Oxymethylene Dimethyl Ether Synthesis starting from Dimethoxymethane and monomeric Formaldehyde

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Abstract: Oxymethylene dimethyl ethers (OME_n; $CH_3(-OCH_2-)_nO-CH_3$, n = 3-5) are investigated as sustainable synthetic fuels with soot-free combustion properties. In this work a novel anhydrous OME_n synthesis route is presented starting from dimethoxymethane and molecular formaldehyde. This homogeneously catalyzed reaction represents a promising new approach towards a sustainable OME_n synthesis with only marginal amounts of impurities.

Keywords: Oxymethylene dimethyl ethers, Homogeneous catalysis, Molecular formaldehyde.

1. Introduction

OME_n are discussed as a novel kind of synthetic fuels, which combust without soot-formation. The synthesis of OME_n requires two structural building units: CH_2O-units (provided e.g. by 1,3,5-trioxane (TRI), para-formaldeyhde (para-FA)) are required for the extension of the oxymethylene chain and methoxy groups are needed for the chain termination (e.g. dimethoxymethane (OME_1), methanol). One differentiates the established OME_n-syntheses into aqueous and anhydrous.[1] Starting from methanol and a FA-source the aqueous synthesis routes is performed in a high scale and uses easily accessible reactants, however the presence of water initiates the formation of side products (e.g. hemiformals, $CH_3(-OCH_2-)_nOH$).[2] The absence of water (anhydrous synthesis), starting from OME_1 and TRI, avoids the creation of side products, but the production of anhydrous TRI is complex and needs a lot of energy.[3] In order to avoid the drawbacks of established OME_n syntheses we want to develop anhydrous and sustainable syntheses based on CO_2 and H_2. To get closer to this goal we developed a novel anhydrous OME_n synthesis by the reaction of OME_1 and monomeric, gaseous FA.

2. Experimental

To realize this intention, we developed a FA-generator (catalytic decomposition of TRI), which produces a continuous FA-stream (5 – 25 Vol.-% FA in N_2; 6 – 36 mmol h^{-1}). This stream was introduced continuously into solutions of OME_1 with different homogeneous catalysts and the resulted OME_n mixtures were analyzed by means of nuclear magnetic resonance spectroscopy.

3. Results and discussion

On the basis of the obtained spectra, selectivity for higher OME_n (n > 1) was determined and compared with simulations (see Figure 1). By the use of these catalysts (0.8–3.0 mol %) the introduced FA reacted instantly to form OME_n (n = 2-6, ca. 99 %) with commonly only marginal amounts of TRI-impurities (ca. 1 %).

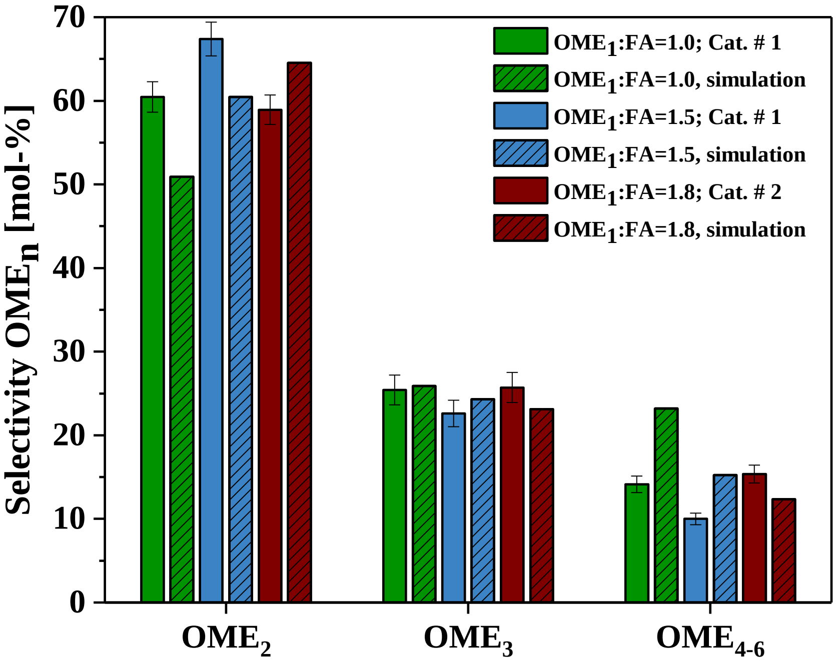

Figure 1. Experimental and simulated OME_n-selectivity with different OME_1:FA-ratios and catalysts.

4. Conclusions

The described OME_n synthesis starting from OME_1 and molecular FA represents a promising new approach towards a sustainable OME_n synthesis.

References

[1] a) Q. Wu, M. Wang, Y. Hao, H. Li, Y. Zhao, Q. Jiao, *Ind. Eng. Chem. Res.* **2014**, *53*, 16254–16260; b) J. Wu, H. Zhu, Z. Wu, Z. Qin, L. Yan, B. Du, W. Fan, J. Wang, *Green Chem* **2015**, *17*, 2353–2357; c) Y. Zheng, Q. Tang, T. Wang, Y. Liao, J. Wang, *Chem. Eng. Technol.* **2013**, *36*, 1951–1956; d) Y. Wu, Z. Li, C. Xia, *Ind. Eng. Chem. Res.* **2016**, *55*, 1859–1865; e) L. Wang, W.-T. Wu, T. Chen, Q. Chen, M.-Y. He, *Chemical Engineering Communications* **2014**, *201*, 709–717; f) X. Fang, J. Chen, L. Ye, H. Lin, Y. Yuan, *Sci. China Chem.* **2015**, *58*, 131–138; g) J. Burger, E. Ströfer, H. Hasse, *Ind. Eng. Chem. Res.* **2012**, *51*, 12751–12761; h) N. Schmitz, J. Burger, H. Hasse, *Ind. Eng. Chem. Res.* **2015**, *54*, 12553–12560; i) M. Ouda, G. Yarce, R. J. White, M. Hadrich, D. Himmel, A. Schaadt, H. Klein, E. Jacob, I. Krossing, *React. Chem. Eng.* **2017**, *2*, 50–59.
[2] J. Burger, E. Ströfer, H. Hasse, *Ind. Eng. Chem. Res.* **2012**, *51*, 12751–12761.
[3] T. Grützner, H. Hasse, N. Lang, M. Siegert, E. Ströfer, *Chemical Engineering Science* **2007**, *62*, 5613–5620.