



Catalytic methanation of carbon dioxide captured from ambient air

Janna V. Veselovskaya^{a, b, *}, Pavel D. Parunin^a, Olga V. Netskina^{a, b}, Lidiya S. Kibis^{a, b}, Anton I. Lysikov^{a, b}, Aleksey G. Okunev^{a, b}

^a Borekov Institute of Catalysis SB RAS, Lavrentiev Avenue 5, Novosibirsk, 630090, Russia

^b Novosibirsk State University, Pirogova Street 1, Novosibirsk, 630090, Russia

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ABSTRACT

A novel process, combining direct CO₂ capture from ambient air using K₂CO₃/Al₂O₃ composite sorbent and CO₂ methanation in the presence of 4% Ru/Al₂O₃ catalyst, has been developed and tested in a cyclic mode. The thermal regeneration of the composite sorbent in these cycles has been carried out in H₂ atmosphere at T = 325 °C with the gas flow going straight from the adsorber outlet to the preheated catalytic reactor. Performance of the ruthenium catalyst in CO₂ methanation process has improved upon cycling, apparently due to *in situ* activation of the supported component. Activation of the catalyst has been studied in a gaseous mixture of CO₂ and H₂ (1:4) at 300 °C. The activation of the catalyst in reductive atmosphere leads to transformation of Ru⁴⁺ surface species to Ru⁰ particles, identified by means of X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy. It has been demonstrated that it is possible to transform the desorbed carbon dioxide to methane with conversion >98% at T = 325–400 °C using the activated Ru/Al₂O₃ catalyst.

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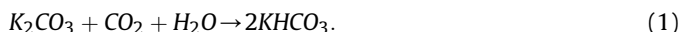
1. Introduction

Carbon dioxide is the major greenhouse gas, which is emitted into the atmosphere by power generation plants, industries and transport vehicles burning fossil fuels [1–3]. The conventional approach for lowering the CO₂ emissions is carbon capture from flue gases at large stationary sources, such as fossil-fuel based power stations and industrial plants. Direct CO₂ capture of from atmospheric air, also known as Direct Air Capture (DAC), is considered as an alternative path for managing CO₂ emissions [4–7], offering more flexibility compared to conventional source point capture because of widespread availability of air.

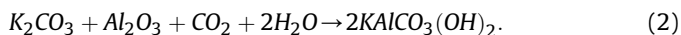
Due to the ultradilute nature of atmospheric CO₂, chemical sorbents with strong CO₂-binding affinities are typically employed for DAC [7]. In 1999 Lackner et al. proposed using aqueous sodium hydroxide solutions for DAC [8]. The major drawback of this approach is that the regeneration of these solutions is generally multi-stage and energy intensive [9]. The resulting solution containing soluble sodium carbonate is supposed to be causticized using calcium hydroxide (quicklime) in order to produce calcium carbonate, which has to be recovered by calcination as calcium

oxide, followed by rehydration, driving off a concentrated CO₂ stream. The calcination is the most energy consuming stage of the process, as high temperatures (>900 °C) are required to break the strong calcium carbonate bond.

Recently, a composite sorbent based on potassium carbonate (K₂CO₃) and porous gamma-alumina (γ-Al₂O₃) has been proposed for application in DAC [10]. Potassium carbonate is a well-known solid inorganic chemisorbent [11], which reacts with atmospheric CO₂ in the presence of water vapor, forming potassium bicarbonate (KHCO₃):



Another reaction, which involves CO₂, takes place inside alumina pores due to interaction between the components of the composite and leads to formation of potassium dawsonite (KAlCO₃(OH)₂) crystalline phase [12]:



It was shown that thermal regeneration of K₂CO₃/γ-alumina composite materials at 300 °C increases CO₂ adsorption capacity of the material in temperature-swing adsorption (TSA) cycles [13], which is due to thermal decomposition of potassium dawsonite [11]. K₂CO₃/γ-Al₂O₃ composite sorbents are regarded as promising materials for DAC because of their ability to absorb CO₂ directly

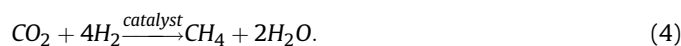
* Corresponding author. Lavrentiev Av. 5, 630090 Novosibirsk, Russia.
E-mail address: jvv@catalysis.ru (J.V. Veselovskaya).

from ambient air without any pretreatment (such as drying) and good thermal stability in multiple TSA cycles [10,14,15].

Carbon dioxide, captured from flue gases or ambient air, can be either stored in geological formations or utilized for production of fuels or other valuable chemical products using renewable energy [16–19]. One of perspective approaches for CO₂ conversion is renewable methane production by the two-step Power-to-Gas (P2G) process [18–23]. The first step of P2G process is hydrogen generation through electrolysis of water utilizing electrical energy produced by renewables:



The second step is Sabatier reaction between generated hydrogen and carbon dioxide:



Thus, excess or off-peak power generated by wind generators or solar arrays can be stored in a form of methane, which is a well-known energy carrier and can be used as fuel for numerous industrial applications. Moreover, the existing natural gas pipeline infrastructure allows transporting synthetic methane over large distances [24].

Supported nickel catalysts are the most widely studied among the materials applied for accelerating Sabatier reaction [16]. However, the formation of mobile nickel subcarbonyls due to the reaction of Ni particles with CO, which results in the deactivation at low temperatures, is considered as a major problem of Ni-based catalysts [25]. Instead, noble metals, such as Ru, Pd, and Pt, are stable at operating conditions and more active for CO₂ methanation than nickel [26]. Supported ruthenium catalysts were found to be the most active ones [16]. Kowalczyk et al. studied the effect of the support on the catalytic properties of Ru nanoparticles in CO₂ hydrogenation and found that TOFs of Ru-based catalysts were dependent on the Ru dispersion and the type of supports [27]. For high metal dispersion, the following order of turnover frequencies (TOF) in the CO₂ hydrogenation reaction was obtained: Ru/Al₂O₃ ($16.5 \times 10^{-3} \text{ s}^{-1}$) > Ru/MgAl₂O₄ ($8.8 \times 10^{-3} \text{ s}^{-1}$) > Ru/MgO ($7.9 \times 10^{-3} \text{ s}^{-1}$) > Ru/C ($2.5 \times 10^{-3} \text{ s}^{-1}$). Thus, porous alumina appears to be the optimal support for ruthenium methanation catalysts.

Potential combination of DAC and P2G technologies offers an opportunity to use ambient air as a feedstock for production of renewable methane. In order to achieve this result, atmospheric CO₂ needs to be captured from air by a regenerable sorbent and then thermally desorbed in H₂ flow in the presence of a heterogeneous catalyst accelerating Sabatier process [10]. Hereinafter, the cyclic process with alternating steps of CO₂ capture from air at ambient temperature and catalytic methanation of desorbed CO₂ at higher temperatures is going to be referred to as the Direct Air Capture/Methanation (DACM) process.

The general aim of our study was to examine the DACM process using K₂CO₃/γ-alumina composite sorbent for capturing CO₂ from ambient air and Ru/γ-alumina catalyst for accelerating Sabatier reaction (eq. (4)). The composite sorbent and the methanation catalyst have been synthesized and then tested in the experimental set-up, consisted of two continuous-flow reactors, connected in series. Additionally, we have studied activation of the catalyst in reductive atmosphere and its effect on CO₂ conversion to methane in the consecutive DACM cycles.

2. Materials and methods

2.1. Synthesis of materials

2.1.1. Composite sorbent K₂CO₃/γ-Al₂O₃ for capturing CO₂ from ambient air

The composite sorbent was prepared by dry impregnation method [10]. Granular mesoporous γ-Al₂O₃ (produced by JSC «Angarsk Catalysts and Organic Synthesis Plant», Russia) with specific surface area of 240 m²/g, total pore volume of 0.59 cm³/g and average pore diameter of 15 nm was used as a host matrix. Cylindrical alumina granules were fractured to obtain pellets with characteristic grain size of 1–2 mm, which were filled with 40 wt % aqueous solution of K₂CO₃, then dried at 90 °C for 24 h and calcinated at 300 °C for 2 h. According to atomic absorption spectroscopy potassium loading in the composite sorbent was 12.5 wt %, which is equivalent to 22 wt % of K₂CO₃.

2.1.2. Ru/Al₂O₃ catalyst for Sabatier reaction

Ruthenium catalyst of methanation was synthesized using mesoporous γ-alumina (produced by JSC “Catalyst”) as a support. Before the synthesis the alumina granules with characteristic size of 0.25–0.50 mm were calcinated at 500 °C. The specific area of alumina after calcination was determined to be 175 m²/g according to Brunauer-Emmett-Teller (BET) method applied to N₂ adsorption isotherms measured at 77 K.

The ruthenium catalyst was prepared by incipient-wetness impregnation of the support with an aqueous solution of Ru(OH)Cl₃ (produced by JSC “Aurat”). The material was air-dried under infrared lamp at 50–60 °C and then in the oven at 130 °C for 2 h. Reduction of the catalyst was carried out at room temperature in an aqueous solution of sodium borohydride with molar ratio Ru:N-aBH₄ being 1:5. Then the catalyst was washed with distilled water and dried in the oven at 130 °C for 2 h. Ru loading in the catalyst was determined to be 4 wt % according to X-ray fluorescence method using a ARL-Advant’x spectrometer with Rh anode X-ray tube.

2.2. Characterization of Ru/Al₂O₃ catalyst samples

2.2.1. X-ray photoelectron spectroscopy

Surface chemistry of the Ru/Al₂O₃ catalyst samples was characterized by means of X-ray photoelectron spectroscopy (XPS) method using a KRATOS ES300 photoelectron spectrometer. Spectra were collected with a non-monochromatized MgKα radiation (photon energy 1253.6 eV). The spectrometer calibration was performed with core-level Au4f_{7/2} line set at binding energy 84.0 eV. The Al2p core-level line was used for an internal calibration of the samples. The E_b(Al2p) = 74.7 eV was employed in accordance with the literature data for γ-Al₂O₃ [28]. To control the composition of the samples the survey spectra were acquired at the analyzer transmission energy of 50 eV and step of 1.0 eV. The charging states of the elements were analyzed with the narrow spectral regions recorded at an analyzer transmission energy of 25 eV and step of 0.1 eV. The experimental curves were fitted with a combination of Gaussian and Lorentzian peaks after the Shirley background subtraction procedure.

2.2.2. High-resolution transmission electron microscopy

High resolution transmission electron microscope (HRTEM) images for the samples of Ru/alumina were obtained using a JEM-2010 electron microscope (JEOL, Japan) with a lattice-fringe resolution of 0.14 nm at an accelerating voltage of 200 kV. The samples for the HRTEM study were prepared on perforated carbon film mounted on a copper grid.

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