

Potassium-Promoted γ -Alumina Adsorbent from K_2CO_3 Coagulated Alumina Sol for Warm Gas Carbon Dioxide Separation

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S Supporting Information



ABSTRACT: This paper provided a practical synthesis method of K-promoted γ -alumina for CO₂ precombustion capture integrating adsorbent pelleting and catalytic active component promotion into one single process. The precursor of the adsorbent, K-promoted pseudo-boehmite (PB), was synthesized from alumina sol and K₂CO₃ powder by mixing, aggregating, drying, and aging. Potassium-promoted γ -alumina was obtained after calcination at 400 °C from K-promoted PB. Characteristic crystallines of several stages of products in the synthesis process have been detected by X-ray diffraction. The optimal Al:K ratio in view of CO₂ capacity and cyclic performance of K-promoted γ -alumina was obtained by a thermal gravimetric analyzer. The optimal ratio of K-promoted γ -alumina showed a capacity of 0.67 mmol/g (dry base) for the first cycle and 0.34 mmol/g (wet base) after 30 pressure swing adsorption (PSA) cycles at 300 °C. K-promoted γ -alumina adsorbent could be favorable for a low energy penalty precombustion CO₂ capture application. It showed a variety of advantages such as low adsorption heat, good mechanical strength, low cost in synthesis, and fair stable capacity.

KEYWORDS: Potassium-promoted γ -alumina, Alumina sol, Warm gas cleanup, Precombustion CO₂ capture, Carbon dioxide adsorbent

INTRODUCTION

Fossil fuel-based power generation brings about a large amount of anthropological CO₂ emissions, which gives rise to global warming. However, CO₂ capture from the power generation process is energy consuming; consequently, thermal efficiency of power plants decreases by 8–10%.¹ Precombustion CO₂ capture in a warm gas cleanup process has two advantages. First, volumetric concentration of CO₂ in shift gas is 15–40%, relatively higher compared to its post-combustion counterpart. Second, if solid adsorbents were used in the elevated temperature range (250 °C–400 °C) of syngas or shift gas, another 0.2–0.7% of higher heating value (HHV)-based thermal efficiency penalty caused by carbon capture will be saved compared to cold cleanup such as Selexol. Moreover, it is possible to decrease the additional regeneration heat if pressure swing adsorption (PSA) is adapted for cyclic CO₂/H₂ separation process.² From this concept, a combination of water–gas shift and CO₂ precombustion capture, called

sorption-enhanced water–gas shift (SEWGS), has been comprehensively studied by various scientists.^{3–7}

Selection of proper adsorbents/sorbents is the priority in turning SEWGS into practice. Appropriate adsorbents/sorbents should meet the following requirements: (1) relatively fast adsorption and desorption kinetics, in order to match fast PSA processes, (2) stable cyclic CO₂ capacity in the temperature range of 250–400 °C, and (3) low adsorption heat/regeneration heat to meet the demand of PSA. Therefore, magnesium and aluminum oxide-based chemical adsorbents, including hydrotalcite-like compounds (HTLs), proved to be promising options by previous researchers.^{8–11} The chemical adsorption of CO₂ takes place on the surface by forming partially reversible chemical bonds. Unlike bulk chemical sorbents such as CaO and Li₂ZrO₃ (adsorption heat is 178

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and 160 kJ/mol, respectively), the adsorbents, which are weakly bonded with CO₂, will not transform into new products when adsorption takes place; thus, the adsorption heat is rather small. As shown in the literature, the adsorption heat of CO₂ on MgO and calcined hydrotalcite is 30–39¹² and 10–17 kJ/mol,⁸ respectively. Alkaline potassium salt is often promoted or doped to enhance the CO₂ capacity and adsorption kinetics of pristine magnesium oxide,¹³ aluminum oxide,^{14,15} and HTlc-derived materials.^{16–18} Promoted surface basic sites elevate the adsorption heat to 37.5 kJ/mol for Na₂O-promoted alumina,¹⁹ and 42 kJ/mol for K₂CO₃-promoted hydrotalcite.²⁰ In the above cases, the fact that the adsorption only takes place at the adsorbent's surface ensures continual CO₂ separation by MgO, Al₂O₃, and HTlcs in a PSA process.

For the above applicable surface adsorbents, good reversibility and mechanical stability are essential and will be discussed. Magnesium oxide may show higher capacity than its alumina counterpart; however, it suffers from poor stability in both capacity and mechanical strength. The adsorption temperature of CO₂ on MgO is usually between 25 and 100 °C, while desorption takes place at 400–800 °C.^{13,21} Hydrotalcite (most often discussed HTls) transforms to amorphous adsorbent after calcination at 400 °C.²² It can be viewed as a mixture of magnesium oxide and aluminum oxide at the atomic scale; thus, it combines the advantage of chemically active MgO and inert Al₂O₃. Although irreversible Mg ions are well dispersed at the atomic scale in the calcined hydrotalcite molecule, MgCO₃ is likely to form in pellets after 1200 cycles, giving rise to cyclic capacity degradation and mechanical failure.²³ Additionally, steam concentration and intense pressure change in real SEWGS and PSA processes should be considered. Therefore, the chemically inert and stable Al–O bond is more favorable for PSA than magnesium oxide-based adsorbents in the temperature range of 250–400 °C, especially taking adsorbent costs, cyclic reversibility, and mechanical strength into consideration.

It is reported that surface promotion by basic potassium salts, and analogous alkaline earth or alkaline metal earth salts, enables robust but poor CO₂ capacity alumina to become competitively adsorbent in removal of CO₂ from WGS processes.^{14,15,24–27} Traditionally, in order to obtain adsorbents in pellet form, shaped alumina pellets are directly doped or impregnated by a potassium cation-based solution. Jordan²⁴ studied the interfacial chemistry of K⁺ on molecular alumina in the impregnation process. The K–O–Al bond existed on the liquid–solid surface in the K₂CO₃ solution, and calcination enabled a uniform surface dispersion of K promotion. Walspurger synthesized¹⁵ K-promoted alumina from cheap alumina pellets. K-Dawsonite was formed after the reaction with CO₂ and steam at 300 °C and was regenerated at 500 °C by a temperature swing adsorption process. Wang²⁵ focused on the effects of various potassium salts on the surface basicity of alumina. Previous researches have contributed to a better understanding of the fundamental mechanism and reaction process of CO₂ adsorption on K-promoted alumina. It is time that focus should be paid to K-alumina's cyclic performance in real WGS operation conditions to look for possible applications for industrial use.

On one hand, alumina sol is one of the most used starting materials in adhesive and additive synthesis. On the other, simple electrolytes are often employed as coagulant to condense colloidal alumina or silica in industrial production of functional catalytic supports. A combination of both may

become a potential alternative for the traditional K⁺ solution impregnation method when taking integration of pelleting and promotion in one process into consideration. A mechanically stable functional alumina skeleton will be formed *in situ* to adhere and support the porous material after drying and calcination.

This research synthesized K₂CO₃-promoted γ -alumina by coagulating colloidal alumina sol with a K₂CO₃ electrolyte solution. The optimal ratio and various alkaline metal-based electrolytes have been studied. Crystalline phases of products after each synthesis step, including coagulation, drying, and calcination, are detected by X-ray diffraction (XRD). Cyclic performance of K-promoted alumina with an optimal K:Al ratio was tested isothermally at 300 °C and 1 atm, both in dry and wet conditions, by a thermal gravimetric analyzer (TGA) setup.

Synthesis of K-Promoted γ -Alumina. Anhydrous potassium carbonate (A.R., Beijing Chemicals) and commercial alumina sol (A-4-20, Snow Chemical, China) are starting materials for synthesizing K-promoted alumina. The main component of alumina sol is a positively charged [AlOOH]_n crystal, and its detailed properties are available in Table 1.

Table 1. Properties of A-4-20 Alumina Sol

AlOOH (wt %)	pH	average particle diameter	appearance	crystal type	impurities
20 ± 2%	4.0	20 nm	slight white liquid, water solvent	boehmite	NO ₃ ⁻ < 0.5% SiO ₃ ²⁻ < 0.1%

In preparation, various kinds of electrolytes of identical molar amounts, including basic K₂CO₃, CaCl₂, Na₂CO₃, and pH neutral KNO₃ powders were mixed with identical weight amounts of alumina sol in separate batches. A total of 0.05 mol of the mentioned salt above and 50 g of A-4-20 were mixed. In order to study the optimal molar ratio of Al to K in K₂CO₃ promoted alumina, various K₂CO₃ weights (Table 2) were selected.

First, electrolyte powder was added into alumina sol and stirred vigorously manually, followed by centrifuging for 10 min. Alumina sol coagulated and transformed to hydrogel gradually in this process. The mixture was dried in a 70 °C oven and aged for 24 h. Finally, the aged crystal was calcined at 400 °C for 6 h.

The stability colloid came from a bilayer electrical balance structure shown in Figure 1. The aggregate, or the micelle, accommodates the alumina sol's crystalline body.^{28,29} Potential-determining ions impart an electric field to adsorb negatively charged ions from the surrounding solution. The positively charged aggregate attracts additional randomly dispersed counterions to form a diffuse layer.

It was speculated that a coagulation process may take place when K₂CO₃ was added into the alumina sol. Solid K₂CO₃ powder was directly mixed with alumina sol, and white gel was quickly formed along with vigorous stirring, accompanied by bulk expansion and an exothermic process. Microscopically, the colloid stability was destroyed by adding electrolyte K₂CO₃ because ion concentration in solvent exceeded coagulation threshold. Carbonate anions, which were opposite in electric charge to that of alumina sol's colloidal particle, destroyed the stability of existing agglomerates, which would form larger

Table 2. Weight Ratio of A-4-20 Alumina Sol and Anhydrous K_2CO_3 in Prepared Samples

A-4-20 (g)	50	50	50	50	50	50	50
K_2CO_3 anhydrous (g)	0	6.325	6.9	7.475	9.25	11.5	13.8
molar ratio of Al to K^{a}	—	0.55	0.6	0.65	0.8	1.0	1.2

^aWeight of $AlOOH$ (solid) is regarded in calculation as 20 wt %.

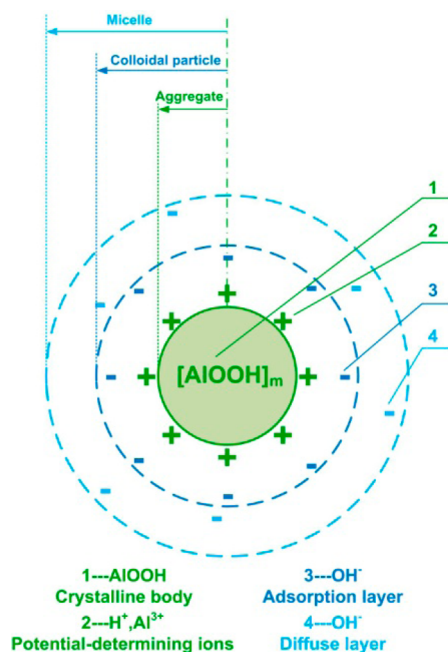


Figure 1. Illustration of alumina sol micelle.

agglomerates until they condensed in solution. The fluidity was lost, and hydrogel was generated under vigorous stirring.

The crystalline phases of products after 70 °C drying, aging, and 400 °C calcinations were detected by a $Cu K\alpha$ radiation Rigaku D-max 2500 XRD detector. A step size of 0.02° was applied, recording from 10° to 80° . In comparison, an identical portion of pristine alumina sol A-4-20, without adding electrolyte, was dried and calcined by the same process. For pure alumina sol, Figure 2 demonstrates that it loses aquatic solvent gradually by drying and aging and then condenses to form well-crystalline pseudoboehmite (JCPDS No. 21-1307). Finally, γ -alumina (JCPDS No. 29-0063) is obtained by calcinations at 400 °C. Characteristic peaks of K_2CO_3 (JCPDS No.49-1093) are found along with PB's characteristic

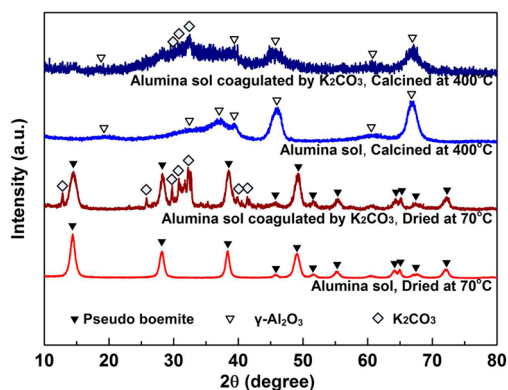


Figure 2. XRD patterns of products in K-promoted γ -alumina synthesis.

peaks. It is deduced by the XRD patterns that the following processes may take place. When foreign ions, K^+ and CO_3^{2-} , are introduced to precipitate a positively charged crystalline body of colloid, carbonate anions will be attracted by the micelle to form larger agglomerates. These agglomerates eventually coagulate and condense. K_2CO_3 crystals are formed after drying and aging. However, as is shown in Figure 2, part of the characteristic peaks of K_2CO_3 of the K-promoted γ -alumina disappear after calcination, illustrating that K_2CO_3 is more likely to be well dispersed on PB's surface in the calcination process.

On the basis of XRD analysis, the synthesis of K-promoted γ -alumina starts to form alumina, and K_2CO_3 is summarized in Figure 3. Foreign ions precipitates positively charged $[AlOOH]$ colloids, which coagulate to form $[AlOOH]_n$ aggregates thereafter. Uniformed K-promoted PB is obtained in the drying and aging process. Well-dispersed K promotion is realized by 400 °C calcination. During the calcination process, the average pore diameter decreases from 10.8 to 7.8 nm, and the BET surface area remains almost unchanged from 33.9 to 32.2 m^2/g .

Other types of electrolytes except K_2CO_3 , for example, basic $CaCl_2$, Na_2CO_3 , and pH neutral KNO_3 , will go through identical processes, including aggregation, condensation, drying, and aging, to form the correspondingly promoted PB and γ -alumina (Figure S1, Supporting Materials). Basic salts, especially alkaline carbonate-promoted γ -alumina, demonstrate better CO_2 capacity over others (Figure S2, Supporting Materials). This may be due to the better condensation effects of the dianionic carbonate and its basic promotion.

Optimal K-Promoted γ -Alumina Cyclic CO_2 Adsorption Tests. CO_2 adsorption was carried out by TGA. All samples were first calcined in situ at 400 °C for 6 h, and then the temperature dropped to 300 °C in atmospheric helium. An adsorption process was carried out at 300 °C for 60 min. The overall flow rate was 100 mL/min. In cyclic tests accorded with the real WGS process, steam was included in the shift gas mixture. A total of 3% (vol.) steam was carried by a bubble bottle in 60 mL/min helium, while 40 mL/min CO_2 gas was controlled by a bypass electro-magnetic valve automatically. The valve was opened for 30 min and closed for another 30 min for 30 cycles.

In order to select the optimal ratio for K_2CO_3 promotion, the effect of the Al:K ratio on the CO_2 capacity at atmospheric 300 °C is provided in Figure 4. The CO_2 capacity reaches a maximum value of 0.67 mmol/g when the molar ratio is 1:0.6. This CO_2 capacity is similar to 0.65 mmol/g of one kind of cylindrical, crushed, K-promoted hydrotalcite pellets from Ding and Alpay's report at 400 °C (wet base)⁸ but lower than around 1 mmol/g CO_2 capacity on K-promoted hydrotalcites powder at about 400 °C from several studies.^{7,16,30} On one hand, K promotion could increase the surface basicity of alumina,^{18,31} which is reported in previous work. It is also similar to the promotion effect of K_2CO_3 in the case of hydrotalcite;³² the K ion disrupts the surface ion arrangement to form more irregular steps, creating more active O^{2-} ions on the basic surface of the

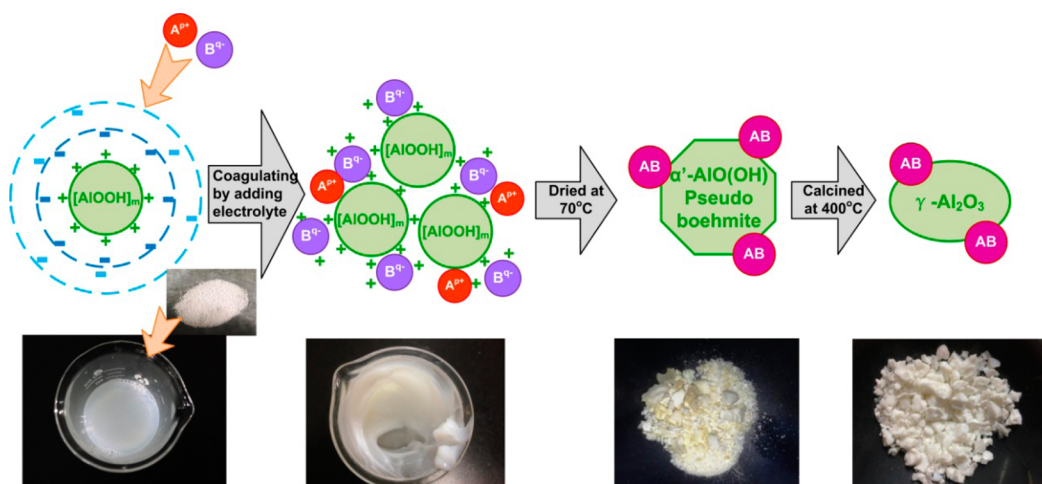


Figure 3. General scheme of synthesis process.

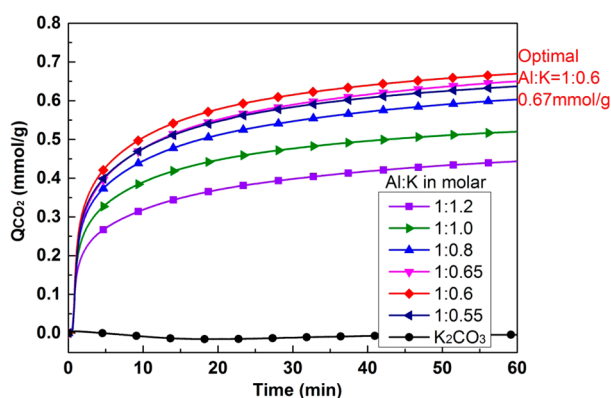


Figure 4. Adsorptive curves of K-promoted γ -alumina with various Al:K ratios.

adsorbents. On the other hand, CO_2 capacity will drop slightly when the Al:K ratio exceeds 1:0.6. Moreover, capacity decreases notably when the ratio is over 1:0.8, which is due to pure anhydrous K_2CO_3 being unable to adsorb CO_2 at 300°C (see round dots in Figure 4).

As mentioned above, the PSA cyclic operation mode is favorable for continuous in situ CO_2 capture from shift gas in the temperature range of about $250\text{--}400^\circ\text{C}$. Therefore, multiple cycle performances of the optimized Al:K ratio K-promoted γ -alumina were studied by TGA trials. As shown in Figure 5, the CO_2 capacity of K-promoted γ -alumina drops dramatically after the first cycle because part of the surface basic sites could reversibly adsorb CO_2 with a relatively weak chemical bond. The tendency of capacity degradation becomes less obvious after the first cycle, indicating that about half of the reversible active sites remain intact after cycles. Such a weak chemical bond as K–O–Al is reversible even in an elevated temperature range, while traditional physical adsorbents, like zeolites and carbon-based materials, often lost CO_2 capacity above 240°C . Similar experimental results could be found in hydrotalcite-based CO_2 adsorbents. It is probable that pressure swing adsorption could be applicable by adsorbents such as aluminum oxides with weak surface basic sites. As the experimental results in Figure 5 show, the values of cyclic capacity of both working conditions finally become stable after about 15 cycles. Approximately 51% and 35% reversible CO_2 capacity remains after 30 cycles, respectively. The effect of

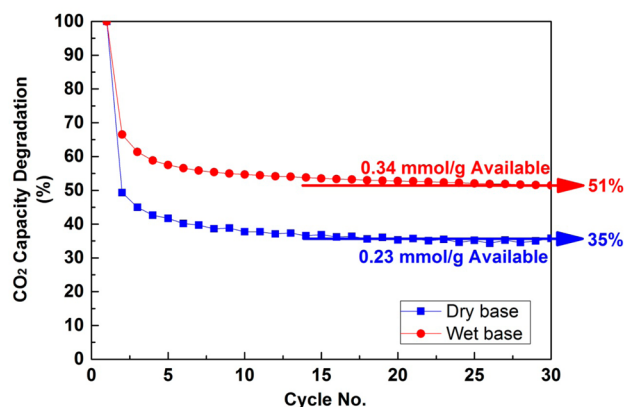


Figure 5. Comparison of cyclic CO_2 capacity of K-promoted γ -alumina in dry and wet conditions, 1 atm, and 300°C .

steam will improve the performance of K-promoted γ -alumina by about 47% in cyclic CO_2 capacity, proving that K-promoted γ -alumina is a potential competitive adsorbent for in situ warm gas CO_2 capture.

CONCLUSION

In this paper, K-promoted γ -alumina as an in situ CO_2 precombustion capture adsorbent was presented. Coagulation of gel by adding promotional electrolytes was adopted in synthesis processes. XRD patterns illustrated the forming of K-promoted PB after drying, aging, and transforming to K-promoted γ -alumina after calcination. This CO_2 adsorbent had a stable capacity of 0.34 mmol/g after 30 cycles with steam bubbling at the unchanged temperature of 300°C . The optimal ratio for Al:K was 1:0.6 for preparing the K-promoted PB precursor.

The synthesis of this adsorbent could have two merits for industrial production. First, it combined the catalyst pelleting process with the addition of the active promoter process. For conventional K-promoted alumina, a wet promotion process should be adopted based on the commercial-shaped adsorbent; while in this study, it was possible to make K-promoted PB pellets directly from starting materials (alumina sol and K_2CO_3) with a binder and an extruder. Second, the adsorbent took advantage of chemically inert alumina, which had a relatively low adsorption heat in favor of PSA operation and inherently

strong mechanical intensity. Moreover, the synthesis method provided a flexible prescription for adding corresponding active catalysts for specialized applications. HTlc and sodium oxide may be good additives for warm gas (250–400 °C) precombustion CO₂ capture adsorbents.

■ ASSOCIATED CONTENT

● Supporting Information

Figure S1 lists the XRD patterns of various electrolyte-promoted PB. Figure S2 compares the CO₂ capacity of various salt-promoted γ -alumina synthesized from precursors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

PB, pseudo boehmite; PSA, pressure swing adsorption; SEWGS, sorption-enhanced water–gas shift; HTlc, hydroxalcalite-like compounds; TGA, thermal gravimetric analyzer; XRD, X-ray diffraction

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