Oxymethylene Dimethyl Ether Synthesis starting from Dimethoxymethane and monomeric Formaldehyde

Andreas Peter, a Mohamed Ouda, b Achim Schaadt, b Eberhard Jacob, c Ingo Krossing, a*

aFreiburg Materials Research Center, Albert-Ludwigs University, Freiburg, 79104, Germany
bDivision Hydrogen Technologies, Fraunhofer ISE, Freiburg, 79110, Germany
cMotors Emissions Concepts UG, Krailling, 82152, Germany
*Corresponding author: +49 (0) 761 203-6001, krossing@uni-freiburg.de

Abstract: Oxymethylene dimethyl ethers (OMEₙ; CH₃(-OCH₂-)ₙO-CH₃, n = 3-5) are investigated as sustainable synthetic fuels with soot-free combustion properties. In this work a novel anhydrous OMEₙ synthesis route is presented starting from dimethoxymethane and molecular formaldehyde. This homogeneously catalyzed reaction represents a promising new approach towards a sustainable OMEₙ synthesis with only marginal amounts of impurities.

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

1. Introduction
OMEₙ are discussed as a novel kind of synthetic fuels, which combust without soot-formation. The synthesis of OMEₙ requires two structural building units: CH₃O-units (provided e.g. by 1,3,5-trioxane (TRI), para-formaldehyde (para-FA)) are required for the extension of the oxymethylene chain and methoxy groups are needed for the chain termination (e.g. dimethoxymethane (OME₁), methanol). One differentiates the established OMEₙ-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, CH₃(-OCH₂-)ₙOH).[2] The absence of water (anhydrous synthesis), starting from OME₁ 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 OMEₙ syntheses we want to develop anhydrous and sustainable syntheses based on CO₂ and H₂. To get closer to this goal we developed a novel anhydrous OMEₙ synthesis by the reaction of OME₁ 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 N₂; 6 – 36 mmol h⁻¹). This stream was introduced continuously into solutions of OME₁ with different homogeneous catalysts and the resulted OMEₙ mixtures were analyzed by means of nuclear magnetic resonance spectroscopy.

3. Results and discussion
On the basis of the obtained spectra, selectivity for higher OMEₙ (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 OMEₙ (n = 2-6, ca. 99 %) with commonly only marginal amounts of TRI-impurities (ca. 1 %).
4. Conclusions

The described OMEₙ synthesis starting from OME₁ and molecular FA represents a promising new approach towards a sustainable OMEₙ synthesis.

References