

Influence of the metallic and acidic component modification on the activity of bifunctional catalysts for one-step DME synthesis from syngas

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Introduction

Dimethyl ether (DME) is one of the most promising benign fuel. It can be used as a diesel substitute due to high cetane number. Because of its low auto-ignition temperature, high oxygen content and absence of C-C bond in molecular structure it undergoes almost smoke-free combustion. Those properties and the variety of possible applications caused an increasing interest in DME [1, 2]. There are two possible chemical routes for synthesis of DME. One, in which two separates reactions occur, is called indirect synthesis of DME. Another strategy is the direct synthesis of DME from synthesis gas combining CO hydrogenation to methanol and the following dehydration to DME in a single step called syngas to DME (STD). The main advantage of the STD process over conventional two-step DME synthesis is that it is more thermodynamically favorable. Thus, during the STD process, the yield of DME is improved and syngas conversion is higher. For that reason, the production cost of DME in STD process is lower than in traditional DME synthesis [3].

Materials and Methods

The metallic components were obtained by carbonate and citric method. Montmorillonite K10 and montmorillonite K10 modified with phosphotungstic acid (TPA) were used as the acidic component. The metallic and acidic functions were combined by physical mixing, the volume ratio: metallic to acid function was equal to 2:1. In order to physicochemical characterization of the metallic components of obtained catalysts, the following measurements were carried out: X-ray powder diffraction, thermo-programmed reduction, the specific surface area and the pore distribution analysis and the copper surface area determination by reactive adsorption of N₂O according to the method described in [3]. The acidic properties of the acidic functions were determined based on pyridine adsorption with FTIR detection.

The activity of bifunctional catalysts in STD process was tested in a high pressure stainless steel fixed-bed flow reactor connected online to gas chromatograph. Before the catalytic experiments, the bifunctional catalysts were reduced and subsequently activated. The catalytic measurements were carried out in the range 280 – 360°C, under the pressure of 40 bars and gas hourly space velocity, GHSV = 3600 h⁻¹.

Results and Discussion

Calculation carried out by the Rietveld method, confirmed that the catalysts obtained by carbonate method contain CuO crystallites, whose sizes are twice as small as in the catalysts from the citric series. Moreover, the addition of the promoters has great impact on the

CuO crystallite sizes. The dispersion is not the only important parameter, which has an influence the activity of the bifunctional catalysts. The second one is the appropriate matching of the metallic and the acidic function in the bifunctional catalysts in order to obtain low concentration of methanol which is the intermediate product in the STD process.

The disparities in activities of the bifunctional catalysts are related with the acidity differences between montmorillonite K10 and TPA-K10. The dependence between Cu dispersion (1/Cu particle diameter) and the activity (STDME) at $\alpha = 0.35$, which is the amount of CO transformed in to DME, for all bifunctional catalysts is obtained and presents the straight line which increase with Cu dispersion (Figure 1).

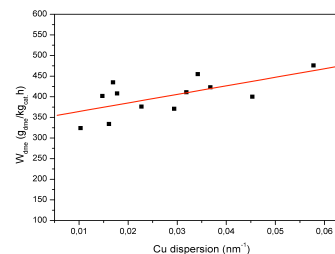


Figure 1. The dependence between Cu dispersion and the activity.

Significance

The metallic components synthesized by the carbonate method exhibit higher copper dispersion, copper surface area and BET surface. The CuO crystal size and its dispersion depend on the presence of promoters (Mn, Ga) and in the case of the metallic components, containing zirconium instead of gallium, additionally depends on the weight ratio between zirconium and the promoter (Zr/P). The activity comparison between the bifunctional catalysts composed of the same acidic function, montmorillonite K10, and various metallic functions reveals that the copper dispersion is one of the crucial parameters responsible for obtaining highly active bifunctional catalysts. Additionally, the activity of bifunctional catalysts can be enhanced by tuning the acidic strength and the number of acidic centers in the acidic component. In the case of bifunctional catalysts for which high concentration of unreacted methanol are observed, the substitution of montmorillonite K10 with TPA-K10 leads to increase in the DME yield.

Acknowledgements

Authors acknowledge the National Science Centre of Poland for financial support in the frame of project 2012/05/B/ST4/00071.

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