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Synthesis and kinetic modeling of functionalized oxymethylene ethers (f-OMEs) based on allyl alcohol as building blocks for the chemical industry

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In the context of a circular economy, the production of chemicals and materials from renewable resources becomes increasingly relevant. One possible approach to reduce the dependence on fossil-based materials is the use of catalyzed acetalization reactions to produce useful building blocks in the chemical sector. Here, aldehydes and alcohols react to form acetals, which are commonly known for their good degradability and non-toxicity. This work focused on the solvent-free synthesis of acetals denominated functionalized oxymethylene ethers (f-OMEs) that are based on allyl alcohol and on formaldehyde, an important C1 feedstock which can be produced from green methanol. Such f-OMEs with unsaturated end groups are employed as useful organic compounds for the production of reactive diluents, cross-linked polymers and epoxides and can therefore be implemented as useful green building blocks in the chemical sector. A catalyst screening and variation of relevant reaction conditions were performed in a batch reactor. The different reactivity of the tested solid acid catalysts is discussed. With zeolite Beta(25), conversion based on allyl alcohol reached values up to 80% and selectivity to f-OMEs up to 90%, depending on reaction conditions. Based on the proposed reaction network, a kinetic model to forecast product distributions was developed, with educt conversion and product yield prediction being mostly within a relative deviation of $\pm 30\%$.

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1. Introduction

The depletion of non-renewable resources and global concern over greenhouse gas emissions has necessitated mankind to innovate the production pathways for fuels, chemicals and materials. In an attempt to produce environmentally friendly synthetic fuels, the production of biodiesel was intensely studied and the transesterification of triglycerides to produce fatty-acid methyl esters (FAME) is nowadays an established industrial production route.^{1–4} In this reaction, glycerol (propane-1,2,3-triol) is formed as a by-product, accounting for approximately 10 wt% of the generated product.^{5–7} In the European Union, biodiesel production has ramped up from 3.7 million tons to 11 million tons between 2006 and 2015 and is expected to keep increasing.⁸ In 2022, biodiesel production in the European Union amounted to approximately 13.7 million tons.⁹ The biodiesel production expansion leads to higher amounts of glycerol in the market, resulting in an increasing supply, demand and disposal issue. In general, the solid bio-residues from biodiesel production

are employed as compost or animal food; however, the refinement of crude glycerol for commercialization is considered expensive.^{5,8} Hence, the upgrading of glycerol into valuable intermediates is considered a valid approach to reduce biodiesel manufacturing costs.^{5,6,8} One of these intermediates is allyl alcohol (AA, prop-2-en-1-ol), which is a readily available chemical with reactivity towards addition, substitution, decomposition, oxidation, rearrangement and polymerization due to the presence of an unsaturated bond and a hydroxyl group.^{10–13} It finds its applications in the cosmetic, fine chemical and pharmaceutical industries, such as in formulations for fragrances, plasticizers, crosslinking agents, reactive diluents and coating additives.^{11,13–16} As an alternative to the propylene-based synthesis (fossil route), the conversion of glycerol to AA is possible (bio route).^{10,11,13,17,18}

In the attempt at developing a more circular economy and reducing dependency on fossil feedstocks, the use of catalyzed acetalization reactions could provide a promising strategy to produce chemicals and materials from the green intermediate AA. In such reactions, a wide range of aldehydes and alcohols can be converted into a multitude of oxygen-containing products known as acetals, which are known for their degradability, recyclability and non-toxicity.^{19–22} These are central properties to be considered when implementing

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sustainable production strategies in a circular economy. Acetalization reactions are generally acid-catalyzed reactions and can be carried out under mild conditions in terms of temperature and pressure.^{23–25} As acetalization reactions are equilibrium-limited,^{23,26–30} acetals can be recycled into their constituent building blocks under controlled acidic solvolysis.^{19–22} A key component in the production of acetals is the use of formaldehyde (FA), which can be produced from green methanol (MeOH), as an important C1 feedstock.^{23,31,32} The acid-catalyzed acetalization reaction of MeOH and FA results in linear acetals denominated oxymethylene ethers (OME), which are currently employed as solvents and studied as alternative diesel fuels.^{23,24,28,33–38} Other alcohols besides MeOH^{39–43} and functionalized alcohols, *i.e.* alcohols with additional functional groups in the molecular structure, are also promising starting materials to tune properties of the synthesized acetals.⁴⁴ This was showcased in our previous work, where acetalization reactions were performed with the lactic acid derivatives ethyl lactate and butyl lactate.⁴⁴ Therefore, AA is a possible renewable candidate for an acetalization reaction to produce functionalized oxymethylene ethers (f-OMEs) with unsaturated end groups to provide promising building blocks for the chemical industry, *e.g.* for cross-linked polymers,^{14–16,45} epoxidation reactions^{14,46–48} or as reactive diluents to substitute styrene-based systems.^{45,49,50} Fig. 1 showcases an overview of possible green pathways for the proposed reaction.

The synthesis of f-OMEs based on AA, also known as diallyl acetals, is described in the literature. One method is composed of refluxing AA with dihalomethanes (dibromomethane or dichloromethane) and tetrabutylammonium bromide in benzene to afford the acetal after distillation.⁵¹ Also possible is mixing AA with aqueous NaOH as well as adding tetrabutylammonium hydrogensulfate and allyl chloride,

followed by a workup involving extraction, drying and distillation steps.⁵² More conventional methods include the acetalization according to Fischer and Giebe as described by Müller *et al.*²⁰ in which alcohols react with aldehydes in an acid-catalyzed reaction. Webb *et al.*¹⁴ and Kazantsev *et al.*⁴⁶ describe the synthesis of diallyl formals by using paraformaldehyde (*p*-FA) or 1,3,5-trioxane (TRI) with AA as reagents and utilizing a mixture of anhydrous calcium chloride and *p*-toluenesulfonic acid as catalytic systems. Furthermore, as an alternative production route and exemplifying the viability of acetals in a circular economy, a chemical recycling concept is demonstrated by Cullen *et al.*,⁵³ in which polyoxymethylene (POM) is depolymerized using AA and bismuth triflate as a catalyst, generating the corresponding diallyl formal with a conversion of 75%.

In the present work, the synthesis of f-OMEs based on the FA source TRI and the glycerol derivative AA was developed. After a screening of catalysts and reaction conditions, the acetals were synthesized with a suitable catalyst in a batch reactor and purified by distillation. Based on these experiments, a reaction network was proposed and a kinetic model developed to forecast conversion and product distribution. The structure of the produced oligomers was verified *via* NMR spectroscopy and GC-MS and relevant properties of the compounds were measured. The novelty of this work in comparison to the literature includes the use of heterogeneous catalysts to facilitate workup steps after reaction (comprised only of catalyst separation and distillation) as well as the characterization of the produced oligomers. Moreover, a novel kinetic model to predict reaction progress was developed, a mandatory step for scale-up. This study concentrated on the development of an environmentally friendly synthesis, performing the reactions without any additional solvent and with materials which can be produced from renewable sources, resulting in recyclable and degradable products.

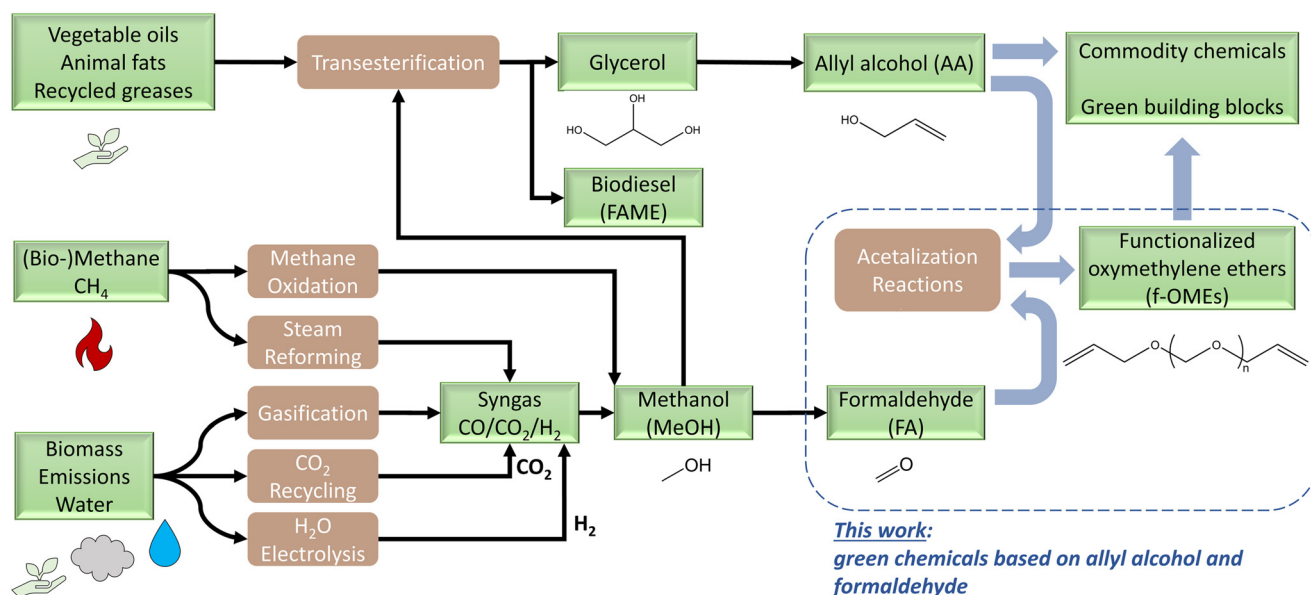


Fig. 1 Overview of possible green pathways for the synthesis of f-OMEs, using allyl alcohol and formaldehyde.

2. Experimental

2.1. Materials

Trioxane (TRI, >99%) and allyl alcohol (AA, 99%) were obtained from Thermo Scientific, *n*-octane ($\geq 99\%$) was obtained from VWR Chemicals and tetrahydrofuran (THF, $\geq 99.5\%$) was obtained from ITW Reagents. Benzene- d_6 (deuteration grade 99.8%) was purchased from Sigma-Aldrich. The catalyst montmorillonite K10 was obtained from Acros Organics. Amberlyst 36 and Amberlyst 46 were obtained from Rohm & Haas. The catalysts Beta(25), Beta(300), ZSM-5(80), ZSM-5(280), Y(12) and Y(80) were obtained from Zeolyst International.

To obtain the active H-form from the zeolites, they were calcined at 500 °C for 5 h in static air. All employed catalysts were dried at 110 °C and 10 mbar overnight prior to use so as to avoid inhibition of catalytic activity by water.^{54,55}

2.2. Reactor setup

The solvent-free reaction mixture consisted of TRI, AA and the catalyst. Batch reactions were performed in glass flasks sealed with a septum and combined with a Dean–Stark apparatus and reflux condenser. Reaction mixtures were magnetically stirred at 500 rpm. A thermostat (CF41, Julabo GmbH) regulated the temperature of the cooling water and an oil bath was used for heating the reaction mixture. Before introduction of the catalyst, the reactants were stirred thoroughly and heated up to reaction temperature. During reaction, continuous sampling of the liquid phase was carried out with a syringe and filtration of samples was made with a 0.2 μm pore width PTFE filter. Samples were diluted with THF and as internal standard for GC analysis a defined amount of *n*-octane was added.

Pure components were obtained by distillation for determination of relevant physicochemical properties and calibration. A 36 mm diameter and 1000 mm height distillation column with a 450 mm Monel spinning band was employed (B/R Instrument) and products were distilled until the GC area was $\geq 95\%$.

2.3. Catalytic tests

>Reaction mixtures without catalyst were prepared for blind testing and no reactivity was measured by GC-FID. During preliminary testing, appreciable conversion was seen beginning at 70 °C and with 0.5 wt% catalyst loading. A screening of different catalytic materials regarding structural and acidic properties was performed and the experiments were carried out for a reaction time of 8 h at 100 °C, 0.57 wt% catalyst loading (in regard to initial mass of reaction mixture) and a molar ratio of allyl alcohol:trioxane ($n_{\text{AA}}:n_{\text{TRI}}$) of 3:1. With the chosen molar ratio, it is possible to ensure that equimolar amounts of reactants are present in the reaction mixture. Furthermore, it is known that water formed during the acetalization reaction can adsorb on acidic sites, reducing catalytic activity.^{54–58} Hence, the temperature of 100 °C was chosen for the catalyst screening, as water can evaporate and then leave catalyst pores, allowing for better comparability. Table 1 gives an overview of the employed solid acid catalysts.

In addition, after choosing a suitable catalyst, a variation of relevant reaction conditions (temperature, catalyst amount, initial educt concentration, reaction time) was performed. The catalyst loading in regard to the initial mass of the reaction mixture was varied at 0.19, 0.57, 1.32 and 1.89 wt%. The initial educt concentration was varied with a molar ratio of allyl alcohol:trioxane ($n_{\text{AA}}:n_{\text{TRI}}$) of 1.5:1, 2:1, 3:1 and 4:1. The temperature variation was made at 70, 80, 90 and 100 °C. Reaction duration was varied between 10 and 80 h, depending on temperature. Moreover, experiments with water addition at the beginning of the experiments were performed to quantify the inhibition effect of water on the acetalization reactions. An overview of the performed experiments and reaction conditions is given in the SI (Table S1).

2.4. Analytical methods

A Hewlett Packard 6890 N series gas chromatograph (GC) coupled with a flame ionization detector (FID) equipped with an Agilent DB-5 MS + DG column (length: 30 m, diameter:

Table 1 Summary of used catalytic materials

Catalyst	Type	Acidity/mmol g ^{−1}	Surface area/m ² g ^{−1}	Pore diameter/Å
Beta(25)	Zeolite	0.60 ^a	680 ^c	6.6 × 6.7 5.6 × 5.6 ^d
Beta(300)	Zeolite	0.17 ^b	620 ^c	6.6 × 6.7 5.6 × 5.6 ^d
ZSM-5(80)	Zeolite	0.32 ^a	425 ^c	5.1 × 5.5 5.3 × 5.6 ^d
ZSM-5(280)	Zeolite	0.07 ^a	400 ^c	5.1 × 5.5 5.3 × 5.6 ^d
Y(12)	Zeolite	n. a.	730 ^c	7.4 × 7.4 ^d
Y(80)	Zeolite	n. a.	780 ^c	7.4 × 7.4 ^d
Amberlyst36 (A36)	Ion-exchange resin	5.4 ^c	33 ^c	240 ^c
Amberlyst46 (A46)	Ion-exchange resin	0.43 ^c	75 ^c	235 ^c
Montmorillonite K10	Clay material, aluminosilicate	0.20 ^c	220–270 ^c	60 ^c

^a Value from Sheikh *et al.*⁵⁹ ^b Value from Aho *et al.*⁶⁰ ^c Manufacturer's data. ^d Value from Baerlocher *et al.*⁶¹

0.25 mm, film: 0.25 μm) and helium as carrier gas was used for the analysis of liquid samples.

Measurements for ^1H , ^{13}C and 2D NMR were recorded under ambient conditions using a Jeol JNM-ECZR series spectrometer equipped with a 9.4 T Oxford cryomagnet (resonance: ^1H @399.905 MHz and ^{13}C @100.556 MHz). Benzene- d_6 (deuteration grade 99.8%) solutions were used for the recording of the spectra together with a Jeol Royal 5 mm probe head. The NMR measurements were carried out using the Jeol software Delta 5.3.3 and the standard Jeol pulse sequences, optimizing them if necessary. The NMR spectra were evaluated using MNova 10 (version 14.2.1-27684).

An Agilent 5977B mass spectrometer (MS) coupled with an Agilent 8890 GC system was used to record mass spectra of the samples. The GC was equipped with an Agilent J&W HP-5 ms Ultra Inert column (length: 30 m, diameter: 0.25 mm, film: 0.25 μm) and helium was used as carrier gas. Mass spectra were evaluated using the software MassHunter Qualitative Analysis from Agilent (version 10.0).

The distillation analysis was performed with the OptiPMD: micro-distillation from PAC (compliant with the standards ASTM D7345 and IP 596 for the distillation of petroleum products and liquid fuels at atmospheric pressure). The flash point was measured using a Pensky–Martens Flash Point Tester PMA 500 from Anton Paar (compliant with ASTM D93 and EN ISO 2719). Density, dynamic viscosity and freezing point were measured using an SVM 3001 Cold Properties kinematic viscometer from Anton Paar.

Pure compounds (GC area $\geq 95\%$) from distillation were used for GC-FID calibration. THF was used as solvent and *n*-octane as internal standard. In the GC-FID, the conversion from area to mass percentage ω_i of component *i* was carried out according to eqn (1):

$$\omega_i = \text{RF}_i \cdot \frac{m_{\text{octane}}}{m_{\text{total}}} \cdot \frac{A_i}{A_{\text{octane}}} \quad (1)$$

where RF_i is the compound specific response factor, A_i is the integration area in the chromatogram referring to component *i*, A_{octane} is the integration area of *n*-octane, m_{octane} is the mass of *n*-octane in the sample and m_{total} is the total sample mass.

Conversion of TRI and the reacting alcohol AA was calculated with eqn (2). Selectivity to product species was calculated based on TRI and AA (eqn (3)):

$$X_i = \frac{n_{i,0} - n_i}{n_{i,0}} \quad (2)$$

$$S_{k,i} = \frac{(n_k - n_{k,0})}{(n_{i,0} - n_i) \cdot \frac{|v_k|}{|v_i|}} \quad (3)$$

where $n_{i,0}$ is the number of moles of educt *i* at the initial point of the experiment before addition of catalyst and n_i is the number of moles of educt *i* at a given point in time after addition of catalyst. Analogously, n_k is the number of moles of product *k*. v is the stoichiometric coefficient of either educt *i* or product *k* of the reaction being investigated.

3. Kinetic modeling

3.1. Reaction network

Some methods for the synthesis of f-OMEs based on AA are described in the literature.^{14,46,51,52} However, a precise description on reaction mechanisms or reaction networks is not available, making detection and interpretation of possible side products challenging. In this work, the heterogeneously acid-catalyzed acetalization reaction as described by Müller *et al.*²⁰ between the FA source TRI and AA was developed. In particular, due to the reactivity under acidic catalysis of FA and the unsaturated bonds present in AA and in the products, side reactions occur and the side products could not be quantified in this study. Thus, they were lumped together. In Fig. S17 and S18 in the SI, an overview of the detected side products of typical GC-FID chromatograms is presented. The assignment of specific side products by GC-MS data remained equivocal; however, the main side product families were identified. Based on performed preliminary studies, a reaction network was proposed to explain the reactivity of the studied system, as shown in Fig. 2. With the reaction network, a basic understanding of the chemical processes is possible and accordingly, a kinetic model for the prediction of conversion and product distribution could be established. This enables reaction control and scale-up.

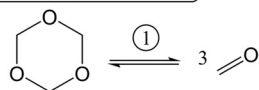
The main observed reactions are denoted with numbers in Fig. 2. Under acidic conditions, TRI decomposes into FA (reaction ①). The acetalization reaction proceeds in two steps. First, FA reacts with AA to form a reactive hemiacetal (reaction ②). Second, a reaction with a capping agent, *i.e.* AA, leads to the stable acetal OMD(AA)₁ (reaction ③), producing water. The chain growth of the acetal OMD(AA)₁ to the acetal distribution OMD(AA)_{*n*} takes place with the reaction of *n* FA (reaction ④). Side reactions occur due to the acidic catalyst, the presence of water from the initial acetalization, the reactivity of FA and the reactivity of unsaturated bonds of the reactants. The main side reaction is possibly the Prins reaction^{14,62–64} (reaction ⑤), which takes place between an aldehyde (here FA) and an alkene (here AA, hemiacetal or acetal) in the presence of H^+ . Depending on reaction conditions, different side products may be formed. Without water, the intermediate reacts to form an allylic alcohol. In the presence of water and a protic acid, a 1,3-diol is the reaction product. With an excess of FA and a low reaction temperature, the product is a cyclic acetal, *i.e.* a 1,3-dioxane. Also possible are side reactions originating from FA, such as the formation of glycols^{26,56,65} due to the presence of water and formation of methyl formate (MeFo)^{26,56,65,66} from Tishchenko-type reactions, which was found in trace amounts. In the presence of water and an acidic catalyst, MeFo can react further to produce formic acid and methanol; however, formic acid decomposes if vaporized and cannot be quantified *via* GC analysis.

The proposed reaction network for AA (Fig. 2) is used as a basis for the kinetic modeling and summarized in the following equations. TRI decomposes to FA (eqn (4)):



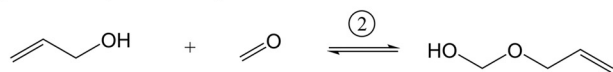
Main reactions

TRI decomposition to FA



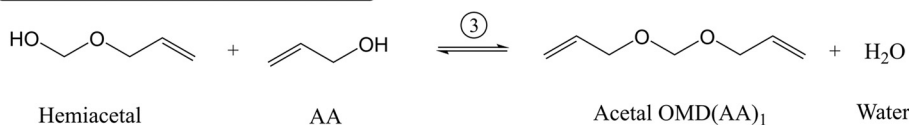
Trioxane (TRI) Formaldehyde (FA)

Formation of hemiacetal

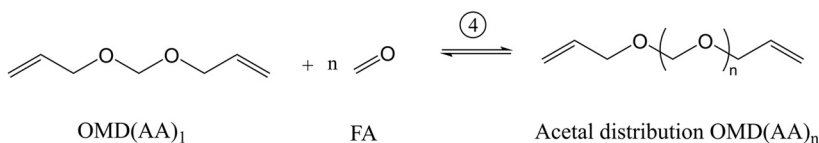


Allyl alcohol (AA) FA Hemiacetal

Formation of acetal distribution OMD(AA)_n



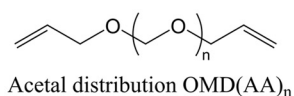
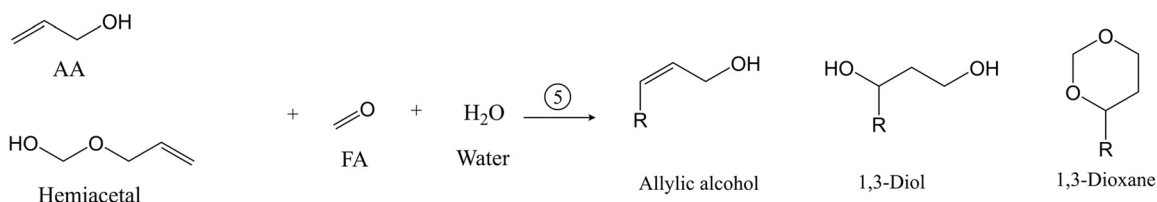
Hemiacetal AA Acetal OMD(AA)₁ Water



OMD(AA)₁ FA Acetal distribution OMD(AA)_n

Side reactions

Prins reactions



R = CH₂OH, for reaction with AA

R = CH₂OCH₂OH, for reaction with Hemiacetal

R = CH₂O(CH₂O)_nC₃H₅, for reaction with OMD(AA)_n

FA side reactions

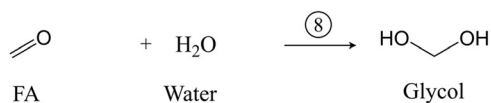
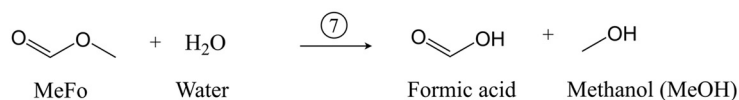
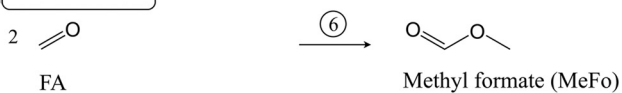
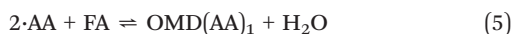


Fig. 2 Proposed reaction network for the acid-catalyzed acetalization reaction of allyl alcohol and trioxane.

The formation of the f-OME molecule with one FA unit $\text{OMD}(\text{AA})_1$ occurs *via* acetalization reaction of AA and FA with formation of water (eqn (5)):

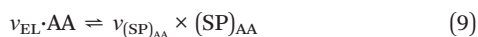
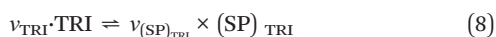


Chain growth of f-OMEs results from the formaldehyde pool in the reaction mixture (eqn (6)) or from transacetalization reactions (eqn (7)):^{66,67}



Since it is described in the literature that the chain growth reaction of OME is fast,^{35,68} it is considered here that the formaldehyde pool approach (eqn (6)) describes the process sufficiently in the kinetic model.^{35,67}

To reduce modeling complexity, side products originating from TRI and AA were lumped together in a hypothetical reaction to close the mass balance during kinetic modeling (eqn (8) and (9)):



where ν_{TRI} and ν_{AA} are the respective stoichiometric coefficients of TRI and AA of the lumped side reactions and $(\text{SP})_{\text{TRI}}$ and $(\text{SP})_{\text{AA}}$ are the side products of TRI and AA and their stoichiometric coefficients $\nu_{(\text{SP})_{\text{TRI}}}$ and $\nu_{(\text{SP})_{\text{AA}}}$, respectively.

3.2. Reaction rates and reactor model

The developed kinetics are based on a pseudo-homogeneous model with concentrations, as described in the literature.^{35,44,67} The reaction system is predicated on the reaction of the educts FA and AA and a successive chain growth with FA units. This leads to a distribution of f-OMEs known as Schulz–Flory distribution.^{69,70} In the considered reaction system, TRI decomposes to FA. When considering eqn (4), the reaction rate of TRI decomposition can be formulated as:

$$r_0 = k_0 \cdot \left(C_{\text{FA}}^3 - \frac{C_{\text{TRI}}}{K_{\text{equil}}} \right) \quad (10)$$

where r_0 is the reaction rate of TRI decomposition ($\text{mol g}^{-1} \text{min}^{-1}$), k_0 is the reaction coefficient ($\text{L}^3 \text{mol}^{-2} \text{g}^{-1} \text{min}^{-1}$), C_i is the concentration of component i (mol L^{-1}) and K_{equil} is the equilibrium constant ($\text{L}^2 \text{mol}^{-2}$). During experiments, no free FA was detected by GC-FID, which is in agreement with the literature.^{35,67,68,71} To quantify TRI decomposition, quasi-equilibrium was assumed, since it is reported that TRI decomposition is fast.^{35,67} Therefore, the following can be derived:⁶⁷

$$k_0 \gg r_0 \rightarrow \frac{r_0}{k_0} \approx 0 \quad (11)$$

$$C_{\text{FA}}^3 - \frac{C_{\text{TRI}}}{K_{\text{equil}}} = 0 \quad (12)$$

$$C_{\text{FA}} = \sqrt[3]{\frac{C_{\text{TRI}}}{K_{\text{equil}}}} \quad (13)$$

The concentration of FA is substituted according to eqn (13) and kinetic parameters were lumped, avoiding the estimation of K_{equil} .⁶⁷ The chain length of $\text{OMD}(\text{AA})_n$ was limited to $\text{OMD}(\text{AA})_3$ for kinetic modeling, since only traces of higher acetals were detected by GC-FID. The reaction rates for the acetalization of AA and TRI are summarized in Table 2.

A temperature-independent inhibition term k_{inh} was introduced to the reaction rates to consider the inhibition effect of water (eqn (14)), which was adapted from Oestreich *et al.*⁵⁶ The inhibition term k_{inh} is calculated by considering the inhibition factor $h_{\text{H}_2\text{O}}$ and the water concentration $c_{\text{H}_2\text{O}}$. The catalyst mass m_{cat} is multiplied by the inhibition term k_{inh} ; hence the effective catalyst mass $m_{\text{cat,eff}}$ is calculated (eqn (15)) and then considered in the reaction rates, resulting in the effective reaction rates.

$$k_{\text{inh}} = \frac{1}{(1 + h_{\text{H}_2\text{O}} \cdot c_{\text{H}_2\text{O}})^2} \quad (14)$$

$$m_{\text{cat,eff}} = m_{\text{cat}} \cdot k_{\text{inh}} \quad (15)$$

An Arrhenius-type approach was employed to describe the temperature dependency of the reaction coefficients. The activation energy E_A (J mol^{-1}) and the pre-exponential kinetic factor k_0 ($\text{g}^{-1} \text{L}^{n-1} \text{mol}^{1-n} \text{min}^{-1}$, unit dependent on reaction order n) of each reaction were calculated. To reduce

Table 2 Summary of reaction rate equations for the acetalization reaction of AA with TRI

Reaction	Reaction rate expression	Eqn no.
$2 \cdot \text{AA} + \text{FA} \rightleftharpoons \text{OMD}(\text{AA})_1 + \text{H}_2\text{O}$ (reaction ② + ③)	$r_1 = m_{\text{cat,eff}} \cdot (k_1 \cdot C_{\text{AA}}^2 \cdot \sqrt[3]{C_{\text{TRI}}} - k_2 \cdot C_{\text{OMD}(\text{AA})_1} \cdot C_{\text{H}_2\text{O}})$	(16)
$\text{OMD}(\text{AA})_n + \text{FA} \rightleftharpoons \text{OMD}(\text{AA})_{n+1}$ (reaction ④) $1 \leq n < 3$	$r_{1+n} = m_{\text{cat,eff}} \cdot (k_i \cdot C_{\text{OMD}(\text{AA})_n} \cdot \sqrt[3]{C_{\text{TRI}}} - k_{i+1} \cdot C_{\text{OMD}(\text{AA})_{n+1}}), 3 \leq i \leq 6$	(17)
$\nu_{\text{TRI}} \cdot \text{TRI} \rightleftharpoons \nu_{(\text{SP})_{\text{TRI}}} \times (\text{SP})_{\text{TRI}}$ (eqn (8))	$r_4 = m_{\text{cat,eff}} \cdot (k_7 \cdot C_{\text{TRI}} - k_8 \cdot C_{(\text{SP})_{\text{TRI}}})$	(18)
$\nu_{\text{AA}} \cdot \text{AA} \rightleftharpoons \nu_{(\text{SP})_{\text{AA}}} \times (\text{SP})_{\text{AA}}$ (eqn (9))	$r_5 = m_{\text{cat,eff}} \cdot (k_9 \cdot C_{\text{AA}} - k_{10} \cdot C_{(\text{SP})_{\text{AA}}})$	(19)
Temperature-independent inhibition term and effective catalyst mass (eqn (14) and (15))	$k_{\text{inh}} = \frac{1}{(1 + k_{11} \cdot c_{\text{H}_2\text{O}})^2}, m_{\text{cat,eff}} = m_{\text{cat}} \cdot k_{\text{inh}}$	(20)

unwanted correlation between the model parameters,⁷² the reference temperature T_{ref} is introduced ($T_{\text{ref}} = 100\text{ }^{\circ}\text{C}$).

$$k(T) = k_{\text{ref}} \cdot \exp \left[-\frac{E_A}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (21)$$

$$\text{with } k_{\text{ref}} = k_0 \cdot \exp \left[-\frac{E_A}{RT_{\text{ref}}} \right]$$

where T is the temperature (K), k_{ref} is the kinetic coefficient at the reference temperature T_{ref} and R is the universal gas constant ($8.314\text{ J mol}^{-1}\text{ K}^{-1}$).

A gradient-free batch reactor (BR) without heat and mass transfer limitations was assumed, as all reagents were thoroughly stirred. A control volume with the liquid phase of the reaction mixture is considered, so as to calculate the variation of the amount of substance (number of moles) n_i (mol) for each component i along the reaction time (eqn (22)).

$$\frac{dn_i}{dt} = m_{\text{cat,eff}} \cdot \sum_{j=1}^N (v_{ij} \cdot r_{ij}) \quad (22)$$

where t (min) is the reaction time after addition of catalyst and N the number of considered reactions.

This system of ordinary differential equations was solved with the Matlab function ode23, with the absolute tolerance set to 10^{-4} and the relative tolerance set to 10^{-6} . The initial conditions for the integration of eqn (22) are given in the SI (Table S1). To avoid numerical instabilities, a non-zero value of 10^{-5} mol was assigned to components with $n = 0$ mol at the initial point.

3.3. Estimation of kinetic parameters

The kinetic model for the batch reactor includes 10 temperature-dependent reaction coefficients (each with its pre-exponential kinetic factor and activation energy) and one temperature-independent water inhibition coefficient (Table 2). During preliminary modeling, the two reaction orders for the accumulation of side products amounted to the value of 1; thus, they were set to this value to formulate a more robust kinetic model with fewer parameters. Following the 5-fold cross-validation method,⁷³ the kinetic fit was implemented with training and validation datasets. A total of 25 experimental runs were considered. These were divided into five groups at random and for each fit, four datasets were used for training, while one was left for validation. The prediction errors from the training and validation datasets are combined and the kinetic fit with the smallest prediction error is deemed the estimation with the best prediction capabilities. Additionally, the standard deviation σ can be calculated as well as the confidence intervals (CI) considering a t -distribution (95% confidence level, 4 degrees of freedom).

The objective function was solved using a chi-square (χ^2) regression method, with the minimization of the sum of the squared deviations between experiment and simulation

of all considered analytes in the reaction system, as shown in eqn (23):

$$\chi^2 = \sum_{j=1}^M \sum_{i=1}^N \left(\frac{\hat{z}_{j,i} - z_{j,i}}{\hat{z}_{j,i}} \right)^2 \quad (23)$$

where j are the considered experimental data points, i the considered components, $z_{j,i}$ the measured mole number (mol) and $\hat{z}_{j,i}$ the simulated mole number (mol). The normalization occurred with the simulated values $\hat{z}_{j,i}$ since this provided more accurate and stable results during parameter fitting. The global minimum is found using the Matlab function fminsearch.

As a first estimate for initial values for the kinetic fit, the reaction coefficients were determined separately for each temperature and an Arrhenius correlation was performed. Consequently, the pre-exponential kinetic factor and the activation energy for each reaction were calculated (eqn (21)) as well as the reaction orders for the side products (eqn (8) and (9)) and the temperature-independent water inhibition coefficient (eqn (14)). Considering the training dataset N_T , the objective function χ_{Train}^2 is calculated and considering the validation dataset N_V the total squared deviation χ_{Total}^2 can be calculated. The kinetic fit with the lowest χ_{Total}^2 is considered the best fit among the optimizations performed. The 95% confidence intervals of the fitted parameters are calculated using the 5-fold cross-validation method, with $G = 5$ groups of datasets, *i.e.* 4 degrees of freedom. More detailed information can be found in the SI (Fig. S1).

The mean relative error $\text{MRE}(i)$ is calculated for each component i considering all available data points M .

$$\text{MRE}(i) = 100\% \cdot \frac{1}{M} \cdot \sum_{j=1}^M \sum_{i=1}^N \frac{|z_{i,j} - \hat{z}_{i,j}|}{z_{i,j}} \quad (24)$$

4. Results and discussion

4.1. Catalyst screening

Most of the existing studies describing the synthesis of diallyl acetals^{14,46,51,52} were not based on heterogeneously catalyzed acetalization reactions, which require an FA source and the corresponding alcohol (in this case AA). Therefore, an initial catalyst screening for the reaction system based on AA and TRI was carried out. In Fig. 3 the results for the different catalysts are shown. The utilized catalytic materials were the clay montmorillonite K10, the ion exchange resins A36 and A46 and the zeolites with FAU (Y type), MFI (ZSM-5 type) and BEA (Beta type) framework (Table 1). The catalyst screening was performed for a total reaction time of 8 h at $100\text{ }^{\circ}\text{C}$, 0.57 wt% catalyst loading (in regard to initial mass of reaction mixture) and an educt molar ratio $n_{\text{AA}}:n_{\text{TRI}}$ of 3:1. The results in Fig. 3 are shown for a reaction time of 2 h, 4 h and 8 h in order to gather data for a comprehensive reactivity profile of the employed catalysts. The temperature of $100\text{ }^{\circ}\text{C}$ was chosen for the catalyst screening to reduce the inhibiting

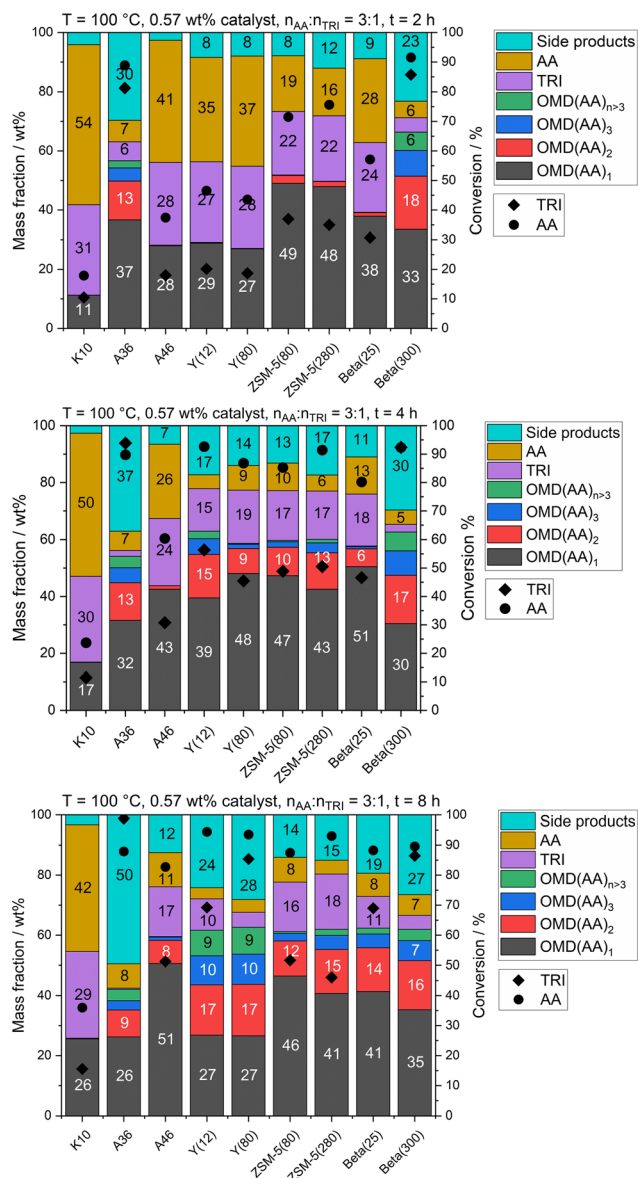


Fig. 3 Results of catalyst screening at atmospheric pressure for the reaction system AA and TRI, with conversion of AA and TRI being depicted as data points and axis on the right side, while mass fractions of reactants and products are shown as bars on the left axis (values below 5 wt% are not shown).

effect of water.^{54–57} The OMD(AA)_n acetals up to a chain length of $n = 3$ are considered individually; acetals with more FA units are lumped together as OMD(AA)_{n>3}.

The clay montmorillonite K10 showcases the lowest conversions among the tested catalysts in this study (10–16% for TRI and 18–36% for AA). Even though conversion is low, selectivity towards OMD(AA)₁ is high at approximately 98%, with little side product formation (<5 wt%). The Amberlyst ion-exchange resins display different reactivity towards f-OMEs. On the one hand, A36 demonstrates one of the highest conversion values among the tested catalysts, though showing significantly higher side product formation. After 2 h, A36 seems to have achieved chemical equilibrium and the

continued reaction favors the formation of side products and a slow degradation of products (37 wt% OMD(AA)₁ at 2 h vs. 26 wt% OMD(AA)₁ at 8 h). On the other hand, A46 shows lower conversions than A36; however, it exhibits higher selectivity specifically towards the f-OME with one FA unit. It demonstrates the highest concentration of OMD(AA)₁ amongst all considered catalysts in this study, with 51 wt% at the end of the experiment. Broadly speaking, the employed zeolites perform similarly in the acetalization reactions. Similarly to the ion-exchange resin A36, zeolite Beta(300) achieves equilibrium after 2 h but with higher selectivity towards f-OMEs, with only 23 wt% side product compared to 30 wt% of A36. When considering only zeolites, after 2 h the Y zeolites demonstrate lower conversion and lower product yield. No substantial differences can be identified when using zeolites with the same framework but different Al/Si ratios. The only exception is that Beta(300) achieves its equilibrium faster than Beta(25). Zeolites of one framework with higher Al/Si ratio show a higher tendency to produce side products. After 8 h, the Y-zeolites exhibit lower selectivity towards the acetal with one FA unit OMD(AA)₁ (Y(12) and Y(80) both with 27 wt%) when compared to the other zeolites (35–46 wt%). For the zeolites, total product yield is overall similar at the end of the experiment. The zeolites ZSM-5 and Beta lead to similar product distributions, as the total fraction of OMD(AA)_n denotes values around 60 wt% and the distribution of f-OME being described by a Schulz–Flory distribution.⁷⁰

Based on the performed catalyst screening, some conjectures can be made to explain the different reactivity of the studied catalysts. The clay montmorillonite K10 is a sheet-structured aluminosilicate, with its layers composed of an octahedral alumina sheet sandwiched between two tetrahedral silica sheets, thus being described as a 2:1 clay.^{74–76} It can partially absorb water and therefore remove it from the reaction system, resulting in formation of less side products.^{44,77} This is supported by the experimental findings, as montmorillonite K10 showcases the least side product formation of the studied catalysts (<5 wt%). The lower conversion of montmorillonite K10 can partially be explained by the lower acid site density in comparison to non-clay materials (Table 1). However, zeolites with comparable or lower acid site density, *e.g.* Beta(300) or ZSM-5(280), still showcase a higher conversion than montmorillonite K10 and a production of f-OMEs with higher number of FA units. This can be explained by the stronger Brønsted acid sites in zeolites due to framework-bound bridging hydroxyl groups (Si–O(H)–Al) rather than the edge silanol groups or weaker hydrated proton sites found on layered clays like montmorillonite K10. This results in higher reactivity of the zeolites in comparison to the clay material.^{78–81}

Furthermore, the accessibility of acid sites seems to significantly influence selectivity towards OMD(AA)_n. This is substantiated by the experimental findings with the studied ion-exchange resins and the zeolites of the catalyst screening.

Table 3 Detailed breakdown of product distribution for each catalyst in the catalyst screening after 8 h

Catalyst	OMD(AA) ₁ /wt%	OMD(AA) ₂ /wt%	OMD(AA) ₃ /wt%	OMD(AA) _{n>3} /wt%
K10	25.55	0.23	0.00	0.00
A36	26.21	8.99	3.09	3.78
A46	50.55	7.75	1.07	0.18
Y(12)	26.78	16.76	9.59	8.51
Y(80)	26.57	17.18	9.92	8.96
ZSM-5(80)	46.50	11.56	2.51	0.61
ZSM-5(280)	40.71	14.53	4.70	2.02
Beta(25)	41.35	14.44	4.60	1.95
Beta(300)	35.28	16.22	6.68	3.79

The employed ion-exchange resins are both sulfonated styrene-divinylbenzene copolymers with $-\text{SO}_3\text{H}$ as the acid group. A36 is considered an oversulfonated resin, as it presents 1 to 1.2 $-\text{SO}_3\text{H}$ groups per aromatic ring and thereby showcases higher acid capacity and acid strength.^{59,82} A46 exhibits essentially double the surface area of A36 and is only sulfonated at the catalyst surface, making the active catalytic centers more accessible, however presenting smaller values for acid capacity than A36.^{59,82} These structural properties are reflected in their reactivity, as A46 demonstrates higher selectivity towards f-OMEs, especially towards OMD(AA)₁ when compared to A36. The lower conversions in the case of A46 indicate a smaller acid capacity compared to A36. Additionally, the relevance of accessibility of active acid sites in this reaction system can be further backed up by analyzing the zeolite frameworks used in this work. Broadly speaking, the FAU framework is characterized by a large 12-membered ring (pore diameter *ca.* 7.4 Å) with interconnected cages, the BEA framework features also a 12-member ring (pore diameter *ca.* 6.0 Å), while the MFI framework has medium-sized pore systems with intersecting channels (pore diameter *ca.* 4.7 Å).^{83–85} The larger pore system (also called “supercages”) is a tentative explanation for the higher propensity of FAU zeolites to produce higher amounts of long-chain f-OME after prolonged reaction durations, followed by the BEA and then the MFI framework, as shown in Table 3 (*e.g.* weight fraction of OMD(AA)_{n>3} Y(80): 8.96 wt% and ZSM-5(80): 0.61 wt%).

Considering the studied zeolites, after 8 h AA conversion stays basically the same. With higher Si/Al ratios, a higher side product formation and a higher concentration of long-chain f-OMEs are observed. With the exception of the MFI framework, higher Al/Si ratios lead to higher TRI conversion. These findings indicate that the higher side product formation is not necessarily coupled with higher TRI conversion and could have a different underlying cause. A possible explanation could be a higher stability of the long-chain OMD(AA)_n molecules in a catalytic environment with lower acid site density, as acetalization reactions are generally equilibrium-limited.^{23,27–29} A higher acid site density of the zeolites with lower Al/Si ratios could lead to a higher probability of OMD(AA)_n molecules breaking down to their constituent building blocks and thus reducing the amount of long-chain f-OMEs. Concomitantly, with higher

concentrations of long-chain f-OMEs in the case of zeolites with higher Al/Si ratios, a higher probability of side-product formation originating from unsaturated bonds (*e.g.* Prins reactions) could be given.

The consideration of Brønsted and Lewis acidity is also important to understand the reactivity profile of the employed catalysts. In regard to the zeolites, the ZSM-5 type is known for having predominantly Brønsted acid sites, while the Y type has weaker Brønsted acid sites compared to the ZSM-5 type. Generally, the Beta type has the lowest concentration of Brønsted acid sites, but also the highest Lewis acidity among the three framework types.^{68,86–89} The higher concentration of Brønsted acid sites in the ZSM-5 type might be an explanation for the higher reactivity towards OMD(AA)₁ in the first 2 h of the catalyst screening. Also, ZSM-5(80) and ZSM-5 (280) have similar acid site strengths,⁵⁹ explaining the overall similar reactivity. The same can be seen with Y(12) and Y(80), as both have similar acid site strengths and thus comparable reactivity profiles.^{59,90} Beta(300) showcases high reactivity towards OMD(AA)_n already in the first 2 h of the experiment. Due to lower acid site density and acid site strength, but still with the same framework as Beta(25),⁶⁰ this reactivity profile might be induced by a synergy of Brønsted and Lewis acid sites, which is described for the OME synthesis.^{66,68,91} Ion-exchange resins are known for exhibiting exclusively Brønsted acidity, as they are sulfonated styrene-divinylbenzene co-polymers with $-\text{SO}_3\text{H}$ as the active acid group.^{59,92–94} By comparing A36 and A46, it is possible to infer that a high Brønsted acid site density leads to higher conversion but at the expense of selectivity.

Considering all data gathered in this catalyst screening, a clear decision for the utilization of a specific catalytic system for the highest product yield is not straightforward. Each studied catalyst system presented advantages and drawbacks and an argument for each system can be made. Montmorillonite K10 is an aluminosilicate which is known for good ion-exchange properties.^{74–76} Even though conversion is low, it has demonstrated high selectivity towards OMD(AA)₁ and it could be modified for higher acid capacity to achieve higher educt conversion, making it a potential viable and eco-friendly catalytic material for the proposed synthesis.^{76,95,96} The ion-exchange resin A46 showcases the importance of availability of catalytic sites, but

clearly demonstrating a one-sided reactivity towards short-chain f-OMEs due to a comparatively weaker acid capacity among ion-exchange resins. However, this behavior could be advantageous for a two-step synthesis. If OMD(AA)₁ is selectively produced and purified from the reaction mixture, *e.g.* by distillation, a further chain growth step could be performed with a zeolite by introducing a dry FA source, such as TRI. A dry FA source leads to higher selectivity towards f-OMEs, as water has an inhibiting effect on acetalization reactions and an anhydrous pathway would be feasible.^{23,35,54,66} Considering the zeolites, all denote useful reactivity towards f-OMEs and zeolite Beta(25) showed a good compromise between conversion and selectivity towards OMD(AA)_n. Therefore, the subsequently conducted variation of experimental conditions and kinetic modeling was performed based on this catalytic system.

4.2. Parameter estimation and model validation

The kinetic parameters for the system AA and TRI are shown in Tables 4 and 5. According to the confidence intervals, all parameters showcase statistical significance.

In particular, due to the lack of information regarding the specific reactions for side product formation, relative deviations on the order of magnitude of $\pm 30\%$ are present in the batch reactor model, as demonstrated in the parity plots in Fig. 4.

For the developed kinetic model, a total of 25 experimental runs were considered, with 255 experimental data points overall. Most of the data points fall within a relative deviation of $\pm 30\%$ and the majority of validation data points also stay within the relative deviation of $\pm 30\%$, demonstrating good predictive capabilities of the kinetic model. The MRE for TRI conversion is at 33%, for AA conversion at 22%, for number of moles of OMD(AA)₁ at 29% and for the sum of moles of OMD(AA)₁₋₃ at 22%. Considering the parity plots, it can be observed that at higher conversion values, the kinetic model has a tendency to underestimate

educt conversion and selectivity towards OMD(AA)₁. Deviation towards OMD(AA)₁₋₃ is randomly distributed. Due to the difficulty of quantifying side products and therefore determining the specific chemical reactions, higher deviations occurred, especially when considering TRI conversion and the corresponding reactivity of FA as well as complex side products from AA (Fig. 2). With a more profound mechanistic understanding of side product formation, specific equations can be formulated, thereby resulting in more precise modeling. Also, at 70 °C higher deviations of the kinetic model's predictive capabilities were observed, which could be an indication of a stronger water inhibition effect when compared to higher temperatures where water has a higher tendency to evaporate and leave the active sites of the catalyst. Water formed during the acetalization reaction not only may lead to side product formation but it also may adsorb on acidic sites, reducing catalytic activity.⁵⁴⁻⁵⁸ Baranowski *et al.*⁵⁴ describe the inhibition effect of water in Beta zeolites during classical OME synthesis. A competition takes place between productive TRI dissociation to FA and unwanted reaction of TRI with water to form methylene glycol units. Furthermore, water competitively adsorbs to silanol and Brønsted acid sites of the catalyst, hindering the adsorption of reactants. All in all, the prediction accuracy of the kinetic model could be improved by conducting experiments with smaller increments in the variation of water addition at different temperatures and with a more profound mechanistic understanding of side product formation and water inhibition.

4.3. Influence of reaction conditions: temperature

The reaction was performed at 70, 80, 90 and 100 °C. In Fig. 5 and 6 a comparison of the temperature variation with constant catalyst load and constant feed composition is demonstrated. Due to lower reaction rates at lower temperatures, the experiments at 70 and 80 °C were

Table 4 Kinetic parameters with confidence intervals for the system AA and TRI for the batch reactor system employing Beta(25) as the catalyst. For parameter description see Table 2. fwd = forward, bwd = backward and *n* = chain length of the considered acetal

Parameter	Value/ $\text{g}^{-1} \text{L}^{n-1} \text{mol}^{1-n} \text{min}^{-1}$, unit dependent on reaction order <i>n</i>	Parameter	Value/ J mol^{-1}	Description
$k_{0,1}$	$1.0953 \times 10^{12} \pm 1.0926 \times 10^{11}$	$E_{A,1}$	$9.6022 \times 10^4 \pm 1.1238 \times 10^3$	fwd reaction, <i>n</i> = 1, eqn (16)
$k_{0,2}$	$1.0081 \times 10^{16} \pm 5.3996 \times 10^{14}$	$E_{A,2}$	$1.3133 \times 10^5 \pm 4.3622 \times 10^3$	bwd reaction, <i>n</i> = 1, eqn (16)
$k_{0,3}$	$9.8218 \times 10^{13} \pm 1.2795 \times 10^{13}$	$E_{A,3}$	$1.0311 \times 10^5 \pm 4.0493 \times 10^3$	fwd reaction, <i>n</i> = 2, eqn (17)
$k_{0,4}$	$9.8488 \times 10^{19} \pm 7.1293 \times 10^{18}$	$E_{A,4}$	$1.4501 \times 10^5 \pm 3.7296 \times 10^4$	bwd reaction, <i>n</i> = 2, eqn (17)
$k_{0,5}$	$5.4393 \times 10^{23} \pm 3.4103 \times 10^{22}$	$E_{A,5}$	$1.6757 \times 10^5 \pm 1.7132 \times 10^3$	fwd reaction, <i>n</i> = 3, eqn (17)
$k_{0,6}$	$5.7460 \times 10^{29} \pm 6.5154 \times 10^{28}$	$E_{A,6}$	$2.0681 \times 10^5 \pm 1.6981 \times 10^4$	bwd reaction, <i>n</i> = 3, eqn (17)
$k_{0,7}$	$5.0865 \times 10^{15} \pm 2.6104 \times 10^{14}$	$E_{A,7}$	$1.1724 \times 10^5 \pm 1.4768 \times 10^3$	fwd reaction, eqn (18)
$k_{0,8}$	$1.0203 \times 10^{19} \pm 4.6907 \times 10^{17}$	$E_{A,8}$	$1.5134 \times 10^5 \pm 1.1987 \times 10^4$	bwd reaction, eqn (18)
$k_{0,9}$	$1.5255 \times 10^{15} \pm 1.5430 \times 10^{14}$	$E_{A,9}$	$1.1440 \times 10^5 \pm 3.6401 \times 10^3$	fwd reaction, eqn (19)
$k_{0,10}$	$2.9832 \times 10^{17} \pm 1.6073 \times 10^{16}$	$E_{A,10}$	$1.4202 \times 10^5 \pm 1.3331 \times 10^4$	bwd reaction, eqn (19)

Table 5 Further kinetic parameters for the system AA and TRI for the batch reactor system employing Beta(25) as the catalyst

Parameter	Value/—	Description
k_{11}	$3.1348 \pm 1.3964 \times 10^{-1}$	Water inhibition coefficient (eqn (14))

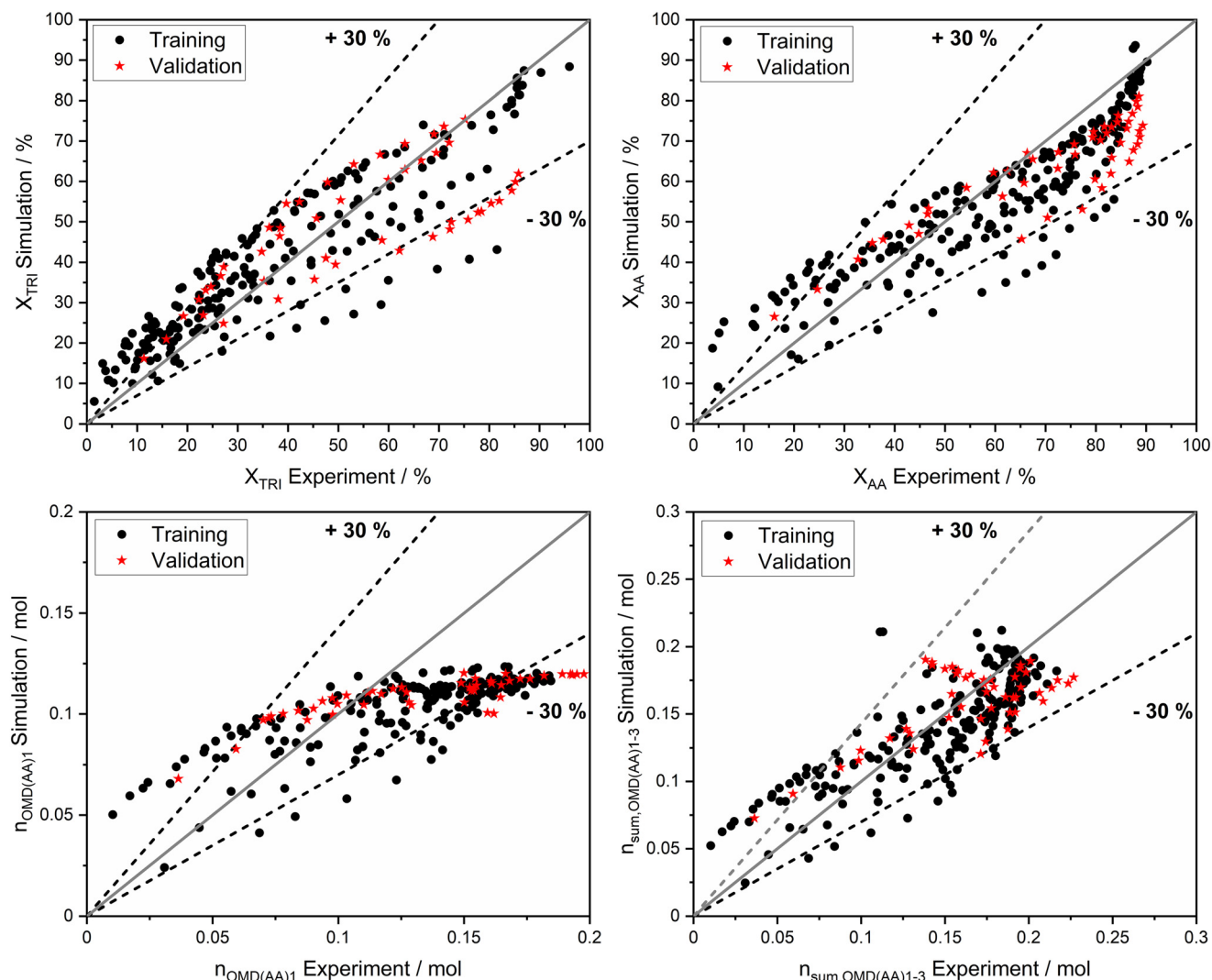


Fig. 4 Parity plots for relevant indicators employing the catalyst Beta(25), i.e. conversion of trioxane X_{TRI} , conversion of allyl alcohol X_{AA} , sum of moles of the acetal with one FA unit $n_{\text{OMD(AA)}_1}$ and sum of moles of acetal distribution with up to 3 FA units $n_{\text{sum,OMD(AA)}_{1-3}}$.

performed with longer reaction times. Experimental and simulation results are shown and compared. Selectivity towards f-OMEs up to chain length $n = 3$ is considered.

Good agreement is seen between experimental data points and simulation. Conversion of TRI and AA increases with higher temperature, which corresponds to known kinetic effects (eqn (21)). Additionally, with increasing temperature, lower selectivity towards OMD(AA)_n is observed, especially when considering TRI. Due to the reactivity of FA under acidic catalysis, a higher propensity to side product formation exists (Fig. 6). At 70 °C, higher deviations between simulation prediction and experimental data are observed. This can be tentatively explained by a higher water inhibition at a lower temperature of 70 °C. Water can be removed from the active sites of the catalyst at higher temperatures, resulting in a reduced inhibiting effect. Hence, the simulation overestimates conversion and underestimates selectivity at 70 °C. Moreover, it can be observed that at 70

°C, even though conversion is low in comparison to higher temperatures (5 h reaction time, X_{TRI} at 12% and X_{AA} at 27%), 99% selectivity towards OMD(AA)_1 is achieved. Even after 24 h of reaction time, selectivity stays high at 95%. By contrast, with higher temperatures starting at 80 °C, selectivity commences with high values of 90% or higher (sampling after 1 h), while at the end of the experimental run, the selectivity plummets to values of 50–80% depending on reaction conditions. This demonstrates that the reaction to long-chain oligomers and side reactions are limited by temperature. Further data comparing experimental data and simulation prediction can be seen in the SI (Fig. S2–S5).

4.4. Characterization of synthesized compounds

The characterization encompasses NMR spectroscopy and GC-MS as well as determination of some relevant physicochemical properties. The assignment of peaks and

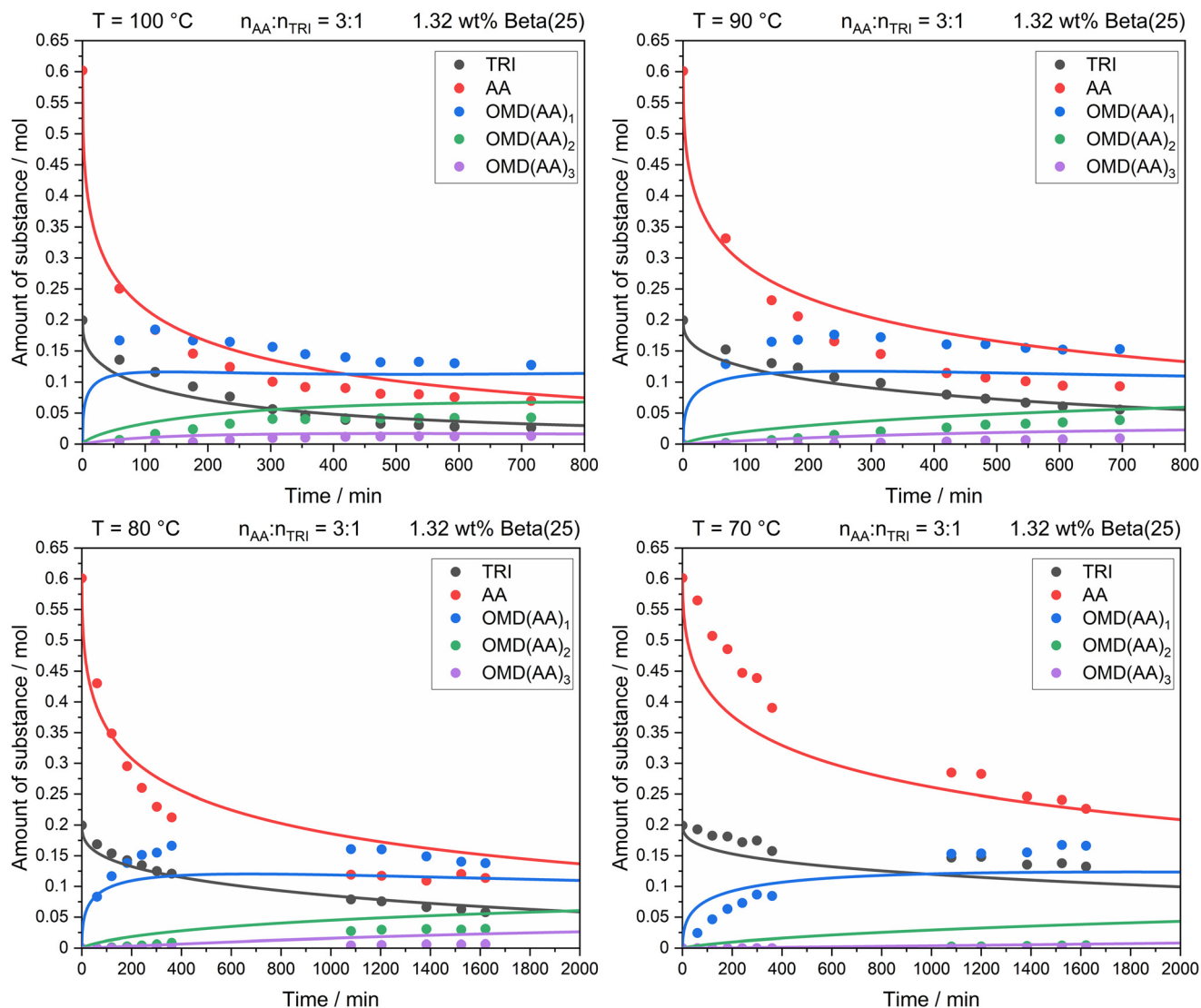


Fig. 5 Experimental runs employing the catalyst Beta(25) and performed at atmospheric pressure, showing the amount of substance of the educts TRI and AA and the acetal distribution of OMD(AA)_n with up to three FA units as a function of time (experimental values as data points and simulation as solid line).

structures from NMR spectroscopy and GC-MS analyses is compatible with data from comparable OME structures.^{40,43,44} Considering NMR, different complementary methods can be employed to clarify the structure of the synthesized f-OMEs, *e.g.* by correlating the information gained from 1D methods (*e.g.* standard ¹H and ¹³C measurements using a DEPT135 pulse sequence) and from correlated 2D NMR spectra, in this case heteronuclear single quantum coherence (HSQC). In Fig. 7, a 2D ¹³C,¹H-correlated spectrum is shown for the f-OME with one FA unit OMD(AA)₁. In the 2D HSQC method ¹H and ¹³C information are interconnected (¹³C signals are shown along the f1 (y) axis, ¹H signals along the f2 (x) axis). Hence, proton-carbon connectivity can be determined as well as carbon multiplicity, *i.e.* discerning CH and CH₃ groups from CH₂ groups. Thus, the structure of the produced compounds can be elucidated and the synthesis success evaluated.

The peak assignment for OMD(AA)₁ is straightforward (see SI Fig. S9 and S10 for more detailed information on chemical shifts and integrations for the corresponding signals and molecule fragments). The vinyl groups (fragments 1_{a,b}) show typical quartet coupling patterns due to different chemical environments of the configuration of the unsaturated bonds at 4.9 ppm for fragment 1_a and 5.1 ppm for fragment 1_b. The following CH fragment of the vinyl group (fragment 2) presents a multiplet at 5.7 ppm, being the group with the highest chemical shift in this molecule. The methylene group (fragment 3) shows a multiplet at the lowest field at 3.8 ppm. At 4.5 ppm, a typical signal representing the central methylene group from the oxymethylene bridge in acetals can be observed (fragment 4). Since it is shielded by two oxygen atoms, no coupling interactions with other protons are possible, resulting in a singlet. The ¹³C NMR spectrum shows the

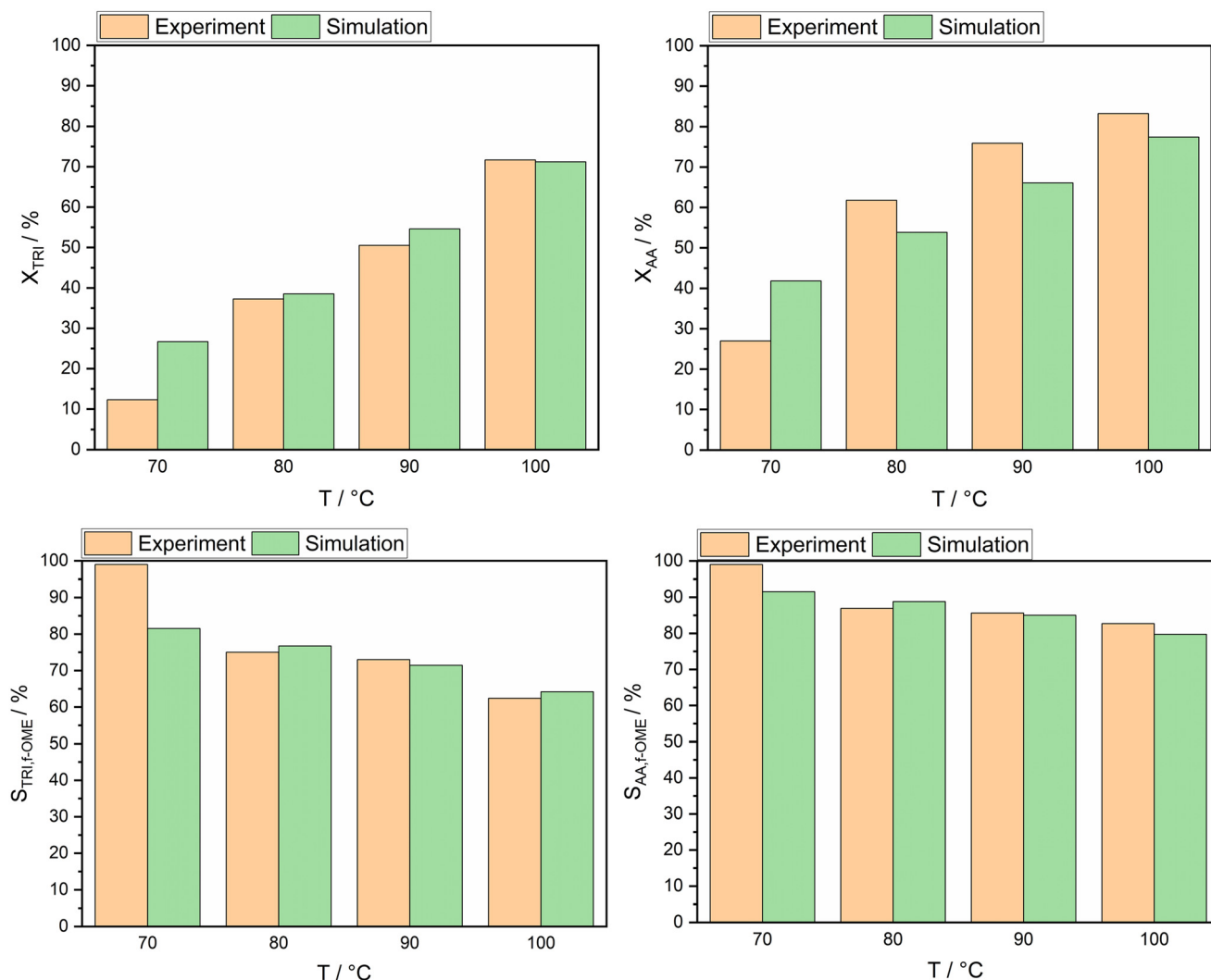


Fig. 6 Overview of temperature variation for the batch system AA and TRI, showing conversion of trioxane X_{TRI} , conversion of allyl alcohol X_{AA} and f-OME selectivity in relation to trioxane S_{TRI} and in relation to allyl alcohol S_{AA} . Reaction conditions: $t = 5$ h, 1.32 wt% Beta(25) as catalyst, $n_{\text{AA}}:n_{\text{TRI}} = 3:1$, atmospheric pressure.

corresponding C atoms seen in the molecule. The carbon atoms from the vinyl group are seen with the highest chemical shift at 116 ppm (fragment 1) and 135 ppm (fragment 2). The carbon from the oxymethylene bridge is seen at 94 ppm (fragment 4) and the carbon closest to it at 68 ppm (fragment 3).

Further NMR spectra (Fig. S9–S16), GC-MS data (Fig. S6–S8) and physicochemical properties at different temperatures (Tables S2–S4) of the synthesized f-OMes, are shown in the SI.

5. Conclusions

The solvent-free synthesis of diallyl f-OMes based on the FA source TRI and AA was investigated. A broad catalyst screening was performed and zeolite Beta(25) exhibited a good compromise between selectivity and conversion among the tested catalysts. The compounds were synthesized and purified by distillation and molecular structures were verified by NMR spectroscopy and GC-MS. Experiments were

performed in a batch reactor, with a variation of temperature, catalyst amount, initial composition and reaction time. Higher temperatures ($T > 70$ °C) lead to higher conversions and a higher concentration of long-chain oligomers; however, side product formation also becomes more pronounced. Performing the reaction at lower temperatures of 70–80 °C in a batch reactor with longer reaction times would be a possibility to reduce unwanted side reactions. Following the proposed reaction network, a kinetic model was developed and validated using the 5-fold cross-validation method, with most of the data being within a relative deviation of $\pm 30\%$. By further studying the reaction mechanism, clarification of side product reactions can be achieved. Implementing them in the kinetic model would lead to higher accuracy in the prediction of relevant process parameters.

This study provides valuable insights for the synthesis of customizable f-OMes structures as green building blocks for the chemical industry. Further work could involve the optimization of the catalyst system towards higher

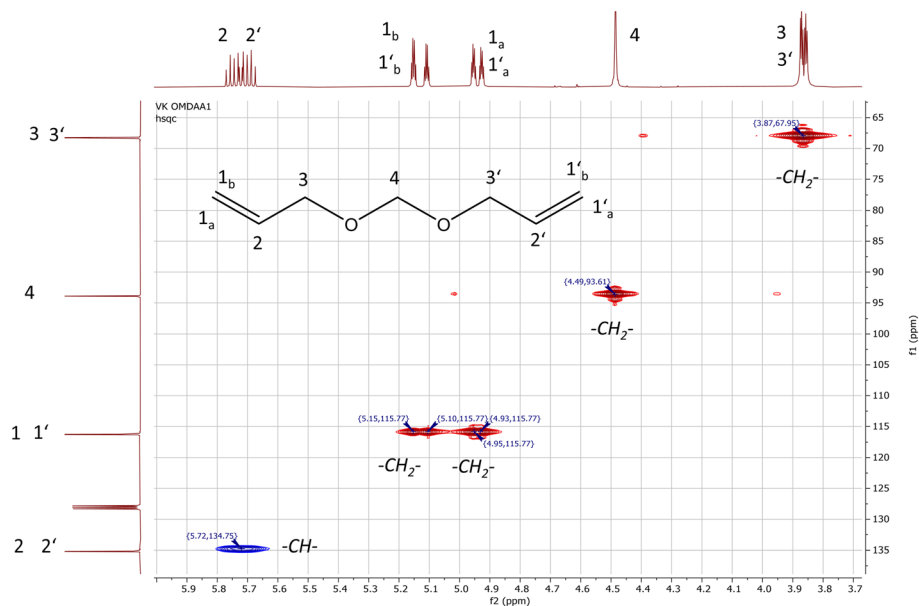


Fig. 7 ^1H , ^{13}C HSQC 2D NMR spectrum of OMD(AA)₁: chemical shift δ in ppm, measured in benzene- d_6 .

selectivity and conversion. As seen from the catalyst screening, different acidic catalysts showed promising results, such as the ion-exchange resin A46 with a high selectivity mainly towards OMD(AA)₁ or the clay material montmorillonite K10 demonstrating almost no side-product formation but with low conversion. By catalyst modification, higher conversion could be achieved in a shorter reaction time and selectivity could be maintained. By modifying the production process, it would be possible to employ a zeolite (e.g. Beta(25)) or ion-exchange resin (e.g. A46) to produce selectively OMD(AA)₁ and after purification, a dry formaldehyde source (e.g. TRI) could be used to selectively perform chain growth to OMD(AA)_n. The evaluation of long-term catalyst stability and recycling possibilities are also of relevance for a potential scale-up. In addition, the demonstration of specific applications of the produced f-OMEs would be of relevance to validate acetal chemistry as a valuable instrument to further develop a circular economy. Potential applications of the produced f-OMEs could be established in the fine chemicals and polymer sector, such as employing them as reactive diluents, as (co-)monomers in the production of polyacetals as degradable polymers with thermoset properties or as reagents in epoxidation reactions leading to useful materials for epoxides and polyurethanes.

Author contributions

Victor Kühnpast: conceptualization, methodology, formal analysis, investigation, data curation, writing – original draft, writing – review & editing, visualization. Thomas A. Zevaco: methodology, investigation, writing – review & editing, visualization. Ulrich Arnold: writing – review & editing, supervision, funding acquisition. Jörg Sauer: writing – review & editing, supervision, funding acquisition.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI).

Supplementary information is available. See DOI: <https://doi.org/10.1039/d6cy00901h>.

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