PRE-COMBUSTION CO_2 CAPTURE AT HIGH TEMPERATURE WITH ALKALINE PROMOTED ALUMINAS AND HYDROTALCITES: THE CRUCIAL ROLE OF ALKALINE CATIONS IN CO_2 ADSORPTION[‡].

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Abstract

Alkali promotion effects on CO_2 sorption have been characterised by a series of complementary analytical techniques on γ-alumina, magnesia, hydrotalcites and alkaline promoted corresponding materials under conditions representative for WGS conditions. Alkaline carbonates are destabilised when interacting with solid surface as evidenced by thermogravimetric analyses and temperature programmed desorption. Structural rearrangements have been observed in alkali promoted hydrotalcite at the temperature used for capture. Moreover, in the presence of CO_2, the reconstruction of hydrotalcite cooled at room temperature after the experiment could not be observed most probably due to the formation of new carbonate species at high temperature that are stable while temperature decreases and prevent the reconstruction of crystalline hydrotalcite. In addition, in situ vibrational spectroscopies (Raman and DRIFT) showed that carbonates rearrange while heating and that alkali ions strongly interact with carbonate groups coordinated to aluminium oxide centres. Indeed both techniques highlight remarkably the loss of symmetry for carbonates group and comparison between parent material's fingerprints evidenced that basic (KAl_nO_{2n}/CO_3)-like species play a key role in CO_2 fixation at 400°C.

Introduction

Power Generation from coal with reduced CO_2 emissions can be achieved by using Integrated Gasification Combined Cycle (IGCC) with CO_2 capture and storage (CCS) in the near future. This configuration should allow the reduction of the efficiency penalty due to CO_2 capture and be competitive in terms of LHV efficiency with currently widespread used coal-pulverized combustion technologies.[1] Among pre-combustion carbon capture options, the Sorption-Enhanced Reaction Process (SERP) has attracted great interest because of the optimization of reaction yield, hydrogen purity[2] and CO_2 separation from the fuel[3-5]. Process simulations have shown that SERP using the pressure swing adsorption mode (PSA) has a high potential for lower efficiency penalties.[6,7] Gasification products mainly consist of CO which has to be converted into H_2 and CO_2 via the water-gas-shift reaction. In sorption enhanced water-gas-shift (SEWGS) the equilibrium of the reaction is shifted to the product side by removing one of the products using a sorbent.

$$H_2O + CO \leftrightarrows H_2 + CO_2 \qquad (\Delta H_{298}^0 = -41 \text{ kJ/mol})$$

The development of such a process has been started by Air Products in the 1990s.[2] Attention has been focused especially on hydrotalcites because they offer i) relatively fast reversible adsorption/desorption, ii) a stable capacity for CO_2 during long term cyclic experiments, iii) fairly good mechanical strength in high pressure steam and iv) there is no interaction with the physically mixed

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water-gas-shift catalyst.[8,9] Using hydrotalcites (HT) as sorbent, the process has been operated successfully at temperatures between 300 and 500°C in a PSA unit (pressure between 1 and 30 bars) on a bench scale (Single Column 2 m tall, 38 mm diameter, CACHET project) for more than 6 months at the Energy research Centre of the Netherlands.[10]

In parallel, investigations on HT and derivative materials are ongoing at lab scale. Despite previous studies on CO_2 sorption using HT-based sorbents in water-gas-shift conditions,[8,9,11-13] the true nature of species involved in CO_2 reversible adsorption at such temperatures is still not clearly identified. In particular, the present study is focused on the role of alkali promoters which have been earlier found to significantly increase the reversible CO_2 sorption capacity of HT.[6,14-16] Particularly, HT as acid-base materials[17] may contain sites with an optimal basic strength for CO_2 fixation at high temperature.

Our approach was based on a systematic comparative study of HT "parent" materials such as alumina and magnesium oxide and their potassium carbonate promoted forms. Characterization of these materials has been performed by 1) sorption experiment, 2) in situ XRD to check phase transformation and 3) by infrared spectroscopy to identify rearrangements that occur at high temperatures and the CO_2 adsorption mechanism.

Results and discussions

Reversible capacity and carbonate decomposition

Hydrotalcites used in this study have been synthesized as described earlier[18] and have been first calcined at 400°C, promoted by potassium carbonate by incipient wetness and then dried at 120°C. In the following discussion the material is noted as HT*, alumina is noted as AO and magnesium oxide as MO. These materials have first been investigated for their reversible CO_2 adsorption in the presence of relatively high partial pressure of steam at 400°C. It was found earlier that the presence of steam in the gas stream has a significant effect on the reversible CO_2 capacity, in the case of HT.[13,19,20] Increasing the steam/CO_2 ratio facilitates a quick and efficient desorption and has a positive influence on adsorption capacity as demonstrated recently.[20]

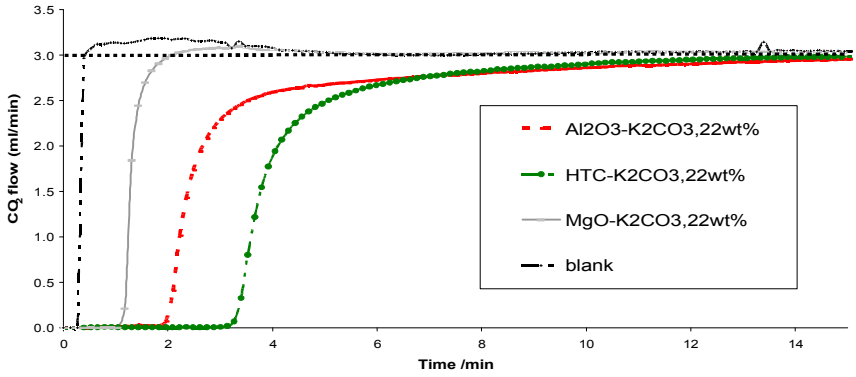

Figure 1: CO_2 breakthrough curves in sorption capacity measurement using 5.8% CO_2, 10.7% H_2O, N_2 balance as gas feed for adsorption step at 400°C, 1 bar. (black) blank, (grey) K_{22}MO, (red) K_{22}AO, and (green) K_{22}HT*.

Figure 1 shows the typical breakthrough curves for various potassium carbonate loaded materials. Reversible capacities for other materials have been measured using the same method and the results after the third cycle are presented together with nitrogen sorption results in table 1. It is worth to note that generally there was only a very small difference between the 2nd and 3rd cycles and longer tests carried out for some of these materials have confirmed that capacity does not vary significantly after

the 3rd cycle under these conditions. Obviously modification by potassium carbonate strongly enhances CO_2 capacity of HT* as demonstrated earlier.[13]

Table 1: CO_2 reversible sorption capacities for hydrotalcite, potassium carbonate promoted hydrotalcites and other selected materials measured after 3 cycles and their specific surface area.

Sample	K_2CO_3 loading (weight%)	BET Specific Surface Area (m^2/g)	CO_2 reversible sorption capacity (mmol/g) at 400°C
K_0HT*	0	48	0.06
K_5HT*	5	41	0.19
K_{11}HT*	11	40	0.30
K_{22}HT*	22	18	0.37
K_0AO	0	256	0
K_5AO	5	-	0.01
K_{11}AO	11	-	0.07
K_{22}AO	22	113	0.27
K_{44}AO	44	-	0.26
K_0MO	0	86	0
K_{22}MO	22	6	0.06

These experiments confirm that there exists an optimal loading of K_2CO_3 on hydrotalcites and that the surface area drops dramatically at high loading.[21] The same conclusion could be drawn from the results obtained with promoted aluminas. Although unpromoted γ-alumina did not show any affinity for CO_2 under the experimental conditions, it clearly appeared that potassium carbonate promotion allows CO_2 fixation despite a pronounced drop in specific surface area. Lower surface area found for high K_2CO_3 loadings are most probably caused by pore or surface blockage due to the formation of bulk K_2CO_3 aggregates as evidenced by the SEM photos (figure 2).

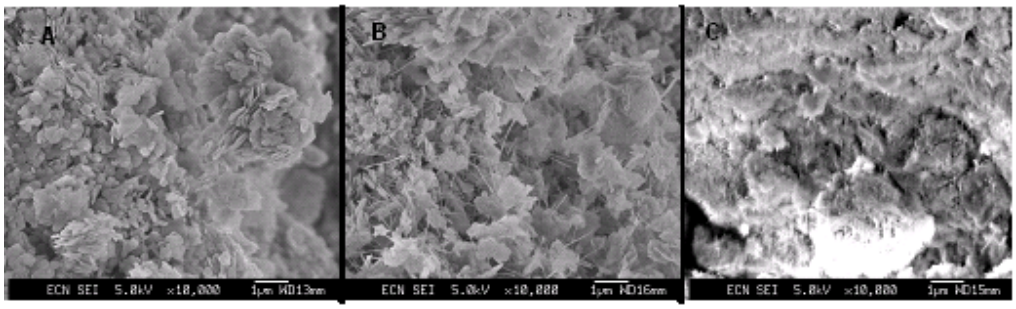

Figure 2: SEM picture of unpromoted HT (A), 22wt% K_2CO_3 promoted HT (B) and 22wt% K_2CO_3 promoted γ-alumina (C)

The typical platelets-like HT particles of the initial material are partially covered by some needle shaped material after potassium carbonate impregnation. In full agreement with the recent contribution of Rodrigues et al. on potassium modified HY,[22] small needle shaped material can also be clearly seen on γ-alumina surface. Although EDX analysis did not allow a definitive answer, it may be assumed that the needles are hydrates of potassium carbonate.[23] It is clear that at least part of the material deposited on the surface is responsible for the increased CO_2 sorption capacities for all those materials. In contrast, it has to be mentioned that commercial bulk potassium carbonate as well as magnesium oxide and other magnesium oxide precursors (Brucite and hydromagnesite) did not show any CO_2 reversible adsorption capacity under the experimental conditions used. Moreover potassium carbonate promoted magnesium oxide showed only a very low reversible CO_2 adsorption capacity compared to the promoted aluminium oxide based materials. Hence it seems that the interaction between γ-alumina

surface or aluminium oxide centres and potassium carbonate does play a key role in the formation of sites[24-26] that do actively and reversibly fix carbon dioxide under the experimental conditions used (1bar- about 60mbar CO_2).
Temperature programmed desorption was carried out to analyse the decomposition of carbonates for various samples. The released CO_2 was analysed by mass spectrometer for HT and aluminas with increasing potassium carbonate loadings and for a potassium carbonate promoted magnesium oxide (Figure 3).

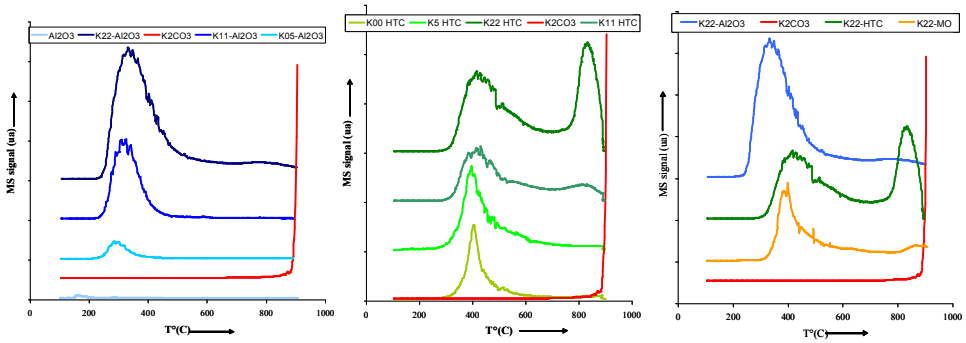

Figure 3: Temperature programmed desorption of CO_2 for K_0AO, K_5AO, $K_{11}AO$, $K_{22}AO$ on the left graph, K_0HT^*, K_5HT^*, $K_{11}HT^*$, $K_{22}HT^*$ on the center graph and $K_{22}AO$, $K_{22}MO$, $K_{22}HT^*$ on the right graph, the red line corresponds to the TPD curve of K_2CO_3 bulk.

For unpromoted HT the desorption profile under standard conditions (heating in a flow of nitrogen (50ml/min) to 900°C at a rate of 10°C min^{-1}) showed a maximum at about 400°C with a rather narrow shape although a small tail was present at higher temperature denoting carbonates decomposing at higher temperature. Although the curve was clearly broadened due to the higher concentration of carbonate in the HT promoted with 5wt% potassium carbonate, the decomposition temperature peak was not shifted towards higher temperatures. More interestingly, with higher loadings the maximum of the decomposition peak shifted toward higher temperature while its profile was significantly broadened. Note that with 22 wt% K_2CO_3, a significant second CO_2 peak was observed at 830°C probably due to the presence of bulk carbonate at the surface of the mixed oxide (originally HT). Although commercial bulk potassium carbonate started decomposing above 900°C under these experimental conditions, it can be assumed that bulk potassium carbonate deposited on the surface of the solid (as observed by SEM) is responsible for the CO_2 release at such a high temperature. The corresponding experiments on γ-alumina and promoted γ-alumina are depicted at the left-side of figure 3. As expected unpromoted γ-alumina did not show any carbonate decomposition at high temperature and only a minor amount of residual CO_2 is desorbed between 100 and 200°C. Increasing the amount of potassium carbonate on the surface led to an increasing amount of CO_2 release between 250 and 450°C. Interestingly samples with increased amount of potassium carbonate showed a gradual shift for the maximum of carbonate decomposition from 290 to 335°C with a strong broadening of the temperature range at which CO_2 was released toward high temperatures. Furthermore the shift of the maximum decomposition peak toward higher temperature has been confirmed in extra experiments with various heating rates (not shown here). Most probably, some carbonates more strongly bonded to the surface, which are formed at higher surface coverage, may be responsible for the modification of the TPD profile.
Finally it is of the greatest interest to compare the decomposition profile for potassium carbonate impregnated on various supports, namely alumina, hydrotalcite and magnesium oxide. In comparison

to bulk potassium carbonate it is obvious that potassium carbonate impregnated on these supports undergoes a transformation that decreases the initial decomposition temperature of K_2CO_3. Apparently, γ-alumina can destabilize potassium carbonate to a high extent since some CO_2 was already released at 250°C. However the results from the thermal decomposition curves can hardly be directly correlated to the reversible CO_2 sorption properties shown in table 1. In other words it would be rather difficult to assign a specific group of carbonates responsible for the increased CO_2 reversible capacity on the basis of carbonates decomposition.

It has to be noted that one can try to analyze the results from carbonates decomposition in terms of basic strength. Indeed CO_2 as an acid probe is entrapped in carbonate form on the solid surface. The desorption of CO_2 may restore the initial basic site and as a result the temperature of carbonates decomposition may reflect, to some extent, the bond strength between CO_2 and the basic site, or in other words, it may give insights on the basic strength of the surface sites. Following this concept it appears from TPD profiles that the higher the carbonate loading, the more sites of higher basic strength are formed on the surface, confirming the results found by Wang et al.[25,27,28] It might be that a population of sites with appropriate basic strength is specifically involved in the reversible CO_2 sorption at 400°C. In situ structural analysis and spectroscopic investigations were therefore carried out to identify rearrangements happening in the sorbent under very similar conditions.

Hydrotalcite structural rearrangement during CO_2 capture

In-situ XRD experiments with variable temperature were performed with HT and promoted HT in the presence of steam (35 mbar) with and without carbon dioxide (120 mbar) (Figure 4).

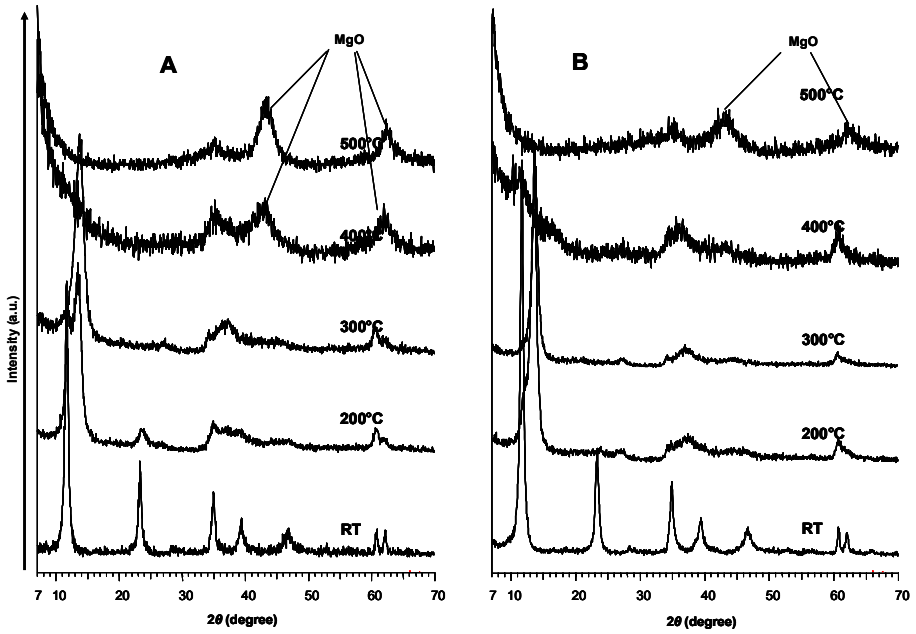

Figure 4: In situ X-Ray powder diffractograms for KoHT* at variable temperature in steam/nitrogen (A) and for KoHT* at variable temperature in steam/nitrogen/CO_2 (B).

Unpromoted hydrotalcite (K_0HT*) and 22 wt% potassium carbonate promoted hydrotalcite (K_{22}HT*) were heated gradually to 500°C in the chosen gas stream and diffraction patterns were recorded at various temperatures. Figure 4A displays the pattern obtained for K_0HT* in a mixture N_2/steam. Note that the diffraction patterns taken at room temperature shows the HT crystalline structure that has been reformed (reconstructed) after calcination at 400°C with subsequent impregnation with water at room

temperature and drying at 120°C overnight. The well known decomposition of HT crystalline phase corresponding to the collapse of the layered structure is clearly observed together with the formation of magnesium oxide crystals,[29-32] although neither the $MgAl_2O_4$ spinel crystalline form (at high temperature) nor crystalline magnesium carbonate could be observed under these conditions.[12] The temperature dependence of the crystalline rearrangement was only slightly different for the other experiments. With CO_2 addition in the gas stream crystalline magnesium oxide appeared only at temperature above 400°C (above 300°C without CO_2) for both unpromoted hydrotalcite (Figure 4B) and K_2CO_3 promoted hydrotalcite (not shown here). In the latter case, with CO_2 in the stream, crystalline potassium carbonate was also observed during the experiment.

Remarkably the main differences were observed while cooling the samples to room temperature in a fixed gas stream after the heat treatment at 500°C (Figure 5). Indeed samples in permanent contact with CO_2 (Figures 5 B and 5 D) did not re-crystallise to HT structure contrary to the samples that were flushed with nitrogen/steam where the memory effect of activated HT was confirmed (Figures 5 A and 5 C).

CO_2 might help stabilizing some carbonates species at the surface which are poorly crystalline or non-crystalline and thus it might hinder the HT re-crystallisation. In addition, it seems that potassium promoted HT is reconstructed faster than the unpromoted HT in N_2/steam (figures 5A and 5C).

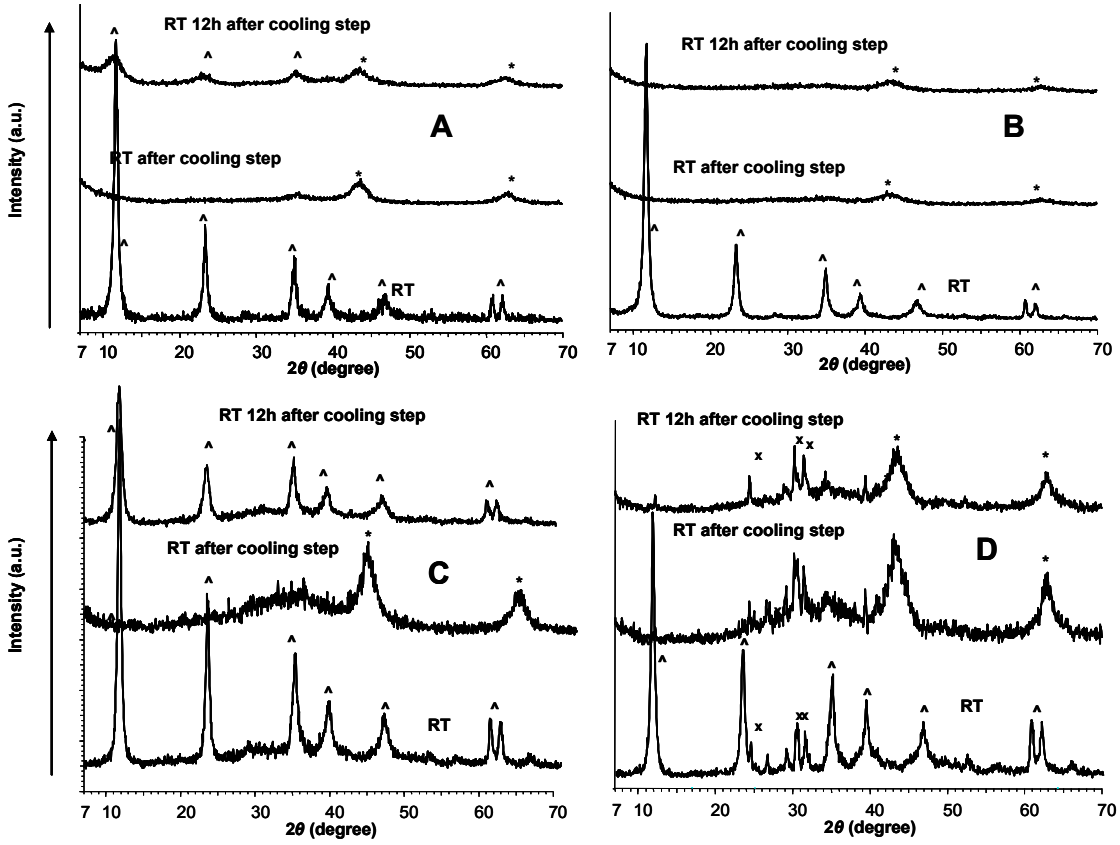

Figure 5: In situ X-Ray powder diffractograms for KoHT* before heating at 500°C, after heating at 500°C and 12h after heating at 500°C flushing with water/nitrogen (A); KoHT* before, after and 12h after experiment flushing with water/nitrogen+$\underline{CO_2}$ (B); for K_{22}HT* before, after and 12h after experiment flushing with water/nitrogen (C); K_{22}HT* before, after and 12h after experiment flushing with water/nitrogen+$\underline{CO_2}$ (D); Crystalline HT (^), MgO (*) and K_2CO_3 (x)

Surface rearrangement during CO_2 capture

In-situ Diffuse Reflectance Infrared Fourier Transformed Spectroscopy (DRIFTS) study was carried out to identify the rearrangements involved in the solids at variable temperature (RT to 400°C) in the presence of N_2/steam. Figure 6 shows the spectra in the 800-2000 cm^{-1} wave numbers range obtained from unpromoted hydrotalcite, 22wt% K_2CO_3 promoted hydrotalcite, γ-alumina and 22wt% K_2CO_3 promoted γ-alumina respectively. Before the heat treatment, a broad absorption band is observed at 1655 cm^{-1} for all samples which is typical of O-H bending mode from water.[34-37] Accordingly, this band disappears after thermal treatment at temperature between 100 and 200°C and reappeared after rehydration of the sample at room temperature (not shown here). It should be noted at this point that this band might also hint at the presence of bicarbonate species at low temperature which are known to decompose at rather low temperature.[21,34]

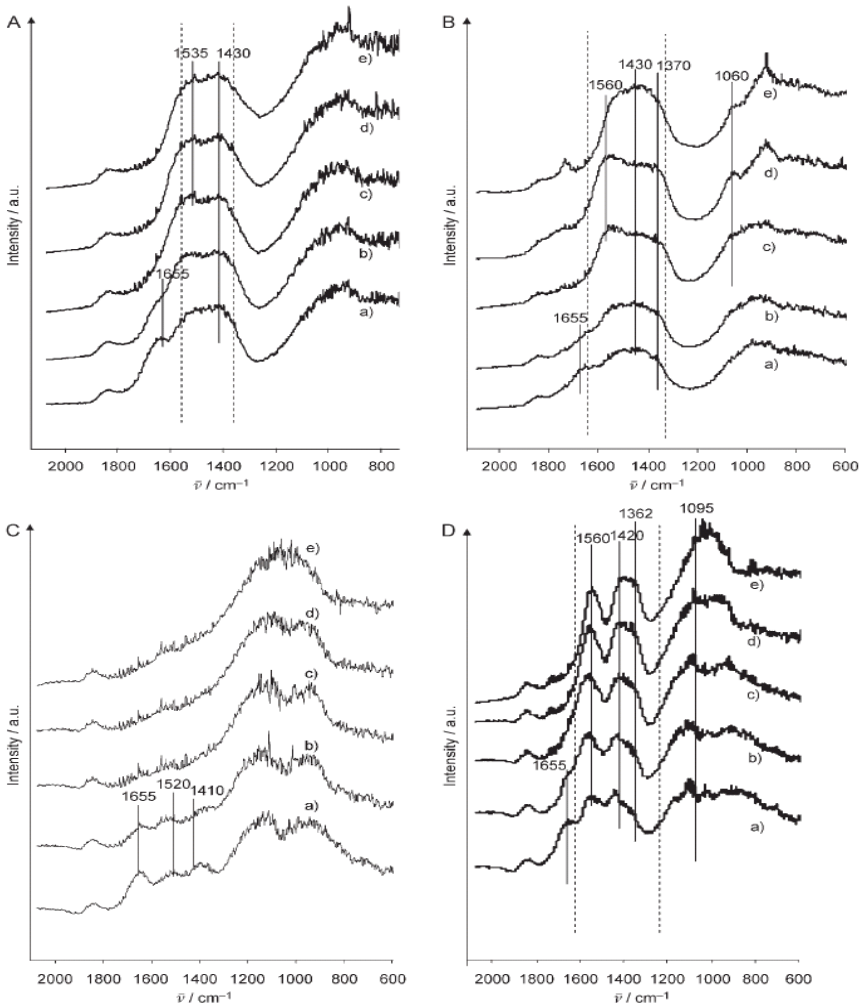

Figure 6: DRIFT spectra of K_0HT^* (A) $K_{22}HT^*$ (B) K_0AO (C) $K_{22}AO$ (D) in the carbonate region at RT in N_2/steam stream at room temperature (a), 100°C (b), 200°C (c), 300°C (d), 400°C (e)

The unpromoted HT sample exhibited a strong and broad absorption band between 1400 and 1600 cm^{-1}. When the temperature is increased there are clearly two maxima appearing at 1535 cm^{-1} and 1430 cm^{-1} (Figure 6A). These bands are generally assigned to ν_3 asymmetric stretching of carbonate groups.[34,36-40] The splitting is most probably caused by the rearrangement of surface carbonates that

involves a lowering of their symmetry. According to Busca et al.[41] the splitting $\Delta\nu$ 105cm^{-1} can be assigned to bidentate carbonates in this case, because the polarisation might be rather low for Mg-Al atoms. For the 22 wt% K_2CO_3 promoted HT (Figure 6B), band splitting also occurs when the temperature is increased. Between 200 and 400°C there are two broad bands peaking at 1560 and 1370 cm^{-1} corresponding to the ν_3 vibrational mode of carbonate groups. Strikingly, the splitting is increased to $\Delta\nu$ 190cm^{-1} denoting a stronger perturbation of the symmetry in carbonate groups which is confirmed by the appearance of the band at 1060 cm^{-1}, infrared inactive for symmetric carbonates. The main reason for this significant change may be the close interaction of surface carbonates with potassium ions provided by potassium carbonates. The band at 1430 cm^{-1} and the weak absorption band at 1740 cm^{-1} maximised at 400°C can be unambiguously assigned to the vibration frequencies ν_3 and $2\nu_2$ (harmonic signal of ν_2, usually found at 870-880 cm^{-1}) respectively of bulk potassium carbonate present in large amount, in agreement with the observation made by TPD and SEM [42].

In contrast, experiment on non-promoted γ-alumina (Figure 6C) showed that no carbonates were present on the surface at high temperature. At room temperature in the presence of steam and residual CO_2 from the atmosphere bands were observed at 1655, 1520 and 1410 cm^{-1} corresponding most probably to surface bicarbonates formed during the storage of the material in ambient atmosphere.[43]

More interestingly 22 wt% K_2CO_3 promoted γ-alumina showed a very clear picture on rearrangement of surface carbonates occurring at elevated temperature (Figure 6D). Two bands peaking at 1560 and 1362 cm^{-1} ($\Delta\nu$ 198cm^{-1}) corresponds to ν_3 stretching frequencies for bidentate carbonates. The second band is rather large probably because of the presence of some bulk potassium carbonate with its typical single ν_3 frequency around 1430 cm^{-1}. Furthermore the bands broadening may be explained by the presence of K-O-(CO)-O-Al species which usually exhibit a split ν_3 frequency and ν_1 at 1550, 1420 and 1095 cm^{-1} respectively.[44,45] These species have previously been invoked to rationalize the enhanced basic strength of alkali promoted aluminium oxides. [24,46,47]

Hence the observed similarities between hydrotalcites and K_2CO_3 promoted γ-alumina may be of the utmost importance for the comprehension of the promoting mechanism. Carbonates provided by the addition K_2CO_3 are rearranged at the surface as proved by the splitting of ν_3 frequency for both materials. Moreover by comparison of the splitting values observed for promoted hydrotalcite and promoted γ-alumina it clearly appeared that the carbonates symmetry may be affected in a similar way. Thus it is obvious that aluminium centres play a major role in the destabilisation of potassium carbonate and may be at the origin of the increased CO_2 capacity observed in our experiments at 400°C in agreement with previous reports.

Although Raman spectroscopy was found to be of limited help concerning HT carbonates analysis because of a pronounced fluorescence which prevents a proper analysis, the comparison between potassium bicarbonate and $K_{22}AO$ has confirmed that γ-alumina destabilises potassium carbonate (figure 7).

Very interestingly, Raman spectroscopy allows to observe very clearly ν_1 stretching frequency of carbonate groups which absorb intensively in the region 1000-1150cm^{-1} contrary to DRIFTS. As a reference, potassium bicarbonate shows a single absorption band at 1027cm^{-1} at 100°C, whereas its decomposition product at 400°C (potassium carbonate) exhibits a band at 1061cm^{-1}. Although $K_{22}AO$ suffered from some interference due to fluorescence, two bands could be clearly detected at 100°C. The one around 1060cm^{-1} can probably be assigned to residual bulk potassium carbonate, whereas the one around 1094cm^{-1} is to be assigned to a carbonate group with a completely different symmetry. At 400°C it seems that both types of carbonate are still present although the relative intensity i.e. presence, obviously changed. Raman spectroscopy investigations are ongoing.

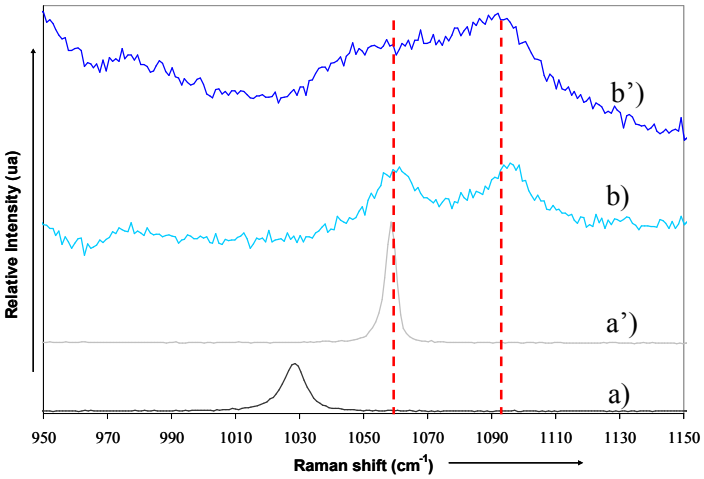

Figure 7: in situ Raman spectra -within 950-1150 cm^{-1}- of potassium bicarbonate at 100°C (a) 400°C (a') and 22wt% K_2CO_3 on γ-alumina at 100°C (b) and 400°C (b')

Conclusion

Hydrotalcites, potassium carbonate promoted hydrotalcite and potassium carbonate promoted γ-alumina have been proved to be excellent materials for in situ CO_2 capture during water gas shift process (SEWGS). Significant enhancement of CO_2 capacity can be achieved by alkaline promotion of the sorbents. We have unambiguously demonstrated that potassium carbonate is destabilized or transformed at the surface of metal oxides and particularly γ-alumina and hydrotalcites. Although no new carbonates structure or species could be identified by *in situ* XRD studies we showed that fixed CO_2 at 300-500°C hinders the reconstruction of hydrotalcites at room temperature most probably because of the formation of carbonate species. Moreover the *in situ* DRIFTS study confirmed that surface carbonates rearrangement occurs at high temperature and that the interaction between aluminium oxides centres and potassium carbonate plays a crucial role in the formation of active sites (strongly basic) for CO_2 capture at 300-500°C. These findings are furthermore corroborated by the very low sensitivity to potassium promotion of magnesium oxide.

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