



Direct synthesis of dimethyl ether from synthesis gas: Experimental study and mathematical modeling



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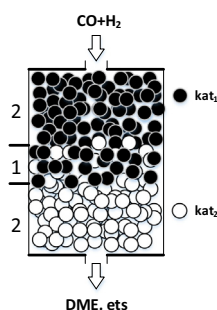
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HIGHLIGHTS

- Direct synthesis of dimethyl ether (DME) from syngas was studied.
- Thermodynamic analysis of the equilibrium mixtures was modeling.
- The variants loading of Cu-Zn-Al and a γ -Al₂O₃ catalysts was studied.
- The effect of operating conditions on DME yield was investigated.
- The optimal reaction conditions were determined.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Available online 2 May 2017

Keywords:

Direct synthesis of dimethyl ether
Syngas
Mathematical modeling

ABSTRACT

Direct synthesis of dimethyl ether (DME) from syngas, was investigated over a CuO-ZnO-Al₂O₃ catalyst for methanol synthesis and a γ -Al₂O₃ catalyst for a methanol dehydration. On the base of mathematical modeling, thermodynamic analysis was carried out in a wide range of pressures (10–100 bar) and temperatures (220–280 °C) for binary mixtures (H₂ + CO) with an H₂/CO = 1–6 M ratio. The influence of reaction conditions on the equilibrium content of components in the mixture was modelled. The effect of the loading method of catalysts of the methanol synthesis and its dehydration (layerwise loading, mixing) in the DME synthesis in a single reaction step on the CO conversion and the yield of DME was experimentally studied. It has been demonstrated that the layerwise combined loading with the intermediate mixed layer of CuO-ZnO-Al₂O₃ catalysts of the methanol synthesis and the γ -Al₂O₃ catalyst for the DME synthesis (2:1:2, ratio parts, i.e. two parts of the catalyst of the methanol synthesis, one part of a mixture of the catalysts and two parts of the catalyst of the methanol dehydration) allow to obtain the higher yield of DME. The effect of operating conditions (pressure, temperature, ratio H₂/CO, time on stream, and catalyst stability) on the CO conversion and yield of DME was studied. The optimal conditions for loading variant 2:1:2 are: the pressure is 30 bar, the temperature is 280 °C and the initial ratio of H₂/CO is equal to 2. At that, the CO conversion remains practically constant during 180 h reaction run.

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1. Introduction

Dimethyl ether (DME) finds its wide application as raw materials for the chemical industry, the solvent and refrigerant, in cosmetic industry (aerosol propellant), but particular interest has currently been aroused regarding its use as a clean and economical

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alternative fuel [1–5]. DME can be obtained from oil alternative raw materials (coal, natural gas, and biomass) via synthesis gas [6–10], but the most promising one is represented by natural gas owing to its availability.

There are two strategies for the production of dimethyl ether from synthesis gas. The first method includes a two-step process: the synthesis of methanol on a metallic catalyst and then the dehydration of methanol on an acid catalyst. In this case, the stage of the methanol dehydration is considered as a separate step in the conversion of methanol to DME [11–15]. At present, much attention is paid to the development of another method – an STD-process (synthesis gas to dimethyl ether), which consists in the obtainment of dimethyl ether in a single step using a bifunctional catalyst [16–20]. This method due to the lower thermodynamic limitations allows the process to be carried out at higher temperatures and lower pressures [21].

In the literature, considerable attention has been paid to the search of optimal catalysts. For the process of the methanol synthesis, catalytic systems Cu/Zn/Al/O and Cu/Zn/Cr/O are used. In a number of papers, it has been demonstrated that the active phase is represented by the copper in the dispersed state. The catalysts are obtained by coprecipitation of zinc and chromium salts or by dry mixing of oxides, by a sol–gel method. In order to enhance the dispersity of copper particles and to increase the specific surface, all kinds of promoters are also used, including such metallic elements as Pd [22], Cr [23,24], Mn [25,26], Zr [27–29], and Ca [30]. For the synthesis of dimethyl ether from methanol, the catalysts of acid type are applied: aluminum oxide, combined aluminum–silicon oxides, zeolites. For the effective progression of the reaction, the presence of a high concentration of acid sites is of great importance. The use of γ -Al₂O₃ as a dehydration agent is connected with the existence of several types of active Lewis centers of different intensities [31–37]. Different modifications of catalysts are possible for the increase of the surface acidity.

In the direct synthesis of the single-step DME synthesis from the synthesis gas, bifunctional (hybrid) catalysts that possess two types of active centers inherent in the methanol formation and its dehydration are used. The interaction of two types of active centers influences the catalytic properties of bifunctional catalysts. The catalysts are obtained by means of mixing the catalysts of the methanol synthesis and its dehydration up to dimethyl ether, by coprecipitation, by sol–gel, by impregnation and by the method of physical mixing [23,25,32,37,38]. The ratio among the components of bifunctional catalysts becomes significant and a determining factor in the increase of the activity. The study of the STD-process has been aimed not only at a hybrid catalyst improving, but at the effect of operating conditions as well.

The objective of the paper was a theoretical and experimental study of the influence of reaction conditions (pressure, temperature, ratio H₂/CO, time on stream) as well as the loading variants of catalysts of the methanol synthesis and its dehydration (layer-wise loading, mixing) on CO conversion and the dimethyl ether yield in a direct synthesis of DME from syngas.

2. Experimental

2.1. Preparation of catalysts

The CuO–ZnO–Al₂O₃ catalyst for the methanol synthesis was prepared by decomposition at 623 K in air of the corresponding mixed hydroxycarbonate with aurichalcite-like structure [39]. The hydroxycarbonate was precipitated from the 10% wt aqueous solution of Cu²⁺ and Zn²⁺ nitrates by Na₂CO₃ solution at 70 °C and pH = 7, washed thoroughly by distilled water and dried overnight under IR lamp and finally calcined at 350 °C for 4 h

and granulated. The dry sample was crushed to a grain size of 0.25–0.5 mm. This 27 wt% ZnO/13 wt% CuO/60 wt% Al₂O₃ catalyst (R-1) is similar to Katalco-58 which has been used in industry for methanol production.

2.2. Characterization of catalysts

The composition of the catalyst samples was analyzed using an Agilent 4100 atomic emission spectrometer of microwave plasma. Sample specimens were decomposed in strong acid. 5 ml of nitric acid was added to the sufficient amount of sample specimens. The decomposition of sample specimens was conducted for a day. The porous structure and the specific surface of the samples were determined by BET using an automatic TriStar II 3020 analyzer of Micromeritics (USA). The value of the specific surface area was determined from the data of nitrogen adsorption isotherms observed at 76 K. The investigation of the samples by the method of the temperature-programmed reduction was carried out using a Chemisorb 2750 chemisorption analyzer in a flow of the 10% H₂ mixture in argon.

2.3. Catalytic procedure

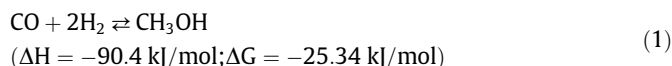
Gaseous hydrogen and carbon monoxides were used as components of the initial reaction mixture. The catalyst with a particle size in the range of 0.5–1.0 mm was used; 5.0 cm³ of the samples was loaded. Before catalytic studies, the samples were being reduced in a flow of hydrogen at 300 °C for 3–5 h. The conditions are as follows: P = 1–5 bar, T = 220–280 °C, H₂/CO = 0.5–2, contact time 6 s. Gas chromatographic analysis of the product was carried out on a Crystal 5000.2 gas chromatograph with two packed columns: Porapak N for the analysis of DME(g), H₂O(g), CH₃OH(g); and a carbon molecular sieve “Activated charcoal” for the analysis of H₂, CO, CH₄, CO₂.

3. Results and discussion

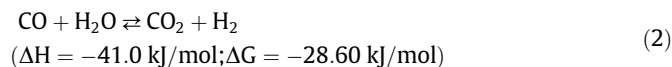
3.1. Thermodynamic study

In the course of the synthesis of dimethyl ether from H₂, CO and CO₂ in a single reaction step, four basic reactions proceed: hydrogenation of carbon monoxide, the reverse water–gas shift reaction, the dimethyl ether (DME) formation, which proceeds as a result of methanol (MeOH) dehydration and the reaction of carbon dioxide hydrogenation. A scheme with the following reactions has been considered [40–42]:

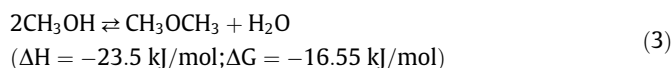
Hydrogenation of CO:



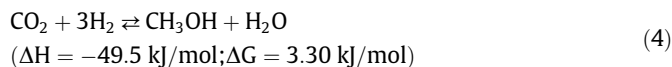
Reversed water–gas shift reaction:



Dehydration of methanol to DME:



Hydrogenation of CO₂:



For studying the influence of the conditions of reactions performance on the equilibrium concentration of methanol and dimethyl ether, the calculations on determination of the mixture composi-

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