

SORBENTS FOR HIGH-TEMPERATURE REMOVAL OF ALKALI METALS AND HCl FROM MUNICIPAL SOLID WASTE DERIVED SYNGAS

Field of Invention

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The current invention relates to a sorbent for use in the removal of alkali metals and HCl from syngas and/or flue gas. Additionally, methods to make and use the sorbent for its intended purpose are also disclosed herein.

10 Background

The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

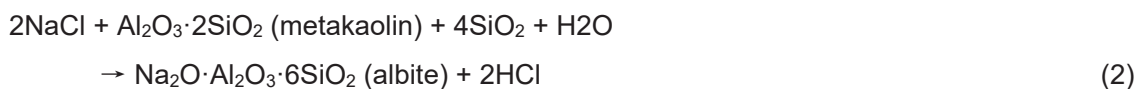
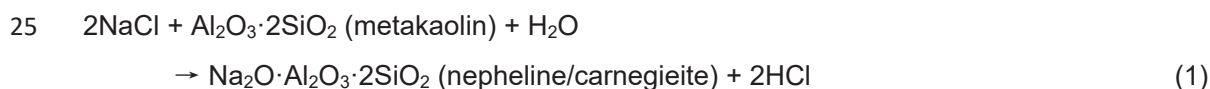
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Globally, a total of 2 billion tonnes of municipal solid waste (MSW) was generated in 2018 and it has been projected to increase to 2.2 billion tonnes by 2025 and 3.4 billion tonnes by 2050. The management of MSW usually includes landfilling, recycling, incineration, waste-to-energy (WTE) conversion, and bioprocessing. Among them, WTE conversion provides an excellent
20 alternative to fossil fuel for energy production. Emissions including dioxins, furans, sulfur dioxide, hydrochloric acid, particulates, etc. from the WTE facilities were found to be less than comparable fossil fuel facilities. Gasification converts MSW into a gaseous fuel (syngas), which mainly contains CO, H₂, CH₄, CO₂, water and some impurities, such as tar compounds, HCl, sulfur species and alkali metals. However, the HCl can cause high-temperature corrosion
25 of boiler during the utilization of syngas. The alkali metals in syngas or flue gas can induce fouling, slagging, agglomeration, contamination, and serious high-temperature corrosion to heating recovery system. Furthermore, the condensation of alkali metals could potentially cause more severe issues to boiler than gaseous HCl.

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Purification techniques have been developed to address the issues with alkali metals (P. J. Woolcock & R. C. Brown, *Biomass Bioenergy* **2013**, 52, 54-84). One method is by pretreatment such as water washing (H. Vuthaluru *et al.*, *Fuel Process. Technol.* 1996, 46, 117-132; and H. Vuthaluru *et al.*, *Fuel* **1999**, 78, 419-425). Another approach is by injecting sorbent/additive to the free board, which is simpler and more economical compared to the
35 pretreatment (W. Punjak, M. Uberoi & F. Shadman, *AIChE Journal* **1989**, 35, 1186-1194; S. Kyi & B. L. Chadwick, *Fuel* **1999**, 78, 845-855; Y. Zheng, P. A. Jensen & A. D. Jensen, *Fuel* **2008**, 87, 3304-3312; and H. Schürmann *et al.*, *Faraday Discuss.* **2002**, 119, 433-444).

Schürmann *et al.* (H. Schürmann *et al.*, *Faraday Discuss.* **2002**, 119, 433-444) reported that the alkali metal species presented as condensed-phase are largely sulfates and silicates, while the gas-phase are mainly chlorides and hydroxides. Chlorides are the dominant gas-phase species lower than 1450 °C and hydroxides become more dominant above that temperature. NaCl and KCl are the major forms of alkali metal species in high-temperature syngas (W. P. Chan *et al.*, *Appl. Energy* **2019**, 237, 227-240), and the alkali metal removal typically consists of the removal of alkali metal chlorides (H. Schürmann *et al.*, *Faraday Discuss.* **2002**, 119, 433-444). Minerals with high alumina and silica content showed good performance in adsorbing alkali metals during coal combustion (H. Schürmann *et al.*, *Faraday Discuss.* **2002**, 119, 433-444). Kaolin containing both alumina and silica was added into a fixed bed reactor and demonstrated that the alkali metal release was suppressed by 20% (K.-Q. Tran *et al.*, *Fuel* **2004**, 83, 807-812). In order to improve the alkali metal sorption at high temperature, Zhang *et al.* (X. Zhang *et al.*, *Fuel* **2017**, 191, 198-203) applied the intercalation-exfoliation method to expand the pore volume and pore diameter of kaolinite, which is beneficial to physisorption. Both physical and chemical sorption occurred in the alkali metals removal process (L. Xu *et al.*, *Energy Fuels* **2014**, 28, 5640-5648). The mechanisms for sodium removal by kaolin minerals at temperatures above the alkali metal dewpoint were investigated by Mwabe *et al.* (P. O. Mwabe & J. O. Wendt, Mechanisms governing trace sodium capture by kaolinite in a downflow combustor. *Symposium (International) on combustion*. 26. Elsevier; **1996**:2447-2453) using a downflow combustor. It was proposed that the removal process was the reaction between activated kaolinite and alkali hydroxide. The mechanisms for sodium capture by kaolin were also studied by Xu *et al.* (L. Xu *et al.*, *Energy Fuels* **2014**, 28, 5640-5648) proposing the following reactions:



Similarly, the mechanism of potassium capture by kaolin was proposed (K.-Q. Tran *et al.*, *Fuel* **2005**, 84, 169-175):



Besides kaolin, alumina was also studied for alkali metals removal. The activated Al_2O_3 for alkali metal (NaCl) removal from gas derived by coal was conducted at 840 °C (B. Dou *et al.*,

Fuel Process. Technol. **2003**, 82, 51-60). It was found that the NaCl vapor removal efficiency was up to 98.2% and the removal process was physical adsorption process in the absence of moisture. In the presence of water vapor, NaCl vapor reacts with activated alumina:



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The physical adsorption of NaCl and KCl by alumina sorbents was also demonstrated at high experimental temperatures (800 - 900 °C) (K. L. Luthra & O. H. LeBlanc Jr, *J. Phys. Chem.* **1984**, 88, 1896-1901). The HCl removal from industrial gases at temperatures up to 650 °C is well established. Na-based and Ca-based sorbents were demonstrated to remove HCl effectively at lower temperatures (N. Verdone & P. De Filippis, *Chem. Eng. Sci.* **2006**, 61, 7487-7496; C. E. Weinell *et al.*, *Ind. Eng. Chem. Res.* **1992**, 31, 164-171; and W. Duo *et al.*, *Chem. Eng. Sci.* **1996**, 51, 2541-2546). At high temperatures (> 750 °C), CaO/K₂O/Na₂O decorated Fe₂O₃/Al₂O₃ exhibited dechlorination efficiency (67 - 75%) during the chemical looping combustion (J. Wang & H. Zhao, *Combust. Flame* **2015**, 162, 3503-3515). Stemmler revealed that Ca-Ba sorbents showed more promising results to remove HCl than Ca-based sorbents for the syngas at 800 - 900 °C in the presence of steam (M. Stemmler, A. Tamburro & M. Müller, *Fuel* **2013**, 108, 31-36). It was reported the chlorine was removed completely by the sorbents, Na₂CO₃, NaHCO₃, and K₂CO₃ at high temperatures up to 960 °C and high pressures (J. Lee & B. Feng, *Front. Chem. Sci. Eng.* **2012**, 6, 67-83). The above-mentioned studies focused on the alkali metals and HCl removed by various sorbents separately.

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Therefore, there exists a need to develop a sorbent that has the capacity for simultaneous removal of alkali and HCl from syngas/flue gas stream, to alleviate the corrosion issues of heating surface.

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Summary of Invention

Aspects and embodiments of the current invention will now be discussed by reference to the following numbered clauses.

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1. A particulate sorbent material suitable for removal of an alkali metal and hydrogen chloride from a syngas and/or a flue gas, the particulate sorbent material comprising:

from 58 to 100 wt% of Al₂O₃ where the Al₂O₃ comprises one or more impurities; and

from 0 to 42 wt% of a binder, wherein:

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the one or more impurities in the Al₂O₃ comprises Na₂O in an amount of from 0.3 to 1.5 wt% of the total weight of the particulate sorbent material; and

the particulate sorbent material has:

a pore volume of from 0.5 to 1 mL/g; and

a pore size of from 10 to 30 Å.

- 5 2. The particulate sorbent material according to Clause 1, wherein the particulate sorbent material comprises:
 - from 58 to 85 wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities; and
 - from 15 to 42 wt% of a binder, optionally wherein the particulate sorbent material comprises:
 - 10 from 70 to 85 wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities; and
 - from 15 to 30 wt% of a binder.
3. The particulate sorbent material according to Clause 1 or Clause 2, wherein the one or more impurities in the Al_2O_3 comprises Na_2O in an amount of from 0.4 to 1.0 wt%, such as
 - 15 from 0.5 to 0.9 wt% of the total weight of the particulate sorbent material.
4. The particulate sorbent material according to any one of the preceding clauses, wherein the particulate sorbent material has a particle size of from 0.01 to 5 mm, such as from 1.8 to 3 mm, such as from 1.9 to 2.8 mm, such as from 2 to 2.5 mm.
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5. The particulate sorbent material according to any one Clauses 1, 2 and 4, wherein, after the particulate sorbent material has been subjected to microwave acid digestion, the resulting mixture has the following composition:
 - from 75 to 96 wt% of Al_2O_3 ;
 - 25 from 0.3 to 1.5 wt% of Na_2O ; and
 - from 1.4 to 16.3 wt% of CaO .
6. The particulate sorbent material according to any one of the preceding clauses, wherein, after the particulate sorbent material has been subjected to microwave acid digestion,
 - 30 the resulting mixture has the following composition:
 - from 82 to 90 wt% of Al_2O_3 ;
 - from 0.4 to 1.0 wt% of Na_2O ; and
 - from 8.6 to 16.3 wt% of CaO .
- 35 7. The particulate sorbent material according to any one of the preceding clauses, wherein the particulate sorbent material has:
 - a pore volume of from 0.6 to 0.8 mL/g, such as from 0.65 to 0.72 mL/g; and/or

a pore size of from 17 to 18 Å.

8. The particulate sorbent material according to any one of the preceding clauses, wherein the binder is a cement, optionally wherein the cement is selected from one or more of the group consisting of calcium aluminate cement, a Portland cement, a rapid hardening cement, a quick setting cement, a sulfate resisting cement, and a blast furnace cement.
9. The particulate sorbent material according to any one of the preceding clauses, wherein the particulate sorbent material has a BET surface area of from 120 to 180 m²/g, such as from 150 to 160 m²/g.
10. A method of manufacturing a particulate sorbent material according to any one of Clauses 1 to 9, wherein the method comprises the steps of:
- (a) providing a slurry formed from water, aluminium hydroxide in an amount of from 58 to 100 solids wt% of Al₂O₃ where the Al₂O₃ comprises one or more impurities, and from 0 to 42 solids wt% of a binder;
 - (b) calcining the slurry at a temperature of from 750 to 1,000 °C for a period of from 4 to 10 hours to provide an unrefined sorbent material; and
 - (c) crushing and sieving the unrefined sorbent material to provide a particle size of from 1.8 to 3 mm, wherein:
the one or more impurities in the Al₂O₃ comprises Na₂O in an amount sufficient to provide from 0.3 to 1.5 wt% of the total weight of the resulting particulate sorbent material.
11. The method according to Clause 10, wherein the slurry comprises water, aluminium hydroxide in an amount of from 58 to 85 solids wt% of Al₂O₃ where the Al₂O₃ comprises one or more impurities, and from 15 to 42 solids wt% of a binder, optionally wherein the slurry comprises water, aluminium hydroxide in an amount of from 70 to 85 solids wt% of Al₂O₃ where the Al₂O₃ comprises one or more impurities, and from 15 to 30 solids wt% of a binder.
12. The method according to Clause 10 or Clause 11, wherein the one or more impurities in the Al₂O₃ comprises Na₂O in an amount sufficient to provide from 0.4 to 1.0 wt%, such as from 0.5 to 0.9 wt% of the total weight of the resulting particulate sorbent material.
13. The method according to any one of Clauses 10 to 12, wherein the particle size obtained in the crushing and sieving step (c) of Clause 10 is from 1.9 to 2.8 mm, such as from 2 to 2.5 mm.

14. A method for removing an alkali metal and hydrogen chloride from a syngas and/or a flue gas in need thereof, the method comprising the steps of:

- (a) providing a reaction chamber comprising a particulate sorbent material as described in any one of Clauses 1 to 9; and
- (b) passing the syngas and/or the flue gas through the particulate sorbent material in the reaction chamber at a temperature of from 600 to 1000 °C to provide a syngas and/or a flue gas with a reduced amount of alkali metal and hydrogen chloride compared to the original syngas and/or flue gas.

15. The method according to Clause 14, wherein the temperature is from 750 - 900 °C.

Drawings

FIG. 1 depicts the scanning electron microscopy (SEM) images showing morphologies of the nanoflakes-like sorbent: (a) low magnification; and (b) high magnification; and (c) elemental mapping of the fresh sorbent (particle size of 2 – 2.8 mm).

FIG. 2 depicts the X-ray diffraction (XRD) pattern of the fresh sorbent and spent sorbent with particle size of 2 – 2.8 mm.

FIG. 3 depicts the X-ray photoelectron spectroscopy (XPS) spectra of fresh and spent sorbents with particle size of 2 – 2.8 mm: (a) survey spectra; (b) Na 1s; (c) Cl 2p; and (d) K 2p.

FIG. 4 depicts the experimental setup.

FIG. 5 depicts the alkali metal removal efficiency versus the particle size of the sorbent for 1 h reaction at 850 °C.

FIG. 6 depicts (a) SEM image; and (b) elemental mapping of the spent sorbent with particle size of 2 – 2.8 mm.

FIG. 7 depicts the HCl removal efficiency versus the particle size of the sorbent for 1 h reaction at 850 °C.

FIG. 8 depicts the equilibrium compositions of NaCl, KCl, and HCl with fresh sorbent. Dots show the amount of the raw material, Lines show the amount after reaction.

FIG. 9 depicts the alkali metal removal efficiency with CaAl_2O_4 addition for 1 h reaction at 850 °C.

5 **FIG. 10** depicts (a) distribution curves of Barrett-Joyner-Halenda (BJH) pore volume; and (b) cumulative pore volume of 85Al-15Ca, activated Al_2O_3 , and kaolin.

FIG. 11 depicts the N_2 sorption isotherms of (a) 85Al-15Ca, (b) activated Al_2O_3 , and (c) kaolin.

10 **FIG. 12** depicts the field emission scanning electron microscopy (FESEM) images showing morphologies of fresh sorbents with low magnification and high magnification: (a) 85Al-15Ca; (c) activated Al_2O_3 ; (e) kaolin; and energy dispersive spectroscopy (EDS) spectrum of the area of high magnification: (b) 85Al-15Ca; (d) activated Al_2O_3 ; and (f) kaolin.

15 **FIG. 13** depicts the XRD patterns of the fresh sorbents with the identified crystalline phases: K = kaolin, M = mullite, I = illite, Q = quartz, γ = γ -alumina, α = α -alumina, δ = δ -alumina, κ = κ -alumina, θ = θ -alumina, ■ = CaO.

FIG. 14 depicts (a) alkali metals removal efficiency versus reaction temperature for 1 h; and
20 (b) alkali metals removal efficiency versus reaction time at 850 °C without HCl in syngas.

FIG. 15 depicts (a) ΔG of the 85Al-15Ca sorbent reacting with NaCl and KCl; (b) equilibrium constant K; and (c) equilibrium distribution of 85Al-15Ca with NaCl and KCl.

25 **FIG. 16** depicts the HCl removal efficiency by 85Al-15Ca at 850 °C and HCl concentrations at the reactor outlet without NaCl and KCl in syngas.

FIG. 17 depicts (a) ΔG of the 85Al-15Ca sorbent reacting with HCl; (b) equilibrium constant K; and (c) equilibrium distribution of 85Al-15Ca with HCl.

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FIG. 18 depicts (a) alkali metals removal efficiency, and (b) percentage of chlorine in sorbents and output of various sorbents after 1 h reaction at 850 °C with NaCl, KCl, and HCl in syngas.

FIG. 19 depicts the FESEM images showing morphologies of spent sorbents with low
35 magnification and high magnification: (a) 85Al-15Ca; (c) activated Al_2O_3 ; and (e) kaolin; and

EDS spectrum of the area of high magnification: (b) 85Al-15Ca; (d) activated Al_2O_3 ; and (f) kaolin.

FIG. 20 depicts the XRD patterns of the spent sorbents, i.e., kaolin, activated Al_2O_3 , and 85Al-15Ca. K = kaolin, M = mullite, I = illite, Q = quartz, γ = γ -alumina, α = α -alumina, δ = δ -alumina, θ = θ -alumina, ■ = CaO, ★ = NaAlO_2 and Na_5AlO_4 , ▲ = $\text{Na}_2\text{Al}_{22}\text{O}_{34} \cdot 2\text{H}_2\text{O}$.

FIG. 21 depicts the HCl concentrations at the reactor outlet with different sorbents at 850 °C.

FIG. 22 depicts the HCl removal efficiency by the different sorbents at 850 °C.

Description

It has been surprisingly found that particulate alumina can form the basis of a suitable material for removal of an alkali metal and/or hydrogen chloride (e.g. in situations where only one of these is present) from a syngas or a fuel gas that solves one or more of the problems identified hereinbefore. Thus, in a first aspect of the invention, there is provided a particulate sorbent material suitable for removal of an alkali metal and hydrogen chloride from a syngas and/or a flue gas, the particulate sorbent material comprising:

from 58 to 100 wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities; and from 0 to 42 wt% of a binder, wherein:

the one or more impurities in the Al_2O_3 comprises Na_2O in an amount of from 0.3 to 1.5 wt% of the total weight of the particulate sorbent material; and

the particulate sorbent material has:

a pore volume of from 0.5 to 1 mL/g; and
a pore size of from 10 to 30 Å.

In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrase, "consists essentially of" and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

As used herein, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise.

10 The Al_2O_3 used herein may be in any suitable form (or a mixture of suitable forms). For example, the Al_2O_3 may be provided with one or more of the α -, θ -, γ -, δ - and κ -alumina crystalline phases.

As noted hereinbefore, the Al_2O_3 used herein is not provided in a form that is 100% pure. Instead, the Al_2O_3 used herein may include one or more impurities. As will be noted from the first aspect of the invention, one of these impurities must be Na_2O , which should be present in an amount to ensure that it forms from 0.3 to 1.5 wt% of the total weight of the particulate sorbent material. Other impurities in the Al_2O_3 may include, but are not limited to, one or more of CaO , MgO , Fe_2O_3 , SiO_2 and K_2O . In particular embodiments that may be mentioned herein, the Na_2O may be present in an amount of from 0.4 to 1.0 wt%, such as from 0.5 to 0.9 wt% of the total weight of the particulate sorbent material.

While the use of Al_2O_3 only having the desired amount of the impurity Na_2O described above may be used as a sorbent, it has been found that the alumina is relatively fragile and tends to fragment into smaller particles that may not adequately retain the desired properties. As such, it is advantageous that a binder is included as part of the particulate sorbent material disclosed herein in order to retain a desirable particle size for the optimal operation of the removal of an alkali metal and/or hydrogen chloride from a syn gas or a fuel gas. Any suitable material that can function to retain the desired particle size of the particulate sorbent material during formation, storage, transport and use may be used herein for this purpose. For example, the binder may be a cement. In particular embodiments that may be mentioned herein, the cement may be selected from one or more of the group consisting of calcium aluminate cement, a Portland cement, a rapid hardening cement, a quick setting cement, a sulfate resisting cement, and a blast furnace cement. In yet more particular embodiments that may be mentioned herein, the binder may be a calcium aluminate cement.

The particle size of the particulate sorbent material disclosed herein may be any suitable size. For example, it may be from 0.01 to 5 mm. More particularly, it may be from 1.8 to 3 mm, such as from 1.9 to 2.8 mm, such as from 2 to 2.5 mm.

- 5 For the avoidance of doubt, it is explicitly contemplated that where a number of numerical ranges related to the same feature are cited herein, that the end points for each range are intended to be combined in any order to provide further contemplated (and implicitly disclosed) ranges. Thus, taking the particle sizes above as an example, there is explicitly disclosed the following ranges:
- 10 from 0.01 to 1.8 mm, from 0.01 to 1.9 mm, from 0.01 to 2 mm, from 0.01 to 2.5 mm, from 0.01 to 2.8 mm, from 0.01 to 3 mm, from 0.01 to 5 mm;
 from 1.8 to 1.9 mm, from 1.8 to 2 mm, from 1.8 to 2.5 mm, from 1.8 to 2.8 mm, from 1.8 to 3 mm, from 1.8 to 5 mm;
 from 1.9 to 2 mm, from 1.9 to 2.5 mm, from 1.9 to 2.8 mm, from 1.9 to 3 mm, from 1.9 to 5
 15 mm;
 from 2 to 2.5 mm, from 2 to 2.8 mm, from 2 to 3 mm, from 2 to 5 mm;
 from 2.5 to 2.8 mm, from 2.5 to 3 mm, from 2.5 to 5 mm;
 from 2.8 to 3 mm, from 2.8 to 5 mm; and
 from 3 to 5 mm.

- 20 It is noted that a range of from around 2 (e.g. from 1.9 or 1.9 mm) to around 2.8 mm (e.g. to 2.5 or 3 mm) may provide a particulate sorbent material with particularly good properties.

- As noted above, it is particularly preferred that the particulate sorbent material include a binder.
- 25 Thus, in particular embodiments that may be mentioned herein, the particulate sorbent material may comprise:

- from 58 to 85 wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities; and
 from 15 to 42 wt% of a binder, optionally wherein the particulate sorbent material comprises:
- 30 from 70 to 85 wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities; and
 from 15 to 30 wt% of a binder.

- As will be appreciated, the compounds that make-up the particulate sorbent material will be affected by the types of impurities present in the Al_2O_3 , but also in the choice of the binder
- 35 material. In order to more readily analyse the composition of the particulate sorbent material it may be subjected to microwave acid digestion (see the protocol in the examples for how this is conducted). The resulting material may then be analysed using inductively coupled plasma

- optical emission spectrometry (ICP - OES), as all of the materials present will be converted to the oxides based on the complete oxidation state. As such, in certain embodiments of the invention that may be mentioned herein, after the particulate sorbent material has been subjected to microwave acid digestion, the resulting mixture may have the following

5 composition:

from 75 to 96 wt% of Al_2O_3 ;

from 0.3 to 1.5 wt% of Na_2O ; and

from 1.4 to 16.3 wt% of CaO .

10 In more particular embodiments of the invention, after the particulate sorbent material has been subjected to microwave acid digestion, the resulting mixture has the following composition:

from 82 to 90 wt% of Al_2O_3 ;

from 0.4 to 1.0 wt% of Na_2O ; and

15 from 8.6 to 16.3 wt% of CaO .

For example, after microwave acid digestion, the binder calcium aluminate cement (CaAl_2O_4), will provide Al_2O_3 and CaO as products.

20 As noted hereinbefore, the particulate sorbent material has:

a pore volume of from 0.5 to 1 mL/g; and

a pore size of from 10 to 30 Å.

In particular embodiments that may be mentioned herein, the pore volume may be from 0.6 to 0.8 mL/g, such as from 0.65 to 0.72 mL/g. In alternative or the same embodiments, the pore size may be from 17 to 18 Å. As will be appreciated, as the particulate sorbent material is in the form of particles, the resulting material will have a surface area as well. Any suitable surface area commensurate with the particles sizes noted hereinbefore may be used. For example, the particulate sorbent material may have a BET surface area of from 120 to 180 m^2/g , such as from 150 to 160 m^2/g .

In a second aspect of the invention, there is provided a method of manufacturing a particulate sorbent material as described hereinbefore, wherein the method comprises the steps of:

(a) providing a slurry formed from water, aluminium hydroxide in an amount of from 58 to 100 solids wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities, and from 0 to 42 solids wt% of a binder;

(b) calcining the slurry at a temperature of from 750 to 1,000 °C for a period of from 4 to 10 hours to provide an unrefined sorbent material; and

(c) crushing and sieving the unrefined sorbent material to provide a particle size of from 1.8 to 3 mm, wherein:

5 the one or more impurities in the Al_2O_3 comprises Na_2O in an amount sufficient to provide from 0.3 to 1.5 wt% of the total weight of the resulting particulate sorbent material.

When used herein, the term “solids wt%” refers to the total dry weight of the components added to the water. For the avoidance of doubt, the weight percentages above may include
10 the components in a hydrated form (e.g. the alumina may be provided in the form of aluminium hydroxide hydrate).

In certain embodiments that may be mentioned herein, the slurry may comprise water, aluminium hydroxide in an amount of from 58 to 85 solids wt% of Al_2O_3 where the Al_2O_3
15 comprises one or more impurities, and from 15 to 42 solids wt% of a binder. In yet further embodiments that may be mentioned herein, the slurry may comprise water, aluminium hydroxide in an amount of from 70 to 85 solids wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities, and from 15 to 30 solids wt% of a binder. As will be appreciated, the one or more impurities in the Al_2O_3 in the alumina should be sufficient to provide Na_2O in an amount
20 to provide a particulate sorbent material as described hereinbefore. For example, the one or more impurities in the Al_2O_3 may comprise Na_2O in an amount sufficient to provide from 0.4 to 1.0 wt%, such as from 0.5 to 0.9 wt% of the total weight of the resulting particulate sorbent material.

25 Any suitable particle size may be obtained from the crushing and sieving step (c) in the method above – certainly all of the particle sizes mentioned above may be obtained. In particular embodiments of the invention that may be mentioned herein, the particle size obtained in the crushing and sieving step (c) of the method above may be from 1.9 to 2.8 mm, such as from 2 to 2.5 mm.

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As will be appreciated, the particulate sorbent material described herein is particularly useful for removing unwanted contaminants from syngas and/or a flue gas, as the case may be. Thus, in a further aspect of the invention, there is provided a method for removing an alkali metal and hydrogen chloride from a syngas and/or a flue gas in need thereof, the method comprising
35 the steps of:

(a) providing a reaction chamber comprising a particulate sorbent material as described in any one of Claims 1 to 9; and

(b) passing the syngas and/or the flue gas through the particulate sorbent material in the reaction chamber at a temperature of from 600 to 1000 °C (e.g. from 750 to 900 °C) to provide a syngas and/or a flue gas with a reduced amount of alkali metal and hydrogen chloride compared to the original syngas and/or flue gas.

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Further aspects and embodiments of the invention will now be discussed by reference to the following non-limiting examples.

Examples

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Materials

Aluminum hydroxide hydrate ($\text{H}_3\text{AlO}_3 \cdot x\text{H}_2\text{O}$) which contains ~1.5 wt.% Na_2O , was provided by Sigma-Aldrich. Calcium aluminate cement (CaAl_2O_4) with a purity of 99% was provided by Alfa Aesar. Activated aluminum oxide (Al_2O_3) with the molar weight of 101.96 g/mol, nitric acid (HNO_3 , 70%), hydrofluoric acid (HF, 48%), boric acid (H_3BO_3 , $\leq 100\%$), hydrochloric acid (HCl, 37%), sodium chloride (NaCl , $\leq 100\%$), and potassium chloride (KCl, 99.0-100.5%) were purchased from Sigma-Aldrich. Kaolin was produced in China (purchased from SG Labware Pte. Ltd., Singapore).

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Analytical techniques

XRD analysis

The crystal phase change of the sorbents was determined by XRD (Bruker D8 Advance).

Inductively coupled plasma-optical emission spectrometry (ICP-OES)

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ICP-OES was performed on Perkin Elmer Optima 8300.

Ion chromatography (IC)

IC was performed on Dionex ICS-1100.

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Field emission scanning electron microscope with energy dispersive spectroscopy (FESEM-EDS)

The morphology of the sorbents were analysed by FESEM-EDS (JSM-7200F, JEOL).

N_2 adsorption-desorption isotherms

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The porous characteristics of the sorbents were analysed by N_2 adsorption-desorption isotherms measured at -196 °C on a Quadrasorb SI (Quantachrome Instrument).

XPS spectroscopy

An AXIS Supra (Kratos) was used to measure the XPS.

General procedure for ICP-OES sample preparation

- 5 The elements tested by ICP-OES were converted to the oxides based on the complete oxidation state after microwave acid digestion (ETHOS One, Milestone Inc.).

85Al-15Ca and activated Al₂O₃

The microwave acid digestion was performed by the following procedure:

- 10 1. weigh ~0.25 g of sample (85Al-15Ca or activated Al₂O₃) directly into a digestion vessel
 2. add HNO₃ (70%, 10 mL) drop by drop into the digestion vessel, immersing the sample
 3. visually look for a reaction
 4. allow the reaction to subside completely for about 20 min
 5. seal the vessel with a cap for microwave digestion. The temperature was raised to
 15 180 °C within 10 min, then kept at 180 °C for 20 min.

Kaolin

Kaolin (0.25 g) was digested by HNO₃ (70%, 8 mL), HF (48%, 0.5 mL), and HBO₃ (4.5%, 3 mL), which is because SiO₂ in the kaolin is not soluble in HNO₃. The microwave acid digestion

- 20 was performed by the following procedure:

1. weigh 0.25 g of sample directly into a digestion vessel
 2. add HNO₃ (70%, 8 mL) drop by drop into the digestion vessel, immersing the sample
 3. visually look for a reaction
 4. allow the reaction to subside completely for about 20 min
 25 5. add HF (48%, 0.5 mL) drop by drop into the digestion vessel
 6. visually look for a reaction
 7. allow the reaction to subside completely for about 10 - 20 min
 8. seal the vessel with a cap for microwave digestion. The temperature was raised to
 180 °C within 10 min, then kept at 180 °C for 20 min.
 30 9. after cooling, open the vessel and check whether the sample is totally digested
 10. add 3 mL of saturated HBO₃ (4.5%, 3 mL) solution into the sample
 11. seal the vessel with a cap for microwave digestion. The temperature was raised to
 150 °C within 10 min, then kept at 150 °C for 20 min.

- 35 General procedure for thermodynamic modelling

The HSC Chemistry 9.0 (GEM, Outotec) was used to explore the interactions between sorbents and syngas impurities in thermodynamic calculations. The Gibbs energy

minimization method was used to measure equilibrium composition of each compound. The calculations were carried out using all species with related elements, i.e. experimental syngas composition (i.e., H₂ 10 vol% CO 10 vol%, CO₂ 10 vol%, N₂ 45 vol%, H₂O 25 vol%) with impurities (i.e., NaCl 0.44 g/Nm³, KCl 0.56 g/Nm³, and HCl 0.26 g/Nm³), sorbents (i.e., 85Al-15Ca, activated Al₂O₃, and kaolin), the sorbent amount of 10 kmol and the total syngas amount of 100 kmol.

Example 1. Sorbent preparation and property

10 *Sorbent preparation*

The sorbent was prepared by a facile mechanical mixing method. H₃AlO₃·xH₂O (85 g) and CaAl₂O₄ (15 g) with the mass percentage of 85% and 15%, respectively, were mixed with deionised (DI)-water (100 mL, mass ratio of solid : water = 1 : 1) under stirring. The two chemicals were mixed at a temperature of approx. 50 °C on a heating plate until most of the water was evaporated. Then, the slurry was transferred to a crucible and calcined at 850 °C for 5 h. Afterwards, the obtained sorbent was crushed and sieved to the size ranges of 0.063 - 0.212 mm, 0.5 - 1.4 mm and 2 - 2.8 mm.

Characterization

20 According to Table 1, the raw material H₃AlO₃·xH₂O contained the impurities: 0.7% of CaO, 1.5% of Na₂O, 0.8% of MgO, etc. Correspondingly, this has led to the fresh sorbent having the impurities: Na₂O, MgO, etc. Table 2 shows that the sorbents with different sizes had similar surface area of 156 - 159 m²/g, pore volume of 0.69 - 0.72 mL/g, and pore size of 17 - 18 Å.

25 **Table 1.** Composition of the aluminum hydroxide hydrate (H₃AlO₃·xH₂O) and fresh sorbent tested by ICP-OES.

Material	Al ₂ O ₃ (wt.%)	CaO (wt.%)	Na ₂ O (wt.%)	MgO (wt.%)	Fe ₂ O ₃ (wt.%)	SiO ₂ (wt.%)	K ₂ O (wt.%)
H ₃ AlO ₃ ·xH ₂ O	96.6 ± 0.7	0.7 ± 0.1	1.5 ± 0.1	0.8 ± 0.1	0.1 ± 0.1	0.3 ± 0.1	0.1 ± 0.1
85Al-15Ca	89.8 ± 0.3	8.7 ± 0.1	0.8 ± 0.1	0.6 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1

Table 2. Surface area, pore volume and pore size of fresh 85Al-15Ca sorbents with different size ranges.

Sorbent size (mm)	BET surface area (m ² /g)	Pore volume (mL/g)	Pore size (Å)
0.063 - 0.212	159	0.69	17

0.5 - 1.4	156	0.70	17
2.0 - 2.8	156	0.72	18

The morphology and element distribution of the fresh sorbent are shown in FIG. 1. The morphology resembles nanoflakes with porous structure, which could be responsible for the large surface area and pore volume of material as shown in Table 2. The XRD pattern of the fresh sorbent is shown in FIG. 2.

According to the study by Nayar *et al.* (P. Nayar *et al.*, *Thin Solid Films*, **2014**, 568, 19-24), crystalline peaks for Al_2O_3 with maximum intensity at 37.4° , 45.8° , 61.0° and 66.9° were detected at 800°C . The peaks at 37.4° (δ), 45.8° (γ , δ) and 61.0° (γ , δ) match well with γ - and δ -phases, while the broad peak at 66.9° could be the superposition of peaks due to γ and δ -alumina. New peaks were detected at 32.0° (γ , δ), 36.2° (δ), 37.4° (γ , δ), 39.5° (γ , δ), 45.8° (γ , δ), 61.0° (γ , δ), and 66.8° (γ , δ) at 950°C . The fresh sorbent synthesized at 850°C gave crystalline peaks with maximum intensity at 19.5° (δ , θ), 25.6° (α), 29.4° (κ) (P. S. Santos, H. S. Santos & S. Toledo, *Mater. Res.*, **2000**, 3, 104-114), 32.0° (γ , δ), 35.1° (α), 36.2° (δ), 37.4° (γ , δ), 37.8° (α), 39.5° (γ , δ), 43.4° (α), 45.8° (γ , δ), 52.6° (α), 57.5° (α), 61.0° (γ , δ), 66.6° (α), 66.8° (γ , δ), and 68.2° (α) (P. Nayar *et al.*, *Thin Solid Films*, **2014**, 568, 19-24; and F. R. Feret, D. Roy & C. Boulanger, *Spectrochim. Acta B: At. Spectrosc.*, **2000**, 55, 1051-1061). The XPS spectra of the fresh sorbent are presented in FIG. 3. The peaks corresponding to Na 1s, O 1s, Ca 2p, and Al 2p are found in the XPS spectra of the fresh sorbent (N. Ohtsu *et al.*, *Surf. Coat. Technol.*, **2013**, 218, 114-118; and B. Shen *et al.*, *J. Solid State Electrochem.*, **2016**, 21, 1195-1201).

Example 2. Performance test

The performance of the sorbents was tested in a fixed bed reactor as shown in FIG. 4. The reactor is a quartz tube with an inner diameter of 15 mm, which was heated by an electric furnace to the desired temperature ($750 - 900^\circ\text{C}$). In the middle of the reactor, a fritted silica disc with gas distributor was used as sample holder. A K-type thermocouple was used to monitor the reaction temperature of the sample inside the reactor. It was 10 mm above the fritted quartz disc and inserted 1 mm inside the sorbent bed. The amount of sorbent in each test was constant, i.e. 2 g (in order to remove alkali metal sufficiently, excessive amount of sorbent (2 g) was used). The system was heated up to the operation temperature while purged with nitrogen (100 mL/min). The simulated syngas consisted of 10 vol% CO , 10 vol% H_2 , 10 vol% CO_2 , and 25 vol% H_2O balanced in N_2 . NaCl, KCl and HCl were respectively dissolved

into H₂O to simulate the concentrations of NaCl (0.44 g/Nm³), KCl (0.56 g/Nm³), and HCl (0.26 g/Nm³), which are typical to syngas from municipal solid waste formulated based on our previous study (W. P. Chan *et al.*, *Appl. Energy*, **2019**, 237, 227-240). Samples from the impinger bottles were measured by IC. The flow rate of the simulated syngas was maintained at 250 mL/min for each test. The exposure time of the sorbent to syngas was 1 - 6 h. The effluent gas was washed with ultrapure DI water in a 125 mL impinger bottle for Cl⁻ capture.

The data shown in the figures and tables are from triplicated experiments and the error bars are the standard deviations. The metal content and chloride content in sorbents were characterized by microwave acid digestion described above, followed by ICP-OES and IC. The total Cl⁻ input was tested by IC and the Cl⁻ in NaCl and KCl were converted by Na and K tested by ICP-OES. The Cl⁻ in HCl was the difference between the total Cl⁻ input and the Cl⁻ in NaCl and KCl. The thermodynamic calculation was calculated using HSC Chemistry 9.0. The Na and K removal efficiencies of the sorbent were calculated by comparing the Na and K content in the sorbent to the total Na and K in the injected gas.

The removal efficiency (η) of the sorbent was calculated by:

$$\eta (\%) = m_1/m_0 \times 100\% \quad (5)$$

in which

$$m_1 (\text{g}) = m_s \times f \quad (6)$$

$$m_0 (\text{g}) = C \times t \quad (7)$$

where m_s (g) stands for the mass of the sorbent, f stands for the mass fraction of Na, K, or Cl in sorbent, and C (g/min) and t (min) are the flow rates of Na, K, or Cl injected into the reactor and reaction time, respectively.

The alkali metals breakthrough time and HCl breakthrough time were defined at the removal efficiency of 80% (G. Liu *et al.*, *Combust. Flame* **2021**, 223, 230-242). The alkali metals exhaustion time and HCl exhaustion time were defined as the time intervals during which the removal efficiency decreased to 20%. The alkali metals breakthrough capacity (q) and the HCl breakthrough capacity (q_b) were defined as the alkali metals sorption amount and the HCl sorption amount per unit mass of sorbents at the breakthrough time, and were calculated as:

$$q (\text{mmol/g}) = n/m_s \quad (8)$$

$$q_b (\text{mmol/g}) = (n_{blk} - n_b)/m_s \quad (9)$$

where n (mmol) is the alkali metals amount in the sorbent, n_{blk} (mmol) and n_b (mmol) are the HCl amounts released from the reactor without and with sorbents at the breakthrough time, respectively, and m_s (g) is the mass of the sorbent.

Example 3. Alkali metals removal by sorbents with different sizes

The alkali metal removal activity of the different-sized sorbents prepared in Example 1 was evaluated by following the protocol in Example 2 except the simulated syngas contained only NaCl and KCl, the reactor temperature was set at 850 °C and the exposure time of the sorbent to syngas was 1 h.

Results and discussion

FIG. 5a shows the removal efficiency of Na, K, and total removal efficiency of Na and K with respect to the sorbent size for 1 h reaction. The removal efficiency of the sorbent for Na was relatively constant, i.e. 93%, 94%, and 92% for the sorbent sizes of 0.063 - 0.212, 0.5 - 1.4, and 2.0 - 2.8 mm, respectively. However, a significant increment was found for the removal efficiency of K with increased sorbent particle size. The removal efficiency increased from 54% to 77% for K and the total removal efficiency of Na and K increased from 73% to 85%. The P values of t-test for the removal efficiencies of Na and K for the sorbents with size of 0.063 - 0.212, 0.5 - 1.4, and 2.0 - 2.8 mm were 0.0004, 0.0009, and 0.0249, respectively. This illustrates the significant difference between the removal efficiency of Na and K. The sorbents have a higher Na capacity than K. Table 3 further presents the Na and K masses in the fresh sorbent and spent sorbent. The mass of Na, which is the mass difference between the fresh sorbent and spent sorbent, captured by the sorbents were constant at approx. 3 mg/g for different sorbent sizes, while the mass of K captured by the sorbents increased with increasing sorbent size.

Table 3. Alkali metal weight in the spent sorbent tested by ICP-OES.

Element	Fresh sorbent	Spent sorbent		
		0.063 - 0.212 mm	0.5 - 1.4 mm	2.0 - 2.8 mm
Na (mg/g)	5.3 ± 0.7	8.4 ± 0.1	8.4 ± 0.2	8.3 ± 0.2
K (mg/g)	0.1 ± 0.1	2.0 ± 0.1	2.1 ± 0.2	2.7 ± 0.2

Table 4 shows the porous properties of the sorbents after the reaction. The surface area of the sorbent with particle size of 2.0 - 2.8 mm decreased by 30.3% from 155 m²/g (Table 2) to 108 m²/g. However, the surface area decreases for sorbents with particle sizes of 0.063 - 0.212 mm and 0.5 - 1.4 mm were only 22.6% and 20.5%. The decrease of surface area is

possibly due to the sintering by growing bonds between contacting materials during heating (R. M. German, *JOM* **2016**, 68, 878-884). Therefore, the sorbent with size of 2.0 - 2.8 mm has the highest alkali metal removal efficiency.

5 **Table 4.** Porous characteristics of the spent sorbent after reaction.

Sorbent size (mm)	BET surface area (m ² /g)	Pore volume (mL/g)	Pore size (Å)
0.063 - 0.212	123	0.56	18
0.5 - 1.4	124	0.52	16
2.0 - 2.8	108	0.64	23

Additionally, the spent sorbent was characterized by XRD and XPS in FIG. 2 and 3, respectively. The peak of the XRD pattern in FIG. 2 shifted from 29.4° (κ) in the fresh sorbent to 32.0° (γ , δ) in the spent sorbent, which is possibly due to the change of crystal form during reaction. The product of sodium aluminate led to more reflections with diffraction at $2\theta = 21$; 22.5; 32; 40; 52.2; 54.4° (A. V. Agafonov *et al.*, *J. Sol-Gel Sci. Technol.* **2015**, 76, 90-97). In FIG. 3, except for the peaks corresponding to Na, O, Ca, and Al, the peaks corresponding to K 2p and Cl 2p can also be found in the survey spectra of the spent sorbent (K. Siegbahn *et al.*, *Phys. Scr.* **1970**, 1, 272; and C. Park, W. Choi & H. Kang, *Radiat. Eff. Defects Solids* **1990**, 115, 65-72). The intensity and area of Na 1s of spent sorbent are larger than the fresh sorbent as shown in FIG. 3. Na and K are also shown in the elemental mapping images in FIG. 6.

Example 4. HCl removal by sorbents with different sizes

20 The HCl removal activity of the different-sized sorbents prepared in Example 1 was evaluated by following the protocol in Example 2 except the simulated syngas contained only HCl, the reactor temperature was set at 850 °C and the exposure time of the sorbent to syngas was 1 h.

25 Results and discussion

FIG. 7 shows the HCl removal efficiency by the synthesized sorbents in the range of 70 - 95%. The HCl removal decreased as the sorbent size increased. The total chloride input to the reactor was around 14.04 mg as calculated from Table 5. The chloride collected in the impinger bottles with DI water (outlet chloride) was much less as compared to the chloride captured by the sorbent (chloride removed by sorbents) (Table 6). The HCl concentrations calculated from Tables 5 and 6 were reduced from 0.26 g/Nm³ to 0.08 g/Nm³. The total chloride

after the reaction was around 14 - 15 mg, which is close to the total chloride input to the reactor and approaching the mass balance. It indicates that no matter what kind of species (HCl, NaCl and KCl) the chloride is in, the sorbent is effective to capture it. Moreover, the small particle size is beneficial for the HCl adsorption as opposed to the alkali metal capture. The effective component for HCl removal in the sorbent may be the impurities Na₂O and K₂O in the aluminum hydroxide hydrate (H₃AlO₃·xH₂O), and the product NaAlO₂ and KAlO₂ from the reaction between the sorbent and alkali metal (B. Dou *et al.*, *Energy Fuels* **2007**, *21*, 1019-1023; and M. Nunokawa, M. Kobayashi & H. Shirai, *Powder Technol.* **2008**, *180*, 216-221), which is calculated and shown in FIG. 8. The large error of the removal efficiency is possibly due to the complicated combined mechanism of alkali metal removal and HCl removal.

Table 5. Input flow rate of chloride in different species during 1 h of reaction, tested by ICP-OES and IC.

	Total Cl ⁻ input	Cl ⁻ in HCl	Cl ⁻ in NaCl	Cl ⁻ in KCl
Flow rate (mg/min)	0.234	0.097	0.085	0.052
Percentage (wt.%)	100	41.5	36.3	22.2

Table 6. Chloride content after 1 h of reaction, tested by IC.

Particle size (mm)	Chloride removed by sorbents (mg)	Outlet chloride (mg)	Total chloride (mg)
0.063 - 0.212	13.7 ± 0.8	0.02 ± 0.01	13.72 ± 0.76
0.5 - 1.4	13.5 ± 1.7	0.96 ± 0.05	14.46 ± 1.28
2.0 - 2.8	12.9 ± 1.5	1.51 ± 1.23	14.41 ± 1.43
No sorbent	0	13.80 ± 0.43	13.80 ± 0.43

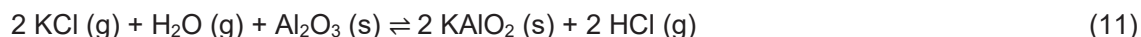
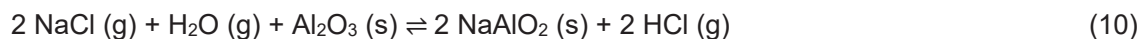
Example 5. Interaction between sorbents and syngas impurities

To explore the interaction between sorbents and syngas impurities, thermodynamic calculations were conducted.

Results and discussion

Table 7 shows the inputs for the calculation, according to the input materials ratio of the experiment. FIG. 8 shows the equilibrium compositions of fresh sorbent with NaCl, KCl, and HCl. As performed in the thermodynamic calculation, NaCl and KCl decrease but HCl

increases. This suggests that the sorbent removes the NaCl and KCl from simulated syngas at temperature 800 - 900 °C through a reaction as shown in Eq. (10) and (11), which is consistent with the study by Lee *et al.* (S. H. Lee, R. F. Henry & K. M. Myles. *Removal of alkali vapors by a fixed granular-bed sorber using activated bauxite as a sorbent.* in *Turbo Expo: Power for Land, Sea, and Air.* **1985.** American Society of Mechanical Engineers). The decrease of Al₂O₃ is also attributed to the formation of Ca-Al composites (e.g. CaO·2Al₂O₃ and CaO·Al₂O₃) in the equilibrium. Moreover, NaAlO₂ and KAlO₂ which are produced from the NaCl and KCl removal can react with HCl and produce NaCl and KCl, which is consistent with the study by Nunokawa *et al.* (M. Nunokawa, M. Kobayashi & H. Shirai, *Powder Technol.* **2008**, *180*, 216-221). For HCl removal, the active component may be NaAlO₂ and KAlO₂ (the stable species of Na₂O and K₂O in the sorbent), as shown in Eq. (12) and (13). The increase of HCl in the figure is possibly due to the equilibrium shifting to Eq. (10) and (11) as the chemical reactions for alkali metal removal and HCl removal are reversible. However, NaCl, KCl, and HCl were decreased by 70% - 90% in Examples 3 and 4. The difference between thermodynamic calculation and experiment results may be attributed to the existence of physical adsorption for NaCl and KCl, besides the chemical sorption (S. H. Lee, R. F. Henry & K. M. Myles. *Removal of alkali vapors by a fixed granular-bed sorber using activated bauxite as a sorbent.* in *Turbo Expo: Power for Land, Sea, and Air.* **1985.** American Society of Mechanical Engineers). The NaCl and KCl vapor are proposed to react with Al₂O₃:



For the HCl removal, the reaction is proposed to be:

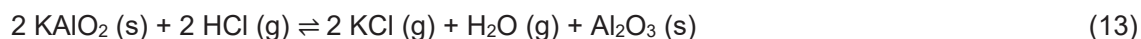
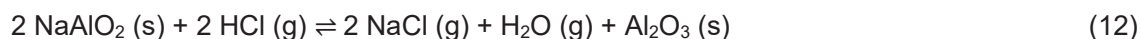


Table 7. Inputs for thermodynamic calculations.

	N ₂	Al ₂ O ₃	CaO	NaCl	KCl	HCl	H ₂ O	Na ₂ O	K ₂ O
Amount (mol)	302.46	17.65	3.10	0.14	0.09	0.16	166.52	0.26	0.01

Example 6. xAl-yCa sorbent preparation and property

The sorbents with varying Al and Ca content were prepared from CaAl_2O_4 and $\text{H}_3\text{AlO}_3 \cdot x\text{H}_2\text{O}$ by following the protocol in Example 1 except the obtained sorbents were crushed and sieved to the size range of 2 - 2.8 mm, and the selected contents of CaAl_2O_4 in the dry mixture of $\text{H}_3\text{AlO}_3 \cdot x\text{H}_2\text{O}$ and CaAl_2O_4 were 0 wt.%, 15 wt.% and 30 wt.%. The sorbents were labeled as xAl-yCa corresponding, where x equals to 100, 85 or 70 and y equals to 0, 15 or 30, Al stands for $\text{H}_3\text{AlO}_3 \cdot x\text{H}_2\text{O}$ and Ca stands for CaAl_2O_4 .

Characterization

The compositions of the sorbent measured by ICP-OES after microwave acid digestion are listed in Table 8. There is a slight difference between the composition weight percentage of 100Al-0Ca and $\text{H}_3\text{AlO}_3 \cdot x\text{H}_2\text{O}$ (see Table 1), which attributes to the calcination and measuring error, such as residual impurities in the muffle furnace and different measuring time.

Table 8. Compositions of the fresh sorbents tested by ICP-OES.

Material	Al_2O_3 (wt.%)	CaO (wt.%)	Na_2O (wt.%)	MgO (wt.%)	Fe_2O_3 (wt.%)	SiO_2 (wt.%)	K_2O (wt.%)
100Al-0Ca	96.6 ± 0.3	1.5 ± 0.1	0.9 ± 0.1	0.6 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
85Al-15Ca	89.8 ± 0.2	8.7 ± 0.1	0.8 ± 0.1	0.6 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
70Al-30Ca	82.5 ± 0.3	16.2 ± 0.1	0.4 ± 0.1	0.5 ± 0.1	0.3 ± 0.1	0.1 ± 0.1	0.1 ± 0.1

Example 7. Alkali metals removal by xAl-yCa sorbents

The alkali metal removal activity of the xAl-yCa sorbents prepared in Example 6 was evaluated by following the protocol in Example 2 except the simulated syngas contained only NaCl and KCl, the reactor temperature was set at 850 °C and the exposure time of the sorbent to syngas was 1 h.

Results and discussion

FIG. 9 shows the removal efficiencies of Na, K, and total removal efficiency of Na and K by the sorbents with different percentages of CaAl_2O_4 . The removal efficiencies of Na and K by the three sorbents were slightly different, illustrating that CaAl_2O_4 did not contribute significantly to alkali metal removal. The P values of t-test for the removal efficiencies of Na and K for the 100Al-0Ca, 85Al-15Ca, and 70Al-30Ca were 0.0126, 0.0249, and 0.0587, respectively.

Example 8. 85Al-15Ca, kaolin and activated Al_2O_3 sorbent preparation and property

85Al-15Ca

The 85Al-15Ca sorbent was prepared by following the protocol in Example 1 except the obtained sorbent was crushed and sieved to the size range of 2 - 2.8 mm.

5 Kaolin

The massive kaolin was crushed to small particles by Ball Mill and sieved to 2 - 2.8 mm.

Activated Al_2O_3

The activated Al_2O_3 was with the size range of 0.06 - 0.30 mm.

10

Characterization

The compositions of the sorbent measured by ICP-OES after microwave acid digestion are listed in Table 9. Based on the acid digestion analysis by ICP-OES, the fresh 85Al-15Ca sorbent contained approximately 90 wt% of Al_2O_3 . The other three main components were
 15 CaO, Na_2O , and MgO from the parents $H_3AlO_3 \cdot xH_2O$ and $CaAl_2O_4$. The raw $H_3AlO_3 \cdot xH_2O$ contained 0.7 wt% of CaO, 1.5 wt% of Na_2O , 0.8 wt% of MgO, etc. The composition of activated Al_2O_3 was similar to 85Al-15Ca, but had a higher content of Al_2O_3 and a lower content of CaO. Kaolin mainly contained 55.0 wt% of Al_2O_3 and 44.4 wt% of SiO_2 .

20 **Table 9.** Compositions of the fresh sorbents tested by ICP–OES.

Material	Al_2O_3 (wt.%)	CaO (wt.%)	Na_2O (wt.%)	MgO (wt.%)	Fe_2O_3 (wt.%)	SiO_2 (wt.%)	K_2O (wt.%)
Kaolin	55.0 ± 2.9	0.4 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	44.4 ± 1.6	0.1 ± 0.1
Activated Al_2O_3	94.5 ± 0.2	4.5 ± 0.2	0.6 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
85Al-15Ca	89.8 ± 0.2	8.7 ± 0.1	0.8 ± 0.1	0.6 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1

The pores with a diameter between 2 to 50 nm is generally characterized as mesopores (J. Yu, J. A. Lucas & T. F. Wall, *Prog. Energy Combust. Sci.* **2007**, 33, 135-170). The BJH pore volume (FIG. 10) of the 85Al-15Ca and activated Al_2O_3 sorbents were mainly provided by
 25 mesopores. N_2 sorption isotherms of the sorbents are shown in FIG. 11. Table 10 shows the porous characteristics of the fresh sorbents. The mesoporous 85Al-15Ca had the largest surface area and pore volume of 158 m²/g and 0.71 mL/g, respectively. The surface area of activated Al_2O_3 was close to 85Al-15Ca, but the pore volume was less than half of the 85Al-15Ca. Kaolin had the smallest surface area and pore volume of 1 m²/g and 0.01 mL/g.

30

Table 10. BET specific characteristics of the fresh sorbents.

Sorbent	BET surface area (m ² /g)	Total pore volume (mL/g)	Pore size (Å)
85Al-15Ca	158	0.71	17
Activated Al ₂ O ₃	140	0.25	7
Kaolin	1	0.01	23

The surface morphologies of the sorbents are shown in FIG. 12. The morphology of 85Al-15Ca resembles nanoflakes with porous structure, which is consistent with the large surface area and pore volume of the material. The area of high magnification was analyzed using EDS and shown as Al-Ca sorbents (FIG. 12b). The surfaces of activated Al₂O₃ and kaolin were cracked and had few porous structures, which were significantly different from 85Al-15Ca and consistent with their lower surface area and pore volume. The areas of their high magnification were analyzed as Al₂O₃ and Al-Si sorbents (shown in FIG. 12d and f), respectively. The XRD patterns of the sorbents are shown in FIG. 13. Only γ -alumina could be observed in activated alumina. The kaolin was mainly composed by kaolinite, mullite, quartz SiO₂ and illite. For the prepared 85Al-15Ca sorbent, CaO and various phases of Al₂O₃, including γ -phase, δ -phase, and α -phase were observed. The formation of various Al₂O₃ phases (i.e., γ -, δ -, and θ -alumina) could have co-existed after the calcination at 800 - 900 °C (K. A. Matori *et al.*, *Int. J. Mol. Sci.* **2012**, 13, 16812-16821) and α -alumina was from the CaAl₂O₄.

Example 9. Alkali metals removal by 85Al-15Ca

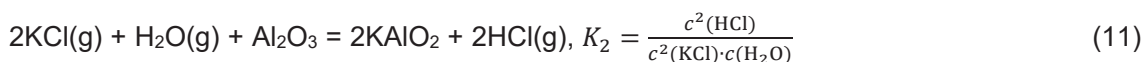
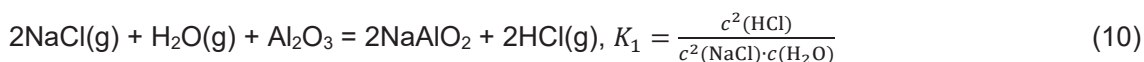
The alkali metal removal activity of the sorbents prepared in Example 8 was evaluated by following the protocol in Example 2 except the simulated syngas contained only NaCl and KCl.

Results and discussion

FIG. 14a presents the removal efficiencies of Na, K, and overall removal efficiency of the sorbent 85Al-15Ca at different temperatures after 1 h. At 750, 800, and 850 °C, the removal efficiency of Na was relatively constant, i.e., 96%, 95%, and 92%, respectively. The removal efficiency of K slightly decreased from 84% to 77% as the reaction temperature increased from 750 °C to 850 °C. The overall alkali metals removal efficiency remained relatively stable at 750 - 850 °C. However, a significant decrease was found for the removal efficiency of Na and K at higher temperature (900 °C). The overall removal efficiency of Na and K decreased to 43% at 900 °C, which is possibly ascribed to the reaction temperature of 900 °C being higher than the synthesizing temperature (850 °C) and then affected the structure of the sorbents (P. S. Santos, H. S. Santos & S. Toledo, *Mater. Res.* **2000**, 3, 104-114). The inverse

temperature dependence was also found by Xu *et al.* (L. Xu *et al.*, *Energy Fuels* **2014**, *28*, 5640-5648), showing that the increase in temperature to 1000 - 1400 °C resulted in the decrease in Na removal efficiency from 70% to 50% due to the structural change of kaolin upon heating. FIG. 14b presents the removal efficiency of Na, K, and overall efficiency as a function of the reaction time at 850 °C. According to the result, the removal efficiency was stable for the first 2 h and decreased afterwards. This suggests that the sorbent was gradually saturated with the alkali metals, thus the adsorption activity was dramatically reduced. As the breakthrough point was defined as the time at the removal efficiency of 80%, the breakthrough capacities for Na and K were 0.16 mmol/g and 0.11 mmol/g, respectively. Notably, the removal efficiency of Na by the sorbents was higher than that of K, which is consistent with the result reported in literature (A. Waindich & M. Müller, *Fuel* **2014**, *116*, 889-893). This could be explained by the thermodynamic calculations conducted in FIG. 15, which explored the interactions between sorbents and alkali metals in syngas.

- 15 The ΔG for the reaction of Al_2O_3 with NaCl and KCl vapor was positive at 750 - 900 °C, suggesting that the NaCl and KCl removal by Al_2O_3 is not thermodynamically favorable. However, the reactions



- 20 with the $c^2(\text{HCl})/c^2(\text{NaCl}) = K \cdot c(\text{H}_2\text{O}) = 0.32$ and $c^2(\text{HCl})/c^2(\text{KCl}) = K \cdot c(\text{H}_2\text{O}) = 0.008$, which the equilibrium concentration of HCl is comparable to NaCl and KCl, imply that the reactions of 85Al-15Ca with NaCl and KCl is possible. For both reactions, the ΔG values increased as temperature increased. The equilibrium distributions were carried out using all species with related elements in FIG. 15c. The amounts of NaCl and KCl vapor respectively decreased to around 3 mol and 12 mol compared with the inputs of 17 mol in the reaction temperature range of 750 - 900 °C, with the reaction products being NaAlO_2 , KAlO_2 and HCl. Excessive amounts of NaAlO_2 and KAlO_2 were from the fresh sorbent 85Al-15Ca. The small amounts of other alkali compounds like NaOH and KOH in the products can be ignored. To conclude, the 85Al-15Ca sorbent performed better in NaCl removal than KCl removal.

- 30 The XPS spectra of the fresh and spent 85Al-15Ca sorbents are presented in FIG. 3. According to FIG. 3a, the peaks corresponding to Na 1s, O 1s, Ca 2p, and Al 2p were found in the fresh sorbent. Except for the peaks corresponding to Na, O, Ca, and Al, the peaks corresponding to K 2p and Cl 2p could also be found in the survey spectra of the spent sorbent, implying the K and Cl were adsorbed by 85Al-15Ca. Cl 2p (FIG. 3c) could be separated into

two peaks: 197.8 eV and 199.1 eV. The binding energy of 197.8 eV was close to the result of NaCl (198.4 eV, W. E. Morgan, J. R. Van Wazer JR & W. J. Stec, *J. Am. Chem. Soc.* **1973**, 95, 751-755), or KCl (198.3 eV, W. E. Morgan, J. R. Van Wazer JR & W. J. Stec, *J. Am. Chem. Soc.* **1973**, 95, 751-755), while the binding energy of 199.1 eV was close to the result of NaCl (199.1 eV, M. Prestat *et al.*, *ChemElectroChem* **2018**, 5, 1203-1211) or KCl (199.5 eV, W. E. Morgan, J. R. Van Wazer JR & W. J. Stec, *J. Am. Chem. Soc.* **1973**, 95, 751-755). Furthermore, the intensity and area of Na 1s (FIG. 3b) and K 2p (FIG. 3d) of spent sorbent were higher than the fresh sorbent. This indicates that Na and K could be effectively removed by the 85Al-15Ca. Meanwhile, Cl in the formation of NaCl and KCl in the survey spectra of the spent sorbent demonstrated physical adsorption is a pathway for NaCl and KCl removal (B. Dou *et al.*, *Fuel Process. Technol.* **2003**, 82, 51-60).

Example 10. HCl removal by 85Al-15Ca

The HCl removal efficiency of 85Al-15Ca prepared in Example 8 was evaluated by following the protocol in Example 2 except the simulated syngas contained only HCl.

Results and discussion

The breakthrough point was the time when the HCl concentration reached 50 ppmv at the reactor outlet as defined before. FIG. 16 shows the HCl concentrations at the reactor outlet and the HCl removal efficiency by the 85Al-15Ca sorbent. For the blank test in the absence of sorbent, HCl concentration at the outlet of the reactor stabilized approximately 320 ppmv after 50 min of measurement. Using 85Al-15Ca sorbent, the HCl concentration at the outlet was around 50 ppmv at 40 min. Thus, the breakthrough point for HCl removal by 85Al-15Ca was 40 min. The HCl removal efficiency decreased with time and almost lost its HCl removal ability after 3 h. The HCl breakthrough capacity was 0.03 mmol/g. The HCl removal ability could be ascribed to the NaAlO₂ and KAlO₂ in the sorbent (the stable species of Na₂O and K₂O). Additionally, considering composition of the sorbent and reaction products of 85Al-15Ca with NaCl and KCl (i.e., NaAlO₂ and KAlO₂), the thermodynamic calculations for HCl removal are shown in FIG. 17. In FIG. 17a, the ΔG values for the reactions of Na₂O, K₂O, NaAlO₂, and KAlO₂ with HCl are negative at 750 - 900 °C, suggesting the formation of chlorides over these species. The ΔG values increased as temperature increased for all materials. Notably, as can be seen in FIG. 17c, nearly 0 amount of CaCl₂ was produced at 750 - 900 °C. This indicates the reaction of CaO with HCl was unfavorable in this temperature range. Therefore, NaAlO₂ and KAlO₂ in the 85Al-15Ca are the main components for HCl removal by chemical sorption. The products NaCl and KCl could be further removed by physical sorption by the sorbent. The

obtained data from experiments and thermodynamic calculations illustrate that the 85Al-15Ca sorbent can remove HCl from syngas at 850 °C.

Example 11. Simultaneous alkali metals and HCl removal by sorbents

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According to the discussion in Examples 9 and 10, the sorbent 85Al-15Ca exhibited great performance on alkali metals and HCl removal separately. For simultaneous alkali metals and HCl removal, the performance of the prepared 85Al-15Ca sorbent in Example 8 was compared with kaolin and activated Al_2O_3 sorbents prepared in Example 8, which are widely studied as
 10 alkali sorbents in literature (H. Schürmann *et al.*, *Faraday Discuss.* **2002**, 119, 433-444; K.-Q. Tran *et al.*, *Fuel* **2004**, 83, 807-812; L. Xu *et al.*, *Energy Fuels* **2014**, 28, 5640-5648; P. O. Mwabe & J. O. Wendt, Mechanisms governing trace Na capture by kaolin in a downflow combustor. *Symposium (International) on combustion*. 26. Elsevier; **1996**:2447-2453; K.-Q. Tran *et al.*, *Fuel* **2005**, 84, 169-175; B. Dou *et al.*, *Fuel Process. Technol.* **2003**, 82, 51-60;
 15 and K. L. Luthra & O. H. LeBlanc Jr, *J. Phys. Chem.* **1984**, 88, 1896-1901), by following the protocol in Example 2 except the reactor temperature was set at 850 °C and the exposure time of the sorbent to syngas was 1 h.

Results and discussion

20 The removal efficiencies of Na, K, and overall removal efficiency by the three sorbents are shown in FIG. 18a. In the presence of HCl, the Na and K removal by 85Al-15Ca decreased 5% - 10% compared with the removal efficiency without HCl in syngas (FIG. 14). Thus, the presence of HCl in syngas lowers the alkali metals removal efficiency. This is ascribed to excessive HCl inhibiting chemical adsorption of alkali metals. The kaolin sorbent showed
 25 approximately 34% of Na removal efficiency and the K removal efficiency was only half of the Na removal efficiency. The Na and K removal efficiencies of activated Al_2O_3 were 63% and 46%, respectively. The 81% of overall alkali metals removal efficiency of the 85Al-15Ca was higher than the overall alkali metals removal efficiency using kaolin (26%) and activated Al_2O_3 (54%). In general, materials with a large surface area and pore volume are more likely to be
 30 excellent sorbents, which is essential for the mass transport of gaseous phases (N. M. Laurendeau, *Prog. Energy Combust. Sci.* **1978**, 4, 221-270). The BET specific characteristics listed in Table 10 shows that the 85Al-15Ca sorbent had the largest surface area and pore volume, which was beneficial to adsorption in physical aspect compared with the other two sorbents.

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To investigate the chlorine removal, the contents of chlorine in sorbent and output are presented in FIG. 18b. The chlorine removal efficiencies by kaolin and activated Al_2O_3 were

less than 10%, while chlorine removal efficiency by 85Al-15Ca was approximately 71%. As shown in FIG. 16, the sorbent exhibited great HCl adsorption performance as 70 - 95% of HCl was removed by the 85Al-15Ca sorbent in 60 min. The presence of NaCl and KCl impeded the chlorine removal efficiency. As discussed before, the effective components for HCl removal by 85Al-15Ca were NaAlO₂ and KAlO₂ (B. Dou *et al.*, *Energy Fuels* **2007**, 21, 1019-1023; and M. Nunokawa, M. Kobayashi M & H. Shirai, *Powder Technol.* **2008**, 180, 216-221). The products NaCl and KCl during the reactions between HCl and sorbents could be further trapped by physical adsorption. Table 11 presents the chlorine content removed by the sorbent and collected in the reactor outlet. The total chlorine input to the reactor was 14.04 mg. The total chlorine after the reaction was 14 - 15 mg, which is close to the total chlorine input to the reactor and approaching the mass balance. The lower chlorine contents were in the sorbents kaolin and activated Al₂O₃, but outlet chlorine contents were higher compared with 85Al-15Ca. The 85Al-15Ca sorbent with the large surface area and pore volume demonstrated excellent ability for alkali metals and HCl removal simultaneously.

Table 11. Chlorine content after 1 h of reaction tested by IC.

Sorbent	Chlorine removed by sorbents (mg)	Outlet chlorine (mg)	Total chlorine (mg)
85Al-15Ca	10.9 ± 1.5	3.51 ± 1.23	14.41 ± 1.43
Activated Al ₂ O ₃	0.63 ± 0.59	14.28 ± 0.46	14.91 ± 0.53
Kaolin	0.91 ± 0.77	13.64 ± 1.28	14.55 ± 0.98
No sorbent	0	13.80 ± 0.73	13.80 ± 0.73

Example 12. Characterization of the spent sorbents

The structural changes in sorbents 85Al-15Ca, activated Al₂O₃, and kaolin after processing in Example 11 was characterized.

Results and discussion

The structural changes in sorbents 85Al-15Ca, activated Al₂O₃, and kaolin after processing were studied using FESEM (FIG. 19). For 85Al-15Ca, the nanoflakes surface was densified after reaction, which is possibly due to the chemical reaction between 85Al-15Ca and alkali metals and HCl. The EDS mapping of the selected area indicated that Na, K, and Cl were present on the 85Al-15Ca surface, suggesting that the NaCl and KCl could be removed by physical adsorption as NaCl and KCl were converted into NaAlO₂ and KAlO₂ by chemical

adsorption. The porosity was decreased in the morphology of activated Al_2O_3 due to adsorption occurring on the surface layer of sorbent (B. Dou *et al.*, *Fuel Process. Technol.* **2003**, 82, 51-60). Na, K, and Cl can be also detected in the EDS mapping of the selected area for activated Al_2O_3 . Compared to the fresh sorbent, the scale shaped pattern displayed on the surface of kaolin could be responsible for the high temperature reaction. The EDS mapping of the selected area of kaolin showed that only Na and K were present on the surface, indicating that the chlorine is hardly removed by the sorbent. In addition, the BET characteristics of the spent sorbents are listed in the Table 12. After reaction, all the sorbents presented reduced surface area and expansion of their pore size, but the pore volume decreased only for 85Al-15Ca. The decrease of surface and pore volume could be a result of alkali metals adsorption.

Table 12. BET specific characteristics of the spent sorbents.

Sorbent	BET surface area (m^2/g)	Total pore volume (mL/g)	Pore size ($\text{\AA}$)
85Al-15Ca	97	0.64	26
Activated Al_2O_3	84	0.26	12
Kaolin	0.3	0.01	200

The XRD patterns of the spent sorbents are presented in FIG. 20. Sodium aluminates including NaAlO_2 , Na_5AlO_4 , $\text{Na}_2\text{Al}_{22}\text{O}_{34} \cdot 2\text{H}_2\text{O}$ were found in the sorbents 85Al-15Ca and activated Al_2O_3 , further indicating the chemical adsorption of alkali metals by the sorbents. Al_2O_3 of α -phase was found in the spent activated Al_2O_3 , which is ascribed to the change of crystal during 1 h of high temperature reaction (850°C). Except for the strong peak at 57.5° in the XRD pattern of the spent kaolin which did not match any material, the remaining was similar to the fresh kaolin due to the poor removal efficiency.

As evidenced by Examples 9-12, both physical and chemical sorption occurred in the NaCl removal process, while physical sorption was dominant for the KCl removal. HCl was removed by the 85Al-15Ca sorbent with the products of NaCl and KCl, whereas NaCl and KCl were further removed by the sorbent. The characteristics of porosity, surface area, and elemental composition enabled 85Al-15Ca to have the highest alkali metals and HCl removal efficiency compared with kaolin and activated Al_2O_3 .

Comparative Example 1

The HCl removal performance of 100Al-0Ca and 85Al-15Ca prepared in Example 6 was compared with Cu-Fe-Ba-Al catalytic sorbent (WO2021150169) by following the protocol in Example 2 except the reactor was a quartz tube with an inner diameter of 11 mm, the reactor temperature was set at 850 °C, the input direction of the syngas was from the bottom of the reactor to the top, only HCl was dissolved in H₂O to simulate an HCl concentration of 289 ppmv in the syngas and heated to 165 °C for total evaporation, and the exposure time of the sorbent in syngas and HCl was set at 50 min.

Preparation of Cu-Fe-Ba-Al

The Cu-Fe-Ba-Al catalytic sorbent with the composition of 40 wt.% CuO, 45 wt.% iron ore, 5 wt.% Al₂O₃, and 10 wt.% BaO, was synthesized by wet impregnation method described in WO2021150169.

Results and discussion

FIG. 21 shows the HCl removal efficiency of the different sorbents. The blank test was measured without any sorbent loading. In the absence of sorbent, HCl concentration at the outlet of the reactor was 200 - 250 ppmv after 30 min of measurement. Compared to the blank test, both the sorbents could remove HCl from syngas at the reaction temperature. The breakthrough times of Cu-Fe-Ba-Al and 100Al-0Ca corresponding to 50 ppmv HCl in the outlet gas were 35 min, while the breakthrough time of 85Al-15Ca was 42 min. In FIG. 22, the HCl removal efficiency of 85Al-15Ca sorbent decreased gradually as the time increased, and remained higher than 70% in about 50 min, whereas that of Cu-Fe-Ba-Al catalytic sorbent decreased dramatically after 30 min.

According to the comparison with Cu-Fe-Ba-Al catalytic sorbent, the 85Al-15Ca sorbent has comparable HCl removal performance at high temperature and high moisture content condition. Due to the presence of calcium compound (calcium aluminate cement) and Na impurity from aluminum hydroxide feedstock, the 85Al-15Ca sorbent has the capacity for HCl removal. According to the publication (G. Liu *et al.*, *Combust. Flame* **2021**, 223, 230-242), Ca-based sorbents are weaker than Ba-based sorbents in the high temperature and high moisture condition. However, the 85Al-15Ca sorbent has a great porous structure with high surface area and Na impurity, thus its HCl removal capacity is comparable to Ba-based catalytic sorbent.

Claims

1. A particulate sorbent material suitable for removal of an alkali metal and hydrogen chloride from a syngas and/or a flue gas, the particulate sorbent material comprising:
 - from 58 to 100 wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities; and
 - from 0 to 42 wt% of a binder, wherein:
 - the one or more impurities in the Al_2O_3 comprises Na_2O in an amount of from 0.3 to 1.5 wt% of the total weight of the particulate sorbent material; and
 - the particulate sorbent material has:
 - a pore volume of from 0.5 to 1 mL/g; and
 - a pore size of from 10 to 30 Å.
2. The particulate sorbent material according to Claim 1, wherein the particulate sorbent material comprises:
 - from 58 to 85 wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities; and
 - from 15 to 42 wt% of a binder, optionally wherein the particulate sorbent material comprises:
 - from 70 to 85 wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities; and
 - from 15 to 30 wt% of a binder.
3. The particulate sorbent material according to Claim 1 or Claim 2, wherein the one or more impurities in the Al_2O_3 comprises Na_2O in an amount of from 0.4 to 1.0 wt%, such as from 0.5 to 0.9 wt% of the total weight of the particulate sorbent material.
4. The particulate sorbent material according to any one of the preceding claims, wherein the particulate sorbent material has a particle size of from 0.01 to 5 mm, such as from 1.8 to 3 mm, such as from 1.9 to 2.8 mm, such as from 2 to 2.5 mm.
5. The particulate sorbent material according to any one Claims 1, 2 and 4, wherein, after the particulate sorbent material has been subjected to microwave acid digestion, the resulting mixture has the following composition:
 - from 75 to 96 wt% of Al_2O_3 ;
 - from 0.3 to 1.5 wt% of Na_2O ; and
 - from 1.4 to 16.3 wt% of CaO .

6. The particulate sorbent material according to any one of the preceding claims, wherein, after the particulate sorbent material has been subjected to microwave acid digestion, the resulting mixture has the following composition:

from 82 to 90 wt% of Al_2O_3 ;

from 0.4 to 1.0 wt% of Na_2O ; and

from 8.6 to 16.3 wt% of CaO .

7. The particulate sorbent material according to any one of the preceding claims, wherein the particulate sorbent material has:

a pore volume of from 0.6 to 0.8 mL/g, such as from 0.65 to 0.72 mL/g; and/or

a pore size of from 17 to 18 Å.

8. The particulate sorbent material according to any one of the preceding claims, wherein the binder is a cement, optionally wherein the cement is selected from one or more of the group consisting of calcium aluminate cement, a Portland cement, a rapid hardening cement, a quick setting cement, a sulfate resisting cement, and a blast furnace cement

9. The particulate sorbent material according to any one of the preceding claims, wherein the particulate sorbent material has a BET surface area of from 120 to 180 m^2/g , such as from 150 to 160 m^2/g .

10. A method of manufacturing a particulate sorbent material according to any one of Claims 1 to 9, wherein the method comprises the steps of:

(a) providing a slurry formed from water, aluminium hydroxide in an amount of from 58 to 100 solids wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities, and from 0 to 42 solids wt% of a binder;

(b) calcining the slurry at a temperature of from 750 to 1,000 °C for a period of from 4 to 10 hours to provide an unrefined sorbent material; and

(c) crushing and sieving the unrefined sorbent material to provide a particle size of from 1.8 to 3 mm, wherein:

the one or more impurities in the Al_2O_3 comprises Na_2O in an amount sufficient to provide from 0.3 to 1.5 wt% of the total weight of the resulting particulate sorbent material.

11. The method according to Claim 10, wherein the slurry comprises water, aluminium hydroxide in an amount of from 58 to 85 solids wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities, and from 15 to 42 solids wt% of a binder, optionally wherein the slurry

comprises water, aluminium hydroxide in an amount of from 70 to 85 solids wt% of Al_2O_3 where the Al_2O_3 comprises one or more impurities, and from 15 to 30 solids wt% of a binder.

12. The method according to Claim 10 or Claim 11, wherein the one or more impurities in the Al_2O_3 comprises Na_2O in an amount sufficient to provide from 0.4 to 1.0 wt%, such as from 0.5 to 0.9 wt% of the total weight of the resulting particulate sorbent material.

13. The method according to any one of Claims 10 to 12, wherein the particle size obtained in the crushing and sieving step (c) of Claim 10 is from 1.9 to 2.8 mm, such as from 2 to 2.5 mm.

14. A method for removing an alkali metal and hydrogen chloride from a syngas and/or a flue gas in need thereof, the method comprising the steps of:

- (a) providing a reaction chamber comprising a particulate sorbent material as described in any one of Claims 1 to 9; and
- (b) passing the syngas and/or the flue gas through the particulate sorbent material in the reaction chamber at a temperature of from 600 to 1000 °C to provide a syngas and/or a flue gas with a reduced amount of alkali metal and hydrogen chloride compared to the original syngas and/or flue gas.

15. The method according to Claim 14, wherein the temperature is from 750 - 900 °C.