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An in-situ IR study on the adsorption of CO₂ and H₂O on hydrotalcites

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ABSTRACT

In-situ IR technique was used to study the reversible adsorption of CO₂ and H₂O at elevated temperatures on a potassium-promoted hydrotalcite for its use in sorption-enhanced water-gas shift (SEWGS). It was found that mainly bidentate carbonate species are responsible for the reversible (cyclic) adsorption capacity of the sorbent. The presence of H₂O can enhance the decomposition of bidentate carbonates bond to the stronger basic surface-sites. The basic strength of the involved adsorption sites for bidentate formation appears to be highly heterogeneous. At higher operating temperatures, reversible formation of bulk carbonates seem to participate in the reversible adsorption for CO₂. The presence of H₂O on the sorbent can lead to the formation of bi-carbonate, especially at lower operating temperatures of 300 °C. The transient absorbance of the main absorption bands for carbonate species identified during this study can be used in the development of a detailed description of the reversible adsorption/desorption kinetics reported before using thermogravimetric analyses.

1. Introduction

Hydrotalcites and hydrotalcite-based materials are widely used in several base-catalyzed reactions such as self-condensation and the cross-adol condensation of aldehydes and ketones owing to their basic properties [1]. Hydrotalcite-based materials can also adsorb large quantities of CO₂ in a wide range of temperatures and pressures [2]. Recently, potassium promoted hydrotalcite has been investigated as a potential catalytic adsorbent in the sorption-enhanced water-gas shift (SEWGS) reaction. In SEWGS, CO₂ adsorption to a solid material shifts the equilibrium of the water-gas shift (WGS) reaction, so that a high concentration of hydrogen can be obtained. SEWGS is typically carried out between 350 and 550 °C and allows converting a mixture of CO and water into a nearly pure hydrogen stream [3].

The general formula of hydrotalcite is M₁₋ₓM’ₓ(OH)₂(Al³⁺O²⁻)ₓ/n•mH₂O, where M²⁺ is a divalent cation, such as Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Cu²⁺, Ni²⁺, Zn²⁺, or Ca²⁺, whereas M’¹⁺ is a tri-valent cation, such as Al³⁺, Cr³⁺, Mn³⁺, Fe³⁺, Co³⁺, or La³⁺, and A²⁻ is an anion [4]. The most common stoichiometry for hydrotalcite is Mg₆Al₂(OH)₁₆CO₃·4H₂O, where the molar ratio of Mg/Al normally varies between 1.7 and 4 [5]. A higher Mg/Al ratio can be beneficial for the adsorption of sour gases because of their higher basicity [6]. On the other hand, mechanical stability issues have been reported for Mg-rich potassium-promoted hydrotalcites due to the formation of MgCO₃ at high partial pressures of CO₂ and H₂O [7–9].

The basicity of hydrotalcite-based adsorbents can be further improved by promotion with alkaline anions [9]. It has been frequently reported that K₂CO₃ promotion can increase the sorption capacity of CO₂ [10–12]. Another important aspect is that the initial layered structure of the anionic clay disappears when the material is heated at elevated temperatures. During the heating process the original brucite structure changes to a Mg(Al)Oₓ mixed metal oxide, releasing CO₂ and H₂O [6,13]. Typical calcination temperatures for hydrotalcites in air after K₂CO₃ promotion are between 673 and 773 K. Higher calcination temperatures can lead to irreversible decomposition of potassium carbonate species, resulting in a lower cyclic working capacity of the adsorbent [11].

Potassium-promoted hydrotalcite sorbents will be exposed to high partial pressures of CO₂ and H₂O (in the order of up to 20 bar of H₂O and CO₂) during their use for SEWGS [14–18]. Therefore, the adsorption and desorption for CO₂ and H₂O adsorption was investigated in the past for a commercially available potassium-promoted hydrotalcite. A complex mechanism was postulated to describe the influence of H₂O on the cyclic working capacity of CO₂ and vice versa [19]. It has been found that at least four different sites are needed to describe the performed thermogravimetric (TGA) and packed-bed reactor (PBR) reactor experiments. However, in which way CO₂ and H₂O are adsorbed by the material and chemically bond to it, is not fully understood yet. Different characterization methods were used in the past to investigate the sorption mechanism of CO₂ on hydrotalcite based materials. X-ray diffraction has been used in various studies to investigate the phases being formed in the material due to the incorporation of CO₂ in its structure [20–23]. However, characterization of the adsorbent is not

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fully representative, because exposure to ambient will lead to take up of CO2 and H2O from the atmosphere. In situ-measurements have shown the formation of Dawsonite (KAl(CO3)(OH)2) at temperatures below 300 °C for potassium-promoted alumina at high partial pressures of CO2 and H2O [24]. For hydrotalcites, the formation of bulk MgCO3 has been reported, which is unwanted [7-9]. X-ray diffraction is not suitable to study the sorption of CO2 and H2O as the material is poorly crystalline [25]. FTIR has been frequently used to investigate carbonate species present in hydrotalcites [11,23,26-28]. Du et al. reported that CO2 reversibly forms unidentate, bidentate and bridged carbonate species, with the formation of bidentate carbonate species being favored at short CO2 exposure times. The very slow adsorption and desorption properties of CO2 were assigned to the formation of bulk polydentate carbonates [27]. Bidentate carbonates have been identified as one of the major carbonate species relevant for the CO2 adsorption mechanism [11], although others have underlined the importance of unidentate carbonate species formed by adsorption of CO2 on strong basic sites [23]. In order to investigate the desorption of CO2 and the decomposition of carbonate species, the sorbent is usually exposed to CO2 at low temperature followed by heating to study desorption. A study where the sample is exposed to CO2, H2O and their mixtures as relevant for SEWGS applications and necessary to further investigate the adsorption mechanism is lacking [23,26,29].

In the recent literature, different hydrotalcites and mixed metal oxides were investigated using IR-spectroscopy to determine mainly the different basic strengths of the sites involved in the CO2 capture mechanism. The basic strength of an adsorption site can depend on the coordination degree of the surface oxygen atoms. The main species formed upon CO2 adsorption reported are chelating or bridging bidentate carbonates, monodentate carbonates, hydrogen carbonates and CO2 linear coordinated on M++ sites [26] and are depicted in Fig. 1. The presence of different carbonate species can lead to the need of multiple adsorption sites, if the adsorption and desorption of CO2 on these types of sorbents is going to be modeled.

It has been reported in the literature, that the free carbonate in D3h symmetry has an active IR band at 1415 cm⁻¹ (asymmetric ν(CO) vibration). In the adsorbed state the symmetry is lowered and the species formed are usually presented by two ν(CO) bands on both sides of the wavenumber of 1415 cm⁻¹. The distance between both bands on each site of the wavenumber 1415 cm⁻¹ is usually reported as Δν3 splitting [30], which is considered to be a measure of the basic strength of the sites available on the sorbent. A smaller splitting represents stronger basic sites, where unidentate (Δν3 = 100 cm⁻¹), bidentate (Δν3 = 300 cm⁻¹) and bridged species (Δν3 = 400 cm⁻¹) are assigned to be representative carbonate species [30]. In general, different authors in the literature have assigned different carbonate species on potassium-promoted hydrotalcites according to the Δν3-splitting measured in the experiments. However, it is reported that a low Δν3-splitting can also indicate the presence of polydentate (very similar to bulk carbonate). It has also been mentioned that a unidentate carbonate would already decompose at relatively low operating temperature (< 150 °C), whereas polydentate is more thermally stable [11,30,31]. Therefore, it is important to consider both the Δν3-splitting and the operating temperature.

In this work, an in-situ FTIR study was performed on potassium-promoted hydrotalcites under a controlled atmosphere close to SEWGS process conditions relevant for the cyclic exposure to CO2, H2O and mixtures of CO2 and H2O at elevated temperatures between 300 and 500 °C. This allows the validation of the proposed mechanism of adsorption of CO2 and H2O on potassium promoted hydrotalcites.

2. Experimental

The potassium-promoted hydrotalcite sample (KMG30) with a MgO/Al2O3 ratio of 0.54 and about 20w% of K2CO3 from SASOL, which was already characterized in a previous work [25], was pretreated prior to FTIR measurements at 600 °C in N2 for two hours to desorb previously adsorbed CO2 and H2O from the atmosphere. After the pretreatment around 8 mg of sample was pressed into a self-supporting wafer, which was subsequently placed in the sample holder. After introducing the sample holder in the measuring cell of the FTIR the experimental procedure was started.

In-situ FTIR measurements were performed in a Bruker Vertex 70v FT-IR-spectrometer. The closed measuring cell is used with CaF2-windows and the cell walls were heated with an external temperature controller to 70 °C to prevent water condensation on the cell-walls. The sample temperature is controlled and can be increased to a maximum temperature of 550 °C. A manifold was connected to two Brooks mass flow controllers (MFC) for CO2 and N2 with a maximum flow rate of 280 Nl/min. The effective pressure between MFC and the cell was set to 0.6 bar (g). Another MFC for N2 with a maximum flow rate of 200 Nl/min was connected to a saturator. The saturator bottle was filled with H2O and immersed in a temperature controlled bath, which was kept at a constant temperature of 50 °C. The N2 gas stream was humidified by passing through the water bottle. All gas lines after the humidifier were traced and heated to above 80 °C to avoid water condensation in the gas lines. Valves V4, V6 and V7 (Fig. 2) were software controlled to prepare...
different gas mixtures, which were sent to the measuring cell of the FTIR. Dry gases as N₂ and CO₂ were dosed via the manifold, whereas the humidified gas stream was mixed with the dry gas stream behind the manifold. A check-valve was installed to prevent the humid gas stream entering the manifold. A saturated gas stream of N₂ at 50 °C was constantly produced and either bypassed or sent to the IR-Cell by switching V7-A/V7-B (resulting in a constant saturation of the N₂ stream). Fig. 2 shows a PFD of the setup used for the FTIR measurements.

The reactant gas was injected into the cell close to the sample as indicated in Fig. 2. The flow rates for the different mass flow controllers are chosen in such a way that the maximum possible flow rate is used in order to keep the gas phase transition in the cell as short as possible (to prevent slow mixing and therefore possible effects on the adsorption/desorption of sorbate species). The MFC's were calibrated previously to the experiments using a Definer H-220 to ensure accurate gas dosing under the chosen inlet pressure of the MFC’s. The steam content was calculated to be 5%, mixing a dry gas stream (280 ml/min) of CO₂ and N₂ with 195 ml/min of N₂ saturated with water at 50 °C (PH₂O = 0.122 bar). The steam content could not be increased due to limitations of the experimental setup (avoiding condensation of steam on the IR cell walls and windows). Table 1 shows the carefully designed measurement sequence containing multiple experiments programmed using in-house designed software. Each experiment took 25 min and was divided in 5 sub-segments of 5 min at constant gas flow rate. Every 5 min during a certain experiment, an IR-spectra between 600 and 4000 cm⁻¹ was recorded.

In order to be able to follow the changes on the material during in situ IR, blank measurements have been carried out to measure the absorbance of the gas phase which was used later to correct the recorded spectra with the solid sample. Therefore, three measurements of each gas composition (gas compositions from Table 1, EXP 2, 3, 9 and 21) were carried out. Prior to the blank measurements, the cell was purged with the desired gas composition for 25 min. In order to improve the accuracy, the blank procedure was carried out twice. Blank measurements were conducted for 300, 400 and 500 °C at identical conditions as for the experiments. Five spectra were recorded for each concentration with a 25 min of N₂ purge in between the measurements.

3. Results and discussion

3.1. Background gas-phase spectra

Recorded spectra for three different gas phase compositions, viz. CO₂/N₂, H₂O/N₂ and CO₂/H₂O/N₂ as listed in Table 1, are shown in Fig. 3. Typical absorption bands for CO₂ are located at 2300 cm⁻¹ corresponding to the asymmetric stretching mode of CO₂ and small peaks in the range 3600–3800 cm⁻¹ corresponding to combination bands [32]. For gaseous water two broad bands at around 1600 cm⁻¹ and 3600 cm⁻¹ are visible. The band at 1600 cm⁻¹ is divided into multiple small bands, corresponding to the bending mode of H₂O, whereas the other branches at 3600 cm⁻¹ correspond to the symmetric and antisymmetric stretching mode of H₂O [32]. It was ensured that subtraction of a single gas spectrum (CO₂/N₂ or H₂O/N₂) from a mixed gas spectrum (CO₂/H₂O/N₂) would result in the same spectrum measured previously for the remaining gas phase (Fig. 3b). Based on this test it was concluded that indeed a gas phase correction is possible under the selected conditions.

An example for the background gas-phase correction is plotted in Fig. 4, showing the uncorrected spectrum, the spectrum after subtracting the IR spectrum of the same sample before CO₂ adsorption and the corrected spectrum obtained by subtracting the contribution of gaseous CO₂ in order to evaluate the changes at the sorbent surface during adsorption/desorption of CO₂, H₂O.

3.2. Pretreatment of KMG30

To qualify the changes in KMG30 during pretreatment, spectra were recorded prior to pretreatment at room temperature under N₂ atmosphere and after pretreatment (EXP1, Table 1) at an operating temperature of 400 °C. It can be seen (Fig. 5a) that the background absorption of the IR is reduced which can be explained that one background is recorded at 50 °C and the other at 400 °C leading to an absolute change in absorbance. The broad absorption band at 3300 cm⁻¹ together with the shoulder at 1650 cm⁻¹ disappeared during the heating process to 550 °C during the pretreatment (Step 1, Table 1). The two bands at 1500 cm⁻¹ and 1400 cm⁻¹ and the band at 1100 cm⁻¹ also appear less intense.
The disappearance of the broad peak around 3300 cm⁻¹ is caused by desorption of H₂O from the sample. Bands at 3400 cm⁻¹ are typically for symmetric O−H stretching and at 3506 cm⁻¹ for asymmetric O−H stretching. Various carbonate species such as free carbonate anion (hydroxyl carbonate) and unidentate and bidentate carbonate species decompose resulting in reduced absorbance in the 1400–1500 cm⁻¹ range and at 1100 cm⁻¹ [29,33]. These changes are consistent with the reported release of H₂O and CO₂ during pretreatment by TGA and TGA-MS [25]. Despite the release of CO₂, the IR spectrum shows that some carbonate species persist after the pretreatment procedure. Based on the low Δν₃-splitting (150 cm⁻¹) for the two remaining absorption bands at 1535 and 1380 cm⁻¹ and the high thermal stability of the remaining carbonates, we conclude that these are strongly bound bulk or polydentate carbonate species [11,30,31,33]. The small remaining band at 3500 cm⁻¹ (Fig. 5b) reveals that still small number of OH-groups are present on the sorbent surface after the pretreatment.

### Table 1

Experimental procedure used for the in-situ FTIR study, which was carried out at three different operating temperatures (300, 400 and 500 °C). The table shows the procedure for 400 °C.

| EXP | TEMP °C | Time Min | Gas feed – | P N₂ bar | P CO₂ bar | P H₂O bar |
|-----|---------|----------|------------|----------|-----------|-----------|
| 1   | 550     | 120      | N₂         | 1.00     |           |           |
| 2   | 400     | 25       | N₂         | 1.00     |           |           |
| 3   | 400     | 25       | N₂/CO₂     | 0.50     | 0.50      |           |
| 4   | 400     | 25       | N₂         | 1.00     |           |           |
| 5   | 400     | 25       | N₂/CO₂     | 0.50     | 0.50      |           |
| 6   | 400     | 25       | N₂         | 1.00     |           |           |
| 7   | 400     | 25       | N₂/CO₂     | 0.50     | 0.50      |           |
| 8   | 400     | 25       | N₂         | 1.00     |           |           |
| 9   | 400     | 25       | N₂/H₂O     | 0.95     | 0.05      |           |
| 10  | 400     | 25       | N₂         | 1.00     |           |           |
| 11  | 400     | 25       | N₂/H₂O     | 0.95     | 0.05      |           |
| 12  | 400     | 25       | N₂         | 1.00     |           |           |
| 13  | 400     | 25       | N₂/CO₂     | 0.50     | 0.50      |           |
| 14  | 400     | 25       | N₂         | 1.00     |           |           |
| 15  | 400     | 25       | N₂/H₂O     | 0.95     | 0.05      |           |
| 16  | 400     | 25       | N₂         | 1.00     |           |           |
| 17  | 400     | 25       | N₂/CO₂     | 0.50     | 0.50      |           |
| 18  | 400     | 25       | N₂         | 1.00     |           |           |
| 19  | 400     | 25       | N₂/H₂O     | 0.95     | 0.05      |           |
| 20  | 400     | 25       | N₂         | 1.00     |           |           |
| 21  | 400     | 25       | CO₂/H₂O    | 0.45     | 0.50      | 0.05      |
| 22  | 400     | 25       | N₂         | 1.00     |           |           |
| 23  | 400     | 25       | N₂/H₂O     | 0.95     | 0.05      |           |
| 24  | 400     | 25       | N₂         | 1.00     |           |           |
| 25  | 400     | 25       | CO₂/H₂O    | 0.45     | 0.50      | 0.05      |
| 26  | 400     | 25       | N₂         | 1.00     |           |           |
| 27  | 400     | 25       | N₂/H₂O     | 0.95     | 0.05      |           |
| 28  | 400     | 25       | CO₂/H₂O    | 0.45     | 0.50      | 0.05      |
| 29  | 400     | 25       | N₂/H₂O     | 0.95     | 0.05      |           |
| 30  | 400     | 25       | CO₂/H₂O    | 0.45     | 0.50      | 0.05      |
| 31  | 400     | 25       | N₂/H₂O     | 0.95     | 0.05      |           |
| 32  | 400     | 25       | N₂         | 1.00     |           |           |
| 33  | 400     | 25       | CO₂/H₂O    | 0.45     | 0.50      | 0.05      |
| 34  | 400     | 25       | N₂/CO₂     | 0.50     | 0.50      |           |
| 35  | 400     | 25       | CO₂/H₂O    | 0.45     | 0.50      | 0.05      |
| 36  | 400     | 25       | N₂/CO₂     | 1.00     |           |           |
| 37  | 400     | 25       | N₂         | 1.00     |           |           |

3.3. Adsorption of CO₂ and desorption with N₂

Fig. 6a shows the changes in the IR spectrum upon exposure of the pretreated sample to CO₂ at 400 °C between 1000 and 1900 cm⁻¹, since only visible changes in the IR-spectra were detected in this region. Exposure to CO₂ increases the intensity of the bands at 1570, 1340 and 1060 cm⁻¹. The most prominent increase is observed in the first 5 min followed by a slower increase during the total exposure of 20 min. These kinetics are in keeping with the CO₂ uptake observed in TGA-MS studies [19].

Upon exposure to N₂ for 25 min (Fig. 6b) the absorption bands at 1570 cm⁻¹, 1340 cm⁻¹ and 1060 cm⁻¹ decrease again. Not all CO₂ adsorbed in step 3 can be desorbed under these conditions. The decreased Δν₃-splitting can be attributed to the heterogeneity in CO₂ binding. That is to say, during CO₂ desorption first relatively weakly adsorbed CO₂ is released followed by stronger bound CO₂. Based on the Δν₃-splitting of 235 cm⁻¹ (after CO₂ adsorption) and 220 cm⁻¹ (after desorption of CO₂ with N₂), we can conclude that mainly bidentate carbonate species are formed during the adsorption of CO₂ on KMG30, as unidentate carbonate species are usually not stable at 400 °C [31].
According to the literature, most probably chelating bidentate or bridged carbonate structures are present under these conditions ($\Delta \nu_3 < 250 \text{ cm}^{-1}$) [11,30,31]. The band CO$_2$ at 1060 cm$^{-1}$ becomes slightly IR-active upon CO$_2$ adsorption for various carbonate species as unidentate and bidentate [23,30].

Comparing the spectra after adsorption of CO$_2$ after the second adsorption cycle with the first adsorption cycle (Fig. 6c, EXP5), some differences can be seen. The total absorbance is increased compared to the first cycle. It is known that a steady state between adsorption and desorption is established after a certain number of cycles [25]. Therefore, the increased absorbance is attributed to a higher loading of CO$_2$ in the form of carbonate species. Again, an increase in $\Delta \nu_3$-splitting (235 cm$^{-1}$) can be obtained from Fig. 7 indicating the reversible formation of weaker bond bidentate.

Fig. 5. Spectra recorded before and after the pretreatment. Assignments of absorption bands before (a) and after (b) pretreatment of KMG30.

Fig. 6. a) Spectra recorded at different times during the first adsorption of CO$_2$ at 400 °C (EXP3) b) Spectra recorded at different times during desorption of CO$_2$ with N$_2$ at 400 °C (EXP4) c) Spectra recorded at different times during the second adsorption cycle of CO$_2$ at 400 °C (EXP5).
3.4. Adsorption of CO₂ and desorption with H₂O

The IR spectra during adsorption of H₂O during experiment 9 is plotted in Fig. 8a, together with the last recorded spectrum of experiment 8 as reference (time zero). A broad absorption band at 3500 cm⁻¹ and a small increase in the absorption band at 1430 cm⁻¹ is visible in this step (Step 9, feed of N₂ and H₂O). The broad band at 3500 cm⁻¹ can be assigned to the adsorption of H₂O (symmetric and asymmetric O–H stretching) on the sorbent.

The absorbance of the absorption bands at 1565, 1365 and 1060 cm⁻¹ strongly decreases, which can be attributed to the decomposition of bidentate carbonate upon exposure to H₂O and N₂. The maximum of the absorption bands are shifted (1565 → 1550 cm⁻¹, 1350 → 1365 cm⁻¹) during this experiment, similar to the desorption step of CO₂ with N₂. The further decrease in Δν₃-splitting (indicated by the shift in the maximum of the absorption bands) to 185 cm⁻¹ (Fig. 7) indicates that the CO₂ desorbed from the sorbent during this step was indeed strongly bound, confirming our hypothesis, that very heterogeneous sites are present on the sorbent for CO₂ adsorption. It seems that adsorbed H₂O can reduce the amount of available strong basic adsorption sites for CO₂ and therefore initiating the decomposition of stronger bond carbonate species. This explains the decrease in desorption rate because the remaining carbonate species on the material were formed on more basic sites (for both desorption with N₂ and desorption with H₂O). Again the major decomposition of carbonate takes place during the first 5 min as reported earlier using TGA [19]. In contrast to the desorption with N₂ where both absorption bands were decreasing in the same way, in case of H₂O being present, the band at 1550 cm⁻¹ has decreased significantly more and a small shoulder at 1490 cm⁻¹ becomes visible. The shape of the remaining bands (similar to the remaining carbonates after the pretreatment) indicates that some bulk carbonate or polydentate and additionally some bicarbonates (band at 1490 cm⁻¹) are formed.

If the material is exposed to N₂ during experiment 10 (Fig. 8b), only a small decrease of the absorption band at 3500 cm⁻¹ can be observed, whereas the other bands seem to remain nearly unchanged. If CO₂ is fed again to the material, the bands at 3500 and 1430 cm⁻¹ can be observed, whereas the bands at 1550, 1365 and 1060 cm⁻¹ are increasing. If the material is exposed to N₂ during experiment 10 (Fig. 8b), only a small decrease of the absorption band at 3500 cm⁻¹ can be observed, whereas the other bands seem to remain nearly unchanged. If CO₂ is fed again to the material, the bands at 3500 and 1430 cm⁻¹ can be observed, whereas the bands at 1550, 1365 and 1060 cm⁻¹ are increasing.
These results show that during the CO2 adsorption additional H2O is desorbed. It was already reported, that adsorption of CO2 leads to additional desorption of H2O, which is now also confirmed by these results using in-situ IR [19]. Both, the very fast adsorption of H2O postulated in the previous publication and the rapid replacement is confirmed. It becomes evident, that probably only one carbonate species is responsible for the adsorption mechanism at high temperature. However, the strength of the interaction between CO2 in adsorbed state and the basic oxygen atoms seem to be different and not homogeneous.

The increase of the absorption band at 1490 cm\(^{-1}\) is exceptional since the other absorption bands in this region show a decrease in absorbance as expected. A possible explanation could be that strongly bond bidentate carbonate which could not be desorbed, is converted into bi-carbonate (hydrogen carbonate) due to the presence of H2O on the surface of the sorbent like illustrated in Fig. 9. However, a clear identification is difficult because the expected presence of the absorption bands around 1650 and 1220 cm\(^{-1}\) (typical for hydrogen carbonate) was not observed from the recorded spectra.

During the adsorption of CO2 in experiment 13, the decrease in the broad band at 3500 cm\(^{-1}\) indicates a further desorption of H2O. It has
been found in earlier studies that indeed CO$_2$ is required to desorb additional amount of H$_2$O, which cannot be removed with N$_2$. The band at 1430 cm$^{-1}$ decreases in the same way as it increased during the adsorption of H$_2$O in experiment 9. In the literature this single absorption band is assigned to the formation of bulk carbonates [11]. This would imply that H$_2$O can lead to the formation of reversible bulk carbonate. The bands at 1550, 1365 and 1060 cm$^{-1}$ are reaching the same net absorbance as during experiment 5, indicating that the same carbonate species are formed as prior to the exposure of the material to H$_2$O.

3.5. Adsorption of CO$_2$/H$_2$O and desorption with H$_2$O and N$_2$

Co-adsorption of CO$_2$ and H$_2$O was studied with experiment 21. Fig. 10a shows the changes of the absorption bands during the adsorption of CO$_2$ and H$_2$O. Similar to the experiments where only CO$_2$ was used, the bands at 1565, 1345 and 1060 cm$^{-1}$ are increased significantly. Again, the broad absorption band at 3500 cm$^{-1}$ is increasing upon adsorption of H$_2$O. However, differently to the previous experiment, a strong increase of the band at 1430 cm$^{-1}$ can be observed during this experiment. It was reported that indeed upon CO$_2$/H$_2$O exposure the adsorbent showed a significant weight increase during TGA experiments, which can be explained now by the formation of bulk carbonates [19].

In Fig. 10b the changes in the recorded IR-spectra are plotted when either N$_2$ or H$_2$O is used after the adsorption of CO$_2$/H$_2$O. Note that the plotted absorbance is the net change compared to the spectra recorded previously after CO$_2$/H$_2$O adsorption. The decrease in the absorption bands between 1600 and 1000 cm$^{-1}$ is significantly higher if the sorbent is exposed to H$_2$O. The broad absorption band at 3500 cm$^{-1}$ remains unchanged during the experiment with H$_2$O, whereas a decrease can be obtained if N$_2$ is used instead. The difference in absorbance decrease of the bands at 1580, 1490, 1330 and 1060 cm$^{-1}$ shows that the desorption of CO$_2$ is improved if H$_2$O is used during the desorption step. The absorption band at 1430 cm$^{-1}$ shows a smaller intensity decrease compared to the experiment where N$_2$ was used. This can be explained with the reversible formation of bulk carbonates. Surface OH groups can only be desorbed if the partial pressure of H$_2$O is lowered (feed of N$_2$).

3.6. Competitive adsorption effects

To further study the effect of H$_2$O inducing desorption of CO$_2$ and vice versa during experiments 33–36 the partial pressure of CO$_2$ was kept constant while changing the partial pressure of H$_2$O. It was decided to study the replacement effect of CO$_2$/H$_2$O after dry CO$_2$, since it is known from recorded gas phase spectra that small amounts of H$_2$O seem to be present in the cell still after 5 min, which therefore cannot be used if we want to study the immediate effect on the sorbent. It can be seen from Fig. 11a that indeed only small changes are visible between the two spectra. The absorption bands at 3500 and 1430 cm$^{-1}$ are increased slightly, whereas the absorption bands at 1565 and 1345 cm$^{-1}$ are decreased slightly if a CO$_2$/H$_2$O gas stream is fed to the cell. The net change in absorbance (Fig. 11b) provides a better view to the changes on the material. It can be seen that the bands at 3500 and 1490 cm$^{-1}$ are increasing and both bands at 1600 and 1320 cm$^{-1}$ decreasing. Decrease in absorbance seems to be time independent (no change after 5 min) where the increase in the band at 1490 cm$^{-1}$ seems to be slower.
and not finished after 25 min.

One has to notice that the partial pressure of H₂O used during this experiment is quite low and therefore the replacement effect is expected to be small in this case due to the relative high partial pressure of CO₂ compared to H₂O. Taking into account the Δν3-splitting of the decreasing absorption bands being 280 cm⁻¹, bidentate carbonate is desorbed from the sorbent during this step. This would explain the instantaneous replacement and fast kinetics for this adsorption site which we have reported earlier [19]. The increased absorption of the band at 1490 cm⁻¹ again can be explained by the formation of hydrogen carbonate due to the presence of H₂O and CO₂ on the sorbent. It was observed that indeed if the feed gas was changed to dry CO₂ the observations described here are reversible.

Fig. 13. Absorbance evolution of different wavelengths at different temperatures as function of time (and experiment number). The distinct colors indicate a change in the gas phase composition during a specific experiment. Arrows are indicating the legend for a certain monitored wavenumber.

Fig. 14. Proposed mechanism for H₂O and CO₂ adsorption on KMG30 and IR bands assigned to different adsorption based on the experimental results.
3.7. Influence of temperature on carbonate species

Experiments were conducted according to Table 1 at 300 and 500 °C and compared to the results obtained for 400 °C in order to study the influence of operating temperature on the reversible formation of carbonates. Fig. 12(a–d) show the recorded spectra at different operating temperature for four different feed gas compositions.

Fig. 12a shows the spectra recorded during experiment 2 using a dry CO₂ gas stream. The net change in absorbance of the bands 1570, 1345 and 1060 cm⁻¹ are very similar, with a somewhat higher absorbance of the band at 1570 cm⁻¹ at lower temperature. The absorbance for the bands at 1490 and 1430 cm⁻¹ is increased at higher operating temperature. The small differences between the spectra indicate that the amount of CO₂ adsorbed at different operating temperature is the same, which has been reported using TGA previously [25]. The difference of the bands at 1430 and 1490 cm⁻¹, however, show that the carbonate species formed do not have to be the same. At higher operating temperature, more bulk carbonate seem to be formed which could be explained by an increased diffusion of carbonate species from the surface to the bulk of the sorbent. The higher absorbance for the band at 1570 cm⁻¹ for lower temperatures indicates that the amount of weaker bond CO₂ is increased.

After CO₂/H₂O adsorption (Fig. 12b, EXP19) most of the absorption bands are decreasing with an increasing operating temperature. This can be expected, since it is known that at lower temperatures a higher irreversible adsorption of CO₂ is taking place, caused by slower desorption kinetics [19]. The reduced absorbance for the band at 3500 cm⁻¹ indicates a lower amount of H₂O being adsorbed at higher temperature. However, it would be expected that at higher temperature the formation of bulk carbonate (1490 cm⁻¹) would be enhanced like in the experiment with a dry feed gas. It seems that the presence of adsorbed H₂O somehow can enhance the formation of bulk carbonates. At 300 °C a small shoulder is visible at 1650 cm⁻¹ indicating the formation of some bicarbonate.

During a desorption step with either N₂ or H₂O in both cases a larger decrease in the absorbance is obtained at higher temperature (Fig. 12c and d). Due to in general increased desorption kinetics at higher operating temperatures, the results are supporting previous measurements, that indeed the CO₂ loading on the sorbent is decreased by increasing the operating temperature. This is confirmed by the lower absorption of the bands at 1680–1060 cm⁻¹.

If H₂O is used for the regeneration of adsorbed CO₂ (Fig. 12d), the absorbance of the different bands is further decreased compared to the regeneration with N₂. It can be obtained that the absorption of all bands is again decreased for a higher temperature indicating that more of the previously adsorbed CO₂ can be desorbed. Due to the strong decrease of the band at 1550 cm⁻¹ (which is lower at higher temperature) the band at 1490 cm⁻¹ becomes more visible. Together with the fact that the Δν₂-splitting seems to be reduced at higher temperatures we can conclude that at higher temperatures even stronger bond carbonate species can be desorbed. The desorption of CO₂ (by feeding N₂) at higher operating temperature can be increased in the same way as using H₂O as a feed at lower temperature. A combination of both (high operating temperature and H₂O present during desorption of CO₂) is therefore the reason for a higher cyclic working capacity obtained in earlier TGA measurements. The clearly visible band at 1490 cm⁻¹ (Fig. 12d) at lower temperature indicates that some bicarbonate is remaining. Since also H₂O cannot be desorbed at lower operating temperature it can be expected that this carbonate species remains. This hypothesis is confirmed in the literature where K-dawsonite (K(Al₂O₃)(CO₃)(OH₂)₂) formation has been reported for this sorbent which has been detected at lower operating temperature (and could be one possible species formed on the sorbent). If the operating temperature is increased this phase seems to disappear [8,20]. The complete disappearance of the band at 1060 cm⁻¹ at 500 °C indicates that the remaining carbonates are probably some bicarbonates and bulk carbonates (polydentate) with a

| Material     | band position | Material     | band position |
|--------------|---------------|--------------|---------------|
| MgO          | 1450          | MgO          | 1450          |
| MgO          | 1430          | MgO          | 1430          |
| MgO          | 1410          | MgO          | 1410          |
| MgO          | 1390          | MgO          | 1390          |
| MgO          | 1370          | MgO          | 1370          |
| MgO          | 1350          | MgO          | 1350          |
| MgO          | 1330          | MgO          | 1330          |
| MgO          | 1310          | MgO          | 1310          |
| MgO          | 1290          | MgO          | 1290          |
| MgO          | 1270          | MgO          | 1270          |
| MgO          | 1250          | MgO          | 1250          |
| MgO          | 1230          | MgO          | 1230          |
| MgO          | 1210          | MgO          | 1210          |
| MgO          | 1190          | MgO          | 1190          |
| MgO          | 1170          | MgO          | 1170          |
| MgO          | 1150          | MgO          | 1150          |
| MgO          | 1130          | MgO          | 1130          |
| MgO          | 1110          | MgO          | 1110          |
| MgO          | 1090          | MgO          | 1090          |
| MgO          | 1070          | MgO          | 1070          |
| MgO          | 1050          | MgO          | 1050          |
| MgO          | 1030          | MgO          | 1030          |
| MgO          | 1010          | MgO          | 1010          |
| MgO          | 0990          | MgO          | 0990          |
| MgO          | 0970          | MgO          | 0970          |
| MgO          | 0950          | MgO          | 0950          |
| MgO          | 0930          | MgO          | 0930          |
| MgO          | 0910          | MgO          | 0910          |
| MgO          | 0890          | MgO          | 0890          |
| MgO          | 0870          | MgO          | 0870          |
| MgO          | 0850          | MgO          | 0850          |
| MgO          | 0830          | MgO          | 0830          |
| MgO          | 0810          | MgO          | 0810          |
| MgO          | 0790          | MgO          | 0790          |
| MgO          | 0770          | MgO          | 0770          |
| MgO          | 0750          | MgO          | 0750          |
| MgO          | 0730          | MgO          | 0730          |
| MgO          | 0710          | MgO          | 0710          |
| MgO          | 0690          | MgO          | 0690          |
| MgO          | 0670          | MgO          | 0670          |
| MgO          | 0650          | MgO          | 0650          |
| MgO          | 0630          | MgO          | 0630          |
| MgO          | 0610          | MgO          | 0610          |
| MgO          | 0590          | MgO          | 0590          |
| MgO          | 0570          | MgO          | 0570          |
| MgO          | 0550          | MgO          | 0550          |
| MgO          | 0530          | MgO          | 0530          |
| MgO          | 0510          | MgO          | 0510          |
| MgO          | 0490          | MgO          | 0490          |
| MgO          | 0470          | MgO          | 0470          |
| MgO          | 0450          | MgO          | 0450          |
| MgO          | 0430          | MgO          | 0430          |
| MgO          | 0410          | MgO          | 0410          |
| MgO          | 0390          | MgO          | 0390          |
| MgO          | 0370          | MgO          | 0370          |
| MgO          | 0350          | MgO          | 0350          |
| MgO          | 0330          | MgO          | 0330          |
| MgO          | 0310          | MgO          | 0310          |
| MgO          | 0290          | MgO          | 0290          |
| MgO          | 0270          | MgO          | 0270          |
| MgO          | 0250          | MgO          | 0250          |
| MgO          | 0230          | MgO          | 0230          |
| MgO          | 0210          | MgO          | 0210          |
| MgO          | 0190          | MgO          | 0190          |
| MgO          | 0170          | MgO          | 0170          |
| MgO          | 0150          | MgO          | 0150          |
| MgO          | 0130          | MgO          | 0130          |
| MgO          | 0110          | MgO          | 0110          |
| MgO          | 0090          | MgO          | 0090          |
| MgO          | 0070          | MgO          | 0070          |
| MgO          | 0050          | MgO          | 0050          |
| MgO          | 0030          | MgO          | 0030          |
| MgO          | 0010          | MgO          | 0010          |
high thermal stability.

3.8. Transient behavior of carbonate formation

To show the relative absorbance of the different adsorption bands, changing during the experiments as a function of time, the relative net absorbance of different characteristic wavenumbers is plotted in Fig. 13. The first two rows show the absorption bands which has been assigned to carbonates. On the third row the absorbance of the band at 3500 cm\(^{-1}\) is plotted, which has been assigned to H\(_2\)O adsorbed by the adsorbent. As indicated in the legend, the different background color indicates which mixture of gases was present in the cell.

It can be observed that the net change in absorbance is higher for higher temperatures for the bands 1060, 1350 and 1570 cm\(^{-1}\), confirming that the amount of CO\(_2\) being exchanged is increased in higher temperatures. In general, a larger irreversible formation of carbonate species due to the slower desorption kinetics of certain adsorption bands (e.g. 1060 and 1570 cm\(^{-1}\)) can be obtained from these figures, which are supporting results earlier obtained by TGA measurements [19]. It is remarkable how the measured weight change by TGA experiments is directly comparable to the absorbance of certain bands. This shows how in-situ IR can be extremely useful to follow CO\(_2\) adsorption on hydrotalcite-based sorbents and how H\(_2\)O influences CO\(_2\) adsorption. Even if the partial pressure of CO\(_2\) is kept constant it can be seen that the absorbance of certain absorption bands is higher with dry CO\(_2\) as a feed gas compared to a wet gas stream which is more distinct at higher temperatures (Fig. 13 first row, 1570 cm\(^{-1}\)). The net absorbance change of the carbonate species in this region seems to match the measured weight change as function of time. In general, it can be derived that both the initial adsorption/desorption are quite fast, where the change in absorbance (e.g. adsorption/desorption of CO\(_2\)) appears to be slower. These results show that the amount of the remaining carbonate species could be further decreased by increasing the desorption time which has been described in the past using TGA measurements [25].

The net absorption of the band at 3500 cm\(^{-1}\) is increased at lower temperature. We have already reported that the cyclic working capacity for H\(_2\)O is significantly increased at lower temperatures due to the higher adsorption capacity for H\(_2\)O of the sorbent at lower temperatures. It has been reported in the literature using coupled TGA and in-situ IR, that the absorbance of the region between 3000 and 3500 cm\(^{-1}\) increases in the same way as the adsorption of water [34,35]. These observations are supported by our measurements which show the same behavior comparing the net change in absorbance to TGA measurements conducted at different operating temperatures.

Comparing the obtained results during this study to a previous study using thermogravimetric analysis and packed bed reactor experiments [19] to determine the cyclic working capacity of CO\(_2\) and H\(_2\)O on KM30, the proposed mechanism can be confirmed. The absorption bands at 1060, 1335 and 1570 cm\(^{-1}\) can be assigned to the two sites necessary to describe the adsorption of CO\(_2\) and H\(_2\)O. Considering the Δν\(_2\)-splitting, it seems that a very heterogeneous site strength distribution of mostly bidentate carbonate species is responsible for the adsorption of CO\(_2\). The regeneration with H\(_2\)O can enable the decomposition of stronger bond bidentate carbonate species. This conclusion is based on the lower Δν\(_2\)-splitting of the remaining carbonates and can be attributed to site C. With this the two sites B (1570 & 1335 cm\(^{-1}\)) and C (1550 & 1345 cm\(^{-1}\)) for CO\(_2\) can be described (Fig. 14).

The irreversible adsorption and activation of an additional site by feeding CO\(_2\) and H\(_2\)O to the adsorbent is confirmed by the significant changes of the bands at 1430 and 1490 cm\(^{-1}\) and therefore to the formation of bulk carbonate and some bicarbonates which can be attributed to the proposed site D for CO\(_2\). A longer desorption time can reduce the amount of site D required to describe the adsorption capacities on the sorbent due to the slow continuous desorption of the stronger bond carbonate species which was proved recently with TGA experiments.

The adsorption of H\(_2\)O indicated by the broad adsorption band at 3500 cm\(^{-1}\) can be assigned to the proposed site A.

If we compare the adsorption bands detected during this study with results obtained and reported in the literature (Table 2) one can conclude that the results are comparable to some of the results already published in the literature. The band at 1490 cm\(^{-1}\) has been identified as a hydrogen carbonate (which usually comes together with two bands at 1220 and 1650 cm\(^{-1}\) [41]) which can be present due to the formation of K-dawsonite (KAl(CO\(_3\))(OH\(_2\))). This has been reported in the literature for the same adsorbent [11,24]. The formation of bidentate carbonate (1590–1535 cm\(^{-1}\) and 1090 cm\(^{-1}\)) was reported by various authors for similar types of sorbents, confirming our findings, that indeed this type of carbonate is mainly responsible for the CO\(_2\) sorption capacity on this sorbent. Reversible bulk carbonate formation and the formation of bicarbonate were reported at different experimental conditions. However, no studies have been found using in-situ IR under realistic operating conditions using both CO\(_2\) and H\(_2\)O as sorbate species.

4. Conclusions

In-situ IR has been used to elucidate the adsorption of CO\(_2\) and H\(_2\)O on a hydrotalcite based adsorbent (KMG30). It has been shown that mostly a heterogeneous distribution of thermally stable bidentate carbonate sites with different basic strength are determining the adsorption and desorption kinetics of CO\(_2\) on the sorbent. The presence of H\(_2\)O seems to enable the decomposition of even stronger bound bidentate carbonate sites leading to an increase in the cyclic working capacity, as reported by various authors in the literature, confirming also results published recently. It has been shown that the desorption kinetics are determining the cyclic CO\(_2\) working capacity of the material due to the increased bond strength of remaining carbonate species on the sorbent, leading to a decrease in the desorption rate if the CO\(_2\) loading on the material decreases.

In addition, it could be confirmed that feeding CO\(_2\) to a hydroxylated sorbent (feeding CO\(_2\)/H\(_2\)O) seems to initiate the formation of some bicarbonates. K-dawsonite formation can be one possible compound formed on the sorbent. Both a higher operating temperature and the presence of H\(_2\)O seem to enhance the formation of some bulk carbonates.

At constant partial pressures of CO\(_2\) additional CO\(_2\) can be adsorbed if the partial pressure of water is lowered. In the same way we could obtain an additional desorption of H\(_2\)O if the sorbent was exposed to a dry CO\(_2\) stream. These observations are important and supportive to results published earlier where TGA and packed-bed breakthrough experiments have been used to determine the cyclic working capacity for CO\(_2\) and H\(_2\)O of the adsorbent.

Finally, it could be confirmed that the increase in the cyclic working capacity at higher operating temperature is due to the decomposition of stronger carbonate species and therefore leading to a lower CO\(_2\) loading of the sorbent at the end of a desorption step.

These results support the development of a model for the adsorption and desorption kinetics of CO\(_2\) and H\(_2\)O mixtures on hydrotalcites for the design and optimization of SEWGS processes.

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References

[1] S. Abelló, F. Medina, D. Tichit, J. Pérez-Ramírez, X. Rodríguez, J.E.E. Sueiras, P. Salgueiro, Y. Costeiro, Study of alkaline-doping agents on the performance of reconstructed Mg-Al hydroxides in aldol condensations, Appl. Catal. A Gen. 281.
