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SUMMARY

„The kinetics of methanol synthesis from carbon dioxide and hydrogen over the Ga modified Cu/Zn/Zr oxide catalyst”

The worldwide climate change – likely to have been caused by the increase of carbon dioxide concentration in the atmosphere, and the exhaustion of fossil fuel stores have been becoming a major challenge for the world population. The catalytic conversion of carbon dioxide to methanol is a promising and ecologically sound method that can help to resolve the problem of utilizing the excess of anthropogenic CO_2. Methanol is an important chemical compound with a wide range of applications in many industries. It is also one of liquid “energy carriers” which can be transferred into hydrogen used in fuel cells.

The catalyst used in methanol production should be characterized by high yield, high selectivity towards methanol formation and high resistance to sintering as well as poisoning with sulphur and water. Commercial copper-zinc catalysts used in industrial methanol production from syngas are not suitable for the methanol synthesis from CO_2-rich gas as they undergo deactivation. Therefore, the investigations over developing the catalyst for methanol synthesis from carbon dioxide and hydrogen are intensively proceeding. The most common way to find such a catalyst is a modification a classical copper catalyst through the implementation of promoters (like metal oxides from groups of transition elements). Results from the vast majority of research related to hydrogenation of carbon dioxide to methanol demonstrate that the modification of Cu/Zn/Zr catalyst using either Ce, Cr, Ga oxides, or a mixture thereof – if compared to unmodified Cu/Zn/Zr one, improves the yield and the selectivity (activity) towards methanol formation.

The aim of this study is investigation of the influence of the Ce, Cr, Ga oxides – each of them or their mixtures on the activity of Cu/Zn/Zr catalyst. The obtained catalysts were evaluated from a physicochemical characteristics aimed at determining their chemical composition, structure properties and reducibility. Based on this, the most suitable catalyst was selected for the next step which were the kinetic studies. The final result of kinetic investigations of methanol synthesis was determine the kinetic equations and its parameters.

The Cu/Zn/Zr/Ga catalyst that achieved a high (over 200 $g \cdot kg^{-1} \cdot h^{-1}$) methanol yield was the only one from the selected catalysts, which demonstrated a stable (ca. 70%) selectivity towards formation of methanol in the temperature range of 503 – 513 K. Taking

into account the results of the activity tests, the catalyst Cu/Zn/Zr/Ga has been selected for kinetic testing.

The parameters of the kinetic tests were as follows: T= 433–513 K; p= 3−8 MPa; GHSV= 1660–10000 h^{-1} and the initial gas compositions: H_2: 30–70 mol.%, CO_2: 5–22 mol.%, CO: 0–7 mol.%. It was found that the CO_2 conversion was strongly dependent on the reaction temperature as well as the initial reaction gas composition. The finally obtained results of kinetic tests were developed in the form of kinetic equations of Langmuir–Hinshelwood's type. The computations were performed using numerical Levenberg–Marquardt method. Five different system of kinetic equations have been analysis. For all of than the value of kinetics parameters were determined and the value average relative error were evaluated. It turned out that the best were equations based on the Yang–Hougen concept, with exponents in denominators equal to a =3 and b =2. The kinetic equations obtained here can be used in design and optimization of industrial scale reactors.