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# Catalytic process for methane production from atmospheric carbon dioxide utilizing renewable energy

Janna V. Veselovskaya<sup>a,b,\*</sup>, Pavel D. Parunin<sup>c</sup>, Aleksey G. Okunev<sup>a,b</sup>

<sup>a</sup> Novosibirsk State University, Pirogova Str. 2, 630090 Novosibirsk, Russia

<sup>b</sup> Borekov Institute of Catalysis, Lavrentieva Av., 630090 Novosibirsk, Russia

<sup>c</sup> Skolkovo Institute of Science and Technology, Nobel Street 3, 143026 Moscow, Russia

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## ABSTRACT

Kinetics of CO<sub>2</sub> methanation reaction over the commercial nickel catalyst NKM-2V was studied in a perfectly mixed reactor at T = 250–350 °C. It has been shown for the stoichiometric mixture of CO<sub>2</sub> and H<sub>2</sub> that both the catalyst activity and CO<sub>2</sub> conversion increase with temperature. The decrease in CO<sub>2</sub>:H<sub>2</sub> ratio at T = 300 °C have led to the rise of CO<sub>2</sub> conversion to methane. The composite material K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, which is a promising solid adsorbent for direct CO<sub>2</sub> capture from ambient air, has been synthesized and studied in the temperature-swing adsorption cycles. It has been shown that the increase in the adsorbent temperature from 200 to 325 °C during the thermal regeneration step enhances the utilization extent of the composite sorbent in the cycle with the total CO<sub>2</sub> uptake rising from 1.9 to 4.4 wt.%. The process combining thermal regeneration of the composite sorbent in hydrogen atmosphere at T = 325 °C and CO<sub>2</sub> methanation reaction over the commercial nickel catalyst NKM-2V at T = 425 °C has been studied using the catalytic reactor connected to the outlet of the adsorbent. It has been demonstrated that it is possible to transform CO<sub>2</sub> into methane with conversion > 99%.

## 1. Introduction

Large scale integration of wind and solar energy into the electrical grid is challenged due to volatility of power supply [1]. Hence, there is a need for a technology allowing storing excess electricity produced by these fluctuating sources of renewable energy. Power-to-Gas (P2G) process is a perspective approach to renewable energy storage in chemical media [2]. The first step of P2G process is hydrogen generation through electrolysis of water using excess electrical energy generated by renewables:



Considering safety issues regarding hydrogen transportation and storage, it is reasonable to use it on site. One of possible options for H<sub>2</sub> utilization is renewable methane production by Sabatier reaction [3]:



Thermodynamics of Reaction (2) allows theoretically a very high methane yield, in particular at low temperatures. However, this is not found practically, because Sabatier reaction is kinetically limited. This kinetic barrier can be overcome using heterogeneous catalysts. Supported nickel catalysts are the most widely studied among the materials

for accelerating Sabatier reaction [4].

The synthetic renewable methane, also referred as SNG (synthetic natural gas), can be injected into the existing gas network or stored and utilized on demand as fuel for transportation or for heating market. Moreover, the existing natural gas pipeline infrastructure allows transporting SNG great distances [5]. For purposes of greenhouse gas mitigation, production of SNG from captured CO<sub>2</sub> and renewable H<sub>2</sub> can potentially be carbon neutral, if renewable energy sources are used to drive the process.

Renewable methane production by Sabatier process (2) requires a sustainable source of carbon dioxide, which is the major greenhouse gas emitted into the atmosphere due to fossil fuels use [6–8]. Carbon dioxide can be concentrated from ambient air, which contains ~400 ppm CO<sub>2</sub>, via direct air capture (DAC) process [9–12]. Incorporation of the DAC unit with into the renewable energy storage system offers an opportunity to use anthropogenic carbon dioxide as a valuable feedstock for the production of SNG.

Carbon dioxide capture from ambient air is more challenging than conventional carbon capture from flue gases because of very low concentration of CO<sub>2</sub> in air 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

\* Corresponding author at: Lavrentieva Av. 5, 630090 Novosibirsk, Russia.  
E-mail address: [jvv@catalysis.ru](mailto:jvv@catalysis.ru) (J.V. Veselovskaya).

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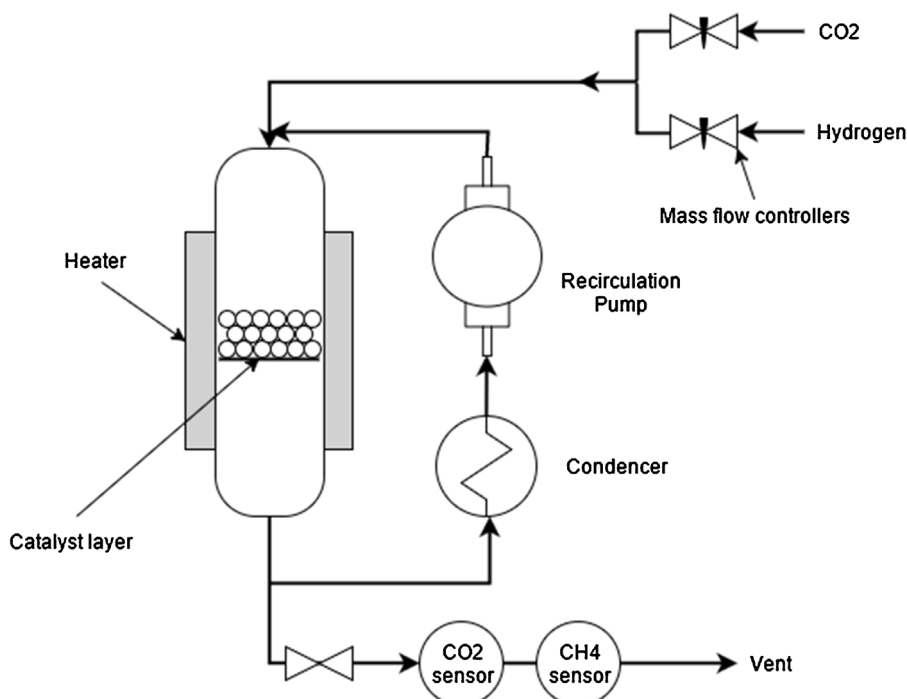


Fig. 1. Scheme of the experimental apparatus for measuring kinetics of Sabatier reaction.

aqueous alkali solutions [9]. 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  $\text{CO}_2$  in the presence of water vapour forming potassium bicarbonate:



Low rate of Reaction (3) is the main problem in regards to using bulk potassium carbonate for  $\text{CO}_2$  absorption purposes [13]. An effective way to increase the reaction rate is dispersing  $\text{K}_2\text{CO}_3$  particles inside a porous medium. Composite materials “ $\text{K}_2\text{CO}_3$ /porous matrix” are known to be effective sorbents for capturing carbon dioxide from wet flue gases [13–15] and are regarded as promising materials for DAC [16–18].

The main goal of our research is to design the Direct Air Capture/Methanation (DACM) process, which will effectively combine  $\text{CO}_2$  capture from ambient air and methane production from captured  $\text{CO}_2$  by Sabatier Reaction (2). In this paper we investigate  $\text{CO}_2$  methanation reaction over the commercial NKM-2V catalyst. In particular, we discuss the effects of gas mixture composition and temperature on catalytic activity of the catalyst and  $\text{CO}_2$  conversion to methane based on kinetics study of Sabatier reaction in a perfectly mixed reactor. Additionally, we study the process combining thermal regeneration of  $\text{K}_2\text{CO}_3$ /alumina composite sorbent and Sabatier process for methane production from desorbed  $\text{CO}_2$ .

## 2. Materials and methods

### 2.1. Methanation catalyst NKM-2V

Commercial granulated nickel methanation catalyst NKM-2V (produced by Novomoskovsk Institute of Nitrogen Industry, Russia) was used for accelerating rate of Sabatier process. According to elemental analysis by atomic emission spectroscopy the catalyst contains 23.4 wt.% of Ni, 13.3 wt.% of Al, 7.36 wt.% of Ca, 0.57 wt.% of Si. Phase composition of the catalyst was studied by XRD analysis before and after activation by stoichiometric mixture of  $\text{CO}_2$  and  $\text{H}_2$  (1:4) at

$T = 300^\circ\text{C}$  (Figs. S1 and S2 in Supplementary material). The catalyst in the initial state contains dispersed nickel oxide NiO and also crystalline phases of cement components:  $\text{CaCO}_3$  (calcite and aragonite),  $\text{CaSO}_4 \cdot 0.67\text{H}_2\text{O}$  (bassanite),  $\text{Al}(\text{OH})_3$  (nordstrandite) and  $\text{SiO}_2$  (quartz). The activation of the catalyst in  $\text{H}_2$  atmosphere results in NiO reduction with formation of metallic Ni. The catalyst heating also leads to dehydration of  $\text{Al}(\text{OH})_3$  and  $\text{CaSO}_4 \cdot 0.67\text{H}_2\text{O}$ , which transform into  $\text{Al}_2\text{O}_3$  and  $\text{CaSO}_4$ , respectively.

### 2.2. Composite sorbent $\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$

The composite sorbent was prepared by dry impregnation method, described in detail in our previous work [16]. Granular mesoporous  $\gamma\text{-Al}_2\text{O}_3$  (produced by JSC «Angarsk Catalysts and Organic Synthesis Plant», Russia) was used as a host matrix. Cylindrical alumina granules were fractured to obtain particles with characteristic grain size of 1–2 mm, which were filled with 40 wt.% aqueous solution of  $\text{K}_2\text{CO}_3$ , then dried at  $90^\circ\text{C}$  for 24 h and calcinated at  $300^\circ\text{C}$  for 2 h. Potassium loading for the as-synthesized composite sorbent determined by means of atomic absorption spectroscopy is 12.5 wt.%, which is equivalent to 22.1 wt.% of  $\text{K}_2\text{CO}_3$ . According to XRD analysis (Fig. S3 in Supplementary material), the composite material after  $\text{CO}_2$  absorption from air contains crystalline phases of potassium bicarbonate  $\text{KHCO}_3$ , mixed potassium carbonate-bicarbonate sesquihydrate  $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$  and potassium dawsonite  $\text{KAlCO}_3(\text{OH})_2$ . It has been previously shown that all these crystalline phases convert to highly dispersed  $\text{K}_2\text{CO}_3$  upon thermal regeneration of the material [16].

### 2.3. Kinetic study of Sabatier reaction over NKM-2V catalyst

Kinetics of Sabatier reaction using the NKM-2V catalyst was studied in an experimental apparatus schematically shown in Fig. 1. The methanation catalyst (0.60 g) was placed inside a cylindrical reactor with the inner diameter of 19 cm, which was located inside an electrical heater. Heating control of the reactor was carried out automatically by a proportional–integral–derivative (PID) controller Termodat-13K2 (produced by Termodat, Russia) using a K-type thermocouple located inside the outer electrical heater of the reactor. Temperature inside the

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