Facile Two-Phase Catalysis: From Dimethoxymethane and Monomeric Formaldehyde towards Oxymethylene Ethers (OMEs)

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An efficient, biphasic route towards oxymethylene dimethyl ethers (OMEs) allowing for catalyst recycling and reuse is presented (OMEs–CH₂(–OCH₂–)ₙO–CH₃, n = 3–5). OMEs are an interesting novel class of non-toxic, diesel-like synthetic fuels with soot-free combustion properties. A solution of commercial OMe₃BF₄ in the ionic liquid (IL) 1-ethyl-3-methylimidazolium tetrafluoroborate acts as the immobilized catalyst. Upon addition of dimethoxymethane (OME₃) and anhydrous formaldehyde (FA) very pure OMEs form in the upper phase of the biphasic mixture. In the lower IL-phase, the catalyst remains immobilized. After phase separation and removal of the top OME layer, the catalytically active IL-phase is reusable for at least ten times without loss of activity and selectivity.

Climate change and air pollution are two of the most critical health and sustainability challenges facing society today. They are also closely related: the major sources of CO₂ emissions are the most significant sources of air pollution. So it would seem only logical to seek joint solutions to these two problems.[1] Amongst others, the mobility sector makes a huge contribution to CO₂ emission (ca. 23%).[2] This sector could be reduced drastically by substituting conventional fossil-based fuels by sustainable synthetic fuels, which are produced on the basis of CO₂ and H₂. In this context oxymethylene dimethyl ethers (OMEs) with the general formula CH₂(–OCH₂–)ₙO–CH₃ (n = 3–5) have diesel-like properties, are suited for the substitution of diesel and are classified as nontoxic.[3–5] Furthermore, based on the lack of covalent C-C-bonds and the high oxygen content, OMEs have soot-free combustion properties and can reduce the emission of nitrogen oxides (NOₓ) significantly.[6,7] In addition, Hank et al. elaborated in a well-to-wheel analysis a potential reduction of CO₂ emissions of up to 86% by using OMEs instead of diesel fuel.[7] However, the diesel consumption is enormous (e.g. 38.7 Mt in Germany in 2017),[8] whereas the largest OME-production plants produce 400 kt a⁻¹ and an optimized sustainable and technically viable OME production route is still lacking.[9] Conventional OME-syntheses are differentiated into aqueous and anhydrous syntheses. The aqueous route starts from methanol (MeOH) and aqueous formaldehyde (FA) solution, whereas anhydrous synthesis routes typically start from a FA-source (e.g. 1,3,5-trioxane, TRI; para-FA) and dimethoxymethane (OME₃) or dimethyl ether (DME).[10,11,12] The easily available educts MeOH and aqueous FA seemingly favor the aqueous route. However, the presence of water produces a large amount of side products (ca. 65%), the separation of which requires about a third of the OME₃ energy content.[9,13] Instead, the avoidance of water in the anhydrous synthesis route provides relatively pure OME-mixtures. Yet, conventional anhydrous syntheses require the use of very energy-intensively synthesized anhydrous TRI,[11,14,15] largely increasing the CO₂ footprint of this route. In contrast to these syntheses, our anhydrous route avoids TRI and yields pure OME-mixtures, which can be used without larger workup. By replacing the commonly used TRI with monomeric FA (if formed from dehydrogenation of methanol) as in Eq. (1), it is possible to reduce the overall H₂ consumption by 22%, therefore preserving up to 87% of the employed energy in the OME based on stoichiometric evaluation (instead of 67% for conventional synthesis via TRI).[12,16,17]

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\text{[O}_3\text{O]} + n \text{H} + \text{H} \quad \rightarrow \quad \text{[O}_3\text{O]}_n \quad \text{(1)}
\]

This energy saving can be assumed for all OME-syntheses which are based on molecular FA, however using anhydrous reaction conditions, byproducts can be avoided and product workup is facile. We have shown[17] that reaction (1) can be performed batch-wise with catalytic amounts of the novel trimethyloxonium-salt OMe₃[Ai(OR)₃]⁻ (R = C(CF₃)₃) in pure OME₃. However, the reaction only works with the very large and

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weakly coordinating, but also rather expensive custom-made \([\text{Al(OR)}_3]^+\) anion. Yet, FA is taken up instantaneously yielding OME-mixtures with only marginal impurities. This is in agreement with a recent computational study that proved the initiation barriers of Brønsted acidic catalysts for OME-synthesis to be higher than those with the methyl-donating trimethyloxonium-cation.\(^{[20]}\) But catalyst separation in homogeneous catalysis is difficult and up to now the dissolved and custom-prepared specialized catalyst had to be quenched to stop the reaction.\(^{[17]}\) Therefore, in this contribution a novel synthesis-procedure is devised, which makes use of the highly active molecular trimethyloxonium catalysts in a commercial form and enables catalyst separation and reuse (Figure 1). By using ionic liquids (ILs) to dissolve and immobilize the catalysts, a catalytically active phase (IL-catalyst phase, IL-Cat.-phase) forms, which is not soluble in OMEs or higher OMEs \((n > 1)\). This approach makes it possible to simply separate the produced OME mixture from the biphasic IL-catalyst solution mixture, i.e. with a syringe for lab scale application (Figure 1).

In contrast to literature known OME-syntheses, where Brønsted-acidic ILs themselves are used as catalysts,\(^{[15,19]}\) the application of this aprotic IL-Cat.-solution uses the polar nature of ILs to dissolve and immobilize a preferably commercial molecular catalyst like OME\(^{\text{3}}\ BF_4^−\).

**Choice of the preferred IL:** To establish the biphasic reaction setup, the properties of the IL are crucial: It should be inert towards the catalyst and should be able to dissolve it completely. In addition, the IL should be insoluble in OMEs to form a biphasic mixture, but the OMEs need at least to be sparingly soluble in the IL-phase to enable reactivity. In order to systematically vary the IL-polarity and the associated solubility characteristics,\(^{[20]}\) we chose a set of 1-alkyl-3-methylimidazolium-based cations to be combined with the anions \([\text{BF}_4]^−, [\text{N(SO}_3\text{CF}_3)]^−\text{(NTf}_2^−)\) and \([\text{PF}_6(C_6F_5)_3]^−\text{(FAP)}\); Figure 2). The imidazolium alkyl-chains were ethyl, butyl and hexyl (EMIM, BMIM, HMIM). In this set of room-temperature-ILs, the solubility behavior stretches from hydrophilic (e.g. EMIM\(^{\text{3}}\ BF_4^−\)) to hydrophobic (e.g. BMIM\(^{\text{3}}\ FAP\)).\(^{[21]}\)

**Catalyst solubility and stability in the ILs:** At first, solubility experiments were performed to analyze the solubility and stability of the catalysts in the ILs. Therefore, the investigated trimethylxonium catalysts \((\text{OME}_n\text{BF}_4^−; \text{OME}_n\text{[Al(OR)}_3]^+\)) were mixed with the selected ILs, observing their solubility and analyzing the solutions via nuclear magnetic resonance (NMR)-spectroscopy (Table 1 and Supporting Information SI – Section 1). The commercially available OME\(^{\text{3}}\ BF_4^−\) catalyst dissolves completely in the comparatively polar tetrafluoroborate ILs, whereas the trimethylxonium-catalyst with the perfluorinated alkoxyaluminate OME\(^{\text{3}}\ [\text{Al(OR)}_3]^+\) dissolves in the nonpolar FAP-ILs. Regarding the stability of the IL-Cat.-solution towards temperature, the solutions of OME\(^{\text{3}}\ BF_4^−\) in EMIM\(^{\text{3}}\ BF_4^−\) (Table 1, Entry 1) and OME\(^{\text{3}}\ [\text{Al(OR)}_3]^+\) in EMIM\(^{\text{3}}\ FAP\) (Table 1, Entry 6) were analyzed exemplarily via NMR-spectroscopy at 25°C, 45°C, 65°C, 85°C, 100°C. In each case, the samples were

![Figure 1. Schematic illustration of the biphasic reaction of OME\(_1\) and FA for the formation of OME\(_n\) \((n = 1–6)\). OME\(_1\) and the solution of the catalyst, dissolved in an IL (IL-Cat.-solution) is stirred, forming an emulsion (A). Subsequently gaseous FA is introduced continuously. After a defined initiation time the FA-introduction and the stirring is stopped and two phases are formed (B). The bottom phase consists of the IL-Cat.-solution, whereas the upper phase contains the desired OME\(_n\)-mixture.](image1)

![Figure 2. Selected cations and anions to be used as ILs. R=−C\(_3\)H\(_7\), C\(_6\)H\(_{13}\), C\(_3\)H\(_{12}\) (equals EMIM, BMIM, HMIM).](image2)

**Table 1. Solubility and stability of the different catalysts in the selected ILs.** The numbers in parentheses describe the required time for dissolving the catalyst. 0.2 ml IL were added to 20 mg of the trimethylxonium-species and stirred at room temperature.

| IL          | Solubility OME\(_1\)\text{BF}_4^− | Solubility OME\(_n\)\text{[Al(OR)}_3]^+ | Biphasic\(^{[1]}\) | Share of OME\(_n\) in IL-phase [mol%] |
|-------------|-------------------------------------|------------------------------------------|-------------------|-------------------------------------|
| 1           | EMIM\(^{\text{3}}\) BF\(_4^−\)      | x                                        | yes               | 39                                  |
| 2           | BMIM\(^{\text{3}}\) BF\(_4^−\)      | (30 min)                                 | x                  | 54                                  |
| 3           | HMIM\(^{\text{3}}\) BF\(_4^−\)      | (48 h)                                   | x                  | 54                                  |
| 4           | EMIM\(^{\text{3}}\) NTf\(_2^−\)     | x\(^{[2]}\)                               | yes\(^{[2]}\)     | 82                                  |
| 5           | BMIM\(^{\text{3}}\) NTf\(_2^−\)     | x\(^{[2]}\)                               | yes\(^{[2]}\)     | 82                                  |
| 6           | EMIM\(^{\text{3}}\) FAP             | x\(^{[2]}\)                               | no                | –                                    |
| 7           | BMIM\(^{\text{3}}\) FAP             | x\(^{[2]}\)                               | no                | –                                    |

\(^{[1]}\) = catalyst dissolves in IL; x = catalyst does not dissolve in IL; \([a]\) Formation of two phases after addition of OME\(_1\); \([b]\) The formation of two phases required an excess of OME\(_n\); \([c]\) Methylation of NTf\(_2^−\) forming Me-NTf\(_2^−\).
left for 30 minutes at each temperature (SI – Section 2). In this series, OMe\textsubscript{3} ‘BF\textsubscript{4}’ was stable with partial decomposition in EMIM\textsuperscript{+} BF\textsubscript{4} until 65 °C (93 %), but decomposes further when heated to 85 °C (83 %) and more rapidly when heated to 100 °C (49 %). OMe\textsubscript{3} ‘[Al(OR)\textsubscript{4}]\textsuperscript{-}’ in EMIM\textsuperscript{+} FAP decomposes analogously at the beginning of the heating series (94 % stability after heating to 65 °C for 30 minutes), but is more stable at higher temperatures (77 % after heating to 100 °C). After 3.5 months the IL-Cat-solutions (stored in inert NMR tubes at room temperature) were analyzed again. Both solutions still contained the active catalyst species (OMe\textsubscript{3} ‘BF\textsubscript{4}’ in EMIM\textsuperscript{+} BF\textsubscript{4}; 34 %, OMe\textsubscript{3} ‘[Al(OR)\textsubscript{4}]’ in EMIM\textsuperscript{+} FAP; 69 %). Using NTf\textsubscript{2}-based ILs, the NTf\textsubscript{2}-anion is methylated quantitatively by the catalyst forming Me–NTf\textsubscript{2} and releasing dimethyl ether (SI – Section 1), analogously to the described methylation of acetonitrile by OMe\textsubscript{3} ‘-cations giving Me–C≡N–Me\textsuperscript{+}’ and OMe\textsubscript{3} ‘.[17]

**Solubility of OMe\textsubscript{3}:** The two-phase reaction concept requires a low solubility of the IL-catalyst- and OME-phase in each other. Therefore, OME\textsubscript{3} was added to the different ILs (1:1 v/v) to analyze, if phase separation occurs (Table 1). Only the relatively polar BF\textsubscript{4}-based ILs (EMIM\textsuperscript{+} BF\textsubscript{4}, BMIM\textsuperscript{+} BF\textsubscript{4}) formed biphasic reaction mixtures with a OME\textsubscript{3}/IL-ratio of 1:1 (v/v), whereas the other ILs formed a solution. The share of OME\textsubscript{3} in the IL-phase (determined by NMR-spectroscopy) increases with the length of the alkyl chain (EMIM\textsuperscript{+} BF\textsubscript{4}: 39 mol%, BMIM\textsuperscript{+} BF\textsubscript{4}: 54 mol%, HMIM\textsuperscript{+} BF\textsubscript{4}: 68 mol%; Table 1). Favorably, the transfer of the IL into the OME-phase remains below 1 mol%. Therefore, the combination of EMIM\textsuperscript{+} BF\textsubscript{4} and OME\textsubscript{3} ‘BF\textsubscript{4}’ appeared suitable for the biphasic reaction concept.

We note that OMe\textsubscript{3} ‘BF\textsubscript{4}’ could not be used as a catalyst in pure OME\textsubscript{3} and only induced FA-polymerization.[17] Only with addition of toxic acetonitrile as solvent, the catalysis proceeded.

**OME-syntheses:** OME-syntheses were performed using a solution of catalytic amounts of OMe\textsubscript{3} ‘BF\textsubscript{4}’ (ca. 100–150 mg, 2.0–3.0 mol% relating to OME\textsubscript{3}) in EMIM\textsuperscript{+} BF\textsubscript{4} (1.0 mL) and adding OME\textsubscript{3} (3.0 mL; OME\textsubscript{3}:IL = 3:1 v/v) and gaseous FA. For this purpose, the recently described FA-generator, which produces a continuous gaseous FA-stream (ca. 55 mmol h\textsuperscript{-1}) and the described synthesis setup was used with minor changes.[17] A series of experiments varying temperature, catalyst loading and FA-introduction time were performed (Table 2).

Occurrence of side products, cross-contaminations of both phases and OME-selectivity was analyzed by NMR-spectroscopy using our against GC data evaluated approach.[17] Furthermore, the experimental selectivities were evaluated against the expected equilibrium selectivities simulated using Aspen Plus® (Figure 3a and SI section 3). Control experiments using the IL, but no catalyst (Exp. 6, Table 2) were futile. In addition, also the solution of OMe\textsubscript{3} ‘BF\textsubscript{4}’ in BMIM\textsuperscript{+} BF\textsubscript{4} at 30 °C was not suited for the reaction (Exp. 5, Table 2). However, Exp. 1 to 4 proceeded favorably. A change of catalyst loading (2.0 or 3.0 mol%;

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**Table 2.** Reaction parameters of the performed OME-experiments. Experimental and expected selectivity simulated using Aspen Plus®.

| Exp. | Catalyst [mol%] | IL | T [°C] | FA Introduction [min] | OME\textsubscript{3}-Conversion [Exp.] [mol%] | OME\textsubscript{3}-Conversion [Sim.] [mol%] |
|------|-----------------|----|--------|----------------------|---------------------------------------------|---------------------------------|
| 1    | 2.0             | EMIM\textsuperscript{+} BF\textsubscript{4} | 30     | 39                   | 33                                           | 34\textsuperscript{[a]}       |
| 2    | 3.0             | EMIM\textsuperscript{+} BF\textsubscript{4} | 30     | 39                   | 34                                           | 34\textsuperscript{[a]}       |
| 3    | 3.0             | EMIM\textsuperscript{+} BF\textsubscript{4} | 45     | 39                   | 32                                           | 34\textsuperscript{[a]}       |
| 4    | 3.0             | EMIM\textsuperscript{+} BF\textsubscript{4} | 45     | 46                   | 39                                           | 39\textsuperscript{[a]}       |
| 5    | 2.0             | BMIM\textsuperscript{+} BF\textsubscript{4} | 30     | 39                   | polymerization –                             | –                              |
| 6    | –               | EMIM\textsuperscript{+} BF\textsubscript{4} | 45     | 39                   | polymerization –                             | –                              |

[a] Simulated conversion for OMe\textsubscript{3} ‘: FA = 2.0. [b] Simulated conversion for OMe\textsubscript{3} ‘: FA = 1.6. Experiments were performed with ca. 100–150 mg OMe\textsubscript{3} ‘ BF\textsubscript{4} (2.0–3.0 mol% relating to OME\textsubscript{3}) in EMIM\textsuperscript{+} BF\textsubscript{4} (1.0 mL) or BMIM\textsuperscript{+} BF\textsubscript{4} (1.6 mL). OME\textsubscript{3} (3.0 mL; OME\textsubscript{3}:IL = 3:1 v/v) was added to the IL-Cat-solution and gaseous FA was introduced continuously (ca. 55 mmol h\textsuperscript{-1}).

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**Figure 3.** a) Experimental and expected simulated OME-selectivity for experiments 1 to 4, Table 2. b) Photo of the biphasic reaction mixture of Exp. 3 after reaction (upper phase: OME-phase, lower phase: IL-phase). c) Experimental selectivity for OMe\textsubscript{3} ‘ and FA conversion for the experiments of the second recycling experiment.
Table 2, Exp. 1 vs. 2) or the reaction temperature (30 or 45 °C; Table 2, Exp. 2 vs. 3) has only marginal influence on the OME-selectivity. The OME-syntheses show good reproducibility (Table 2, Exp. 1–3; FA-introduction time 39 minutes, selectivities suitable to a ratio of OME$_2$:FA = 2.0) and the experimental results are in agreement with simulated selectivity. At a reaction temperature of 30 °C (Table 2, Exp. 1) a slightly turbid OME-product-phase was obtained, which probably results from partial polymerization of the introduced FA. Preferably, the higher reaction temperature (Exp. 3, 45 °C) avoids the formation of polymeric byproducts completely, resulting in very pure OME-solutions, which consist mainly of OMEs with only marginally impairments of TRI (ca. 0.5–1.0 mol%) and methyl formate (ca. 1 mol%) and almost no dissolved IL (<0.1 mol%; photo Figure 3b and SI – Section 4). By increasing the time of FA-introduction (46 minutes) and thus its molar amount, the product distribution can be shifted towards higher OMEs (Table 2, Exp. 4; selectivity according to a ratio of OME$_n$:FA = 1.6). Separation of the catalyst can be easily executed by removing the upper OME-phase with a syringe (Figure 3b). In addition to the IL EMIM $^+$BF$_4$ we tested BMIM $^+$BF$_4$, using the same reaction conditions and catalyst like in Exp. 1 (Table 2, Exp. 5). However, with this IL-Cat.-solution, polymerization of the introduced FA occurred and a separation of pure OMEs was not possible. This underlines the good performance of the OME$_n$:EMIM $^+$BF$_4$-system. Moreover, a control reaction using only EMIM $^+$BF$_4$ without catalyst (Table 2, Exp. 6), led to instant polymerization of the introduced FA and proved the catalytic activity of OME$_n$:BF$_4$ immobilized within the IL.

However, catalyst recycling is crucial and the IL-Cat.-phase had to be tested in terms of deactivation. For this purpose, an initial recycling experiment was performed using the reaction parameters of Exp. 3 and introducing FA in each experiment for 39 min (SI-Section 5 for details). At the end of each reaction, the OME-phase was removed and analyzed. Next, OME, was added again on top of the IL-Cat.-phase. The same procedure was performed for three subsequent reaction runs. The resulting FA-conversions and OME$_{3-6}$ selectivities showed a significant increase in the second and third reaction cycle despite using the same FA-introduction time for each reaction cycle (SI-Section 5). To reproduce these findings and to further analyze the reusability of the IL-Cat.-solution, a second recycling experiment with 10 cycles was performed within three days, with the IL phase being left overnight under inert conditions in a fridge. Analogously to the first recycling experiment the reaction parameters of Exp. 3 were used and FA was introduced for 29 min. The resulting selectivities confirm the reusability of the IL-Cat.-solution and do also show higher FA-conversions and higher selectivity for longer chained OMEs (OME$_{\geq 3}$) with the same FA-introduction time after several experiments (Figure 3c). This might be attributed to an activation of the IL-Cat.-solution by the dissolution of some OMEs. Possibly, the saturation of the IL-Cat.-phase with OMEs leads to an increased solubility of the reaction partners (OME$_n$ and FA) thereby resulting in a complete conversion of the introduced FA. Pre-saturation experiments with EMIM $^+$BF$_4$ and OME$_n$ (Table 1) or a solution of OME$_{1-5}$ (1:1:1:1:1, mol:mol), respectively, confirmed this saturation effect (SI – Section 7). Furthermore, it can be confirmed by the increased conversion after reaction run number 2, which is enhanced from ca. 60 % (Cycle No. 1 and 2) to ca. 84–89 % (Cycle No. 3–5) and 100 % (Cycle No. 6 and 7). At the same time the selectivity for the desired longer chained OMEs (OME$_{\geq 3}$) increases from ca. 33 % (Cycle No. 1 and 2) to ca. 48 % (Cycle No. 6–8) and are further increased to 54 % (Cycle No. 10). However, the shift towards longer chained OMEs was attributed to an increased formation of a white solid inside the OME-phase of Cycle No. 8–10. This solid was analyzed by NMR- and IR-spectroscopy and was identified as a polymer, which consists of oxymethylene units (longer chained OMEs or para-FA; SI – Section 5). The presence of this insoluble polymer could explain the slight decrease in FA-conversion (Cycle No 8–10), since solids are not considered in the NMR analysis. More importantly, the liquid OME-product mixtures of all recycling experiments do only consist of OMEs with marginal impurities of TRI (<1.0 mol%), methyl formate (<0.5 mol%) and dissolved IL (<0.1 mol%).

This second recycling experiment confirmed the reuse possibility of the IL-Cat.-solution for at least 10 reaction cycles. After an activation of the IL-Cat.-phase a FA-conversion of 100 % becomes possible. Apparently and favorable for the process, the relevant OME$_{1-5}$ fraction increases over time (Figure 3c).

In conclusion, based on the established batch OME-synthesis without catalyst reuse starting from OME$_n$, monomeric gaseous formaldehyde and the custom-made expensive catalyst OME$_n$-[Al(OR)$_4$]$_3$, a facile, accessible and recyclable process using the commercially available catalyst salt OME$_n$:BF$_4$ immobilized in the commercial IL EMIM $^+$BF$_4$ was created. With this sustainable approach, the energy expensive use of anhydrous trioxane can be avoided and the consumption of hydrogen can be reduced by 22 %, if FA-synthesis is performed through dehydrogenation of MeOH. In this biphasic OME-synthesis, simple separation of the immobilized molecular catalyst-IL-phase from the OME-product-phase is possible. The catalytically active IL-phase can be reused for at least 10 times after product separation. Moreover, the anhydrous synthesis approach avoids the production of byproducts and yields very pure OME-mixtures. In addition, the reactions are performed at very mild conditions (atmospheric pressure, 30–45 °C). Ongoing work is devoted to activate dimethyl ether with monomeric formaldehyde and conversion of this semi-batch process towards a continuous OME-synthesis process as a potentially interesting industrial synthesis route.

Supporting Information

Experimental details, procedures, weights and NMR spectra of the reactions are deposited. 9 Figures, 7 Tables, 13 pages.
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Conflict of Interest

The authors declare no conflict of interest.

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