Direct CO$_2$ capture from ambient air by K$_2$CO$_3$/alumina composite sorbent for synthesis of renewable methane

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Abstract

A composite sorbent was synthesized by impregnating cylindrical granules of mesoporous $\gamma$-Al$_2$O$_3$ with an aqueous solution of K$_2$CO$_3$. Three fractions of the composite with the characteristic grain size of 1–2 mm, 3–4 mm and 4–6 mm were tested for direct carbon dioxide capture from ambient air in a continuous-flow system. It was shown that dynamic CO$_2$ absorption capacity of the composite sorbent increases significantly with decrease of the characteristic grain size, which indicates that the process is limited by mass transfer. The effect of temperature on thermal regeneration of the composite was also investigated. The change of regeneration temperature from 250 to 300°C enhanced CO$_2$ absorption capacity for all the fractions studied. XRD in situ study showed that the reason of this enhancement is thermal decomposition of potassium dawsonite KAlCO$_3$(OH)$_2$ formed during synthesis of the composite material. The composite sorbent demonstrated a good stability of its CO$_2$ absorption characteristics, therefore it should be considered as a promising material for direct carbon dioxide capture from air.

Keywords: Carbon dioxide, potassium carbonate, alumina, composite material, absorption, regeneration, air, grain size effect

Introduction

One of the main problems of power systems based on renewables, such as wind and solar energy, is volatility of the power supply. Chemical energy storage systems have the potential to become a sustainable and realistic solution to this challenge, which enables an offsetting in the time gap between power production and its consumption.

The surplus electricity generated by renewables can be used for water electrolysis (1) in order to produce hydrogen:

$$2H_2O \xrightarrow{\text{electrolysis}} 2H_2 + O_2 \quad (1)$$

Hydrogen is considered to be a perspective fuel for low-carbon economy, but there are still unresolved safety problems regarding its transportation and storage. Therefore, it is reasonable to use the generated hydrogen for production of a conventional hydrocarbon fuel, e.g., methane, which can be obtained by the Sabatier process [1]:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (2)$$

The synthetic renewable methane, which corresponds to chemically normal natural gas, can be injected into the existing gas network or stored and utilized on demand. It is very important for sustainable development that renewable methane can be potentially produced using carbon dioxide captured from ambient air. It is well known that CO$_2$ is the major anthropogenic greenhouse gas, which contributes to global climate change. Carbon dioxide capture is usually discussed in the context of capturing CO$_2$ from large point sources, such as flue gases from industries and coal-fired power plants. For small distributed sources of CO$_2$, i.e., transport vehicles, capture at the emission source is not favorable from the practical point of view. Therefore, capturing carbon dioxide directly from the atmosphere (“direct air capture”, DAC) is currently under consideration as an option for stabilizing global CO$_2$ concentrations [2,3]. Direct CO$_2$ capture from ambient air offers more flexibility compared to conventional source point capture, because CO$_2$ capture units can easily be located close to CO$_2$ recycling center. The DAC technology has a potential to be “carbon negative”, but only if a renewable energy source is used to drive the process. Incorporation of the DAC unit into the energy...
storage system offers an opportunity to use anthropogenic carbon dioxide as a valuable feedstock for the production of renewable methane, which can be utilized in the heating market or as a fuel for transportation.

Carbon dioxide capture from ambient air is more challenging than conventional carbon capture from flue gases because of very low CO₂ concentration in air (~400 ppm) and the necessity to operate in the presence of moisture excess at ambient temperature and pressure. The most developed DAC technologies are based on carbon dioxide absorption by aqueous alkali solutions. The major drawback of this approach is that the regeneration of these solutions is generally multi-stage and energy intensive.

Potassium carbonate is a well-known solid inorganic chemisorbent, which reacts with atmospheric CO₂ in the presence of water vapor forming potassium bicarbonate [4]:

\[ K_2CO_3 + H_2O + CO_2 \rightarrow 2KHCO_3 \]  

(3)

The main problem with using bulk potassium carbonate for CO₂ absorption purposes is low carbonation rate [5,6]. This problem can be solved by dispersing K₂CO₃ particles inside a porous support material. Composite materials "potassium carbonate inside a porous matrix" are known to be effective sorbents for capturing carbon dioxide from wet flue gases [5-9]. Recently, it was also shown that K₂CO₃/γ-Al₂O₃ composite is a promising material for CO₂ capture directly from ambient air [10]. However, the room for improvement still exists and more in-depth study is needed in order to optimize absorption properties of the composite material. In this paper we will discuss some factors affecting CO₂ absorption capacity by K₂CO₃/γ-Al₂O₃ material under conditions of direct CO₂ capture from ambient air with thermal regeneration in the temperature-swing absorption (TSA) cycles.

Materials and methods
Composite sorbent preparation and characterization
Cylindrical γ-Al₂O₃ granules with diameter of 3 mm and typical length of 4-6 mm were produced by JSC «Angarsk Catalysts and Organic Synthesis Plant». The alumina is a mesoporous material with the average pore diameter of 15 nm.

The composite sorbent K₂CO₃/γ-Al₂O₃ was prepared by dry impregnation method, described in detail in [9]. The pores of the alumina matrix were filled with 40 wt.% aqueous solution of potassium carbonate. After the matrix and the solution contacted for about 1 h, the granules were dried at 90°C for 24 h and then calcinated at 200°C for 2 h. The resulted product was ground in a mortar and sieved to obtain the desired particle size range fractions: 1-2 mm, 3-4 mm and 4-6 mm.

Specific surface area and pore volume of samples of the γ-Al₂O₃ porous matrix and the composite sorbent were determined from nitrogen adsorption isotherms measured at 77 K on a Nova 1200e Surface Area and Pore Size Analyzer (BET method). Before the measurement, the samples were degassed at 150°C under vacuum for at least 3 h.

The phase composition for the composite sorbent was determined from powder X-ray diffraction (XRD) patterns, which were obtained on a Brucker D8 Advance diffractometer using Cu Kα radiation. Diffraction intensities were measured with the LynxEye position sensitive detector (2.9° angular range). XRD patterns were collected in 2θ range 10-70°, with 0.02° step size and 2s collection time. Variation of the phase composition of the composite sorbent owing to heating and cooling of the composite sorbent in air were studied by XRD analysis in situ by Siemens D-500 X-ray diffractometer equipped with graphite monochromator on the diffracted beam using Cu Kα radiation. Diffraction patterns were detected in the 10°-50° (2θ) region by points with the 0.05° (2θ) step. Measurements at elevated temperatures were carried out in a special X-ray chamber under ambient atmosphere. The sample of the as-synthesized composite sorbent was placed in the chamber and heated in air. Temperature of the chamber was gradually increased from 50°C up to 350°C by the step of 50°C. A diffraction pattern for the heated sample was measured after holding the sample at given temperature for about 15 minutes. Then the sample was cooled down to the the room temperature, and a diffraction pattern was detected 12 hours after. Phase analysis was performed using ICDD PDF-2 and ICSD data bases. The size of the coherent scattering domain (CSD) for constituent phases was estimated using by Fundamental parameter approach [11].

CO₂ absorption and desorption experiments
Processes of carbon dioxide absorption from ambient air and consecutive thermal desorption were studied in a cyclic mode (TSA test) in the experimental apparatus schematically shown in Figure 1. Installation of four absorbers connected in parallel was used for simultaneous testing the sorption properties of several samples with different size fractions (Table 1). Heating control and redistribution of the gas stream to the reactors were carried out automatically using the controllers MVU-8 (OWEN, Russia) and Thermodat-13K2 (Thermodat, Russia). The composite sorbent was placed into a cylindrical glass tube.
absorber 6.5 mm ID located inside an electrical heater. Indoor air was pumped through the reactor continuously using the air pump FIAC CCS 100-335. Pressure drop at the absorber inlet was maintained constant during the experiments. Air flow rate was controlled at the absorber outlet by the flow meter SMC PFM510-F01-2.

A single TSA cycle comprised 2 steps: 1) CO₂ absorption from ambient air for 6 h; 2) the composite sorbent thermal regeneration for 2 h. Two regeneration temperatures were used in TSA cycles: 250 and 300°C. The next CO₂ absorption step started right after the regeneration, as the absorber was cooling down to room temperature. Outlet concentrations of CO₂ during regeneration step were measured by the gas analyzer Test-1.1 (BONER, Russia) in the range from 0 up to 5 vol. % with accuracy of 0.05 vol. %. The gas analyzer OPTOGAZ-500.4C (OPTEC, Russia) was used for measuring outlet concentration of CO₂ during cooling (sorption) steps in the range from 0 to 2000 ppm with relative error of 3%. The summary of experimental conditions of TSA tests is presented in Table 2.

Table 1. Samples of the K₂CO₃/γ-Al₂O₃ composite for TSA tests.

| Absorber Fraction, mm | Mass, g |
|-----------------------|---------|
| 1 1-2                 | 2.64    |
| 2 1-2                 | 2.69    |
| 3 3-4                 | 2.59    |
| 4 4-6                 | 2.56    |

Table 2. The experimental conditions of the TSA tests.

| Sorption step | Desorption step |
|---------------|-----------------|
| Step duration 6 hours | Heating rate 12 K/min |
| Air flow rate 20-24 ml/s | Step duration 2 hours |
| Air flow rate 20-24 ml/s | Air flow direction Concurrent |
| Regeneration temperature 250°C; 300°C | |

CO₂ outlet concentration curves c(t) [vol. %] measured during the regeneration step were used for calculation of specific CO₂ flow Q(t) [cm³/s/g] and the absorption capacity of the material aᵣ [cm³/g]:

\[ Q(t) = \frac{U(t) \cdot c(t)}{m}, \]  
\[ aᵣ = \frac{1}{m} \int_{t₀}^{t} U(t) \cdot c(t) dt, \]

where \( U(t) \) [cm³/s] is the air flow rate and \( m \) is the mass of the composite sorbent [g].

The value of the absorption capacity was also calculated in wt. % (\( a_m \)), using the ideal gas approximation:

\[ a_m = \frac{aᵣ \cdot M(CO₂) \cdot 100\%}{V_w}, \]  

where \( V_w \) is the molar volume of the ideal gas (2.44×10⁴ cm³/mol for the standard conditions: ambient temperature and pressure of 298 K and 1 bar, respectively), \( M(CO₂) \) is molar weight of CO₂ (44 g/mol).

Results and discussion

CO₂ absorption and desorption behaviors for different fractions of the composite sorbent

The effect of the grain size on CO₂ absorption and desorption behavior of the composite was investigated in the TSA cycles with \( T_{reg}=250°C \). One can see that the minimal value of outlet CO₂ concentration during absorption differs significantly for the fractions with different characteristic grain size (Figure 2). The lowest prebreakthrough level of CO₂ concentration (about 200 ppm) was reached by 1-2 mm granules. In comparison, for 4-6 mm granules the minimal CO₂ concentration detected during the absorption run was as high as 450 ppm. Nevertheless, one can see that, irrespective of the grain size, at the end of the absorption step outlet CO₂ concentration becomes equal to the inlet one, which indicates that the CO₂ absorption rate becomes negligible.

Figure 2. Outlet concentrations of CO₂ (symbols) and absorber temperature profile (line) during absorption step of the TSA cycle for different fractions of the composite sorbent. Maximum regeneration temperature during preceding step was 250°C. Other conditions were as in Table 2.
granules of 1-2 mm grain size placed inside two different absorbers.

The values of CO₂ absorption capacity, which were calculated from desorption curves, were found to be fairly stable for all the fractions of the composite for ten consecutive TSA cycles with T_{reg}=250°C (Figure 4a). Ultimately, the decrease in the grain size from 4-6 mm to 1-2 mm resulted in increasing CO₂ absorption capacity from 10 to 25 cm³/g.

It was shown that all the fractions of the composite showed a gain in CO₂ absorption capacity as a result of increasing regeneration temperature from 250 to 300°C (Figure 4b). The absolute value of CO₂ absorption capacity in the TSA cycles with T_{reg}=300°C was still strongly influenced by the grain size. The best result was obtained by the sample consisted of granules with 1-2 mm sizes, which demonstrated CO₂ absorption capacity \( \approx 6 \) wt. % and the utilization extent of potassium carbonate about 85%.

The grain size effect on the integral CO₂ absorption capacity of the material indicates that either the absorption or the desorption step of the TSA cycle is limited by the mass transfer within the grain. As a result of this limitation, the part of the supported alkali component in the larger granules is apparently unable to absorb CO₂ from air during the cyclic process. In order to study this effect in more depth we compared some characteristics of the big granules of the composite sorbent before and after TSA cycling.

**Chemical composition of the composite sorbent**

Potassium loadings, which were determined by means of atomic absorption spectroscopy for the samples of the composite sorbent before and after TSA experiments, turned out to be 12.5 and 12.3 wt. %, correspondingly. These values are equivalent to 21.8-22.1 wt. % of K₂CO₃. Thus, the TSA cycling procedure does not lead to the significant loss of the supported alkali component.

**Porous structure of the composite sorbent**

Porous structure of the host matrix and the composite before and after TSA cycling with T_{reg}=250°C was characterized by BET method. The alumina matrix used for synthesis of the composite material is a mesoporous material which demonstrates a bimodal pore size distribution (PSD) with one peak centered at 4 nm and another one characterized by a maximum at 19.5 nm (Figure 5). Modification of mesoporous alumina with the alkali chemisorbent predictably leaded to the decrease in both the specific surface area and pore volume in comparison to those for pure \( \gamma \)-Al₂O₃ (Table 3). The PSD for the as-synthesized composite sorbent differs noticeably from the one for the unmodified alumina (Figure 5) as the first peak at 4 nm decreases and the second peak shifts from 19.5 to 16 nm. The likely explanation for the latter effect is that the supported alkali component covers the inner surface of \( \gamma \)-Al₂O₃ as a thin layer resulting in pore narrowing.

The composite sorbent after TSA cycling is characterized by lower values both the specific surface area and the total pore volume compared to those for the as-synthesized material (Table 3). The comparison of PSDs for the composite
Figure 5. The pore size distributions for pure γ-Al₂O₃ granules (1) and K₂CO₃/γ-Al₂O₃ composite granules before and after TSA cycling with Treg = 250°C (2 and 3, correspondingly).

Table 3. Porous structure of γ-Al₂O₃ and K₂CO₃/γ-Al₂O₃ granules.

| Sample                              | Surface area, m²/g | Pore volume, cm³/g |
|-------------------------------------|--------------------|--------------------|
| γ-Al₂O₃                             | 197                | 0.72               |
| K₂CO₃/γ-Al₂O₃ (before TSA cycling)  | 99                 | 0.35               |
| K₂CO₃/γ-Al₂O₃ (after TSA cycling)   | 80                 | 0.29               |

before and after TSA cycling shows that used material has less mesopores with the characteristic sizes of 4 nm and 10-16 nm, but slightly more mesopores with the characteristic size about 19 nm. This change in the PSD is likely be caused by redistribution of the active alkali component inside the porous media of the alumina matrix.

Phase composition of the composite sorbent

Crystalline phases of potassium-containing species for the composite sorbent have been characterized by means of XRD analysis (Figure 6). The main diffraction peaks observed for the sample of the composite at ambient temperature were attributed to KHCO₃ (Kalicinite, P2/a, ICDD PDF-2 #12-0292) and KAICO₃(OH)₂ (potassium dawsonite, Cmcm, ICSD #153303). Additional peaks at 2θ=30.98, 31.76 and 33.68° were assigned to mixed potassium carbonate-hydrocarbonate phase K₄H₂(CO₃)₃*1.5H₂O (Pbam, ICDD PDF-2 #20-0886). Widths diffraction maxima corresponding KHCO₃ phase for the both samples are narrow and compatible with the widths of a standard sample that indicates the coherent scattering domain (CSD) size is >100 nm. The CSD size of KAICO₃(OH)₂ phase is 18 nm for the as-synthesized material and 14 nm for the composite after TSA cycling with Tₗ = 250°C. The results of XRD analysis indicate that the crystals of potassium dawsonite and bicarbonate seem to be spatially separated in the granule. Potassium dawsonite has the CSD, which is comparable with the average pore diameter of the alumina matrix. Therefore, the KAICO₃(OH)₂ phase is likely to be dispersed inside the pores, on the internal surface of the alumina matrix, as it was previously stated in [12]. On the contrary, the CSD size for potassium bicarbonate phase is >100 nm, which is higher than the typical pore sizes for the mesoporous alumina matrix (see Figure 5). Thus, the KHCO₃ crystals are likely to be located on the external surface of the grain.

In order to explore structural transformations of the composite sorbent in the course of TSA cycling, XRD in situ experiment was carried out. The characteristic XRD patterns are presented in Figure 7. When the as-synthesized composite was heated from 25°C to 50°C, the reflections corresponding to potassium bicarbonate vanished. This temperature is too low for thermal decomposition of potassium bicarbonate, therefore the reflections disappearance is likely to be caused by dissolution of bicarbonate in the water adsorbed on the alumina surface. The aqueous solution is obviously more mobile than the crystalline phases, so the redistribution of the active alkali component inside the granule, which apparently affects the PSD of the composite, seems to be the result of the fluid-aided dissolution–reprecipitation of the supported components. At 250°C intensities of the reflections corresponding to potassium dawsonite phase seem to be lower than at the room temperature, however, thermal destruction of KAICO₃(OH)₂ is not complete until it is heated up to 300°C. It was previously reported that decomposition of KAICO₃(OH)₂ phase occurred in the temperature range of 260–320°C with formation of crystalline K₂CO₃ [13]. However, diffraction maxima, chara-
There are several reasons why the K$_2$CO$_3$/γ-Al$_2$O$_3$ composite should be considered as a promising material for the capture of ambient CO$_2$ and subsequent methane production using renewable energy sources.

K$_2$CO$_3$/γ-Al$_2$O$_3$ composite as a material for DAC combined with methanation process

There are several reasons why the K$_2$CO$_3$/γ-Al$_2$O$_3$ composite material should be considered as a promising absorbent for CO$_2$ capture from ambient air with subsequent methane production. First of all, this composite material absorbs CO$_2$ directly from ambient air without any pretreatment and is thermally stable in multiple TSA cycles. In comparison, zeolites cannot absorb CO$_2$ directly from air due to their high affinity to moisture [14], while supported amine adsorbents suffer from degradation in the presence of oxygen-containing gases [15,16].

The composite sorbent based on potassium carbonate is also favorable for application in the processes combining CO$_2$ capture and methanation, because this material enables production of concentrated CO$_2$ stream during desorption stage, which is required for the effective methanation process. As it was estimated in [10], realization of the DAC/methanation process at ambient pressure means that the equilibrium CO$_2$ pressure over the sorbent must be above 0.17 atm in order to comply with optimal gas composition during combined desorption-methanation step. Using thermodynamic data for the reaction of potassium hydrocarbonate decomposition [17], it was calculated that the partial CO$_2$ and H$_2$O pressures of 0.17 atm are reached at the equilibrium reaction temperature of 135°C, while the further increase in the regeneration temperature results in the higher equilibrium CO$_2$ pressure.

The efficiency of renewable energy storage sequence, which includes direct air capture by K$_2$CO$_3$/γ-Al$_2$O$_3$ composite and the subsequent methanation process, was estimated to be about 50%, taking into account that the heat released due to the reaction of methanation (2) can be utilized for thermal regeneration of the sorbent [10]. Straightforward implementation of the DAC/methanation process will be fulfilled experimentally in the nearest future.

Conclusions

Three different fractions of the composite sorbent K$_2$CO$_3$/γ-Al$_2$O$_3$ were tested in the cyclic process of direct CO$_2$ capture from ambient air with thermal regeneration of the material. It was found that dynamic CO$_2$ absorption capacity of the composite increases with decrease of the characteristic grain size, which indicates that the process is likely to be limited by mass transfer.

The change of regeneration temperature from 250 to 300°C leded to increase of absorption capacity for all the fractions of the composite. As a result, for 1-2 mm fraction absorption capacity reached the level of 6 wt. %. The XRD in situ experiment showed that the reason behind this effect is thermal decomposition of KAlCO$_3$(OH)$_2$ crystalline phase, which is likely to produce highly reactive K$_2$CO$_3$ species as a result of heating.

K$_2$CO$_3$/γ-Al$_2$O$_3$ composite should be considered as a promising material for the capture of air-borne CO$_2$ and subsequent methane production using renewable energy sources.

Competing interests

The authors declare that they have no competing interests.

Authors’ contributions

| Authors’ contributions                  | JVV | VSD | TYK | AGO |
|----------------------------------------|-----|-----|-----|-----|
| Research concept and design            | ✓   | ✓   | --  | ✓   |
| Collection and/or assembly of data     | ✓   | ✓   | ✓   | --  |
| Data analysis and interpretation       | ✓   | ✓   | ✓   | ✓   |
| Writing the article                    | ✓   | ✓   | ✓   | ✓   |
| Critical revision of the article       | ✓   | ✓   | ✓   | ✓   |
| Final approval of article              | ✓   | ✓   | ✓   | ✓   |
| Statistical analysis                   | ✓   | ✓   | --  | --  |

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