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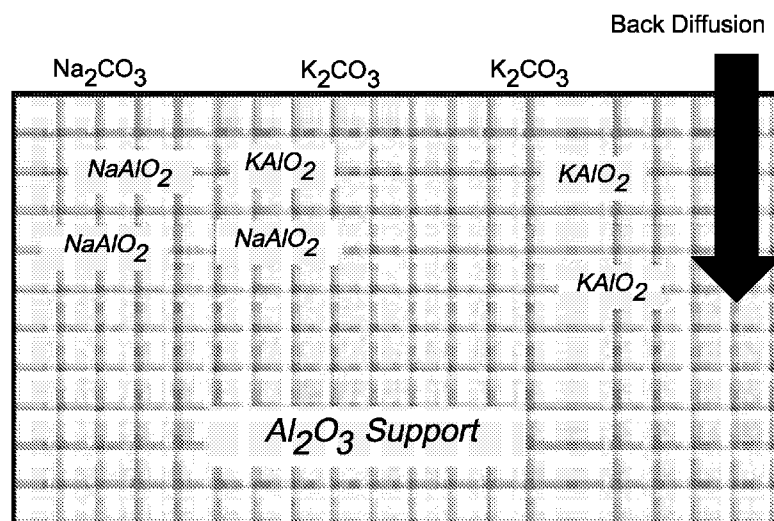


Figure 2A

(57) Abstract: The disclosure generally relates to CCS sorbents, particularly for CO₂/H₂O displacement desorption process. The sorbents include an aluminum oxide support that includes alkali metal salts within the support, in the form of pseudo alkali aluminate. The sorbents also include alkali metal salt impregnated on the support. The sorbents demonstrate improved CO₂ loadings and better H₂O/CO₂ ratios, as well as improved stability. Compositions and methods of making are disclosed.



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HIGH PERFORMANCE CO₂/H₂O DISPLACEMENT DESORPTION SORBENTS AND METHODS OF MAKING SAME

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/466,744, filed 3 March 2017, which is entirely incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] Portions of this disclosure were made with government support under Contract No. DE-FE0012870, awarded by the Department of Energy. The government may have certain rights in the invention.

TECHNICAL FIELD

[0003] The various embodiments of the disclosure relate generally to methods and compositions of high performance sorbents, particularly alkali metal salt aluminum oxide sorbents. The sorbents are particularly useful for CO₂/H₂O displacement desorption, and have been developed with improved stability and performance.

BACKGROUND

[0004] Fossil fuels currently supply the majority of world's energy needs and their combustion is the largest source of anthropogenic carbon dioxide emissions. Carbon dioxide is a greenhouse gas and is believed to contribute to global climate change. Concern over global climate warming has led to interest in capturing CO₂ emissions from the combustion of fossil fuels. The quantities of combustion gas produced in electric power generation are large because of the scale of furnaces and turbines utilized. One measure of the scale of these operations is the amount of CO₂ produced in a typical 500 Megawatt power plant, for coal fired power generation, the rate of CO₂ production is on the order of 100 kg per second; for gas fired power production it is more like 50 kg per second.

[0005] CO₂ can be removed from combustion flue gas streams by various methods, often referred to a carbon capture and sequestration (CCS.) The challenge for CO₂ capture from flue gas is to do it efficiently to minimize the cost. All post-combustion CO₂ capture technologies suffer from the disadvantages that the CO₂ in the flue gas is present at low pressure (1 atmospheric pressure) and in low concentrations (3 to 15%). A large amount of energy is

needed to separate CO₂. Developing methods that minimize the amount of energy and other costs will be necessary if CO₂ removal from flue gas is to be economical. Methods for the removal of CO₂ from flue gas streams include adsorption with a solvent, adsorption with a sorbent, membrane separation, and cryogenic fractionation and combinations thereof. In absorption/adsorption processes to capture CO₂, the energy needed to regenerate the sorbent or solvent is also a large cost element.

[0006] CO₂ displacement desorption process uses a competitive adsorption of H₂O to drive off adsorbed CO₂ on sorbent. During CO₂ capturing step, CO₂ of the flue gas displaces the adsorbed H₂O on the sorbent. Displacement desorption swings the concentrations of H₂O and CO₂. It is an isothermal process and has no need for pressure swing.

BRIEF SUMMARY

[0007] The various embodiments of the disclosure relate generally to CCS sorbents, particularly CO₂/H₂O displacement desorption sorbents, and methods for preparing the same.

[0008] An embodiment of the disclosure can be a method for preparing a CCS sorbent, comprising preparing a support by mixing a mixture comprising an aluminum compound and an aqueous solution of a first alkali metal salt to form a dough, extruding the dough to form an extrudate, and drying the extrudate to form the support, impregnating a second alkali metal salt into the support; and drying the impregnated support to create the sorbent. In some embodiments, the extrudate can be further calcined after drying.

[0009] In some embodiments, the extrudate can be dried at 125-500°C. The extrudate can also be dried at 250-350°C.

[00010] In some embodiments, the aluminum compound can be aluminum oxide, aluminum oxide hydroxide, aluminum hydroxide, boehmite, or pseudoboehmite. In some embodiments, the aluminum compound can be aluminum oxide hydroxide, boehmite, or pseudoboehmite.

[00011] In some embodiments, the first alkali metal salt can be a potassium salt, a sodium salt, or both a potassium salt and a sodium salt. In some embodiments, the second alkali metal salt can be lithium, sodium or potassium; or the second alkali metal salt can be sodium or potassium; or the second alkali metal salt can be sodium and potassium.

[00012] In some embodiments, the support can be a pseudo alkali aluminate. In some embodiments, the support can be a pseudo potassium aluminate, or a pseudo sodium aluminate, or a pseudo mixed potassium-sodium aluminate.

[00013] An embodiment of the disclosure can be a method for preparing a CCS sorbent, comprising impregnating a second alkali metal salt solution into a support; wherein the support is prepared by mixing an aluminum compound and an aqueous solution of a first alkali metal salt to form a dough, extruding the dough to form an extrudate, and drying the extrudate to form the support. In some embodiments, the extrudate is further calcined after drying.

[00014] In some embodiments, the extrudate can be dried at 125-500°C. The extrudate can also be dried at 250-350°C.

[00015] In some embodiments, the aluminum compound can be aluminum oxide, aluminum oxide hydroxide, aluminum hydroxide, boehmite, or pseudoboehmite. In some embodiments, the aluminum compound can be aluminum oxide hydroxide, boehmite, or pseudoboehmite.

[00016] In some embodiments, the first alkali metal salt can be a potassium salt, a sodium salt, or both a potassium salt and a sodium salt. In some embodiments, the second alkali metal salt can be lithium, sodium or potassium; or the second alkali metal salt can be sodium or potassium; or the second alkali metal salt can be sodium and potassium.

[00017] In some embodiments, the support can be a pseudo alkali aluminate. In some embodiments, the support can be a pseudo potassium aluminate, or a pseudo sodium aluminate, or a pseudo mixed potassium-sodium aluminate.

[00018] An embodiment of the disclosure can include a CCS sorbent, particularly a CO₂/H₂O displacement desorption sorbent. The sorbent can comprise a support, having an aluminum compound and a pseudo alkali aluminate, and an impregnated alkali salt.

[00019] In some embodiments, the pseudo alkali aluminate can include potassium, sodium or both potassium and sodium. In some embodiments, the pseudo alkali aluminate comprises potassium and sodium.

[00020] In some embodiments, the impregnated alkali salt can be lithium, sodium or potassium; or the impregnated alkali metal salt can be sodium or potassium; or the impregnated alkali metal salt can be sodium and potassium.

[00021] In some embodiments, the alkali composition of the support can be at least about 3 wt% as M_2O , at least about 5wt%, or at least about 8 wt%. The impregnated alkali salt can be at least about 5 wt% as M_2O of the total sorbent, or at least 7 wt%, or at least 9wt%.

BRIEF DESCRIPTION OF THE DRAWINGS

[00022] Figure 1 illustrates a simplified system of CO_2/H_2O displacement desorption system in which a sorbent of the disclosure would be applied, in accordance with an exemplary embodiment of the disclosure.

[00023] Figures 2A and 2B illustrate an $\gamma-Al_2O_3$ support with Na_2CO_3 and K_2CO_3 , and the denser phase of $KAlO_2$ that stabilizes K_2CO_3 and Na_2CO_3 , in accordance with an exemplary embodiment of the disclosure.

DETAILED DESCRIPTION

[00024] Although preferred embodiments of the disclosure are explained in detail, it is to be understood that other embodiments are contemplated. Accordingly, it is not intended that the disclosure is limited in its scope to the details of construction and arrangement of components set forth in the following description or illustrated in the drawings. The disclosure is capable of other embodiments and of being practiced or carried out in various ways. Also, in describing the preferred embodiments, specific terminology will be resorted to for the sake of clarity.

[00025] It must also be noted that, as used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise.

[00026] Also, in describing the preferred embodiments, terminology will be resorted to for the sake of clarity. It is intended that each term contemplates its broadest meaning as understood by those skilled in the art and includes all technical equivalents which operate in a similar manner to accomplish a similar purpose.

[00027] Ranges can be expressed herein as from “about” or “approximately” one particular value and/or to “about” or “approximately” another particular value. When such a range is

expressed, another embodiment includes from the one particular value and/or to the other particular value.

[00028] By “comprising” or “containing” or “including” is meant that at least the named compound, element, particle, or method step is present in the composition or article or method, but does not exclude the presence of other compounds, materials, particles, method steps, even if the other such compounds, material, particles, method steps have the same function as what is named.

[00029] It is also to be understood that the mention of one or more method steps does not preclude the presence of additional method steps or intervening method steps between those steps expressly identified. Similarly, it is also to be understood that the mention of one or more components in a device or system does not preclude the presence of additional components or intervening components between those components expressly identified.

[00030] Embodiments of this disclosure include sorbent for use in a CCS process, particularly CO₂/H₂O displacement desorption, and methods for preparing or improving the stability of those sorbents. Figure 1 demonstrates a simplified system of CO₂/H₂O displacement desorption, in which a sorbent of this disclosure might be applied. System **100** includes two sorbent bed positions, **101** and **102**, in which the sorbents of this disclosure would be placed. Sorbent bed position **101** contains a sorbent that is initially CO₂ poor. A CO₂ rich stream, **110**, e.g. a flue gas feed from a combustion source, passes across sorbent bed **101**, which absorbs the CO₂, and a CO₂ depleted stream exits the bed. Once sorbent bed **101** is saturated, it can move to sorbent bed position **102**. A steam feed **120** containing water vapor, can enter the CO₂ saturated sorbent bed **102** and cause desorption and displacement of the CO₂ from the sorbent. The exit gas stream is then a CO₂ rich stream that can then be further processed. Once sorbent bed **102** is regenerated, it can return to position **101**. Several applications of this system have been demonstrated, such as in U.S. Patent Nos. 9,504,955; 9,446,343; 9,539,540; and 9,527,029.

[00031] The typical sorbent used in CO₂/H₂O displacement desorption is an alkali metal salt impregnated on an aluminum oxide catalyst, particularly using a potassium salt. K₂CO₃/Al₂O₃ is a preferred sorbent currently. However, this sorbent deactivates on stream, which degrades performance of the system. CCS tests showed the sorbents usually had high initial CO₂ sorption capacities, but they were gradually losing CO₂ sorption capacities on

stream. Sorbent aging also leads to higher $\text{H}_2\text{O}/\text{CO}_2$ molar ratios. Potassium carbonate agglomeration on the support surface gives rise to hydroxyl groups resurfacing, which results in more H_2O sorption onto the sorbents.

[00032] Characterizations of spent sorbent revealed the formation of poison phase potassium aluminate carbonate. Under hydrothermal testing condition, Al_2O_3 slowly converts to aluminum hydroxide ($\gamma\text{-AlOOH}$, boehmite), which reacts easily with K_2CO_3 to form KAlO_2 . The formation of KAlO_2 weakens its affinity towards CO_2 sorption. One route discovered and discussed herein to mitigate sorbent deactivation can include creating a denser phase support structure based on a pseudo MAlO_2 structure. The $\gamma\text{-Al}_2\text{O}_3$ support has a defect spinel structure, with 7/8 of tetrahedral sites and 1/2 octahedral sites that are empty, and these sites can accommodate alkali cations to form pseudo aluminates. Extrusions of Na_2CO_3 and K_2CO_3 with boehmite could form pseudo NaAlO_2 and KAlO_2 phases, acting as denser phases to limit further diffusions of Na_2CO_3 and K_2CO_3 into support, which leads to a stable and high performance CCS sorbent. Thus, to improve sorbent CCS performance, extrusions of sodium carbonate and potassium carbonate with aluminum hydroxide ($\gamma\text{-AlOOH}$, boehmite) were carried out to form supports with denser phases of pseudo NaAlO_2 and KAlO_2 . The dense phase supports limit the further diffusions of Na_2CO_3 and K_2CO_3 into supports. These dense phase pseudo aluminate supports can then be impregnated with alkali metal salts, producing sorbents with excellent and stable CCS performances, high CO_2 loading capacities and low $\text{CO}_2/\text{H}_2\text{O}$ molar ratios.

[00033] The disclosure can include a method for preparing a CCS sorbent, including a $\text{CO}_2/\text{H}_2\text{O}$ displacement desorption sorbents. The method can include the steps of preparing a support, impregnating a second alkali metal salt into the support; and drying the impregnated support to create the sorbent. The support can be prepared by mixing a mixture that includes an aluminum compound and an aqueous solution of a first alkali metal salt to form a dough, extruding the dough to form an extrudate, and drying the extrudate to form the support. The CCS sorbent can also be prepared by impregnating a second alkali metal salt solution into a support; where the support is prepared by mixing an aluminum compound and an aqueous solution of a first alkali metal salt to form a dough, extruding the dough to form an extrudate, and drying the extrudate to form the support. In some embodiments, the extrudate is

preferably further calcined after drying and before impregnation by the second alkali metal salt.

[00034] The disclosure can also include a CCS sorbent, including a CO₂/H₂O displacement desorption sorbent. The CCS sorbent can include a support comprising an aluminum compound and a pseudo alkali aluminate, and an alkali salt impregnated on the support.

[00035] The first alkali metal salt and the aluminum compound can be mixed together by any mixing technique known to one of skill in the art. For example, the first alkali metal salt and the aluminum compound can be milled or grinding together into a mixture containing the two compounds. The mixture can be extruded by any technique known to one of skill in the art, particularly as relates to solid supports used in sorbent technologies. Typically, the mixture is milled as an aqueous solution of the first alkali metal salt and the aluminum compound. However, other polar protic and aprotic solvents could be applied, including particularly an alcohol.

[00036] The extrudate can be dried at any temperature that drives off moisture. The extrudate can be dried at greater than about 125°C, greater than about 150°C, greater than about 200°C, or greater than about 250°C. The extrudate can be dried at up to about 500°C, up to about 450°C, up to about 400°C, or up to about 350°C. The extrudate can be dried at a temperature between about 125°C to about 500°C, about 200°C to about 400°C, or about 250°C to about 350°C. As discussed in a co-pending provisional application filed by the same entity on the same day, and titled CALCINATION OF CO₂/H₂O DISPLACEMENT DESORPTION SORBENTS, which is incorporated by reference in its entirety as if set forth herein, the lower calcination temperatures can provide better support for the techniques disclosed herein.

[00037] Alternatively, the dried extrudate can be further calcined at a temperature of greater than about 400°C, greater than about 450°C, or greater than about 500°C. The extrudate can be calcined at a temperature of less than about 600°C.

[00038] In the disclosure, the aluminum compound includes any general aluminum oxide type compound, such as one of ordinary skill in the art would use in making aluminum oxide-type support structures. In an embodiment, the aluminum compound can be comprises aluminum oxide, aluminum oxide hydroxide, aluminum hydroxide, boehmite, or pseudoboehmite. The aluminum oxides, oxide hydroxides, and hydroxides can include

aluminum oxides including γ -aluminum oxide, θ -aluminum oxide, corundum (Al_2O_3); aluminum oxide hydroxides such as diaspore ($\alpha\text{-AlO}(\text{OH})$), boehmite or böhmite ($\gamma\text{-AlO}(\text{OH})$), akdalaite, including $5\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $4\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, also called tohdite; and aluminum hydroxides such as gibbsite, hydrargillite (hydrargyllite), bayerite, doyleite, nordstrandite, including $\alpha\text{-Al}(\text{OH})_3$, $\beta\text{-Al}(\text{OH})_3$, $\gamma\text{-Al}(\text{OH})_3$. In some preferred embodiments, the aluminum compound comprises aluminum oxide hydroxide compounds, particularly, boehmite, or pseudoboehmite. While traditional Al_2O_3 compounds, as well as other aluminum oxide type compounds can work effectively, and without wishing to be bound by theory, the boehmite and pseudoboehmite compounds appear to be more effective in part because of the added hydroxylation of the alumina composition, prior to drying and optionally calcining the support/extrudate.

[00039] The first alkali metal salt can include any alkali metal salt. By alkali metal is meant a Group 1 metal (group IA), including lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs). Preferably the first alkali metal salt can include sodium, potassium, or a combination of sodium and potassium. The first alkali metal salt can include potassium, or the first alkali metal salt can include sodium.

[00040] The second alkali metal salt can include any alkali metal salt. As used herein the second alkali metal salt can as be known as the impregnating, or impregnated, alkali salt, because this alkali metal salt is added second to the support via impregnation to for the sorbent. By alkali metal is meant a Group 1 metal (group IA), including lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs). The second alkali metal salt (i.e. impregnated alkali salt) can include lithium, sodium, potassium, rubidium, or cesium, or combinations thereof. The second alkali metal salt can include lithium, sodium, potassium, or cesium, or combinations thereof. The second alkali metal salt can include lithium, sodium, or potassium, or combinations thereof. The second alkali metal salt can include potassium and sodium.

[00041] In some instances, the second alkali metal salt can be two different alkali metal salts. For example, impregnating both potassium and sodium can provide improved performance and stability over impregnating with only one alkali metal salt, including particularly only potassium metal salts. As discussed in a co-pending provisional application filed by the same entity on the same day, and titled MIXED METAL SORBENTS FOR

CO₂/H₂O DISPLACEMENT DESORPTION, which is incorporated by reference in its entirety as if set forth herein, poisoning effects and improved performance can be achieved if two salts can be applied as the impregnating salts.

[00042] One of ordinary skill would understand that alkali metal in the context of this disclosure implies the alkali metal cation. As such, synonymous terms include alkali metal salt, alkali metal ion, alkali metal cation, an alkali salt, alkali ion, or alkali cation. The alkali metal salt can also in the context of this disclosure be referred to as an alkali metal composition.

[00043] Because the alkali metal is a cation, it will necessarily have a counterion, i.e. an anion. However, the nature of that anion is not a limiting issue. On the sorbent, particularly during operation, the anion can be a carbonate or bicarbonate counterion, or a hydroxyl or oxide anion that is part of the support to which the alkali metal is impregnated upon. Moreover, during preparation of the sorbents, and also as part of the sorbent when the salt is impregnated on the support, the alkali metal cation can have any counteranion one of ordinary skill would use. Nonlimiting examples of the anion can be hydroxides, halides, carbonates, bicarbonates, nitrates, nitrite, phosphate, hydrogen phosphate, dihydrogen phosphate, and organic acid salts including but not limited to acetate, citrate, gluconate, and benzoic acid, etc.

[00044] The support created by this method, and the support within the CCS sorbents, comprises a pseudo alkali aluminate. As discussed above and as shown in further detail below, alkali metals in the presence of hydroxylated aluminum compounds, particularly for example aluminum oxide hydroxide compounds, can combine under heat to form alkali aluminates, MAIO₂ where M is a alkali metal. Without wishing to be bound by theory, the structural form of this MAIO₂ is not necessarily pervasive throughout the entire support, and portions of the support can include regions of aluminum compounds such as Al₂O₃. However, the process disclosed here and the CCS sorbents created here include a denser phase section that includes the MAIO₂, i.e. alkali aluminate, and is referred to as a pseudo alkali aluminate because the structure is not purely or exclusively MAIO₂. Because of low temperature calcination and non-stoichiometry ratios between alkali metals and alumina support, the interactions between alkali metals and alumina can generate an amorphous phase, or pseudoaluminate, that lacks a long-range periodic ordering between alkali and alumina. High temperature calcination can generate a well-crystallized phase called alkali aluminate, which

can be detected by X-ray diffraction. The pseudo alkali aluminate can be a pseudo potassium aluminate, a pseudo sodium aluminate, a pseudo lithium aluminate, a pseudo rubidium aluminate, or a pseudo cesium aluminate. The pseudo alkali aluminate can be a pseudo potassium aluminate, a pseudo sodium aluminate, or a pseudo lithium aluminate; or can be a pseudo potassium aluminate or a pseudo sodium aluminate, or a combination of a pseudo potassium aluminate and a pseudo sodium aluminate.

[00045] The methods and sorbent of the disclosure, by virtue of creating a pseudo alkali aluminate within the support prior to impregnation, can have two different alkali metal values. The first alkali metal value can indicate the amount of alkali metal within the support as part of the pseudo alkali aluminate. This value would also reflect the amount of alkali added to the mixture used for form the support, such as during mixing, extruding and before drying the extrudate. Thus, in an embodiment, the alkali composition of the support can be at least about 3 wt% of the support, at least about 4 wt% of the support, at least about 5 wt% of the support, at least about 6 wt% of the support, at least about 7 wt% of the support, at least about 8 wt% of the support, at least about 9 wt% of the support, or at least about 10 wt% of the support. The alkali composition of the support can be up to about 30 wt% of the support, or up to about 25 wt% of the support. In another embodiment, the amount of impregnated alkali salt, or the amount of alkali salt added to the support via impregnation during the method of making the support, can be at least about 5 wt% of the sorbent, at least about 6 wt% of the sorbent, at least about 7 wt% of the sorbent, at least about 8 wt% of the sorbent, at least about 9 wt% of the sorbent, at least about 10 wt% of the sorbent, at least about 11 wt% of the sorbent, or at least about 12 wt% of the sorbent. The percent weight of alkali metal is presented as weight M_2O as a percentage of the total weight of the support or sorbent. The weight percent of M_2O is defined as the weight of M_2O /(the weight of alumina support + the weight of M_2O). The weight percent of M_2O usually ranges from 5 wt% to 30 wt%.

EXAMPLES

[00046] The following examples are illustrative, but not limiting, of the methods and compositions of the present disclosure. Other suitable modifications and adaptations of the variety of conditions and parameters normally encountered in the field, and which are obvious

to those skilled in the art, are within the spirit and scope of the disclosure. All patents and publications cited herein are fully incorporated by reference herein in their entirety.

Example 1 - Preparation of 8.6% K₂O/Al₂O₃

[00047] γ -Al₂O₃ extrudates (1/20 inch in diameter, quadlobe shape) were used as support to deposit K₂CO₃. It has surface area of 250 m²/g, 0.85 cm³/g pore volume and pore size centered on 73 Å. An aqueous solution containing potassium carbonate was prepared by dissolving K₂CO₃ in distilled H₂O. The sorbent of K₂O/ γ -Al₂O₃ was prepared by an incipient wetness technique. As an example of sample preparation, 13.8 g of potassium carbonate was dissolved in 50.0 g of distilled water. The total solution volume of K₂CO₃ adjusted with distilled water was 78.9 ml. 100.0 g of γ -Al₂O₃ the extrudates were impregnated with the solution by incipient wetness. The sample was dried in air at 250°F for 16 hours and calcined in air at 1000°F for 3 hours. The furnace was ramped at rate of 5°F/min. During the calcination, the air flow was adjusted to 5 volume/volume solid/minute. The sorbent contains 8.6% K₂O as K loading.

[00048] The metal loading is defined as metal oxides, which does not necessarily represent the final state of the metal precursors on alumina support. 11.03%Na₂O/ γ -Al₂O₃ and 15.85%K₂O/ γ -Al₂O₃ were also prepared. The carbonates, acetates and citrates of Na and K were used as precursor compounds for the sorbent preparations.

Example 2 - Extrusions of 10%K₂O/V-300 Al₂O₃

[00049] 61.372 g of potassium carbonate was dissolved in 325 g of water. 500 g of Versal-300 alumina powders was impregnated with the solution of potassium carbonate (K₂CO₃). The mixture was placed in muller and mulled for 40 minutes. The extrusion dough targeted solid percentage was 49.41%. The mixture dough was extruded into 1/16" quadrilobe extrudates with Diamond America Extruder. After the extrusion, the extrudates were spread into thin layers in the sample trays. The extrudates were dried 16 hours in air at 250°F. After drying, the extrudates were used as supports for the impregnation of solution of sodium and potassium carbonates. A portion of extrudates were also calcined in air at 1000°F for 3 hours. The furnace was ramped at rate of 5°F/min. During the calcination, the air flow was adjusted

at 5 volume/volume solid/minute. The calcined extrudates were also used as supports for the deposition of sodium and potassium carbonates.

[00050] Besides the extrusion of 10%K₂O/V-300 Al₂O₃, the dense sorbent supports with different potassium loadings of 8%K₂O/V-300 Al₂O₃ and 12%K₂O/V-300 Al₂O₃ were also prepared and used as supports for deposition of sodium and potassium carbonates.

[00051] Besides the extrusions of potassium carbonate (K₂CO₃) with Versal-300 Al₂O₃ powders, the extrusions of sodium carbonate (Na₂CO₃) with Versal-300 Al₂O₃ powders were also carried out. The dense phase supports were used for deposition of sodium and potassium carbonates. The supports with various sodium contents were prepared with the following compositions: 6%Na₂O/V-300 Al₂O₃, 8%Na₂O/V-300 Al₂O₃, 10%Na₂O/V-300 Al₂O₃, 12%Na₂O/V-300 Al₂O₃, 16%Na₂O/V-300 Al₂O₃ and 20%Na₂O/V-300 Al₂O₃. The metal loading is defined as metal oxides, which does not necessarily represent the final state of the metal precursors on alumina support.

[00052] Besides the extrusions of potassium carbonate (K₂CO₃) with Versal-300 Al₂O₃ powders and the extrusions of sodium carbonate (Na₂CO₃) with Versal-300 Al₂O₃ powders, the extrusions of both potassium carbonate (K₂CO₃) and sodium carbonate (Na₂CO₃) with Versal-300 Al₂O₃ powders were also carried out. The dense phase supports were used for deposition of sodium and potassium carbonates. The supports prepared with the following compositions: 5.4%K₂O+3.5%Na₂O/V-300 Al₂O₃, 7.7%K₂O+5.1%Na₂O/V-300 Al₂O₃, and 9.9%K₂O+6.5%Na₂O/V-300 Al₂O₃.

[00053] Besides Versal-300 aluminum hydroxide (γ -AlOOH, boehmite) powders were used in extrusions to form dense phase supports, Versal-250 boehmite powders, Versal-700 boehmite powders and Catapal D boehmite powders were also used in extrusions. The dense phase supports were used for deposition of sodium and potassium carbonates.

Example 3 - Preparation of 5.4%K₂O+3.5%Na₂O/10%K₂O/Al₂O₃

[00054] 10%K₂O/Al₂O₃ extrudates both calcined and not-calcined were used as supports for the impregnation of solution of sodium and potassium carbonates.

[00055] The aqueous solution containing sodium and potassium carbonates was prepared by dissolving Na₂CO₃ and K₂CO₃ in distilled H₂O. The sorbent was prepared by incipient wetness. 17.276 g of potassium carbonate and 13.248 g of sodium carbonate were dissolved in

120 g of di-H₂O. 200 g of 10%K₂O/ Al₂O₃ extrudates were impregnated with the solution by incipient wetness. The sample was dried in air at 250°F for 16 hours and calcined in air at 1000°F for 6 hours. The furnace was ramped at rate of 5°F/min. During the calcination, the air flow was adjusted at 5 volume/volume solid/minute.

[00056] In addition to 5.4%K₂O+3.5%Na₂O/10%K₂O/Al₂O₃, compositions containing 7.7%K₂O + 5.1% Na₂O/10% K₂O/ Al₂O₃ and 9.9% K₂O + 6.5%Na₂O/10%K₂O/ Al₂O₃ were also prepared similarly.

Example 4 - CO₂ Sorption/Steam Displacement Fixed Bed Testing

[00057] Simulated flue gas during fixed bed testing contained 13.4% CO₂ and 14.9% H₂O balanced with N₂. The fixed bed volume is 100 cc. With the simulated natural gas conditions the flue gas space velocity during screening conditions was 10.56 SCCM/g for 9 minutes and steam regeneration space velocity was 3.74 SCCM/g for 9 minutes. The temperature during adsorption was about 140°C, increasing to approximately 153°C during sorbent regeneration.

[00058] In the single fixed bed, all flow controllers were calibrated to obtain high accuracy in gas flowrates. Whenever a gas is not in use, the flow controller is completely shut to prevent any gas leakage. During adsorption cycle, N₂ and CO₂ are mixed with steam provided by 500 cc syringe pump. The feed enters the bed by down-flow through a 3-way valve and exits through another 3-way valve. The outlet gas/steam moves through a chiller, and the steam is condensed, collected and measured by an online scale. N₂ and CO₂ gases pass the chiller and exit to a ZRE CO₂ analyzer which measures the breakthrough CO₂ concentration. During regeneration cycle, both the 3-way valves are switched to allow steam controlled by 1000 cc syringe pump to enter the bed by up-flow and exit via a different path toward a second chiller. The steam is condensed and collected by online scale for measurement of water out in regeneration. CO₂ passes the chiller and is diluted with N₂ before entering the ZRE CO₂ analyzer which detects the desorbed CO₂ concentration. Both syringe pumps are continuously running through a 3-way valve which directs the steam either through the bed or to a by-pass line. The downstream N₂ is also used to remove/flush out the condensed water in the exit line at the end of each cycle.

RESULTS AND DISCUSSION

[00059] γ - Al_2O_3 has a defect spinel structure. 7/8 of tetrahedral sites and 1/2 octahedral sites are empty, which can accommodate alkali cations to form aluminates. Extrusions of Na_2CO_3 and K_2CO_3 with boehmite were to perform sorbent supports of pseudo NaAlO_2 and KAlO_2 , acting as denser phases to limit further diffusions of Na_2CO_3 and K_2CO_3 into support as illustrated in Figures 2A and 2B. The sorbents made by impregnations of Na_2CO_3 and K_2CO_3 on the dense phase supports of NaAlO_2 and KAlO_2 have led the development of sorbents with excellent and stable CCS performances, high CO_2 loading capacity and low $\text{CO}_2/\text{H}_2\text{O}$ molar ratios.

[00060] Table 1 summarizes the $\text{CO}_2/\text{H}_2\text{O}$ displacement desorption performances of several CO_2 sorbents developed and incorporated herein.

Table 1 – Summary of CO_2 Sorbent Development

Sorbent Impregnati ng alkali metal Support	Sorbe nt A 12% Na_2O Al_2O_3	Sorbe nt B 15.85 % K_2O Al_2O_3	Sorbent C 9.9%K_2O+6.5% Na_2O Al_2O_3	Sorbent D 5.4%K_2O+3.5% Na_2O 10% $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$	Sorbent E 5.4%K_2O+3.5% Na_2O 10% $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$
CO_2 wt% loading	0.56	0.81	1.03	1.07	1.14
Molar ratio of $\text{H}_2\text{O}/\text{CO}_2$	6.60	5.50	4.31	3.66	3.94
Density (g/ml)	0.60	0.48	0.53	0.62	0.7

[00061] Sorbent A was prepared by extrusion of Na_2CO_3 with Versal-700 Al_2O_3 . CO_2 sorption loading was 0.56 wt%, with molar ratio of $\text{H}_2\text{O}/\text{CO}_2$ of 6.60.

[00062] Sorbent B was prepared by impregnation of K_2CO_3 solution onto alumina support. Higher CO_2 sorption capacity was due to higher dispersion of potassium carbonate on Al_2O_3 .

Formation of poison phase of potassium aluminate carbonate hydrate gradually reduced CO₂ capacity on stream.

[00063] Sorbent C was mixed Na + K sorbents, according to co-pending provisional application filed on the same date and titled MIXED METAL SORBENTS FOR CO₂/H₂O DISPLACEMENT DESORPTION, herein incorporated by reference in its entirety as if fully set forth below. Addition of Na carbonate was to interrupt the crystallization of the poison phase K aluminate carbonate hydrate. The similar counterpart phase with Na cations does not exist. Better sorbent performance compared to 2nd generation sorbent, higher CO₂ sorption capacity of 1.03 wt% and lower H₂O/CO₂ ratio of 4.31.

[00064] Sorbent D was prepared by extrusions of K₂CO₃ with alumina to preform denser phase of pseudo KAlO₂, according to this disclosure. After extrusion, the 10% K₂O/ Al₂O₃ was impregnated with K₂CO₃ and Na₂CO₃ solutions. Stable and high CO₂ loading of 1.07 wt% and much low H₂O/CO₂ ratio of 3.66 were observed. Also the density of the sorbent was increased to 0.62.

[00065] Sorbent E was prepared by extrusions of K₂CO₃ with alumina to preform denser phase support of KAlO₂, according to this disclosure. After extrusion, the support of 10%K₂O/ Al₂O₃ was only dried at 250°F in air before it use as support for Na and K carbonates deposition, according to co-pending provisional application filed on the same date and titled CALCINATION OF CO₂/H₂O DISPLACEMENT DESORPTION SORBENTS, herein incorporated by reference in its entirety as if fully set forth below. Without calcination, more hydroxyl groups on the supports were preserved, which can act as anchoring points for Na and K carbonates dispersions. This leads to higher CO₂ loading of 1.14 wt%. Also the density of the sorbent was further increased to 0.70 g/ml, which indicates that CO₂ sorption loading per volume of sorbent increased.

[00066] It is to be understood that the embodiments and claims disclosed herein are not limited in their application to the details of construction and arrangement of the components set forth in the description and illustrated in the drawings. Rather, the description and the drawings provide examples of the embodiments envisioned. The embodiments and claims disclosed herein are further capable of other embodiments and of being practiced and carried out in various ways. Also, it is to be understood that the phraseology and terminology

employed herein are for the purposes of description and should not be regarded as limiting the claims.

[00067] Accordingly, those skilled in the art will appreciate that the conception upon which the application and claims are based can be readily utilized as a basis for the design of other structures, methods, and systems for carrying out the several purposes of the embodiments and claims presented in this application. It is important, therefore, that the claims be regarded as including such equivalent constructions.

CLAIMS

We claim:

1. A method for preparing a CCS sorbent, comprising
preparing a support by
 mixing a mixture comprising an aluminum compound and an aqueous solution
 of a first alkali metal salt to form a dough,
 extruding the dough to form an extrudate,
 and drying the extrudate to form the support;
impregnating a second alkali metal salt into the support; and
drying the impregnated support to create the sorbent.
2. The method of claim 1, wherein the extrudate is further calcined after drying.
4. The method of claim 1, wherein the extrudate is dried at 125-500°C.
5. The method of claim 1, wherein the extrudate is dried at 250-350°C.
6. The method of claim 1, wherein the aluminum compound comprises aluminum oxide, aluminum oxide hydroxide, aluminum hydroxide, boehmite, or pseudoboehmite.
7. The method of claim 1, wherein the aluminum compound comprises aluminum oxide hydroxide, boehmite, or pseudoboehmite.
8. The method of claim 1, wherein the first alkali metal salt comprises a potassium salt, a sodium salt, or both a potassium salt and a sodium salt.
9. The method of claim 1, wherein the support comprises a pseudo alkali aluminate.
10. The method of claim 1, wherein the support comprises a pseudo potassium aluminate.

11. The method of claim 1, wherein the second alkali metal salt comprises lithium, sodium or potassium.
12. The method of claim 1, wherein the second alkali metal salt comprises sodium or potassium.
13. The method of claim 1, wherein the second alkali metal salt comprises sodium and potassium.
14. A method for preparing a CCS sorbent, comprising impregnating a second alkali metal salt solution into a support; wherein
the support is prepared by
 mixing an aluminum compound and an aqueous solution of a first alkali metal salt to form a dough,
 extruding the dough to form an extrudate,
 and drying the extrudate to form the support.
15. The method of claim 14, wherein the extrudate is further calcined after drying.
16. The method of claim 14, wherein the extrudate is dried at 125-500°C.
17. The method of claim 14, wherein the extrudate is dried at 250-350°C.
18. The method of claim 14, wherein the aluminum compound comprises aluminum oxide, aluminum oxide hydroxide, aluminum hydroxide, boehmite, or pseudoboehmite.
19. The method of claim 14, wherein the aluminum compound comprises aluminum oxide hydroxide, boehmite, or pseudoboehmite.
20. The method of claim 14, wherein the first alkali metal salt comprises a potassium salt, a sodium salt, or both a potassium salt and a sodium salt.

21. The method of claim 14, wherein the support comprises a pseudo alkali aluminate.
22. The method of claim 14, wherein the support comprises a pseudo potassium aluminate.
23. The method of claim 14, wherein the second alkali metal salt comprises lithium, sodium or potassium.
24. The method of claim 14, wherein the second alkali metal salt comprises sodium or potassium.
25. The method of claim 14, wherein the second alkali metal salt comprises sodium and potassium.
26. A CCS sorbent, comprising
a support comprising an aluminum compound and a pseudo alkali aluminate, and
an impregnated alkali salt,
wherein,
the alkali composition of the support is at least about 3 wt% as M_2O , and
the impregnated alkali salt is at least about 5 wt% as M_2O of the total sorbent.
27. The sorbent of claim 26, wherein the pseudo alkali aluminate comprises potassium, sodium or both potassium and sodium.
28. The sorbent of claim 26, wherein the pseudo alkali aluminate comprises potassium and sodium.
29. The sorbent of claim 26, wherein the impregnated alkali salt comprises potassium, sodium or both potassium and sodium.

30. The sorbent of claim 26, wherein the impregnated alkali salt comprises potassium and sodium.
31. The sorbent of claim 26, wherein the alkali composition of the support is at least about 8 wt% as M_2O .
32. The sorbent of claim 26, wherein the impregnated alkali salt is at least about 9 wt% as M_2O .

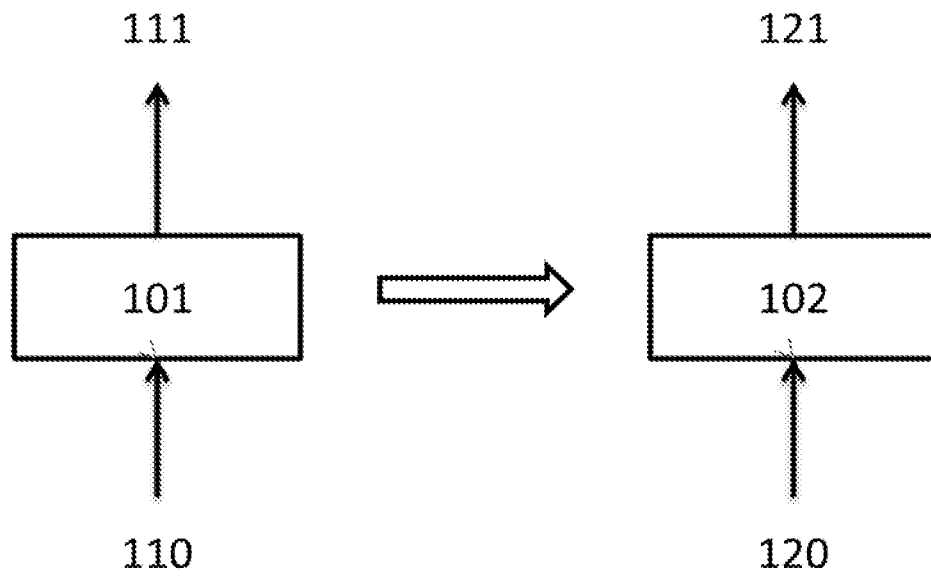


Figure 1

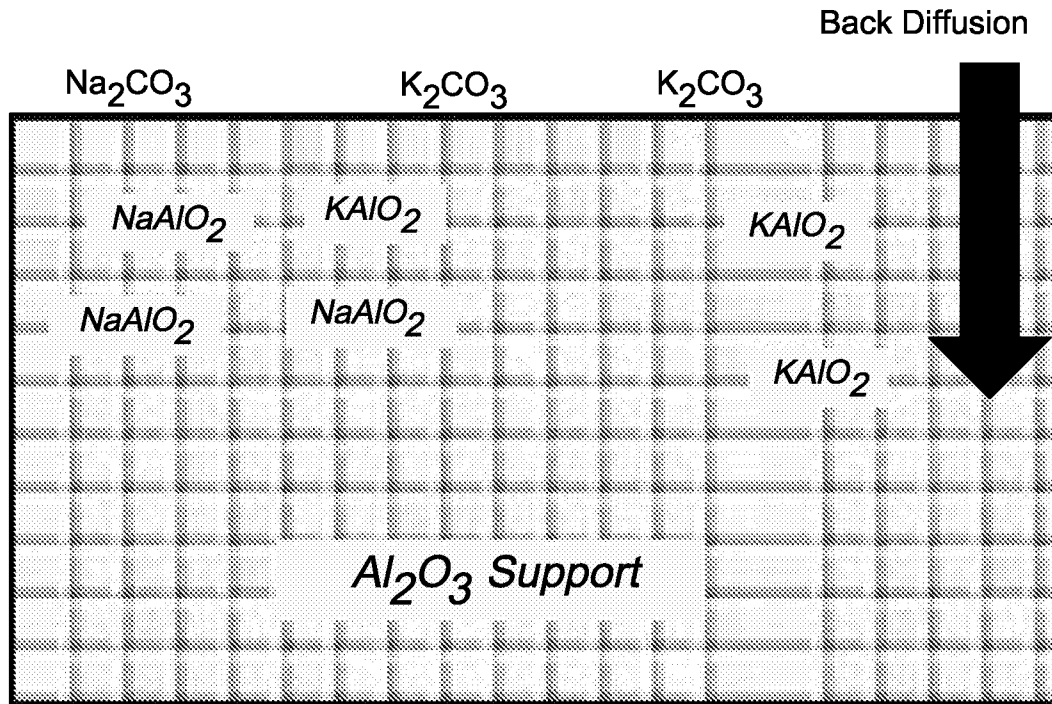


Figure 2A

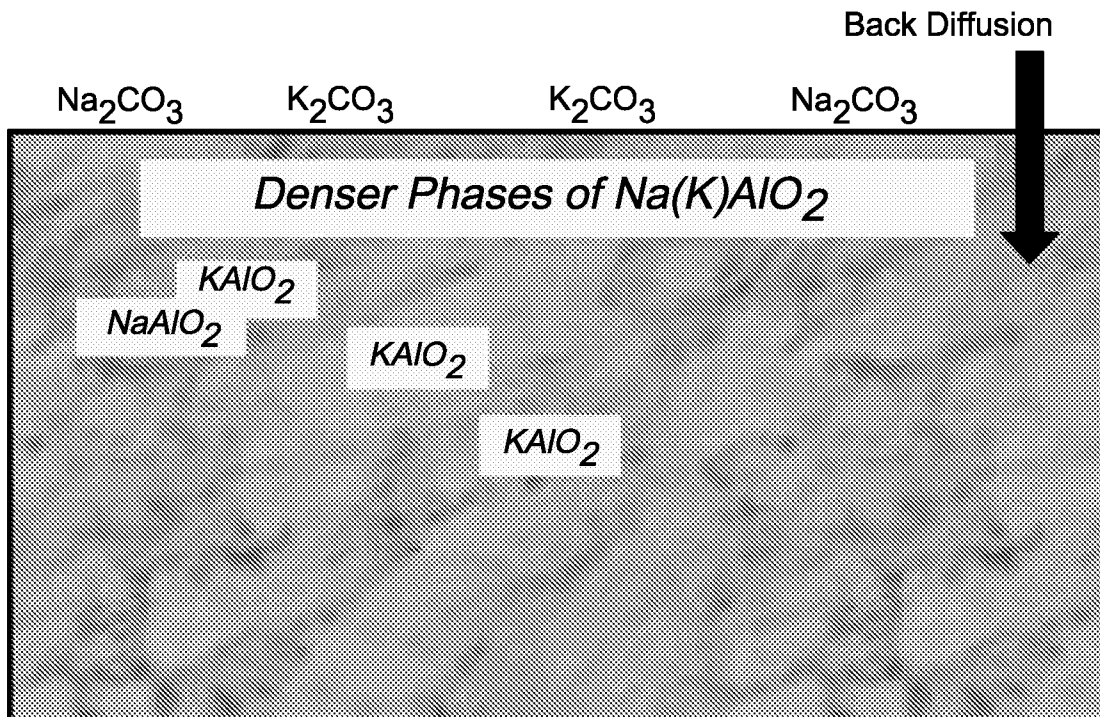


Figure 2B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US18/20606

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B01J 20/02, 20/04, 20/32, 23/00, 23/04 (2018.01)

CPC - B01J 20/02, 20/04, 20/041, 20/3007, 20/32, 20/3202, 20/3204, 23/00, 23/002, 23/007, 23/04;
B01D 53/1475

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	WO 2016/015923 A1 (IFP ENERGIES NOUVELLES) 04 February 2016; see machine translation; abstract; paragraphs [0014], [0017], [0030]-[0032], [0047], [0049]-[0050], [0053], [0068], [0073], [0075]-[0076], [0079]-[0080], [0101]; claim 6	1-8, 11-12, 14-20; 23-24 -- 9-10, 13, 21-22, 25-32
Y	CN 102,234,125 A (CHINA PETROLEUM AND CHEM) 08 November 2011; see machine translation; paragraphs [0006], [0018], [0041], [0057]	9-10, 21-22, 26-32
Y	US 5,935,894 A (KANAZIREV, VI) 10 August 1999; abstract; column 2, lines 46-52; column 4, lines 61-62; column 6, lines 38-40; column 9, lines 63-67	13, 30
Y	US 2015/0008366 A1 (EXXONMOBIL RESEARCH AND ENGINEERING COMPANY) 08 January 2015; paragraphs [0089], [0092]-[0093], [0176], [0208]-[0210]	25, 31

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

13 April 2018 (13.04.2018)

Date of mailing of the international search report

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Name and mailing address of the ISA/

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