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Plasma deposited novel nanocatalysts for CO_2 hydrogenation to methane

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ABSTRACT

The catalytic hydrogenation of CO_2 to methane has been receiving an increasing attention as a method to mitigate the concentration of CO_2 in the atmosphere through the production of synthetic natural gas. Finding the effective catalyst is the key factor to make this process feasible. In the present work, hydrogenation of CO_2 into CH_4 over novel metal oxide nanocatalysts supported on wire gauzes made from kanthal steel (FeCrAl) has been studied. The series of thin films of active phase were prepared by plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD), containing cobalt spinel (Co_3O_4), ruthenium oxide (RuO_2), mixed oxides (RuO_2/Co_3O_4) and iron oxide (Fe_2O_3). The activity of the prepared nanocatalysts was tested in the gradientless reactor in the temperature range of 150–500 °C. The RuO_2 catalyst revealed the highest both the yield of methane and the reaction rate, while the Fe_2O_3 catalyst promoted the CO production through reverse water-gas shift reaction. The results of the present studies are the foundation for further research on a new class of nanomaterials with high catalytic properties for the methanation reaction.

1. Introduction

Carbon dioxide is a greenhouse gas and increase of its concentration in the atmosphere is mainly attributed to high consumption of fossil fuels. The direct option to deal with CO_2 emissions is the carbon capture and storage technology (CCS). However, in recent years, the utilization of captured CO_2 is considered as a better alternative to geological storage [1]. Latest developments in this area are focused on chemical methods of CO_2 recycling, in particular the use of CO_2 as a sustainable feedstock in production of fuels and chemicals [2–4]. Many projects and research activities are focused on mitigating the CO_2 emission by converting CO_2 into synthetic fuels. Among different methods, the catalytic hydrogenation of CO_2 to methane has been receiving a growing attention. Considering the increasing natural gas demand, methanation of captured CO_2 available from CCS facilities for synthetic natural gas (SNG) production seems to be a feasible solution for effective storage of energy while reducing CO_2 emissions. The concept assumes the use of renewable energy for production of hydrogen which is a necessary co-reactant to activate the CO_2 molecule due to its thermodynamic and chemical stability [5,6].

The key reaction of methane synthesis is the Sabatier reaction, a highly exothermic CO_2 reduction expressed as:

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H(298.15K) = -164.75\,\frac{kJ}{mol} \tag{1}$$

Although the reaction (1) is thermodynamically favorable, the process of CO_2 hydrogenation to methane requires an efficient and stable catalyst to obtain an appropriate rate at low temperatures [7]. Nickel-based catalysts are widely used in the methanation reaction due to their low cost and ease of availability. However, nickel catalysts can be deactivated due to sintering of nickel particles, formation of nickel sub-carbonyls or carbon deposits [8,9]. In contrast to nickel-based, ruthenium catalysts are described as the most stable over a wide range of process conditions [10,11]. Other effective metals forming the active phase of catalysts used in the methanation reaction are transition metals including Rh, Co, Fe, which are dispersed on metal oxide supports such as the Al_2O_3, TiO_2, SiO_2, CeO_2 [12].

The progress in the area of catalysts for the methanation reaction, including technical aspects of novel reactor design, has been recently reported in some reviews [13–16]. The latest advancements in research and development of methanation catalyst are widely discussed by Rönsch et al. [17]. In this work,

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different topics covering the kinetics and reaction mechanism, the effects of catalyst active components, promoters, supports and preparation methods on catalyst performance are summarized. It should be stressed, however, that most of catalysts designed for CO_2 hydrogenation were prepared by conventional methods on typical porous supports. Although hydrogenation of CO_2 is a feasible process, as discussed in the cited references, the efficiency of the CO_2 conversion to methane is still low and in addition to catalyst properties themselves, the reactor design plays a crucial role in the successful performance of catalyzed conversion of CO_2 into methane [16].

Conventionally, the processes involving heterogeneous catalysis are realized in packed-bed reactors filled with a fixed or fluidized bed of catalytic grains. These solutions can be regarded as slightly outdated showing high flow resistance and low effectiveness of the catalyst grains, which leads to high spending on catalyst material [18,19]. In turn, the monolithic reactors, currently used for catalytic combustion, provide better performance compared to packed-bed equipment, but it is also far from expectations. Recently, various types of structured catalytic reactors have been developed in order to allow both the high mass and heat transfer coefficients and reasonably low flow resistance. Various metallic fillers formed from wire gauzes, short-channel structures [20] and monolithic metal-foams [21,22] are regarded as prospective catalyst supports ensuring substantial process intensification in terms of mass and heat transfer. Practical application of such metal structures in catalytic reactors faces serious problems associated with the appropriate deposition method of uniform, well adhered and catalytically effective films on the metal surface, without changing the original geometry of such structures after preparation. This requires the use of catalytic compounds in the form of very thin layers. Li et al. [23] developed the effective method for creating and firmly embedding $NiO–Al_2O_3$ composite catalyst layer (~2 μm) into the Ni-foam struts via a modified wet chemical etching (MWCE) method. Another promising method of producing catalytic films (of nanometer thickness) with specific nanostructure, is a cold plasma deposition from metalorganic precursors. The use of plasma technique, instead of conventional catalyst preparation methods, has attracted special attention because of the unusual chemical reactivity that can be achieved in a plasma environment, which in turn allows fabricating nanoscale layers under full control. In addition to the ability of preparing very thin films, the method of plasma-enhanced metal-organic chemical vapor deposition (PEMOCVD) offers the possibility of precise control over molecular structure and nanostructure of such films by selecting appropriate precursors and conditions of the manufacturing process [e.g. 24,25]. This issue is discussed in detail in a recent review [26,and Refs therein].

In the present work, a comparative study on the performance of CO_2 hydrogenation over novel nanocatalysts based on cobalt, ruthenium and iron oxides supported on wire-gauzes has been conducted. The series of thin metal oxide films of the desired chemical structure were prepared on metallic structured supports by the PEMOCVD. The influence of the kind of metal oxide on catalytic activity, methanation selectivity, and reaction yield was investigated in a continuous gradientless reactor. The new generation of nanocatalysts prepared by the cold plasma technique, designed to the requirements of CO_2 hydrogenation into methane, is our unique approach and has not been studied before. It should be emphasized that nanostructured films supported on wire-gauzes have the great potential to enhance the mass and heat transfer compared to typical catalyst grains used commonly in industrial processes.

2. Thermodynamic analysis

In this paper, in order to characterize the most favorable conditions for the CO_2 methanation process, a thermodynamic analysis of the process was performed by applying the total Gibbs free energy minimization method. Simulation was performed using the Gibbs'reactor model of ChemCAD software (Chemstations Inc.). This method enables calculation of equilibrium composition according to the initial reactants composition and given operating conditions. In the present case, two reaction substrates, CO_2 and H_2 were fed to the reactor at stoichiometric ratio of 1:4. Besides the direct CO_2 hydrogenation to methane (Eq. (1)), several side reactions are considered according to the following scheme:

$$CO_2 + H_2 \rightleftarrows CO + H_2O \tag{2}$$

$$CO_2 + 2H_2 \rightleftarrows C + 2H_2O \tag{3}$$

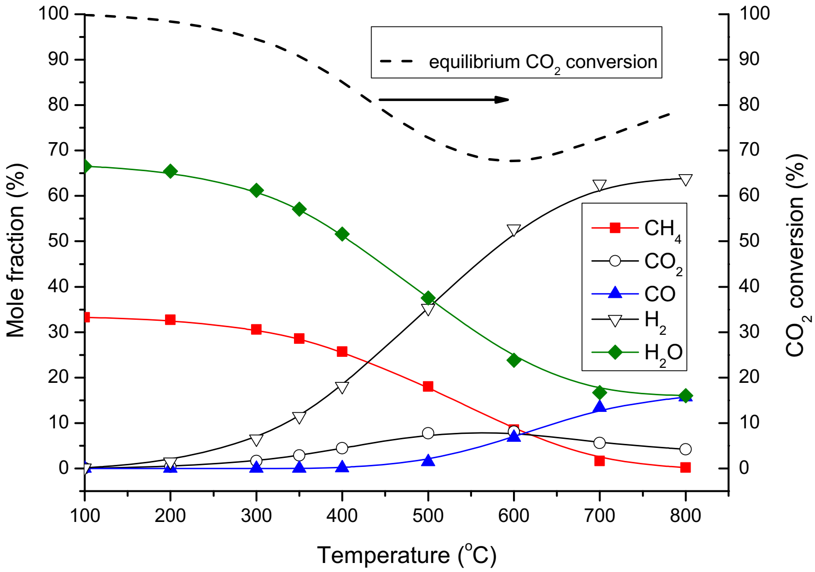

Fig. 1. The equilibrium composition of components as a function of temperature in the hydrogenation of CO_2 at 0.1 MPa (H_2:CO_2=4).