the same way (heating the samples to 600 °C in N2 with a dwelling at 600 °C for 120 min) as reported in an earlier publication [18]. In this publication we will distinguish between different experiments that have been conducted with TGA.

1. In order to investigate the adsorption mechanism and kinetics of the different materials, adsorption of CO2 and H2O were conducted according to the conditions listed in Table 2, where the adsorption/desorption times and the operating temperature (300-500 °C) were varied. The same experiments were carried out for CO2 and H2O as the sorbate species. For CO2 adsorption experiments a partial pressure of CO2 of about 1 bar was used. For H2O we used a partial pressure of 0.34 bar for all experiments.

2. Steam treatment with temperature programmed desorption (TPD): Adsorption of steam during an increase in the operating temperature was performed in order to further understand the sorption phenomena. After steam adsorption of 30 min (P$_{H2O} = 0.34$ bar) the operating temperature was increased from 300 °C to 850 °C keeping the partial pressure of H2O constant. Afterwards, N2 was fed to desorb remaining H2O at 850 °C. The sorbents were cooled down to the operating temperature at 400 °C and the CO2 cyclic working capacity was determined at 400 °C at P$_{CO2} = 1$ bar with a half-cycle time of 30 min.

### 3. Results and discussion

#### 3.1. Characterization of different materials

N2 adsorption isotherms were conducted for the three different materials, in order to determine their surface area. Fig. 2 shows the adsorption isotherms and the resulting surface area (BET method). All materials show an isotherm typical for a mesoporous material. The determined BET surface area decreased for the three materials in the following order: KMG30 > KSORB > KMG70. It has been reported earlier in the literature that the surface areas of the original HTC prior to K2CO3 promotion for KMG30 is higher than for KMG70 [9,20,21]. Since K2CO3 leads to a significant reduction in surface area, one can expect the same order for potassium-promoted materials. However, the measured surface areas reported in the literature do not always show the same trend. This may be caused by different impregnation or calculation methods used. A pore size analysis shows that the pore size of all sorbents is below 40 nm as determined with BHJ method analysis (Fig. 2b). KMG30 has the broadest pore size distribution compared to the other sorbents. From the isotherms it is evident that the pore volume for KMG70 is smallest and about 5 times smaller than for KMG30.

#### 3.2. TGA experiments

##### 3.2.1. CO2 Adsorption experiments

The CO2 cyclic working capacity was determined for the different sorbents using different half-cycle times. It can be seen that for all sorbents the cyclic working capacity can be increased by increasing the half-cycle time (Fig. 3). In general the increase in cyclic working capacity for an increased half-cycle time is a result of more CO2 being desorbed during the regeneration step which was reported earlier for KMG30 [18] and is also valid for the other sorbents, independent of their material composition and difference in morphology. For all sorbents, the cyclic working capacity is nearly doubled when increasing the half-cycle-time up to 600 min. Although 600 min is not a realistic regeneration time for actual applications, the results give an indication on how much the cyclic working capacity could be increased if the regeneration of the sorbent were improved.

During all experiments the sorbents can be sorted according to their

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Mg/Al</th>
<th>Al/K</th>
<th>Mg/K</th>
<th>K$_2$CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic ratio</td>
<td>w%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KSORB</td>
<td>–</td>
<td>5.42</td>
<td>–</td>
<td>20</td>
</tr>
<tr>
<td>KMG30</td>
<td>0.54</td>
<td>3.79</td>
<td>2.06</td>
<td>20</td>
</tr>
<tr>
<td>KMG70</td>
<td>2.95</td>
<td>1.63</td>
<td>4.80</td>
<td>20</td>
</tr>
</tbody>
</table>

The cyclic working capacity was determined for both sorbate species at different conditions according to Eq. (1), where the average of the measured weight change upon adsorption and desorption is divided by the sample mass after pretreatment [18]:

$$c_{w}c = \frac{\Delta m(ads) + \Delta m(des)}{2m_{sample}(pretreated)} \quad (1)$$

#### 3.2.2. CO2 Desorption experiments

The CO2 cyclic working capacity was determined for the different sorbents after desorption experiments at different half-cycle times. It can be seen that for all sorbents the cyclic working capacity can be increased by increasing the half-cycle time (Fig. 3). In general the increase in cyclic working capacity for an increased half-cycle time is a result of more CO2 being desorbed during the regeneration step which was reported earlier for KMG30 [18] and is also valid for the other sorbents, independent of their material composition and difference in morphology. For all sorbents, the cyclic working capacity is nearly doubled when increasing the half-cycle-time up to 600 min. Although 600 min is not a realistic regeneration time for actual applications, the results give an indication on how much the cyclic working capacity could be increased if the regeneration of the sorbent were improved.

During all experiments the sorbents can be sorted according to their

### Table 2

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Temperature °C</th>
<th>Adsorption time min</th>
<th>Desorption time min</th>
<th>Cycles</th>
<th>Adsorption feed</th>
<th>Desorption feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
<td>30</td>
<td>30</td>
<td>20</td>
<td>CO2</td>
<td>N2</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>60</td>
<td>60</td>
<td>20</td>
<td>CO2</td>
<td>N2</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>120</td>
<td>120</td>
<td>10</td>
<td>CO2</td>
<td>N2</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
<td>300</td>
<td>300</td>
<td>10</td>
<td>CO2</td>
<td>N2</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>600</td>
<td>600</td>
<td>5</td>
<td>CO2</td>
<td>N2</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>60</td>
<td>60</td>
<td>5</td>
<td>CO2</td>
<td>N2</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>60</td>
<td>60</td>
<td>5</td>
<td>CO2</td>
<td>N2</td>
</tr>
<tr>
<td>8</td>
<td>400</td>
<td>30</td>
<td>30</td>
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<tr>
<td>9</td>
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<td>60</td>
<td>5</td>
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<td>N2</td>
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<tr>
<td>10</td>
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<td>120</td>
<td>5</td>
<td>H2O</td>
<td>N2</td>
</tr>
<tr>
<td>11</td>
<td>400</td>
<td>300</td>
<td>300</td>
<td>10</td>
<td>H2O</td>
<td>N2</td>
</tr>
<tr>
<td>12</td>
<td>400</td>
<td>600</td>
<td>600</td>
<td>10</td>
<td>H2O</td>
<td>N2</td>
</tr>
<tr>
<td>13</td>
<td>300</td>
<td>60</td>
<td>60</td>
<td>10</td>
<td>H2O</td>
<td>N2</td>
</tr>
<tr>
<td>14</td>
<td>500</td>
<td>60</td>
<td>60</td>
<td>10</td>
<td>H2O</td>
<td>N2</td>
</tr>
</tbody>
</table>
cyclic working capacity in the order of KMG70 > KGM30 > KSORB. According to this, it can be stated that, even if the surface is lowest for KMG70, the highest cyclic working capacity was measured for this sorbent. It is known that the MgO content in the sorbent has a significant influence on the basicity of the material [22], which results in more active adsorption sites for CO2 on a material with a higher MgO content, explaining the obtained results.

We have reported before that usually a higher operating temperature can have a positive effect on the cyclic working capacity for hydrotalcite-based adsorbents due to the increase in the desorption rates at higher operating temperatures [18,23]. We plotted the cyclic working capacity determined for CO2 at different temperatures in Fig. 4 for the different sorbents. It can be seen that for KMG70 the already described trend for KMG30 is confirmed. However, it seems that the cyclic working capacity of CO2 for the potassium-promoted alumina is not increased significantly when increasing the operating temperature.

The reason for this difference is the generally different adsorption and desorption behavior of hydrotalcite-based adsorbents compared to potassium-promoted alumina. From the TGA curves shown in Fig. 5a, it can be seen that for HTC-based adsorbents during the first adsorption cycle, the initially adsorbed amount of CO2 is nearly independent of the operating temperature. However, the amount of CO2 desorbed during the regeneration step is increased at a higher operating temperature, as already indicated. Fig. 5b shows that this is not the case for potassium-promoted alumina. At a lower operating temperature more CO2 is being adsorbed initially, where the adsorption kinetics seem to remain the same, even if the CO2 loading is different (see the small figure inside Fig. 5b). After the first cycle the cyclic working capacity for potassium-promoted alumina remains basically unchanged during the following 10 cycles (Fig. 6), where the cyclic working capacity is slightly higher at lower temperature. One would expect that at higher temperatures less CO2 can be adsorbed due to increasing desorption kinetics (high kinetic energy of gas molecules), which can be seen for the potassium-promoted alumina. It has been reported in the literature that the adsorption of CO2 on potassium-promoted HTC can be described with a bi-Langmuir adsorption isotherm, where both physisorption and chemisorption lead to a similar adsorption capacity at different operating temperature [24].

It is remarkable that during the first adsorption cycle the CO2 adsorption capacity is higher for KSORB than for both HTC based materials at a lower operating temperature. Considering both surface area (adsorption) and bulk basicity one would expect that the HTC based adsorbent would show a higher adsorption capacity. One explanation could be that at lower temperature condensation of CO2 could occur in the very small pores of the potassium-promoted alumina. The theory of a possible condensation of CO2 in nanopores was reported earlier in the literature [25] and could be an explanation for the obtained behavior, since KSORB has the lowest a mean pore diameter of around 10 nm (see Fig. 2b) compared to KMG30 and KMG70. This could explain why pore condensation only occurs for this material or contributes more to the adsorption mechanism. Another reason can be that the integration of K2CO3 species in the HTC-based adsorbents is different. Adsorption sites on KSORB, created by K2CO3 impregnation, are available on the surface and therefore strongly dependent on the surface coverage, whereas for the HTC-based adsorbent CO2 is also bond by a reaction. It has been reported in the literature that the adsorption of CO2 on potassium-promoted HTC can be described with a bi-Langmuir adsorption isotherm, where both physisorption and chemisorption lead to a similar adsorption capacity at different operating temperature [24].
reported that needle shaped crystals on the surface of an adsorbent have been identified as K$_2$CO$_3$ using SEM-EDX and have been found on potassium-promoted alumina to a higher extent than on potassium-promoted HTC [12].

Adsorption and desorption kinetics are very important for the efficiency of the used sorbents especially when using them in cyclic experiments. A comparison of the normalized kinetics of the different sorbents with respect to the total adsorbed mass during the adsorption cycle of 300 min are plotted in Fig. 7. It can be seen that the potassium-promoted alumina has a very fast initial adsorption rate, where equilibrium seems to be established after about 8000 s. The HTC-based sorbents also exhibit a very fast initial adsorption rate, however at approximately 80% normalized weight change a very marked decrease in adsorption rate is observed, followed by a relatively constant but slow adsorption rate. For HTC-based materials this slow adsorption rate contributes to a much larger extent to the total CO$_2$ adsorption capacity. A higher MgO content seems to enhance this effect, which can be explained by a slow reaction of MgO sites with CO$_2$. It has been reported that potassium-promoted HTC can form bulk MgCO$_3$ under higher partial pressures of CO$_2$ and H$_2$O. At low pressure and dry adsorption conditions a possible explanation of the observed behavior could be the migration of adsorbed CO$_2$ on the surface to highly basic adsorption sites in the bulk of the material. It was reported in the literature for a similar material as KMG70 that different adsorption steps (from fast adsorption to diffusion of gaseous CO$_2$ to finally chemisorption in basic sites) can explain the adsorption kinetics on this type of sorbents [26]. During the desorption step this slowly adsorbed CO$_2$ seem to be desorbed quite fast, indicated by the faster relative desorption kinetics for KMG70 compared to KMG30 and the potassium-promoted alumina (KSORB). With two independent reaction mechanisms involved in the HTC-based materials compared to one single adsorption site for KSORB the obtained results for both adsorption and desorption can be described. It was already reported that promotion with potassium increases the amount of basic sites available for HTC and alumina, where alumina itself does not show any significant CO$_2$ adsorption capacity [12]. It was concluded that especially the interactions between K$_2$CO$_3$ and the aluminum centers play a crucial role in the creation of basic adsorption sites [12].

3.2.2. H$_2$O adsorption experiments

Similar to CO$_2$, the influence of the half-cycle-time on the cyclic working capacity of H$_2$O on the different adsorbents was investigated at 400 °C and $P_{CO_2} = 0.34$ bar during the adsorption step. It can be seen from Fig. 8 that KMG30 has the highest cyclic working capacity for H$_2$O followed by KMG70 and KSORB. Considering only the available surface area, one would expect KSORB to show a higher cyclic working capacity for H$_2$O than KMG70. However, when considering the surface

Fig. 5. a) mass change during the first cycle for HTC-based adsorbents; b) mass change for the potassium-promoted alumina during the first cycle with a close-up of the desorption step if the initial weight is set to 0 after the adsorption step to compare the desorption kinetics.

Fig. 6. Adsorption and desorption capacities for KSORB at different temperatures during 10 adsorption/regeneration cycles $P_{CO_2} = 1$ bar during adsorption and $P_{N_2} = 1$ bar during regeneration.

Fig. 7. a) Normalized adsorption kinetics for different adsorbents at 400 °C and $P_{N_2} = 1$ bar for 300 min half-cycle time b) normalized desorption kinetics for different adsorbents at 400 °C and $P_{N_2} = 1$ bar for 300 min half-cycle time.
Basicity and the difference in the materials one can understand that the HTC-based adsorbents show a higher cyclic working capacity for H₂O, since stronger sites are available. Surface basicity becomes very important at higher operating temperatures during adsorption (greater ratio of gas phase molecules and shorter residence time of gas molecules on the surface). In this case, a simple physisorption mechanism for the adsorption is not able to explain the experimental results. However, the fact that the order in highest cyclic working capacity is changed for H₂O confirms that the mechanism for adsorption is different from the mechanism for CO₂ [18].

Similar to CO₂, the cyclic working capacity for H₂O is determined by the relatively slow desorption kinetics. Therefore, an increase in half-cycle-time leads to an increase in cyclic working capacity. However, this increase is less significant for H₂O than for CO₂. One reason for this observed behavior can be found in the normalized adsorption and desorption kinetics of H₂O with respect to the total adsorbed/desorbed amount of H₂O within one step. It can be seen from Fig. 9 that the adsorption of H₂O is extremely fast and reaches adsorption equilibrium even within a very short time. It seems that the adsorption kinetics are the same for the different materials. This suggests that only surface adsorption is taking place on different types of basic sites without any bulk diffusion or reaction like it was observed for CO₂. The same observation can be made for the desorption step (Fig. 9b), where the normalized adsorption kinetics are similar for the different materials. Comparing the desorption kinetics of H₂O (Fig. 9b) to CO₂ (Fig. 7b) it becomes clear that H₂O desorbs much faster and thus an increase in half-cycle-time leads to a less pronounced increase in cyclic working capacity.

Increasing the operating temperature leads to a decrease in cyclic working capacity for H₂O (see Fig. 10) contrary to the observations for CO₂. The differences in cyclic working capacity regarding the different sorbents decrease at higher operating temperatures. It was observed for experiments at higher operating temperatures that during the first few adsorption cycles, the sorbents KMG70 and especially KSORB show a weight decrease in mass after the first rapid increase which was attributed to the desorption of CO₂ due to the presence of steam on the sorbent.

This observed weight loss can be seen in Fig. 11 for the sorbent KSORB and KMG70. For KSORB it can be seen that the during the first adsorption cycle a strong decrease in mass is detected at 500 °C. For KMG70 this weight decrease is less prominent at 500 °C, but it is visible during the following cycles. Both sorbents only show the described behavior if the temperature is increased (> 400 °C). It can be seen that this effect was not observed in the experiments at 300 °C. Since the desorption kinetics (for the experiments at 500 °C) remain unchanged during the cycles it can be concluded that most probably the sorbent releases CO₂ due to the exposure to H₂O at a high operating temperature. We have reported that for potassium-promoted HTC (KMG30) an adsorption site exists which is can be occupied by either CO₂ or H₂O, where one component replaces the other [23]. The existence of this type of site on KMG70 and KSORB could explain the described results. In order to confirm this hypothesis TGA-MS and TGA-TPD were carried out to study this effect and the influence of H₂O on the cyclic working capacity of CO₂.

**Fig. 8.** H₂O cyclic working capacity at different half cycle times at 400 °C P_H₂O = 0.34 bar during adsorption and P_N₂ = 1 bar during the regeneration step.

**Fig. 9.** a) Adsorption kinetics for H₂O at 400 °C for the experiment with 300 min half-cycle time at P_H₂O = 0.34 bar, b) desorption kinetics for H₂O at 400 °C for the experiment with 300 min half-cycle time at P_N₂ = 1 bar.

**Fig. 10.** Cyclic working capacity for different sorbents at different operating temperatures (300–500 °C) at P_H₂O = 0.34 bar during the adsorption and P_N₂ = 1 bar during the regeneration for experiments with a half-cycle-time of 60 min.
3.3. TGA-DSC and TGA-MS

The normalized weight change for the different sorbents and reactor temperature during the TGA-TPD experiment are plotted in Fig. 12a (for a detailed description of the procedure see Section 2), while Fig. 12b shows the mass change during the steam adsorption and TPD during steps 2 and 3 in more detail. In order to compare the weight change in the different sorbents, the initial mass was set to 0 after the pretreatment and both x- and y-axes were set to 0 at the start of the adsorption at 300 °C. After H2O adsorption at 300 °C, all sorbents are losing weight during the increase in temperature to 850 °C. Where KMG30 shows a more or less linear weight loss during the linear increase in temperature, for KSORB at about 500 °C a strong decrease in weight is observed, while at even higher temperatures the weight loss is linear with the increase in operating temperature. For KMG70 the strong weight loss occurs at a higher temperature (about 650 °C, Fig. 12b) and continues until the final temperature of 850 °C is reached. At the end of the adsorption step only a small amount of H2O is left on the sorbent, which is basically the same for all sorbents. This can be seen in the following desorption step, where for all sorbents the same mass decrease is detected upon changing the feed gas from H2O/N2 to N2. It is expected that some of the previous adsorbed H2O desorbs when the temperature is raised due to an increase in the desorption rate shifting the equilibrium constant for H2O. Regarding the linear weight the temperature is raised due to an increase in the desorption rate loss rate of the diadsorption at 300 °C. After H2O adsorption at 300 °C, all sorbents are pretreatment and both x- and y-axes were set to 0 at the start of the change in the diadsorption during steps 2 and 3 in more detail. In order to compare the weight change in the different sorbents, the initial mass was set to 0 after the pretreatment and both x- and y-axes were set to 0 at the start of the adsorption at 300 °C. After H2O adsorption at 300 °C, all sorbents are losing weight during the increase in temperature to 850 °C. Where KMG30 shows a more or less linear weight loss during the linear increase in temperature, for KSORB at about 500 °C a strong decrease in weight is observed, while at even higher temperatures the weight loss is linear with the increase in operating temperature. For KMG70 the strong weight loss occurs at a higher temperature (about 650 °C, Fig. 12b) and continues until the final temperature of 850 °C is reached. At the end of the adsorption step only a small amount of H2O is left on the sorbent, which is basically the same for all sorbents. This can be seen in the following desorption step, where for all sorbents the same mass decrease is detected upon changing the feed gas from H2O/N2 to N2. It is expected that some of the previous adsorbed H2O desorbs when the temperature is raised due to an increase in the desorption rate shifting the equilibrium constant for H2O. Regarding the linear weight loss of KMG30 one would expect that only water is desorbing form the surface of potassium-promoted HTC, which results in an increase in desorption rate at 870 °C. The activation energy for K2CO3 decomposition resulting in a decomposition at much lower temperatures than under dry conditions. The activation energy for K2CO3 decomposition on KGM70 seems to be higher compared to KSORB resulting in the decomposition of these species at a higher temperature. The fact that KMG30 does not show K2CO3 decomposition at higher temperature could be explained with a different incorporation of K2CO3 into the structure of KMG30. It was also reported in the literature, that a very high surface area of the sorbent before impregnation can lead to a better incorporation of K2CO3 into the sorbent structure [27]. Our BET measurements are in line with this hypothesis showing that KMG30 indeed has a high surface area compared to the other two materials after K2CO3 impregnation.

After the treatment with steam, the CO2 cyclic working capacity of the different materials is significantly reduced (Fig. 14). Where the cyclic working capacity for KMG30 is reduced by 50%, KMG70 has only 21% of its capacity compared to the normal pretreatment. A possible explanation could be a significant loss of surface area due to the high temperature (agglomeration of metal species), which could however be excluded for KMG70. It can be seen from Fig. 15a that the N2 adsorption isotherms are quite similar for KMG70 before and after TGA-TPD. The surface area of KMG70 is higher after the experiment in the TGA. It has been reported that CO2 desorption is creating “vent holes” in the surface of potassium-promoted HTC, which results in an increase in surface area [28]. Al-spinel formation after the steam treatment at higher temperatures which could explain the reduction in available surface sites for KMG70, could not be detected using XRD with a closed sample holder (to avoid exposure to humidity and CO2 from the lab atmosphere) (see Fig. 15b). It was reported that steam aging leads to the formation of MgO and Al spinel which reduces the number of basic sites for a HTC similar to KMG70 (without K2CO3 promotion) [29]. However, both recorded XRD spectra show only MgO as detectable crystalline phase of KMG70 before and after the TPD experiment.
Additionally, the potassium promoted Alumina did not show a high loss in sorption capacity, where Mg-Al spinel formation can be excluded due to the absence of Mg in the material. Spinell formation does not explain the obtained results during this study. Irreversible decomposition of the potassium carbonate species and possible interaction with Al and Mg under the presence of steam at high temperature resulting in a significant loss of basic sites available for cyclic CO₂ adsorption is therefore an explanation for the obtained results.

It is very important regarding the use of potassium-promoted sorbent for SEWGS and other applications at elevated temperatures, that the temperature for decomposition of potassium carbonate can be significantly reduced by the presence of steam and this should be avoided in order to prohibit the deactivation of the sorbent. This shows the importance of not only studying the CO₂ adsorption capacity at ideal conditions, but to also consider conditions outside the direct process window. Considering the findings during this study, KMG30 was found to be the best candidate for SEWGS applications regarding the stability of the sorbent and the relatively high cyclic working capacity for CO₂.

4. Conclusions

The CO₂ and H₂O cyclic working capacity was determined for three sorbents with different material compositions for their use in sorption-enhanced water-gas shift processes at a temperature range between 300 and 500 °C. The potassium-promoted hydrotalcite based adsorbent with a high MgO content shows a higher cyclic working capacity for CO₂ at different operating temperatures. More and stronger bulk basic sites are responsible for this increase in cyclic working capacity. For all sorbents the desorption step is limiting the cyclic working capacity due to slower desorption kinetics, which determines the amount of CO₂ that can be adsorbed in the subsequent adsorption step. HTC-based adsorbents exhibited different adsorption kinetics compared to potassium-promoted alumina. After the first fast initial adsorption of CO₂ a sorbent with a higher MgO content adsorbs a larger amount of CO₂ slowly which could be caused by slow formation of bulk carbonates. During a desorption step with N₂ the additionally adsorbed CO₂ can be desorbed relatively fast compared to the slow adsorption. Probably two different independent surface reactions are responsible for this behavior caused by MgO in the sorbent structure. The adsorption and desorption kinetics of H₂O are similar for all sorbents independent of their material composition. A combination of a high surface area and the strength of basic sites could explain that the HTC-based materials show the highest cyclic working capacity for H₂O at three different operating conditions. The presence of steam at high operating temperature can lead to the irreversible decomposition of surface carbonates resulting in a strong decrease in CO₂ cyclic working capacity of the sorbent. It was found that steam seems to be able to reduce the temperature when the.
decomposition of these carbonates occurs. For the use of these sorbents in sorption-enhanced water-gas shift processes this observation is of major importance regarding the selection of the sorbent and optimization of the process conditions. The potassium-promoted HTC KMG30 thus seems to be the best candidate for sorption-enhanced water-gas shift processes.

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