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In Situ XRD Detection of Reversible Dawsonite Formation on Alkali Promoted Alumina: A Cheap Sorbent for CO_2 Capture

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Alkali-promoted aluminas are inexpensive and robust materials with significant basicity that allow CO_2 uptake at relatively high temperature and pressure. In situ XRD experiments show that bulk crystalline carbonate K-Dawsonite [$KAlCO_3(OH)_2$] phase is formed on such materials under relatively high pressure of an equimolar mixture of CO_2 and steam (total pressure of 10 bar) and at temperatures up to 300 °C. In parallel, typical needle-shaped Dawsonite crystallites are observed by SEM after exposure to similar conditions. Furthermore, the in-situ experiments show that the carbonate crystalline phase disappears between 300–400 °C, and that K-Dawsonite crystalline phase can be reformed by lowering the temperature in the range 200–300 °C and contacting the material with both steam and CO_2 at sufficiently high partial pressure. In a fixed-bed reactor a high breakthrough capacity of 1.5–1.7 $mmol\,g^{-1}$ has been measured. The experimental results reported herein highlight the high potential of alkali-promoted alumina for cyclic CO_2 removal in industrial systems.

Introduction

Significant anthropogenic CO_2 emission mitigation can be achieved by capturing CO_2 from large point sources, such as coal-fired power plants, followed by transport and underground storage.[1] Current research on CO_2 sorbents focuses on reducing the cost of capture resulting from both the decrease of plant efficiency due to the capture and the increased capital and operational expenditures of extra unit. Separating CO_2 from a carbonaceous fuel at high temperatures and high pressures has proven to be a good option to significantly reduce the energy penalty associated with capture. Moreover separation of CO_2 from hot gas streams in such large facilities requires robust and cheap sorbent materials that show both high stability and performance under long-term cyclic regenerative conditions at elevated temperatures and pressures. Activated alkali-promoted alumina materials are inexpensive products (obtained as intermediate during aluminium processing[2]) and have been intensively studied throughout the last century in both catalysis[3] and acid gas adsorption[4] due to their unique acid-base properties. Among these applications, alkali-promoted aluminas have shown an interesting potential for power plant flue gas decarbonation as well as for hydrogen/carbon dioxide separation.[5–7]

While the interaction of CO_2 with alkali-promoted alumina materials has been described at relatively low temperatures (ambient to 150 °C) and ambient pressure, only scarce data are actually available on the behaviour of alkali-promoted alumina at higher pressures and temperatures. As CO_2 can be advantageously separated at or close to Water-Gas Shift conditions in pre-combustion carbon capture,[8–10] a thorough understanding of the sorbent material rearrangement and chemistry under these industrially relevant conditions is essential. Information gathered from experiments under realistic pressure and temperature and gas composition may further guide research toward the development of novel smart, robust and cheap materials.

In this work, in situ powder XRD experiments using synchrotron radiation, which have long been recognised as a powerful technique in material research,[11] have been carried out at pressures up to 10 bar and temperatures up to 500 °C at the European Synchrotron Radiation Facility on the Swiss-Norwegian beam lines (BM01B). A sample holder was designed to allow in situ measurements under high pressure gas mixtures, including steam, such that no condensable vapours could interfere with the sample (see Supporting Information). The structural investigations have been correlated with consecutive morphological rearrangements due to CO_2 sorption observed by SEM and cyclic sorption experiments carried out in a fixed-bed reactor.

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Results and Discussion

An alkali-promoted sample, a transitional alumina[12] impregnated with 20 wt.-% potassium carbonate subsequently calcined at 550 °C, was obtained from a commercial vendor and was placed in a 1 mm outer diameter quartz capillary with a wall thickness of 40 µm (Hilgenberg, Germany). The material in the capillary was exposed to an appropriate mixture of gases at a constant flow rate of about 15 mL/min (STP). A full description of the experimental conditions is provided in the Supporting Information.

Initially, the sample was heated to 200 °C under 10 bar dry CO_2. XRD data (Figure 1, a) revealed a rather amorphous material, hinting at a mixture of K_2CO_3 and alumina. This is consistent with SEM analysis of the calcined material that shows a heterogeneous morphology with wormlike structure, probably corresponding to poorly crystalline potassium carbonate, deposited on a bulk alumina material (Figure 2, left).

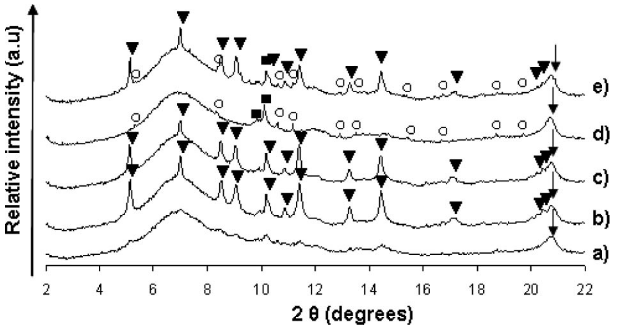


Figure 1. Powder XRD of 20 wt.-% potassium carbonate-promoted alumina: a) at 200 °C under 10 bar CO_2 (dry); b) at 200 °C under 10 bar CO_2/H_2O (1:1); c) at 300 °C under 10 bar CO_2/H_2O (1:1); d) at 400 °C under 10 bar CO_2/H_2O (1:1) and e) at 200 °C under 10 bar CO_2/H_2O (1:1) while cooling down. ▼ K-Dawsonite-type phase (JCPDS 21-979); ■ K_2CO_3 monoclinic phase (JCPDS 016-0820); ○ K-Mullite-type phase $K_{0.67}Al_6O_{9.33}$;[13] ↓ transitional alumina. Broad diffraction peak at around 7° 2θ is due to the quartz capillary.

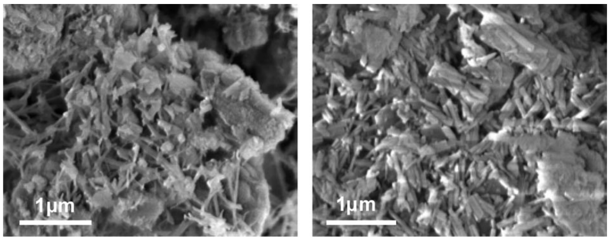
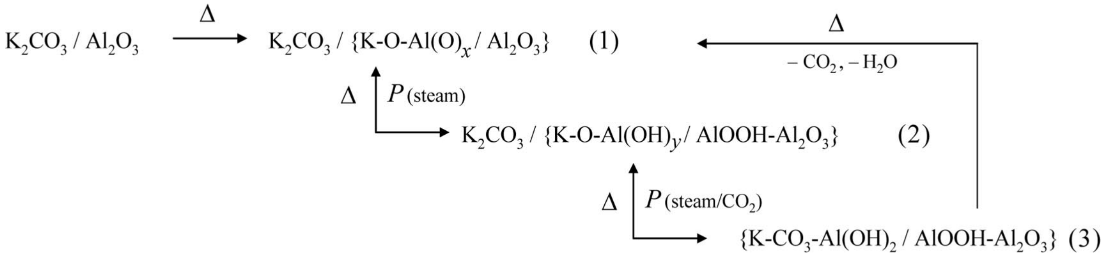


Figure 2. SEM micrograph; left side: freshly calcined 20 wt.-% K_2CO_3-promoted alumina; right side: calcined 20 wt.-% K_2CO_3-promoted alumina after hydrothermal treatment at 260 °C under steam and CO_2 pressure.

Interestingly, as soon as the partial pressure of steam was raised to 5 bar (CO_2/steam ratio of 1:1, 10 bar total pressure), a crystalline K-Dawsonite-type phase exhibiting rather sharp diffraction peaks was formed almost instantaneously, while the temperature remained at 200 °C (Figure 1, b). To the best of our knowledge it is the first time that formation of crystalline Dawsonite has been directly observed from gas-solid reaction under CO_2 capture conditions (with relatively high T and p). Previously, the synthesis of this material (bulk form) has been studied in strongly alkaline aqueous solutions under hydrothermal conditions,[14] and its formation on potassium carbonate-promoted aluminas had been suggested earlier at rather low temperatures.[7,15,16] Besides it is also interesting to note that Dawsonite-type carbonates may play a role in CO_2 mineralisation in underground storage sites.[17] The harsh CO_2 capture conditions [10 bar, CO_2/steam (1:1) at 200 °C] clearly trigger the reaction between the impregnated potassium carbonate and the alumina surface, resulting in the formation of a crystalline phase of potassium aluminium carbonate hydroxide, $KAlCO_3(OH)_2$, K-Dawsonite. In agreement with earlier studies addressing potassium ion rearrangement on the alumina surface and at the subsurface[18–21] it seems that potassium ions that are first brought in close contact with the surface of the alumina as a result of heat treatment (equation 1) are able to take up CO_2 in the presence of steam to form K-Dawsonite-type species by a series of equilibria controlled ostensibly by the presence of steam. For the purpose of clarity, this series of equilibria is described in Scheme 1.

Accordingly, the presence of high partial pressure steam at 200 °C may enhance partial hydroxylation of alumina[12] and potassium ions mobility in such a way that aluminum hydroxy-species react with potassium to form potassium hydroxyalumina species (equation 2). These species would be best described by the mixture $\{K_2CO_3/K\text{-}O\text{-}Al(OH)_y/AlOOH\text{-}Al_2O_3\}$, i.e. bulk potassium carbonate present at the surface of alumina which is partially hydroxylated and present a domain close to the surface in which potassium ions are intimately mixed with hydroxyalumina centres $\{K\text{-}O\text{-}Al(OH)_y\}$. Reaction with sufficiently high pressure CO_2



Scheme 1. Proposed mechanism the reversible formation of K-Dawsonite crystalline phase.

leads to formation of K-Dawsonite type crystalline phase at 200 °C detected in this study (equation 3). Note, at this stage of the experiment, a K-Dawsonite type crystalline phase co-exists with a crystalline transitional alumina phase ($AlOOH-Al_2O_3$) which exhibits a typical broad diffraction peak at $2\theta = 20.7°$. Since the sample Al/K ratio is about 4.5 initially, it is obvious that a K-Dawsonite-type phase (Al/K = 1) cannot be obtained as a single product and is probably built up close to the alumina surface where K^+ ions can migrate[18–21] and react with aluminum (hydr-)oxide centres as a result of both the heat treatment, and the extensive carbonating and humid conditions.

In an ex-situ CO_2 adsorption experiment a 20 wt.-% potassium carbonate-promoted preliminary calcined alumina was treated under hydrothermal conditions at 260 °C and high partial pressure of CO_2 in an autoclave (see experimental section in the Supporting Information). After the experiment the material consisted of sharp needle-like nanostructures packed on bulky assemblies consisting of alumina (Figure 2, right side). Such a morphology for Dawsonite crystals had already been reported for hydrothermally synthesised K-Dawsonite by Zhang et al.[22] who reported that the aspect ratio between particles length and width decreases with decreasing K/Al ratio, which is in support of the present case where a large excess of alumina is present. In addition, the morphological comparison between freshly calcined material (Figure 2) and the material loaded with CO_2 shows very clearly that K-Dawsonite has been formed on top of larger alumina aggregates and supports the proposed mechanism for K-Dawsonite formation.

Further increase of the temperature under 10 bar of CO_2/steam (1:1) resulted in the disappearance of K-Dawsonite type crystalline phase between 300 and 400 °C in agreement with reported experimental data on K-Dawsonite decomposition and thermodynamical properties.[23,24] At 400 °C (Figure 1, d), diffraction peaks of transitional alumina are accompanied by a diffraction pattern with peaks at 2θ 10.1, 9.9 and 9.2 corresponding to the major diffraction peaks of the monoclinic crystalline phase of K_2CO_3 (JCPDS 016-0820). Moreover, a set of weak diffraction peaks appears at 400 °C. According to previous reports, this new phase is a Mullite-type phase $K_{0.67}Al_6O_{9.33}$ corresponding to published crystallographic data.[20,25,26] Although K-Mullite formation from alkali-containing alumina is generally observed after treatment at high temperature,[26,27] MacKenzie et al. have shown that a Mullite-type crystalline phase readily forms at temperature as low as 400 °C if a sufficiently intimate and homogeneous mix of Potassium and alumina is achieved by the preparation method.[25] Accordingly, the enhancement of K^+ mobility by the presence of relatively high pressure of steam could probably explain why K-Mullite-type crystalline phase is formed under these experimental conditions, supporting further the proposed mechanism involving K^+ migration.

In order to assess the potential reversibility of CO_2 fixation through the formation of a K-Dawsonite crystalline phase, the temperature was subsquently decreased while keeping the same flow conditions (steam/CO_2 = 1:1, at 10 bar). As shown in part e of Figure 1, crystalline K-Dawsonite-type phase was readily reformed at 200 °C. Reformation of such phases has been reported recently by Perez–Ramirez et al.[28,29] after contact of calcined Dawsonite material with aqueous alkaline solutions. The present experiment shows for the first time that at higher pressures of CO_2 and steam the reformation of K-Dawsonite by a solid–gas phase reaction occurs. Here again, the reformation process can be explained by enhanced rearrangement mechanisms of alumina under hydrothermal conditions that leads to an intimate mixing between potassium carbonate and aluminium (hydr-)oxide allowing reformation of K-Dawsonite, $KAlCO_3(OH)_2$. Finally the material adsorption capacity was tested in a fixed-bed reactor over 7 cycles by carrying out adsorption at 300 °C and 20 bar total pressure (5 bar CO_2, 5 bar steam and 10 bar N_2) while regeneration was carried out at 500 °C and 1 bar total pressure (0.5 bar N_2 and 0.5 bar steam). The breakthrough time corresponded to a CO_2 breakthrough capacity of about 1.5–1.7 $mmol\,g^{-1}$ which decreased slightly with the number of cycles (Figure 3). Note that breakthrough capacities determined from breakthrough times measured under such conditions may only partially reflect the actual material capacity since bulk K-Dawsonite formation most probably results in slower uptake processes due to mass-transfer limitations. Nevertheless such high breakthrough capacities complete very well the information gathered by the structural study reported herein and support the proposed pathway under relatively high pressure and temperature. In contrast, previous studies on CO_2 sorption on alkali-promoted alumina carried out at ordinary pressure[30] or relative high CO_2 pressure without steam[31] have revealed much lower CO_2 capacities.

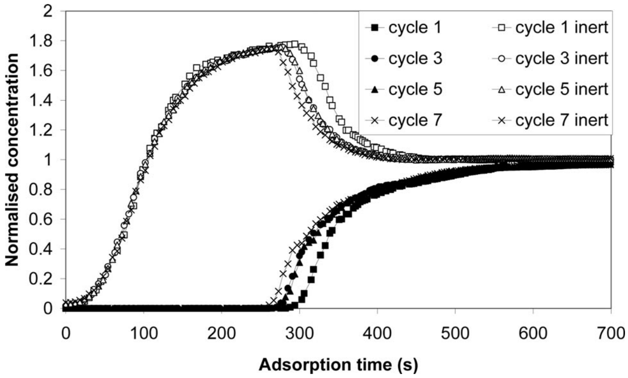


Figure 3. Breakthrough curves during CO_2 adsorption on 20 wt.-% K_2CO_3-promoted alumina at 300 °C under 5 bar CO_2, 5 bar steam and 10 bar N_2 (20 bar total pressure) over 7 cycles. Inert tracer is included for breakthrough time measurement (hollow signs).

Conclusions

In view of the described reversible formation of K-Dawsonite [$KAlCO_3(OH)_2$], alkali-promoted alumina may be used as regenerable CO_2 sorption species in hot wet gas streams in separation applications. For instance, cheap alkali-promoted aluminas, which are intermediate products of the Bayer process in alumina production from Bauxite, could be used as a CO_2 sorbent in a temperature swing absorption mode taking up CO_2 in the presence of steam at temperatures in the range of 200–300 °C and release it upon a temperature increase to about 400–500 °C for further use or storage. CO_2 adsorption isotherm measurements and cyclic CO_2 adsorption under industrially relevant conditions are currently under investigation for Dawsonite-based materials and long-term stability will be evaluated under cyclic experiments to clarify the role of transformation of Dawsonite to Mullite phase.

Supporting Information (see also the footnote on the first page of this article): Detailed in situ XRD measurements conditions and complete description of the gas cell used for the experiments.

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