



# Effect of formaldehyde precursor and water inhibition in dimethoxymethane synthesis from methanol over acidic ion exchange resins: mechanism and kinetics

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**Abstract:** A systematic comparison of the use of trioxane and depolymerized paraformaldehyde as formaldehyde precursors for the acetalization of methanol to dimethoxymethane was performed, using the acidic ion exchange resin, Amberlyst 15, as catalyst. Experiments were carried out under isothermal conditions in batch and continuous fixed-bed reactors. The influence of the main operating parameters, temperature (80–120 °C), space time (2.7–6.2 kg h m<sup>-3</sup>), and feed concentration (12–22 wt% of trioxane/formaldehyde, 2.5 wt% of water on methanol) on reaction rate and product selectivity were evaluated. When using trioxane as reactant, dimethoxymethane is the main reaction product, with more than 90% selectivity. The catalyst was found to be stable during all the experiments (more than 30 h on stream). However, water caused a reversible inhibitory effect on reaction rate, which can be accounted for by using a competitive adsorption model. A mechanistic kinetic model was proposed and validated using the experimental results. When trioxane is used as reactant, its decomposition to formaldehyde was found to be the rate-limiting step of the reaction mechanism (activation energy 73.1 kJ mol<sup>-1</sup>). This was confirmed with additional experiments, in which trioxane was replaced by depolymerized formaldehyde. In this case, reaction rate considerably increased. © 2021 The Authors. *Biofuels, Bioproducts and Biorefining* published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

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Supporting information may be found in the online version of this article.

Key words: synthetic fuels; green solvents; acid catalyst; fixed-bed reactor; kinetic modeling

## Introduction

Dimethoxymethane (DMM), or methylal, is an important, highly valuable organic substance in the chemical industry, especially in recent years. Its wide range of applications, and its physicochemical characteristics make this chemical an environmentally friendly alternative. Dimethoxymethane is used as a green solvent and a raw material in the pharmaceutical, perfume, polymer, and paint industries, among others.<sup>1</sup> Moreover, dimethoxymethane could have a key role in the energy market, as it can be used as fuel additive<sup>2</sup> or raw material in the production of higher oxygenated compounds, such as, poly(oxyethylene) dimethyl ethers (POMDME).<sup>3–6</sup> These oxygenated compounds are added to conventional fuels, like diesel, to reduce soot formation, leading to cleaner and more efficient combustion.

Dimethoxymethane synthesis is based on the liquid-phase acetalization reaction of methanol and formaldehyde.<sup>7,8</sup> Methanol can be obtained from synthesis gas. Formaldehyde is produced by partial oxidation of methanol. The synthesis gas is produced from renewable feedstocks by gasification of biomass. Therefore, since dimethoxymethane can be obtained from renewable biomass resources, dimethoxymethane and its derivated compounds can also be used as new biofuels.<sup>9–11</sup>

The acetalization reaction is typically carried out using homogeneous liquid acid catalysts, such as concentrated sulfuric acid or *p*-toluenesulfonic acid,<sup>12</sup> which cause equipment to corrode,<sup>13</sup> and which generate environmentally unfriendly effluents. Solid acid catalysts constitute some of the best alternatives for dimethoxymethane synthesis from methanol and formaldehyde. These catalysts have the advantages of heterogeneous catalysts, such as the ease of separation and reuse, operation under mild conditions, and avoidance of corrosion problems. Many different solid acid catalysts have been proposed for this reaction, such as, cation-exchange resins,<sup>7</sup> zeolite, supported heteropolyacids ( $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ),<sup>1</sup> sulfonated fluoroalkylene resin derivatives,<sup>14</sup> and crystalline aluminosilicates.<sup>15</sup> The results available in the literature show that polystyrene-based macroporous cation-exchange resins exhibit excellent activity and stability.<sup>16</sup>

The effect of water on the catalyst performance constitutes another important, but rarely studied, limitation of the traditional dimethoxymethane production process. Formaldehyde used as a raw material is commonly supplied as aqueous methanolic formaldehyde solutions, as water

is generated as a product in the formaldehyde production process. Some previous studies had reported an inhibitory effect caused by water adsorption over cation exchange resins, which reduces the active centers available for the reaction.<sup>17–19</sup> For this reason, the use of anhydrous trioxane or paraformaldehyde as raw material could be a good alternative to minimize the inhibition caused by water. Although the water presence is unavoidable, as it is a reaction product, its effects can be reduced by using a water-free feed. Many studies have proposed the use of trioxane in dimethoxymethane and POMDME synthesis,<sup>20</sup> given its greater solubility and stability, although other authors suggested paraformaldehyde as a more economically advantageous educt.

In the recent years, some strategies have been developed to simplify and integrate the process. However, they are not yet completely effective, or they have some limitations. For example, reactive distillation, based on the simultaneous reaction and product separation in a single unit operation, is one of the most attractive alternatives. The continuous removal of dimethoxymethane and water from the reaction mixture accomplished by this method could lead to higher reaction rates and conversion.<sup>13,21</sup> The presence of an azeotrope (92.2% dimethoxymethane and 7.8% methanol) at 41.9 °C constitutes a restriction for this procedure, and more complicated techniques, as extractive reactive distillation,<sup>16</sup> have been proposed to obtain high-purity dimethoxymethane. This technique requires the use of entrainer components, which must be separated and recovered, significantly increasing the cost of the process and, therefore, reducing the efficiency.

Another proposed approach suggests direct methanol oxidation to dimethoxymethane in one single step.<sup>8,22–25</sup> This reaction system operates in the gas phase and requires bifunctional catalysts, with redox sites for methanol oxidation and acidic sites for the acetalization reaction, such as FeMo catalysts,<sup>22</sup>  $\text{H}_{3+n}\text{VnMo}_{12-n}\text{PO}_{40}$  Keggin structures,<sup>26</sup>  $\text{V}_2\text{O}_5\text{-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ ,<sup>23</sup> acid-modified  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts,<sup>24</sup> or bifunctional  $\text{V}_2\text{O}_5/\text{ZrO}_2\text{-Al}_2\text{O}_3$ .<sup>27</sup> This reaction is highly sensitive to active site distribution requiring an appropriate balance between redox and acid sites.

Kinetic studies of the dimethoxymethane synthesis reaction are scarce in the literature. Masamoto and Matsuzaki developed an elementary model based on experiments in a fixed-bed reactor at low formaldehyde concentrations.<sup>28</sup>

Danov *et al.* proposed a simple kinetic model for the reaction performed in a batch reactor catalyzed by silicotungstic heteropoly acid.<sup>1</sup> A pseudo homogeneous activity model was proposed by Drunsel *et al.*<sup>7</sup> to take into account the oligomerization reactions of formaldehyde, water, and methanol to form glycols and hemiformals together with dimethoxymethane. A more complex kinetic model has been developed by Oestreich *et al.*, but in their case the objective of the study is the synthesis of longer chain oxygenates (POMDME) in an autoclave reactor and, therefore, a greater number of reactions are involved in the process.<sup>29</sup>

In summary, acid resins are considered optimal catalysts, trioxane a promising alternative formaldehyde source, and water a non-negligible and unavoidable inhibiting agent for these reactions. However, to the best of our knowledge, there are not systematic studies accounting for these facts. This article tries to fill this gap, comparing the performance of this reaction using trioxane or depolymerized paraformaldehyde as reactant. We also develop and experimentally validate mechanistic models for both determining controlling steps in the reaction and accounting for the inhibitory effect of water on the reaction. To accomplish these purposes, we determined the product distribution and reaction scheme in a batch reactor. Then, a continuous fixed-bed reactor was used to evaluate the catalyst stability and determine the influence on reaction rate of the most important variables (temperature, space-time, trioxane feed concentration and water content). Based on the reaction mechanism, different kinetic models were proposed and fitted to the experimental data, considering both alternative formaldehyde sources.

## Materials and methods

### Catalyst and chemicals

Methanol (VWR International Eurolab, S.L.U., SPAIN, 99% purity), paraformaldehyde (Alfa Aesar, Thermo Fisher (Kandel) GmbH, GERMANY, 98% purity), 1,3,5-trioxane (Sigma-Aldrich, Merck Life Science S.L.U., SPAIN,  $\geq 99\%$  purity), and dimethoxymethane (Sigma-Aldrich, ReagentPlus®, 99% purity) were purchased. The catalyst, the acidic ion-exchange resin Amberlyst 15 (dry, hydrogen form) (Sigma-Aldrich), was supplied as spheres (dry diameter  $< 300 \mu\text{m}$ ) in the protonated form (capacity  $4.7 \text{ mmol H}^+/\text{g}_{\text{dry cat}}$ ).

### Experimental devices

In this work, two reactors were used: discontinuous (batch) and continuous. The discontinuous reactor is a temperature-controlled 0.5 L stirred autoclave reactor (accuracy of temperature measurement  $\pm 0.5 \text{ }^\circ\text{C}$ ). The reactor was loaded with 250 mL of the reactant solution (22 wt% of trioxane on methanol) and 4 g of catalyst. The reactions were carried out under 10 bar of nitrogen and stirred at 700 rpm using a turbine impeller. Samples were taken upon time from the inside of the reactor using a sampling valve.

The continuous reactor (Fig. 1) is a fixed-bed tubular reactor (10.9 mm inner diameter and 600 mm length) made of stainless-steel and surrounded by a PID-controlled electric furnace (accuracy of temperature measurement  $\pm 0.5 \text{ }^\circ\text{C}$ ). The catalyst bed was supported inside the reactor tube using a steel-wool plug and a small supportive bed made of ground

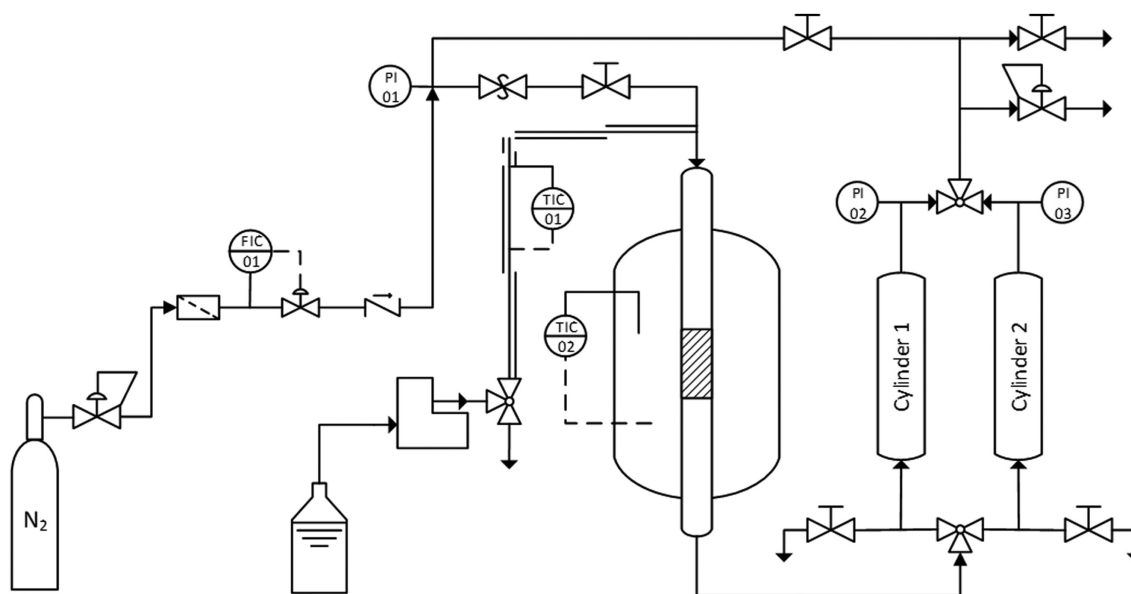


Figure 1. Flowsheet of the experimental device (continuous reactor).

glass (355–710 μm). Ion exchange resins swell in liquid polar media. Amberlyst 15 increases its volume (dry to solvent saturated) by 43% in the presence of methanol and 59% in the presence of water. To prevent the formation of plugs inside the reactor, the catalytic spheres (1 g, wet diameter <340 μm) were wetted in methanol and then introduced in the reactor (wet catalytic bed length 39 mm). On the top of the catalytic bed, glass beads (diameter 1 mm, bed length 200 mm) were used to distribute the feed over the cross-section homogeneously and for pre-heating. The assumption of plug flow is fulfilled for long beds packed with small particles: bed height/particle diameter >50 and bed diameter/particle diameter >10 (in this work, bed height/particle diameter (wet conditions) was 115 and bed diameter/particle diameter was 32).<sup>30</sup>

The liquid feed (2.7 and 6.2 mL min<sup>-1</sup>) was introduced to the system by a dosing pump (Dostec-AC, ITC Dosing Pumps, SPAIN). When paraformaldehyde is used as raw material, the dissolution process requires mixing paraformaldehyde and methanol under stirring at 80 °C, with reflux, for 48 h followed by a subsequent filtration. At the reactor outlet, two sampling cylinders were used alternatively to accumulate the reactor effluent and collect the samples in steady state conditions (liquid was accumulated in each vessel for at least 1 h).

The reactor pressure was maintained at 8.5 bar using a pressure regulator (back-pressure type, GO regulator, CRANE Instrumentation & Sampling, SC, USA), placed downstream of the sampling cylinders.

## Characterization and analytical methods

Nitrogen physisorption at 77 K in a Micromeritics ASAP 2020 analyzer was used for determining the textural properties of the catalyst. Before the tests, the catalyst samples were dried overnight at 100 °C in a stove and then degasified at 120 °C.

Liquid samples were analyzed in a gas chromatograph (Shimadzu GC-2010), equipped with a capillary column (CP-Sil 8 CB, 30 m long) and a flame ionization detector (FID). The carrier gas was He (1.36 mL min<sup>-1</sup>) and the temperature program was: 33 °C maintained constant for 10 min, followed by a ramp of 20 °C min<sup>-1</sup> up to 240 °C and held for 3 min, then ramped at 5 °C min<sup>-1</sup> up to 250 °C and held for 5 min and, finally, ramped at 10 °C min<sup>-1</sup> up to 270 °C and held for 5 min. The error associated with the analysis (based on the standard deviation) was estimated as less than 5%. Quantification of the components was carried out using ethyl acetate and *n*-heptane as internal standards. The accuracy of the measurements was estimated to be <5% per compound (lower than the error associated to the reactor operation and sampling). Formaldehyde quantification was carried out by the sodium sulfite method.<sup>31</sup>

The results of the analysis were used to calculate formaldehyde-equivalent conversion ( $X_{FA_{eq}}$ ), product selectivity ( $S_i$ ), and carbon balance (CB) according to Eqns (1) to (3). The carbon balance was over 95% for all the operating conditions:

$$X_{FA_{eq}} = 1 - \frac{w_{FA_{eq}}}{w_{FA_{eq} in}} \quad (1)$$

$$S_{DMM} = \frac{M_{FA}}{M_{DMM}} \frac{w_{DMM}}{(w_{FA_{eq} in} - w_{FA_{eq}})} \quad (2)$$

$$CB = \frac{w_{FA_{eq}} / M_{FA} + w_{MeOH in} / M_{MeOH} + 3 w_{DMM} / M_{DMM}}{w_{FA_{eq} in} / M_{FA} + w_{MeOH in} / M_{MeOH}} \quad (3)$$

where  $w_i$  and  $M_i$  are, respectively, the mass fraction and molar weight of compound  $i$ , and the subscript *in* refers to initial conditions. The formaldehyde-equivalent mass fraction is equal to the formaldehyde and trioxane mass fraction ( $w_{FA_{eq}} = w_{FA} = w_{Triox}$ ).

## Modeling

The continuous fixed-bed reactor is modeled as an isothermal plug flow reactor:

$$\frac{dF_i}{d\tau_w} = q \sum_j \nu_i r_m \quad (4)$$

where  $F_i$  is the molar flow of compound  $i$ ,  $\tau_w$  is the space time expressed in kg<sub>cat</sub> h m<sup>-3</sup>,  $q$  is the volumetric flow rate,  $\nu_i$  is the stoichiometric coefficient of compound  $i$ , and  $r_m$  is the rate of reaction  $j$  per unit weight of catalyst.

The model, a set of ordinary differential equations, is solved in MATLAB using *ode15s* function. The fitting of the unknown kinetic parameters from the model is accomplished by the least-square method, using the MATLAB *lsqcurvefit* function. The 95% confidence intervals were calculated with MATLAB function *nlparci*, which uses the residuals and Jacobian matrix previously calculated by *lsqcurvefit*.

## Results and discussion

### Reaction scheme

Dimethoxymethane synthesis from methanol and trioxane in the presence of an acid catalyst consists of two main reactions



(Table 1): first, trioxane decomposes to formaldehyde (reaction 1) and then formaldehyde and methanol react yielding dimethoxymethane and water (reaction 2). There are also secondary reactions generating other reaction products and, hence, reducing dimethoxymethane selectivity. At this point, poly(oxymethylene) dimethyl ethers (POMDME<sub>n</sub>) are a family of compounds formed by successive polymerization of dimethoxymethane with additional formaldehyde molecules (reactions 3 and 4).

The discontinuous autoclave-type reactor has been used to study the reaction for long reaction times (up to 24 h) and analyze the reaction scheme. First, experiments using a mixture of 22 wt% of trioxane on methanol as reactor feed, were carried out with a catalyst loading of 16 kg m<sup>-3</sup>. Three reaction temperatures were considered: 80, 100, and 120 °C, as shown in Fig. 2. After 24 h of reaction, 100% trioxane conversion was observed for all the tests (Fig. 2(a)). Consequently, at these operating conditions, it can be said that the reaction is irreversible (e.g. reactants completely shifted towards products). This finding was also confirmed by means of a thermodynamic study carried out in Aspen Plus using UNIQUAC model. Dimethoxymethane is the main product, with a selectivity of 94% (Fig. 2(b)). This selectivity was constant over time (i.e., independent of conversion) at 100 and 120 °C, while it increased at the beginning of the reaction at 80 °C; this suggests a reaction scheme in series as indicated in Table 1.

Figure 2(c) depicts the product distribution at 100 °C, selected as an example. Di(oxymethylene) dimethyl

ether (POMDME<sub>2</sub>) was detected in a low amount with a selectivity of 2% for complete conversion. This compound is formed by dimethoxymethane polymerization with formaldehyde molecules, resulting in the insertion of more oxymethylene groups (reaction 3). This reaction is also catalyzed by acid catalysts, such as Amberlyst 15, as reported in the literature.<sup>6,32,33</sup> However, in these experiments, only POMDME<sub>2</sub> is formed and in very low amounts. To elucidate the catalyst's performance towards this set of secondary reactions, a new experiment has been carried out in the discontinuous reactor, consisting of the reaction of dimethoxymethane and trioxane. At 50 °C and 22 wt% trioxane feed, conversion of trioxane reached 96.5% after 24 h, with the following selectivity distribution: 30.4% to POMDME<sub>2</sub>, 27.9% to POMDME<sub>3</sub>, 18.0% to POMDME<sub>4</sub>, 11.6% to POMDME<sub>5</sub> and 12.0% to longer POMDME (n > 5).<sup>6</sup>

The previous test demonstrated that Amberlyst 15 is able to catalyze the dimethoxymethane polymerization to POMDME<sub>n</sub>. However, such production of POMDME<sub>n</sub> is not observed in the reaction of dimethoxymethane synthesis from trioxane and methanol. In this reaction, water is generated as product (i.e., one mole of water for every mole of dimethoxymethane), but the reactions of dimethoxymethane polymerization to POMDME<sub>n</sub> do not generate water. Some previous works had reported a negative effect of water on the activity of Amberlyst-type catalysts.<sup>6,17,19,29</sup> For this reason, the role of water on the catalyst activity will be addressed in more detail below.

Dimerization of formaldehyde to methyl formate (the Tischenko reaction) is also a possible secondary reaction (reaction 5). However, methyl formate was detected only in trace amounts. In agreement with this fact, other studies have reported that the extent of this reaction is rather limited in these reaction systems (<1% selectivity).<sup>29</sup>

The presence of water in the reaction medium can also promote the formation of glycols by reaction between formaldehyde and water (reactions 6 and 7 in Table 1). These reactions occur spontaneously following non-catalytic mechanisms. As the amount of water in the reaction media was relatively low, because it is a reaction product, the extent of these secondary reactions will be limited. Thus, the remaining 4% selectivity is attributed either to free formaldehyde or glycols, both of which are difficult to quantify using the gas chromatography (GC) analysis. If water is used as a solvent, glycol formation is not negligible, being an important reactant consumption source. Since the glycol formation reactions are reversible, the glycols are decomposed back to generate formaldehyde as the reaction to dimethoxymethane proceeds, and trioxane concentration decreases.

**Table 1. Main and secondary reactions involved in dimethoxymethane synthesis from methanol and trioxane.**

Main reactions	
$(\text{CH}_2\text{O})_3 \rightleftharpoons 3 \text{CH}_2\text{O}$	(1)
$2 \text{CH}_3\text{OH} + \text{CH}_2\text{O} \rightleftharpoons (\text{CH}_3\text{O})_2\text{CH}_2 + \text{H}_2\text{O}$	(2)
Secondary reactions	
$(\text{CH}_3\text{O})_2\text{CH}_2 + \text{CH}_2\text{O} \rightleftharpoons \text{CH}_3\text{O}-(\text{CH}_2-\text{O})-\text{CH}_3$	(3)
$\text{CH}_3\text{O}-(\text{CH}_2-\text{O})_{n-1}-\text{CH}_3 + \text{CH}_2\text{O} \rightleftharpoons \text{CH}_3\text{O}-(\text{CH}_2-\text{O})_n-\text{CH}_3$	(4)
$2 \text{CH}_2\text{O} \rightarrow \text{CH}_3-\text{COO}-\text{CH}_3$	(5)
$\text{CH}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})_2$	(6)
$\text{CH}_2\text{OH}-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH} + \text{CH}_2\text{O} \rightleftharpoons \text{CH}_2\text{OH}-(\text{CHOH})_n-\text{CH}_2\text{OH}$	(7)

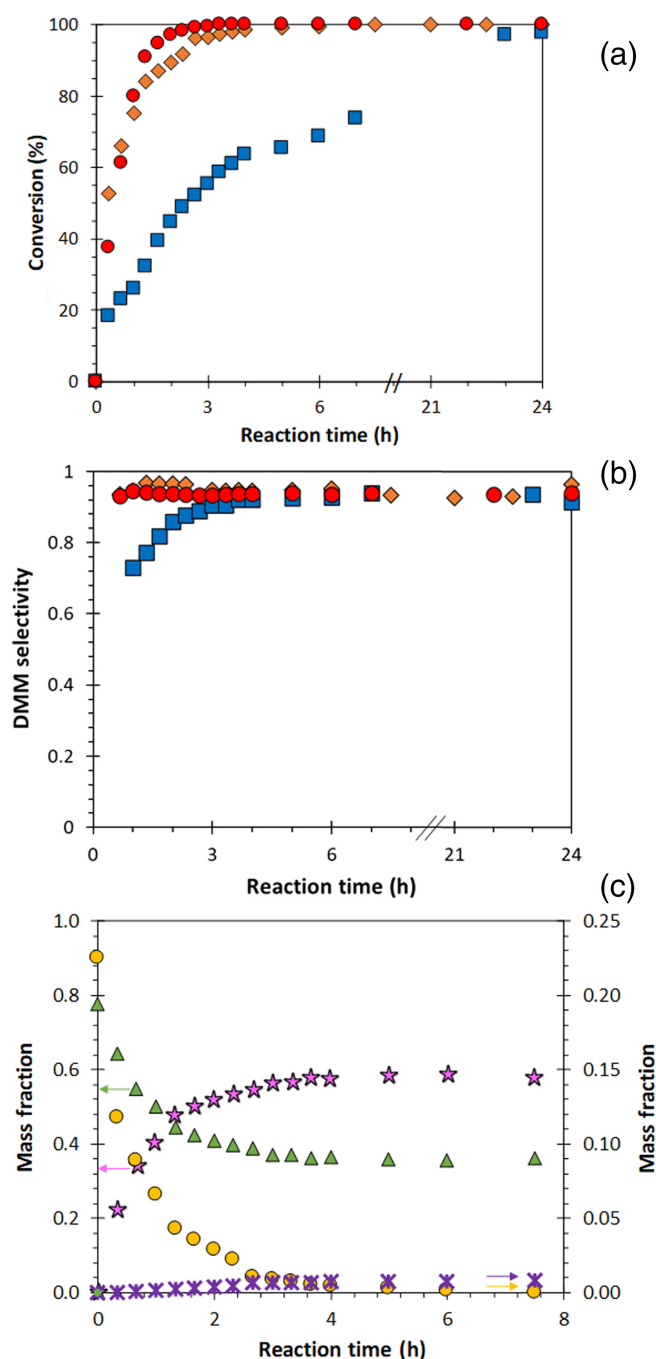


Figure 2. Discontinuous reaction experiments (22 wt% initial trioxane and  $16 \text{ kg m}^{-3}$  of catalyst loading). Influence of temperature ( $\bullet$  120 °C,  $\blacklozenge$  100 °C,  $\blacksquare$  80 °C): (a) conversion and (b) selectivity to DMM. (c) Product distribution at 100 °C ( $\bullet$  trioxane,  $\blacktriangle$  methanol,  $\star$  dimethoxymethane,  $\times$  POMDME<sub>2</sub>).

## Catalyst stability

The stability of the Amberlyst 15 catalyst was studied in the continuous fixed-bed reactor, operated under constant conditions (100 °C and 8.5 bar) for several hours. The reactant

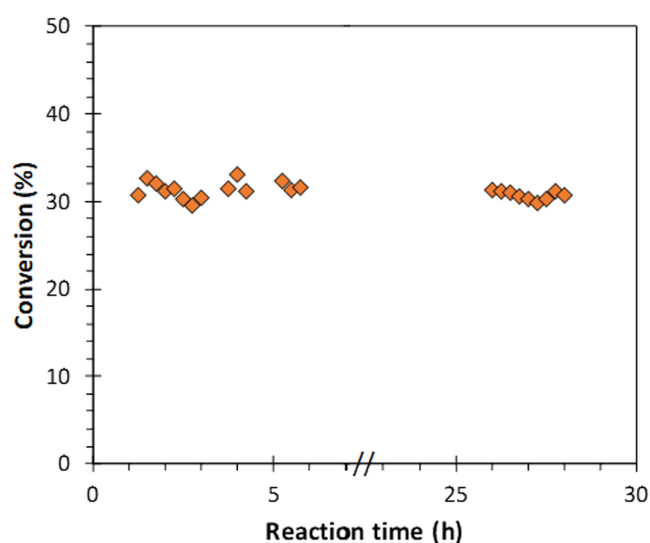


Figure 3. Catalyst stability with reaction time. Operating conditions: 22 wt% fed trioxane, space time of  $5.9 \text{ kg h m}^{-3}$  and 100 °C.

mixture, a solution of 22 wt% of trioxane on methanol, was fed to the reactor at a flow rate of  $3 \text{ mL min}^{-1}$  (space time  $5.9 \text{ kg h m}^{-3}$ ). Trioxane conversion remained constant at 30% for more than 30 h (time on stream) (Fig. 3). Traces of reaction intermediates or by-products (e.g., methyl formate) were detected in the GC analysis, but dimethoxymethane selectivity was above 90% for all this period.

The textural properties of the fresh and used catalysts indicate no significant changes caused by the reaction. Brunauer–Emmett–Teller (BET) surface area decreased from  $80.2$  to  $77.4 \text{ m}^2 \text{ g}^{-1}$  and the pore volume from  $0.442$  to  $0.417 \text{ cm}^3 \text{ g}^{-1}$  (less than 6%). Average pore size remained constant (26 nm).

According to the experimental results, it can be concluded that the catalyst is stable at the reaction conditions.

## Measurement of reaction rate

The reaction rate has been measured in the continuous fixed-bed reactor as a function of space time ( $2.7$  to  $6.2 \text{ kg h m}^{-3}$ ), temperature (80, 100, and 120 °C) and feed concentration (12 and 22 wt% trioxane on methanol). The steady-state trioxane conversion has been used to evaluate the reaction rate using the plug flow reactor model (Eqn 4), as show in Fig. 4. As might be expected, conversion increased on increasing temperature and space time. The highest conversion value was 65% at 120 °C,  $6.2 \text{ kg h m}^{-3}$  and 12 wt% trioxane. Selectivity was found to be independent of trioxane conversion, with an averaged value of 93%.

At low temperatures (80 and 100 °C), conversion was almost independent of trioxane feed concentration. Conversely, at

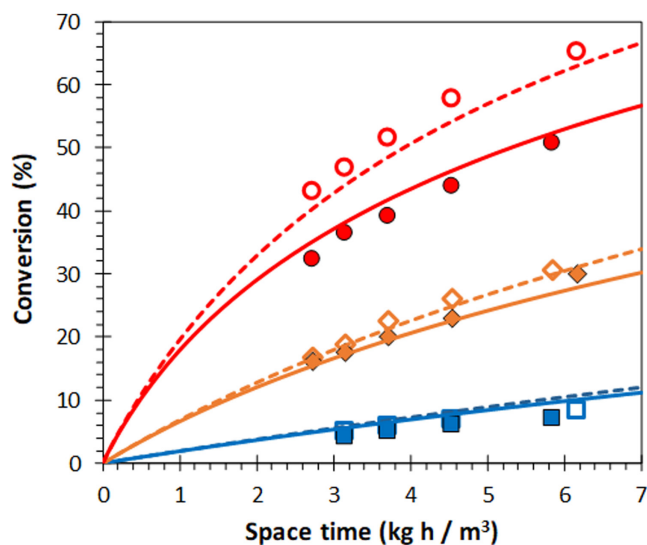


Figure 4. Continuous reaction experiments with trioxane: Influence of space time and temperature (● 120 °C, ◆ 100 °C, ■ 80 °C). Symbols: Experimental data. Lines: Model fitting (according to the reaction rate defined in Eqn 7). Trioxane feed concentration: 12 wt% (empty symbols and dashed lines) and 22 wt% (filled symbols and solid lines).

a high temperature (120 °C), trioxane feed concentration had a marked influence: for example, for the space time of  $4.6 \text{ kg h m}^{-3}$ , conversion decreased from 57.7% to 43.9% when trioxane feed was increased from 12% to 22 wt%

### Effect of water on catalyst performance

A previous work<sup>6</sup> determined that water causes inhibition of the reaction of dimethoxymethane polymerization with trioxane to POMDME<sub>n</sub> on Amberlyst 15 catalyst. The effect of water, through reversible, is very marked, with trioxane conversion decreasing from 78% to 40% for just 1 mol% water co-feeding (80 °C,  $2.8 \text{ kg h m}^{-3}$ ).

For this reason, the influence of water has also been investigated for the synthesis of methylal. Figure 5 shows an experiment carried out with water co-feeding together with the reactor feed ( $5.7 \text{ kg h m}^{-3}$ , 8.5 bar, 22 wt% trioxane). The experiment was repeated for three temperature levels (80, 100, and 120 °C). During the first 2 h, water was not fed, so the activity remained constant (e.g., at 100 °C, 30% conversion and 90% dimethoxymethane selectivity). Then, a feed with 2.5 wt% of water was introduced for 2 h and, finally, water was removed from the feed once again. There is a short delay between the change in the feed and the observed effects on trioxane conversion, attributed to the dynamics of the system (reactor and sampling cylinders). As observed in Fig. 5, there is a decrease in trioxane conversion every time the feed includes water (e.g., at 120 °C, conversion decreases from 54%

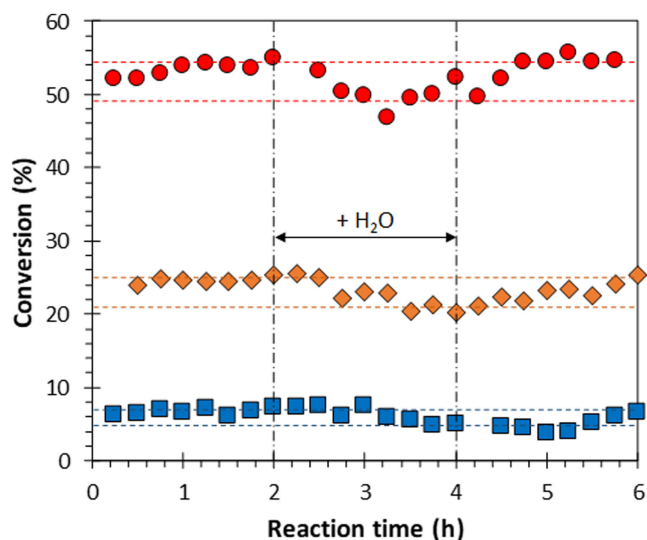


Figure 5. Influence of water on the catalyst activity (water added to the feed: 2.5 wt%) as a function of temperature (● 120 °C, ◆ 100 °C, ■ 80 °C). Operating conditions: 22 wt% fed trioxane and space time of  $5.7 \text{ kg h m}^{-3}$ .

to 49%). This conversion drop is recovered when the original water-free feed is restored. Selectivity to dimethoxymethane is not affected by all these changes in water concentration, being around 93% for all the conditions studied. Consequently, it can be concluded that water is responsible for a reversible inhibition of the catalyst activity.

The observed effect caused by water is not as strong as in the case of POMDME<sub>n</sub> polymerization from dimethoxymethane and trioxane, reported in a previous work.<sup>6</sup> Thus, in the synthesis of dimethoxymethane, water is a reaction product, so the inhibition is already present even without co-feeding. Water might also be responsible for inhibiting the further dimethoxymethane polymerization that otherwise (in the absence of water) would react at a relatively high rate.<sup>6</sup>

### Reaction mechanism and kinetic model

The reaction mechanism of dimethoxymethane synthesis is shown in Table 2. In an acidic environment, first trioxane decomposes to formaldehyde (step 1). The resultant formaldehyde methanolic solution is known to be a highly reactive multicomponent mixture. Formaldehyde and methanol react to form hemiacetals or hemiformals (step 3). This reaction has been widely studied in the literature, its rate being important even under mild conditions and without catalysts. Hemiformal is transformed to dimethoxymethane by an etherification reaction with methanol in the presence of an acid catalyst (step 4). Water is formed as a coupled product of this reaction. Based on the possible reactions involved in the process and the results obtained in the experiments, the steps

**Table 2. Reaction mechanism of dimethoxymethane synthesis from methanol and trioxane.**

Trioxane decomposition	$Triox + 3* \rightarrow 3 FA^*$	(1)
Adsorption	$MeOH + * \rightleftharpoons MeOH^*$	(2)
Hemiformal formation	$MeOH^* + FA^* \rightleftharpoons HF_1^* + *$	(3)
Dimethoxymethane formation	$HF_1^* + MeOH^* \rightarrow DMM^* + H_2O^*$	(4)
Desorption	$DMM^* \rightleftharpoons DMM + *$	(5)
Desorption	$H_2O^* \rightleftharpoons H_2O + *$	(6)

Triox, trioxane; FA, formaldehyde; MeOH, methanol; HF<sub>1</sub>, hemiformal; DMM, dimethoxymethane.

of higher relevance are trioxane decomposition, hemiformal formation, and the dimethoxymethane synthesis reaction. As the hemiformal synthesis reaction is a reaction that occurs almost spontaneously in any condition, it is assumed that its reaction rate will be orders of magnitude greater than that of the rest and, therefore, it is ruled out as a limiting stage for the reaction mechanism.

The kinetic model for the studied reaction has been developed from the previous reaction mechanism, assuming different steps as rate-limiting: models 1 and 2 assume, respectively, that trioxane decomposition (step 1) and dimethoxymethane formation (step 4) are the rate-limiting steps. All the other reaction steps are assumed to be faster and, hence, in quasi-equilibrium. The rate-limiting steps are considered irreversible reactions, in agreement with the discontinuous experiments, which resulted in a complete trioxane conversion. Using these assumptions, the following kinetic equations have been obtained (the detailed development is included in the supplementary information, S1):

Model 1

$$r_{DMM} = \frac{k C_{Triox}}{\left(1 + \frac{C_{DMM} C_{H_2O}}{K' C_{MeOH}^2} + K_1 C_{MeOH} + \frac{C_{DMM} C_{H_2O}}{K' C_{MeOH}} + \frac{C_{DMM}}{K_5} + \frac{C_{H_2O}}{K_6}\right)^3} \quad (5)$$

Model 2

$$r_{DMM} = \frac{k C_{Triox}^{1/3} C_{MeOH}^2}{\left(1 + (K_1 C_{Triox})^{1/3} + K_2 C_{MeOH} + K' C_{Triox}^{1/3} C_{MeOH} + \frac{C_{DMM}}{K_5} + \frac{C_{H_2O}}{K_6}\right)^2} \quad (6)$$

where  $C_i$  is the concentration of compound  $i$  in mol/m<sup>3</sup> (Triox: trioxane, MeOH: methanol, DMM: dimethoxymethane).

Methanol is in excess, so its concentration hardly changes during the reaction and the methanol concentration terms can be lumped and incorporated inside the apparent kinetic and adsorption constants. The inhibitory effect of water on the reaction kinetics has been experimentally demonstrated, as discussed in the previous subsection. Both models account for this inhibition by the competitive adsorption of water molecules on the catalyst active sites. Given the strength of water adsorption reported for this type of catalyst,<sup>17–19</sup> and our experimental findings at reaction conditions, water adsorption is assumed to be the strongest adsorption effect. The kinetic equations are simplified as follows:

Model 1

$$r_{DMM} = \frac{k C_{Triox}}{(1 + K_{H_2O} C_{H_2O})^3} \quad (7)$$

Model 2

$$r_{DMM} = \frac{k C_{Triox}^{1/3} C_{MeOH}^2}{(1 + K_{H_2O} C_{H_2O})^3} \quad (8)$$

When water concentration is low, e.g. for low conversion, the inhibition effect is not significant and the term of the denominator corresponding to water adsorption can be eliminated. Under these conditions, the models are transformed into power-law kinetic equations with trioxane reaction order of 1 and 1/3, respectively, for models 1 and 2.

The experimental results of the continuous fixed-bed reactor have been used to fit the proposed kinetic models. The fitting was based on the least-square technique, as explained in the materials and methods section. A set of 24 experimental data have been considered, from the experiments at different space times, temperatures, and feed concentrations, including those in which water was introduced in the feed mixture. Only data for which trioxane conversion was less than 50% have been used in the fitting. This excludes a few points of high space time in the experiments for 120 °C and 22 wt% of trioxane feed (see Fig. 4). Note that the reaction is exothermic with  $\Delta H_{298}^0 = -96.1 \text{ kJ mol}^{-1}$  and an adiabatic temperature rise of 41 °C under reaction conditions. Hence, limiting conversion to 50% reduces the energy released along the reactor tube and, with the help of the electric furnace, the reactor approaches isothermal conditions.



The fitting procedure is explained as follows. First, a preliminary fitting was done using only the experiments at the same temperature. Three sets of kinetic parameters at each of the reaction temperatures were obtained. Then, the temperature dependence of the kinetic constants was fitted using the Arrhenius equation:

$$k = k_0 e^{-\frac{E_a}{RT}} \quad (9)$$

where  $k_0$  is the pre-exponential factor and  $E_a$  is the activation energy.

Finally, the kinetic parameters obtained in this way were used as estimated solutions in a fitting using all the experimental data. The resulting fitting parameters and their 95% confidence intervals are shown in Table 3. The goodness of fit can be assessed by the sum of square errors (SSE), regression coefficients ( $R^2$ ), and confidence intervals of the parameters.

The model with the best fitting was Model 1 ( $R^2 = 0.997$ ). Model 2 exhibited poorer fitting results with wide confidence intervals for the kinetic parameters, particularly, for the activation energy. Model 1 considers trioxane decomposition as the rate-limiting step of the reaction mechanism and competitive adsorption of water. To evaluate whether the term corresponding to water competitive adsorption was significant, Model 1 was also fitted assuming  $K_{\text{H}_2\text{O}} = 0$ . The quality of the fitting decreased ( $R^2 = 0.974$ ) and the confidence intervals of the kinetic parameters became wider. Hence, water concentration was high enough to affect reaction rate and must be considered.

The predictions of model 1 are depicted as lines in Figs 4 and 6, and compared to the experimental data, which are represented as symbols. The strong agreement between both confirms the validity of the model within the range of operating conditions of the experiments.

For model 1, the activation energy of the reaction,  $E_a$ , was estimated as  $73.1 \text{ kJ mol}^{-1}$ . The adsorption constant of water was found to be independent of temperature, at least within the considered temperature range,  $K_{\text{H}_2\text{O}} = 1.27 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ . This model is similar to the one proposed by Oestreich *et al.*<sup>29</sup> for poly(oxymethylene) dimethyl ether production from methanol and formaldehyde. Their model was hyperbolic, like a Langmuir–Hinshelwood model with temperature-independent inhibiting factors due to water, methanol, and dimethoxymethane. Their experiments were carried out in an autoclave batch reactor using methanol and paraformaldehyde mixtures, as reactants, and Dowex50Wx2, as catalyst. They found that dimethoxymethane formation and further polymerization reactions were the kinetically relevant reactions. However, when trioxane is used as formaldehyde source, several works have suggested that trioxane decomposition into formaldehyde is a critical step of the process.<sup>34</sup> Wang *et al.* reported an activation energy of  $53.2 \text{ kJ mol}^{-1}$  for the trioxane decomposition reaction step, when using acidic ion liquids as catalyst.<sup>35</sup>

The turnover frequency (TOF) has been calculated for 22 wt% of trioxane on methanol as  $0.0024 \text{ s}^{-1}$  and  $0.030 \text{ s}^{-1}$  at  $80 \text{ }^\circ\text{C}$  and  $120 \text{ }^\circ\text{C}$ , respectively (an acid site density of  $4.7 \text{ mol H}^+/\text{kg}$  was considered, as indicated by the catalyst manufacturer).

The extent of external and internal mass transfer limitations was evaluated by means of the Mears criterion and the internal effectiveness factor calculation.<sup>36,37</sup> In the same way, the Mears criterion for external heat transfer evaluation<sup>36</sup> and an internal heat transfer empirical correlation<sup>38</sup> have been used to evaluate heat transfer. Detailed information about the equations can be found as supplementary information (S2). All the criteria were met for the studied operating conditions. For example, at the conditions where reaction rate was the highest,  $120 \text{ }^\circ\text{C}$  and the feed concentration, the internal

**Table 3. Kinetic constants for the kinetic rate equations proposed in this work for dimethoxymethane synthesis.**

Model type	Model parameters	Fitted value with 95% confidence interval	SSE · 10 <sup>-4</sup> (mol m <sup>-3</sup> ) <sup>2</sup>	R <sup>2</sup>
Model 1	$k_0$ (m <sup>3</sup> /kg <sub>cat</sub> s)	$(1.08 \pm 0.10) \cdot 10^6$	1.37	0.997
	$E_a$ (kJ/mol)	$73.1 \pm 4.1$		
	$K_{\text{H}_2\text{O}}$ (m <sup>3</sup> /mol)	$(1.27 \pm 0.29) \cdot 10^{-4}$		
Model 2	$k_0$ ((m <sup>3</sup> ) <sup>7/3</sup> /kg <sub>cat</sub> s mol <sup>4/3</sup> )	$(1.89 \pm 0.16) \cdot 10^6$	88.4	0.830
	$E_a$ (kJ/mol)	$67.5 \pm 5.0$		
	$K_{\text{H}_2\text{O}}$ (m <sup>3</sup> /mol)	$(7.16 \pm 0.43) \cdot 10^{-4}$		
Model 3	$k_0$ ((m <sup>3</sup> ) <sup>3</sup> /kg <sub>cat</sub> s mol <sup>2</sup> )	$14.9 \pm 6.3$	44.8	0.970
	$E_a$ (kJ/mol)	$90.5 \pm 1.2$		
	$K_{\text{H}_2\text{O}}$ (m <sup>3</sup> /mol)	$(1.27 \pm 0.29) \cdot 10^{-4}$		

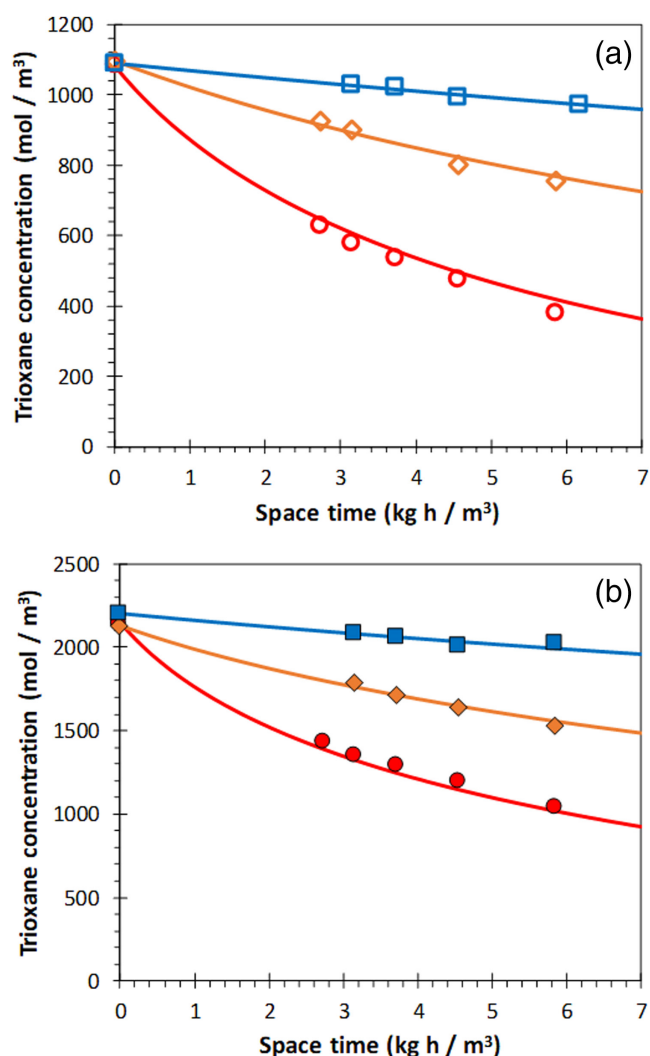


Figure 6. Model fitting on trioxane concentration. Trioxane feed concentration: (a) 12 wt% (empty symbols) and (b) 22 wt% (filled symbols). Temperature: ● 120 °C, ◆ 100 °C, ■ 80 °C. symbols: Experimental data, lines: Model fitting (according to the reaction rate defined in Eqn 7).

effectiveness factor was 0.96 and 0.99, respectively, for the experiments of the continuous and discontinuous reactors.

## Use of paraformaldehyde as reactant

According to the experimental results and the fitted kinetic model, trioxane decomposition was identified as the rate-limiting step of the reaction mechanism. Additional experiments were proposed to verify this finding, where depolymerized paraformaldehyde was used as reactant. Paraformaldehyde is the polymeric form of formaldehyde (8–100 oxymethylene units). Depolymerization of paraformaldehyde was carried out until its complete dissolution in methanol at 80 °C for 48 h under reflux. This solution of 22 wt% formaldehyde on methanol is

used as feed for the continuous reactor (the weight fraction of formaldehyde has been selected to equal that of trioxane in the above experiments).

First, the stability of the catalyst was evaluated for several hours at 100 °C, 8.5 bar and a space time of 5.9 kg h m<sup>-3</sup> (i.e., the same conditions used in the section on catalyst stability above). Conversion was found to be constant over time; a value of 78% was obtained, which is significantly higher than the 30% conversion obtained with trioxane. Dimethoxymethane was the main product, with a selectivity above 95%.

The influence of the main operating parameters (temperature and space time) on reaction rate was also evaluated, as shown in Fig. 7. Given the high activity level exhibited during the stability test, the reaction temperature was decreased to the 60–80 °C range. The increase in reaction rate with respect to the trioxane system is evident: at 80 °C, conversion was higher than 48%, whereas in the case of trioxane reactant it was below 10%. This finding is a direct confirmation of the main hypothesis of the proposed kinetic model: the decomposition of the trioxane to formaldehyde is the rate-limiting step.

The kinetic model proposed above can be complemented using the new experimental results (Fig. 7), once the trioxane limitation has been overcome. Thus, according to the reaction mechanism and assuming dimethoxymethane formation as the rate-limiting step (step 4), the following kinetic equation can be obtained:

Model 3

$$r_{DMM} = \frac{k C_{FA} C_{MeOH}^2}{(1 + K_{H_2O} C_{H_2O})^2} \quad (10)$$

As for Eqns (7) and (8), the kinetic equation has been simplified assuming all the adsorption terms are negligible, except that of water. The inhibition caused by water has been considered using the adsorption constant fitted in the section 3.6,  $K_{H_2O} = 1.27 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ .

The Arrhenius equation has been used to model the dependence with temperature of the kinetic constant. The results of Table 3 have been obtained following the fitting procedure described above. The model predictions are depicted as lines in Fig. 7, and compared with the experimental data, represented as symbols. The quality of the fitting is good given the strong agreement between experimental and predicted values and the value of the regression coefficient,  $R^2 = 0.970$ . The fitted activation energy was 90.5 kJ mol<sup>-1</sup>, which is higher than that obtained for trioxane decomposition. This suggests the temperature dependence of reaction rate is more marked for the present reaction.

The TOF has been calculated as 0.565 s<sup>-1</sup> at 80 °C. For the case of trioxane decomposition reaction, at the same

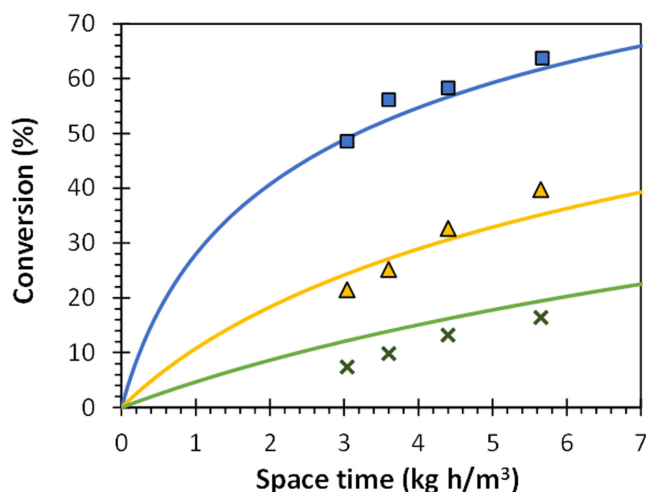


Figure 7. Continuous reaction experiments with formaldehyde: Influence of space time and temperature (■ 80 °C, ▲ 70 °C, × 60 °C). Symbols: Experimental data. Lines: Model fitting. Formaldehyde feed concentration (according to the reaction rate defined in Eq. 10): 22 wt%.

temperature and concentration, the TOF value was  $0.0024 \text{ s}^{-1}$ , which is two orders of magnitude lower.

## Conclusions

Dimethoxymethane synthesis from methanol and trioxane, catalyzed by the acid ion-exchange resin Amberlyst 15, was studied in discontinuous and continuous reactors. This catalyst presented high activity and selectivity towards dimethoxymethane (93%), without any deactivation for at least 30 h on stream. The experimental results showed that trioxane conversion increased with temperature (80–120 °C) and space time (2.7–6.2  $\text{kg h m}^{-3}$ ), while dimethoxymethane selectivity remained independent of trioxane conversion. It has been demonstrated experimentally that the water product is responsible for a reversible inhibitory effect on the catalyst activity. This agreed with a competitive adsorption of water on the catalyst active sites.

The analysis of the reaction mechanism has identified two possible kinetic models for the reaction. Our experimental results suggest that trioxane decomposition yielding formaldehyde is the rate-limiting step of the reaction mechanism. The proposed kinetic model is  $r_{\text{DMM}} = k C_{\text{Triox}} / (1 + K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}})^3$ , with  $k = k_0 e^{-E_a/RT}$ ,  $k_0 = 3.60 \cdot 10^5 \text{ m}^3/\text{kg}_{\text{cat}} \text{ s}$ ,  $E_a = 73.1 \text{ kJ mol}^{-1}$  and  $K_{\text{H}_2\text{O}} = 1.27 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ .

Additional experiments, replacing trioxane with depolymerized paraformaldehyde, resulted in a reaction

rate two orders of magnitude higher than that of trioxane (for the same operating conditions). This confirmed the main conclusion of the present work. The kinetic model was completed with the kinetic equation of the dimethoxymethane formation step ( $E_a = 90.5 \text{ kJ mol}^{-1}$ ).

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