

Catalyst deactivation in the direct synthesis of dimethyl ether from syngas over CuO/ZnO/Al₂O₃ and γ -Al₂O₃ mechanical mixtures

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Abstract

Direct synthesis of dimethyl ether from syngas over mixed catalysts constitutes a novel route aimed to replace the traditional two-step process. Many previous studies about this one-step process showed that catalyst deactivation is unavoidable. The present study wants to characterize the deactivation of CuO/ZnO/Al₂O₃ and γ -Al₂O₃ mechanical mixtures, and develop a deactivation model for predicting catalyst performance in presence of deactivation.

It was demonstrated that water adsorbs over the γ -Al₂O₃ surface, blocking its active sites and causing a sharp conversion drop (mainly observed during the first hours on stream). This effect was reversible and could be avoided by increasing temperature (270°C or above). The other deactivation mechanism was the deposition of carbonaceous species over the catalyst surface. A deactivation model was proposed and fitted to the experimental data.

Keywords: syngas upgrading; syngas-to-chemicals; renewable fuels; process intensification; deactivation models

1. Introduction

Syngas processing into dimethyl ether (DME) has gained great interest in recent years. Traditionally, DME is used as propellant and coolant, but new applications have been proposed, which makes DME a promising platform molecule to synthesize derived chemicals and fuels. DME and its derivatives chemicals are a good replacement for liquefied petroleum gas and diesel fuels. The main advantages of these compounds as fuels are high cetane number, lower NO_x emissions, near-zero soot production and lower engine noise [1, 2]. Furthermore, DME is an intermediate raw material, alternative to methanol, for the production of hydrocarbons [3, 4]; chemicals of interest such as methyl acetate, ethanol [5], formaldehyde [6] or polyoxymethylene dimethyl ethers [7]; and hydrogen [8].

Extensive works have been developed about DME synthesis methods. There are two main strategies for its production: the indirect route, where first methanol is produced from syngas and then dehydrated to DME; and the direct route, with both reactions coupled in the same reactor. Syngas is produced by gasification of biomass/coal or by reforming of biogas/natural gas [9, 10]. The direct route is thermodynamically favored due to the synergetic effect between the reactions involved. This results in a more efficient process than the two-step technology, with higher conversion obtained at milder operating conditions, especially in terms of lower pressure and higher temperature, and without the large recycle stream to the reactor needed in the traditional process [11, 12]. Thus, while typical per-pass conversion in the synthesis of methanol is around 20% (52 bar), the direct method can reach values higher than 80% in fixed bed reactors (30 bar)[12-14].

The catalysts used in the direct route have a hydrogenation function suitable for the methanol synthesis reaction and a solid-acid function for the methanol dehydration reaction to DME. These catalysts could be hybrid or supported bifunctional catalysts according to the preparation method. Hybrid catalysts combine two, or more, catalyst particles with different active phases, while bifunctional catalysts combine the two, or more, active phases on the surface of one catalyst particle. The interaction between the two catalytic functionalities is, therefore, completely different in hybrid and bifunctional systems, due to the physical separation of the two active phases. The most typical hybrid catalysts are prepared by mechanical mixing. Bifunctional catalysts are usually prepared by methods as coprecipitation, impregnation, sol-gel, or other chemical methods (e.g. colloidal approach

[15], capsule [16] or confining of copper nanoparticles within the zeolite matrix [17] and core-shell catalysts [18, 19]).

The CuO/ZnO/Al₂O₃ catalyst is currently used as commercial catalyst for methanol synthesis and, hence, has been deeply proposed for one-step DME synthesis. Regarding to the solid-acid function, γ -Al₂O₃ and zeolites, such as HZSM-5, NaHZSM-5 or HY, are the most common catalysts. Other zeolites and materials have also been studied, as ferrierite, MCM-22, ITQ-2, polymeric Naflon resins, microporous silicoaluminophosphates (SAPO-5, SAPO-11, SAPO-18, SAPO-34) and phosphorus modified alumina [17, 20-22]. The main drawback of alumina-based catalysts as dehydration catalysts, either pure or doped, is their sensitivity toward deactivation by competitive adsorption of water [23]. In this context, zeolites are more stable in the presence of steam but their narrow and slender microporous structure restrain DME diffusion and favors its degradation to carbonaceous compounds, losing activity and selectivity. In addition, most of them present high acidity, which also catalyzes the conversion of DME to hydrocarbons and this hydrocarbons evolve to heavy structures and block active sites, deactivating the catalyst [11, 13, 24]. Newer and more complex catalysts has been designed to overcome deactivation problems, but their preparation is more complex and environmentally unsustainable [13]. The low strong acid sites concentration, its reasonable high activity and stability in terms of mechanical, thermal and chemical resistance, and the low cost, make γ -Al₂O₃ the best option as methanol dehydration catalyst [13].

Previous reviews summarized the performance of different hybrid and supported bifunctional catalysts prepared by several methods [11-14]. The interaction between metallic and acidic functions, as well as the acid site strength, are key factors for DME synthesis. Strong interaction between both functions due to closer positions between the two kinds of active sites leads to detrimental interactions and deactivation as the individual components reacted to each other. García-Trenco *et al.* [25] determined that physical mixing is the best way to prepared the catalysts for this reaction. Sun *et al.* [12] compared CuZnAl/H-MFI400 prepared by physical mixture, impregnation, oxalate coprecipitation and coprecipitation-impregnation; CuZnAl/ γ -Al₂O₃ prepared by physical mixture and coprecipitation; capsule catalysts (CuZnAl@HZSM-5 and Pd-SiO₂@HZSM-5) and others such as CuZn/HZSM-5 prepared by sputtering or catalysts including Fe (CuFeZr + HZMS-5). From

this, the catalyst which allows a better compromise between selectivity and conversion is also that obtained by physically mixing CuO/ZnO/Al₂O₃ and γ -Al₂O₃.

The main problem associated to the use of these catalysts is their deactivation. Several studies have shown that activity decreases substantially after several hours on stream. This negative factor is attributed to two different reasons: a negative inhibitory effect of water over the catalyst and the catalyst deactivation by fouling [12, 26-28].

The role of water over the performance of direct synthesis of DME has been widely reported, since it is a factor with complex effects over the catalyst and reaction [29-31]. Water is formed in the dehydration of methanol to DME and consumed by the water-gas-shift reaction. An increase of water concentration in the reaction mixture leads to CO conversion to H₂ and CO₂, whereas methanol transformation to DME is mitigated. All these factors decrease the rate of methanol formation and, consequently, the global performance of the process. On the other hand, water produces different negative effects on both functions of the mixed catalyst. High water content enhances the deactivation of the acid dehydration catalyst by blockage of the Lewis acid sites through adsorption of water molecules, due to the high hydrophilicity of the γ -Al₂O₃ [32]. Additionally, the deactivation of the hydrogenation component due to morphological changes and hydrothermal leaching of Zn and Al can be promoted by water [33]. The presence of water also accelerates copper sintering on the catalyst surface [34, 35]. At the same time, water is known to attenuate coke and coke precursors formation and deposition over both catalyst functions [36]. This inhibition effect can be attributed to competition for adsorption on the active sites between water and coke precursors, or desorption of these coke precursors when water is present.

Regarding to catalyst deactivation, there are two possible causes: deposition of carbonaceous materials on the methanol synthesis catalyst and sintering of the material. It is known that the use of copper catalysts at elevated temperatures (above 280-300°C) can result in the sintering of the copper particles [37, 38]. This structural rearrangement leads to a decrease in the number of active sites, which is detected as a decrease in activity. This type of process implies an irreversible deactivation of methanol catalyst and, therefore, constitutes one of the main factors to be avoided, since regeneration is not possible.

Deactivation can also be caused by deposition of carbonaceous materials, i.e. coke precursors, over the catalyst surface. These carbonaceous materials could be formed by degradation of the methoxy ions (from dimethyl ether or methanol), generated at the interface between Cu and its support (Al_2O_3) from oxygenated compounds present in the reaction medium [39, 40]. In this case, regeneration of the catalyst is possible by oxidation of the carbonaceous materials. Sierra *et al.* [30, 39] studied the morphology of the coke deposited over a $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ catalysts prepared by wet mixing.

In the present work, a study about the stability of a mechanical mixture of $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ for the one step DME synthesis has been developed. The nature of the deactivation factors that affect to the catalysts performance during the reaction has been also investigated. Based on these results, a model which describes the loss of activity of the catalyst with time has been proposed and validated. The aim is establishing the strategies for improving the viability of the process by increasing the knowledge about the activity of the catalyst.

2. Methodology

2.1. Catalysts and chemicals

The chemicals consisted of gases (Air Liquide, purity >99%): H_2 , CO , CO_2 , N_2 , He , air and DME; and anhydrous methanol (Sigma Aldrich, 99.8% purity), used for calibrations. Regarding to the catalysts, a $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ commercial catalyst, METS-1, (Chempack) and $\gamma\text{-Al}_2\text{O}_3$ (BASF) were used for the reaction, ground to 100-250 μm and mixed in adequate proportions. The fresh catalyst mixture was pretreated inside the reactor using a gas flow of 4% H_2 (N_2 as balance gas) at 220°C (2°C min^{-1} until 220°C, holding for 2 h).

2.2. Catalyst characterization

The catalyst physical and textural properties were characterized in previous works [41] for fresh and used samples. See Supporting Information (Tables S1 and S2) for more details.

Used catalysts were analyzed by Temperature-Programmed Oxidation (TPO) using a Pfeiffer Vacuum Omnistar Quadrupole Mass Spectrometer (MS) placed in the reactor outlet stream. The samples were exposed to an oxidant gas (4% vol. O₂) while the temperature was increased (2°C min⁻¹) from 20°C to 550°C. The evolution of CO and CO₂ concentrations was monitored continuously by MS. Origin Pro 8 software was used for signal processing.

2.3. Experimental device

The experimental device consisted of an isothermal fixed bed reactor (7.5 mm inner diameter, 600 mm length), packed as follows (from top to bottom): bed of glass beads (1 mm) to heat the feed to reaction temperature, catalyst bed (100-250 μm), support bed of glass (355-710 μm) and support bed of steel wool. Reactants flow rates were controlled using mass flow controllers supplied by Bronkhorst High-Tech instruments.

Temperature is measured inside the reactor tube downstream the fixed beds by one thermocouple. This temperature is supplied to a PID feedback controller actuating on the electric furnace that surrounds the reactor. In addition, several thermocouples are placed outside the reactor tube along the wall, which is useful to measure possible temperature profiles in the bed. The temperature profiles measured with the different thermocouples during the experiments allow to confirm isothermal conditions during the experiments, i.e., for reactions with 85% wt. CuO/ZnO/Al₂O₃ and 250°C inside de reactor (thermocouple 3), the readings were 251°C in thermocouple 1 and 253°C in thermocouple 2. When temperature was increased to 270°C (thermocouple 3), the temperature profile was 268°C in thermocouple 1 and 270°C in thermocouple 2.”

Pressure was fixed at 30 bar with a back-pressure regulator placed at the reactor outlet. The reactor effluent was maintained at 150°C using heating tape, which prevented methanol and water condensation.

The global diagram of the experimental device as well as a reactor detail with thermocouples position and catalytic bed configurations are shown in Figure 1.

2.4. Analytical and characterization techniques

The reactor feed and effluent streams were analyzed on-line by gas chromatography (GC) and mass spectroscopy (MS).

For the gas chromatography analysis, a GC Agilent HP 6890N chromatograph equipped with thermal conductivity (TCD) and flame ionization (FID) detectors placed in series was used.

The columns used for the analysis are: HP Plot Q column, which separates CO₂, DME, methanol and water; and HP MoleSieve 5A column, used for the separation of CO, H₂, O₂ and N₂.

Regarding to the mass spectroscopy analysis, a Pfeiffer Vacuum Omnistar Quadrupole Mass Spectrometer (MS) placed in the reactor outlet stream was used for an on-line characterization of the gas streams.

The results of the analysis were used to calculate conversion of CO (X_{CO}) and product yields (Y_i) according to the following expressions:

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

$$Y_{DME} = \frac{2 M_{CO} w_{DME}}{M_{DME} w_{CO\ in}} \quad (2)$$

$$Y_{CH_3OH} = \frac{M_{CO} w_{CH_3OH}}{M_{CH_3OH} w_{CO\ in}} \quad (3)$$

$$Y_{CO_2} = \frac{M_{CO} (w_{CO_2} - w_{CO_2\ in})}{M_{CO_2} w_{CO\ in}} \quad (4)$$

Where w_i and M_i are, respectively, the mass fraction and molar weight of compound i . The mass fraction is used to calculate conversion and yield, instead of mole fraction, due to the important change in the total mole of the reactions.

2.5. Modelling

The fixed-bed reactor is modelled as an isothermal plug flow reactor for non-constant density systems. 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 (this work 460 and 31, respectively). The following mass conservation equation, based on mass fractions, is considered:

$$m_0 \frac{dw_i}{dW_{cat}} = M_i \sum_j v_{ij} r_{mj} a \quad (5)$$

Where m_0 is the total feed mass flow rate, w_i is the mass fraction of compound i , W_{cat} is the total weight of catalyst, M_i is the molecular weight of compound i , v_{ij} is the stoichiometric coefficient of compound i in reaction j , r_{mj} is the rate of reaction j per unit weight of catalyst and a is the activity of the catalyst.

In a previous work [41], the kinetic model of Table 1 was postulated, fitted and validated with experimental data. This model is used to calculate the corresponding rate of the involved reactions, taking into account the corresponding amount of catalyst in the mixture and any possible inhibitory effect due to the presence of water (factor $K_{H_2O} f_{H_2O}$ of the denominator).

Table 1. Kinetic model for the synthesis of dimethyl ether from syngas on CuO/ZnO/Al₂O₃ (catalyst 1) and Al₂O₃ (catalyst 2) [41].

Catalyst	Reaction	Rate law
Cat 1	[I] $CO + 2 H_2 \rightleftharpoons CH_3OH$ $\Delta H_1 = -90.51 \text{ kJ/mol}$	$r_1 = \frac{k_1}{DEN^3} \left(f_{CO} f_{H_2} - \frac{f_{CH_3OH}}{K_{eq1} f_{H_2}} \right)$ $\ln k_1 = 25.25 - 20664/T$
	[II] $CO_2 + 3 H_2 \rightleftharpoons CH_3OH + H_2O$ $\Delta H_2 = -49.51 \text{ kJ/mol}$	$r_2 = \frac{k_2}{DEN^3} \left(f_{CO_2} f_{H_2} - \frac{f_{CH_3OH} f_{H_2O}}{K_{eq2} f_{H_2}^2} \right)$ $\ln k_2 = -5.10 - 457/T$
	[III] $CO + H_2O \rightleftharpoons CO_2 + H_2$ $\Delta H_3 = -41 \text{ kJ/mol}$	$r_3 = k_3 \left(f_{CO} f_{H_2O} - \frac{f_{CO_2} f_{H_2}}{K_{eq3}} \right)$
Cat 2	[IV] $2 CH_3OH \rightleftharpoons C_2H_6O + H_2O$ $\Delta H_4 = -23.5 \text{ kJ/mol}$	$r_4 = k_4 \left(f_{CH_3OH}^2 - \frac{f_{C_2H_6O} f_{H_2O}}{K_{eq4}} \right)$ $\ln k_4 = 2.10$ $DEN = 1 + K_{H_2O} f_{H_2O}, K_{H_2O} = 19 \text{ bar}^{-1}$

* r_j in mol kg_{cat,j}⁻¹ s⁻¹, f_i in bar and T in K.

The reactor model is solved using a MATLAB code, responsible of performing all the calculations and solving the set of ordinary differential equations (*ode15s*). The fitting of unknown parameters from the model is accomplished by the least-square method (*lsqcurvefit*) using conversion and selectivity as estimates (eq. (1) to (4)).

3. Results and discussion

3.1. Catalyst stability

The stability of the catalyst was studied with the reactor operated at constant conditions: feed of 40% CO and 60% H₂ (% mol), 30 bar, 0.20 kg_{cat} h/Nm³ space time (70 % wt. of CuO/ZnO/Al₂O₃ in the catalyst mixture).

Figure 2a shows the evolution of CO conversion and selectivity with time at 250°C. The results indicated that conversion slightly decreases in the first 10 h on stream, but then conversion sharply decreases from 51% to 26%. Despite of this, changes on selectivity are not significant, from 67% to 68.7% for DME and from 33% to 31.3% for CO₂. Afterwards, conversion was maintained almost constant at this last value for other 10 h of reaction. In this situation, temperature was increased to 270°C, which resulted in an increase of conversion to 52.6%, a similar value to that observed before the drop in conversion. The reaction was kept at these conditions during another 15 hours, only a slight decrease on conversion being observed, from 52.6% to 48.5%. Selectivity is practically unaffected by temperature, with 65.3% to DME and 34.7% to CO₂ at 270°C.

In order to elucidate the cause of the observed behavior, a new experiment using fresh catalyst and 270°C from the beginning of the experiment was carried out (Figure 2b). In this case, no sharp decreases in conversion were observed, which confirmed that the phenomenon is dependent of temperature. Conversion decreases slowly from 56.5% to 49.8%, corresponding to a progressive loss of activity. The final conversion value for 18 h of reaction is close to that observed at 270°C at the end of the previous experiment with other catalyst loading (49.9% against 48.5%). Regarding to selectivity, it is maintained constant at 62.0% to DME and 37.8% to CO₂.

According to these results, a temperature of 270°C seems to be the best option, resulting in higher conversion and similar selectivity. Higher temperatures were not considered since they increase the rate of sintering of the CuO/ZnO/Al₂O₃ catalyst and results in an irreversible loss of activity [37, 42, 43]. The manufacturer of the catalyst recommends a maximum temperature of 280°C for industrial-scale operation.

The experimental trials suggested that the observed abrupt decrease in activity is reversible and highly dependent of temperature. For this reason, it is hypothesized that it is caused by water adsorption. Water is generated as product in the dehydration of methanol to dimethyl ether. At 250°C, part of the water product is progressively adsorbed on the γ -Al₂O₃ catalyst. At the beginning of the experiment, conversion was unaffected, because the amount of adsorbed water is low and the γ -Al₂O₃ catalyst is in excess (the dehydration of methanol to dimethyl ether is in equilibrium at reaction conditions). The drop in conversion exhibits a rupture-like curve, as the adsorbed water blocks an increasing amount of active sites on the catalyst surface. When temperature is increased, water desorbs and, therefore, conversion increases.

To demonstrate that the adsorption/desorption of water from the catalyst is responsible of the observed inhibitory phenomena, a new set of experiments were set up to test this hypothesis.

3.2. Inhibition caused by water

The experiments of the previous section showed a decrease in conversion attributed to the adsorption of water on the catalyst surface. To test this hypothesis, additional experiments using nitrogen as a desorption agent were performed, as shown in Figure 3. The operating conditions were the same as in the previous experiments; fresh catalyst was also used. After 10 hours of reaction at 250°C, conversion dropped from 52% to 30%, as in the previous experiments, and then its value remained constant. At this point, the syngas feed was replaced by a nitrogen stream (of equal total flow rate) during 1 hour. Then, the syngas feed was returned back, and a recovery in conversion of 3.8% was observed, Figure 3a. This recovery was temporary and conversion decreased again to 30%. It can be concluded that nitrogen caused a positive effect on the catalyst, acting as sweep gas to promote water

desorption. Any change was detected in selectivity, which remains constant at 63.2% to DME, 33.4% to CO₂ and 3.4% to methanol. The reversibility of this phenomenon was tested in a second trial, where nitrogen was maintained for more time, 2.5 hours. Now, the recovery of conversion was higher (about 88%), though it fell again to the constant value of 30%. The fact that a longer desorption time resulted in a higher recovery of conversion agrees with the hypothesis of being water the responsible of this loss of activity. The analysis of the outlet of the reactor by MS showed a very low water content during all the experiment, including during desorption.

A second set of experiments with fresh catalyst, but with higher fraction of CuO/ZnO/Al₂O₃ in the catalytic bed, 92.5 wt.%, were carried out. Consequently, the total flow rate was changed keeping constant the space time (0.14 kg_{cat} h/Nm³ with respect to the methanol catalyst) and, therefore, the same CO conversion, given that γ -Al₂O₃ is in excess for these conditions. Conversion decreased after 6 h of reaction, Figure 3b, instead of the 10 h required of the previous experiments. Nitrogen was fed for 1 h, which was enough to completely recover the initial conversion and maintain it for 2 h before it started to decrease again. In this experiments, the amount of γ -Al₂O₃ in the formulation of the catalyst is lower (7.5% wt. of γ -Al₂O₃), so the time required to observe the drop in conversion and to desorb water is lower. As in the previous experiment, selectivity was constant despite changes in conversion (62.7% to DME, 35.8% to CO₂ and 4.1% to methanol).

The importance of water in the direct synthesis of DME was also studied using a layered reactor. In this reactor, both catalysts are loaded in fixed-bed as two layers, instead of mixed: the methanol synthesis catalyst is placed in a first layer and then the methanol dehydration catalyst in a second one (in the flow direction). The reaction was performed at the same conditions than in the first experiment (70% wt. CuO/ZnO/Al₂O₃). Figure 4a compare the initial stability of both catalytic beds, mixed and layered, for the reaction at 250°C. It can be seen that, for the layered reactor, no abrupt decrease in conversion is observed; however, conversion is substantially lower (14% for the layered bed against 59% for the mixed one). Regarding to selectivity, the absence of the synergetic effect that takes place in the mixed reactor leads to a decrease on DME selectivity compared with the mixed reactor (from 69 to 63%), with the consequent increase in selectivity to methanol (from 0.1

to 9%). These values remain constant throughout the reaction time, so that deactivation by adsorption of water on the active centers is discarded.

In the mixed catalytic bed, the presence of both catalysts mixed in the same bed makes it possible that water formed as product in the synthesis of dimethyl ether reacts with carbon monoxide to produce carbon dioxide and hydrogen (water-gas-shift reaction catalyzed by CuO/ZnO/Al₂O₃). This synergetic effect does not take place in the layered reactor, where water is formed in the second layer and, since CuO/ZnO/Al₂O₃ catalyst is not present, it does not react by the water-gas-shift reaction and, therefore, does not shift the equilibrium of the overall reaction. For this reason, all the water formed in the dimethyl ether synthesis leaves the reactor with the outlet stream. This is supported by the analysis of the reactor outlet stream by MS. Figure 4b confirms that the amount of water during the reaction is greater for the layered reactor than in the mixed one. It results in a higher water amount at the outlet of the reactor, as well as a higher water desorption with nitrogen, significant in the signal of the MS analysis.

3.3. Catalyst deactivation

Once the adsorption of water over the catalyst surface reaches the saturation, conversion evolves more steadily. Anyway, it can be observed that a progressive decrease on conversion takes place during the next hours of reaction, though it is very slight at some operating conditions.

Figure 5 depicts the evolution of conversion with time for different catalyst fractions (70, 85 and 92.5% wt. CuO/ZnO/Al₂O₃, rest γ -Al₂O₃) and temperatures, 250°C and 270°C. The influence of temperature on deactivation rate was small, though at high temperature deactivation was slightly more pronounced. For example, conversion decreased about a 1.1% in 15 hours when the reaction is performed over a 70% wt. CuO/ZnO/Al₂O₃ catalytic bed at 250°C, and 2.7% at 270°C. Selectivity is not affected for the decreasing on conversion (68.7% to DME and 31.5% to CO₂ at 250°C; and 64.7% to DME and 34.6% to CO₂ at 270°C). On the contrary, there is an important influence of the CuO/ZnO/Al₂O₃ catalyst fraction on the deactivation of the catalytic bed. A greater loss of activity was detected for a reaction under the same operating conditions when the catalyst bed is composed of a higher

percentage of methanol synthesis catalyst. After 15 hours on stream at 250°C, the 92.5% wt. of CuO/ZnO/Al₂O₃ catalyst mixture suffered a loss of conversion of 4%, while for the 70% wt. CuO/ZnO/Al₂O₃ catalyst mixture the decrease was only a 1.1%. Selectivity were 61.6% to DME, 34.5% to CO₂ and 4.0% to methanol when reaction was performed at 250°C; and 61.8% to DME, 37.2% to CO₂ and 2.8% to methanol at 270°C for the 92.5% wt. of CuO/ZnO/Al₂O₃ catalyst mixture. Similarly, with the 85% wt. of CuO/ZnO/Al₂O₃ catalyst mixture selectivities were 66.1% to DME, 30.3% to CO₂ and 3.1% to methanol at 250°C; and 65.5% to DME, 32.4% to CO₂ and 2.3% to methanol at 270°C.

The specific surface area, calculated by the Brunauer-Emmett-Teller (BET) method, slightly decrease for all the catalyst mixtures studied (between 5 and 15%) after using the catalyts (Table S1 of Supporting Information). The pore distribution of the used samples shows a decrease on the pore volume of both catalysts in the mixture, with a reduction of 6.1% attributed to CuO/ZnO/Al₂O₃ pores and 10% to γ -Al₂O₃ pores (Figure S2 of Supporting Information). This decrease, thought being small, can be attributed to the presence of carbonaceous species adsorbed on the catalyst surface of both catalysts of the mixture. To confirm this statement, a temperature-programmed oxidation (TPO) test was performed *in situ* in the reactor. The catalyst sample had been used for a long period of reaction (110 h on-stream) and was not extracted from the reactor or previously exposed to oxidatant conditions (e.g. air). In the TPO test, the sample was exposed to a gas steam containing 4% O₂ (N₂ balance) while temperature was increased from 20°C to 550°C at a rate of 2°C min⁻¹.

Figure 6 shows the signal corresponding to CO₂ in the mass spectrometer. The profile consists of two peaks, corresponding to different types of carbonaceous species on the catalyst [30, 40], as it was previously determined in the surface area analysis. The first peak occurs at low temperature, 180-190°C, and could be attributed to carbonaceous species deposited over the metallic function or the interface between the metallic sites and the Al₂O₃ support. The oxidation takes place at a lower temperature, because the metal acts as catalyst of the oxidation reaction [44, 45]. The second peak, at higher temperatures around 340°C, is assigned to the oxidation of the carbonaceous species deposited over the acid function of the catalyst, γ -Al₂O₃. The nature of the carbonaceous species is non-graphitic, since all of them can be removed at relatively low temperatures (<375°C) [46]. These values are similar to those reported by Sierra et al. [30, 36], where a first peak at 210-260°C, and a

second one at 330-400°C, were detected. The slight discrepancies on temperatures might be attributed to a different amount of coke deposited and some differences on the equipment where the experiment was performed.

Previous works suggested that coke initially deposits on the metallic sites and on the interphase between the metal and the support. As time on stream elapses, the Al₂O₃ of the support is saturated and the deposition starts over the acid function [40]. Considering that the overall synthesis kinetics is controlled by the methanol synthesis and that, in this work, the acid function is in excess, the main reason of catalyst deactivation must be the deposition over the metal function. Copper sintering is discarded since temperature is maintained below the stability limit recommended by the supplier of the catalyst.

Establishing the suitable conditions for the catalyst regeneration is a key factor in the improvement of the process and has to be taken into account in the design of the system. Previous studies found that the removal of carbonaceous species by combustion can be carried out without sintering the metallic phase [27, 30].

3.4. Modelling of catalyst deactivation

The experimental results, Figure 5, show that the rate of deactivation is higher when conversion is high (e.g. high fraction of CuO/ZnO/Al₂O₃ catalyst). At these conditions, higher DME and methanol concentration are present in the reaction medium. These compounds are responsible of the formation of carbonaceous species, since it is produced by the degradation of the methoxy ions generated from oxygenates in the reaction medium [39, 40, 47]. Several studies confirmed this degradation as the cause of deactivation in methanol to hydrocarbons process, and also takes place in similar reactions as those involved in syngas transformation to methanol, to gasoline, Fischer-Tropsch synthesis, or methanation reaction [40, 48]. According to this, the deactivation model proposed in this work includes the concentration of DME and methanol. A term for taking into account the inhibitory effect of water on catalyst deactivation has been also considered in the denominator of eq. (6):

$$-\frac{da}{dt} = \left(\frac{k_d(f_{DME} + f_{CH_3OH})}{1 + K_{H_2O}f_{H_2O}} \right) a \quad (6)$$

The catalyst deactivation has been modelled as a kinetic of pseudo-first order, relating directly the loss of activity of the catalyst with its time on reaction. Since the methanol dehydration catalyst ($\gamma\text{-Al}_2\text{O}_3$) is in excess and reaction IV, in which it participates, is practically in equilibrium, the deactivation model has been applied only to determine the CuO/ZnO/Al₂O₃ catalyst activity, maintaining a value of $a = 1$ for the $\gamma\text{-Al}_2\text{O}_3$ catalyst in all the experiments. Studies available on literature show that coke deposition over CuO/ZnO/Al₂O₃ is a deactivation phenomena which is well-represented by a first order kinetic with respect to the activity. This model is based on that proposed by Sierra *et al.*[39], who related the loss of activity with time by means of a deactivation constant, including the effect of water. In their study, different kinetic models were proposed for deactivation and the best fit was shown to be for a model which considers that deactivation occurs by degradation of the oxygenate compounds (methanol/DME) in series with the main reaction scheme.

Since reaction time is considerably lower than deactivation time, the deactivation model can be solved independently of the reactor model. Hence, assuming little change upon time in the concentration of DME, methanol and water, eq. (6) can be easily integrated as: $a = a_0 e^{-k'_d t}$, where a_0 is the activity of the catalyst at the beginning of the experiment and $k'_d = k_d (f_{\text{DME}} + f_{\text{CH}_3\text{OH}}) / (1 + K_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}})$. This expression is incorporated to eq. (5) and the kinetic model of Table 1 to predict the evolution with time of the catalyst activity. In order to calculate the evolution of conversion upon time, the reactor model is solved in each time interval, using the corresponding activity calculated from the integrated expression. The apparent deactivation constant k'_d is evaluated at the corresponding concentrations encountered at each point along the axial coordinate of the reactor.

According to this procedure, the experimental data of Figure 5, corresponding to two temperatures and three catalyst mixtures, has been used to fit the deactivation constant of the proposed model. Very little dependence with temperature was observed for this constant, and the average value for all the experiment was $k_d = 0.011 \pm 0.001 \text{ h}^{-1} \text{ bar}^{-1}$. The model predictions are depicted in Figure 5. As observed, the model exhibits a good agreement with the experiments.

The rate of deactivation is observed to be higher at high temperature and for high fraction of CuO/ZnO/Al₂O₃ catalyst. The effect of temperature alone may be explained by the temperature dependence of the deactivation constant. However, the most pronounced influence on deactivation corresponds to the fraction of CuO/ZnO/Al₂O₃ catalyst. Both factors contribute to increase reaction rate and conversion, as observed in Figure 5, which determines higher product (DME/methanol) concentration in the reaction media. These compounds are responsible of the formation of carbonaceous species, as reported in the TPO test.

The deactivation model has also been used to fit the deactivation observed during an additional set of experiments carried out using only the CuO/ZnO/Al₂O₃ catalyst (e.g. only the methanol synthesis reaction). The reaction was performed in the same operating conditions than the previous experiments: feed of 40% CO and 60% H₂ (% mol), 250°C, 30 bar, and 0.14 kg_{cat} h/Nm³ space time.

Figure 7 shows the evolution with time of conversion. The absence of γ -Al₂O₃ leads on lower CO conversion, about 9.3%, with methanol and CO₂ as the main products (64.3% selectivity to methanol). The synergistic effect achieved by the interaction of the metal and acid functions in the direct synthesis of DME does not take place in this reaction, so there is no displacement of the reaction equilibrium, which affects CO conversion.

The same deactivation model has been applied to this experiment, resulting in a value of $k_d = 0.027 \pm 0.001 \text{ h}^{-1} \text{ bar}^{-1}$. The model predictions are shown as solid lines in Figure 7 and confirm the good fit of the model to the experimental results. It can be observed that the value of the deactivation constant and, consequently, the deactivation rate, is higher for the case of methanol. This fact can be attributed to the role of water in the synthesis of dimethyl ether. As it was proved in the present work, water has a negative competitive inhibitory effect on the synthesis reaction leading to lower yields. This effect is reversible and can be shifted by an increase in temperature. However, water has also the capacity to avoid the formation or even desorb the carbonaceous species responsible of the observed deactivation. This fact explains that the specific deactivation constant observed in the synthesis of methanol is 2.5 times higher than that of dimethyl ether (0.011 h⁻¹ bar⁻¹ against 0.027 h⁻¹ bar⁻¹).

3.5. Catalyst deactivation: model validation

The aim of this section is to test the adequacy of the deactivation model previously fitted. To do this, the model is used to predict catalyst deactivation for long periods of time. Figure 8 shows the predictions for the experiments with 85% wt. (a) and 92.5% wt. (b) of CuO/ZnO/Al₂O₃ and compares them with the experimental data. In both cases, the reaction time considered is greater than 60 hours. During this time, the catalyst was exposed to different conditions of temperature and space time. Only the experiments at reference conditions of 250-260°C, 30 bar, H₂/CO molar ratio = 1.5, and space time respect to CuO/ZnO/Al₂O₃ of 0.14 kg_{cat} h/Nm³ are depicted. The blank gaps in Figure 8 correspond to experiments in-between where conversion varied due to a kinetic effect in reaction rate, as a result of changes in pressure, feed concentrations and other operating variables. These points were removed from the figure but taken into consideration, at the corresponding conditions of these tests, for the model predictions.

According to the proposed model, deactivation only depends on reaction time and DME, methanol and water concentrations. As a result, the different concentrations along the reactor were used to calculate the apparent deactivation constant of each time interval and, hence, the cumulative deactivation.

The first set of experimental data points of Figure 8 (first 20 h) are those previously used in the fitting of the model (Figure 5). The rest data were not used in the previous fit and, hence, are suitable for the validation of the model. It can be seen that the model predicts in a good way the rate of deactivation, despite the different intermediate reaction conditions and longer period of time. This confirms that catalyst deactivation is only dependent of the concentration of oxygenate compounds and water in the reaction media, as proposed by our model.

Conclusions

Although the direct synthesis of DME from syngas is a promising route for the commercial production of DME, the deactivation of the catalyst can be an issue. In the present work, the

main reasons of this loss of activity have been studied experimentally for a mechanical mixture of CuO/ZnO/Al₂O₃ and γ -Al₂O₃ catalysts.

Stability studies at 250°C showed an abrupt conversion drop after a few hours of operation. It was demonstrated that this drop was caused by the adsorption of water on the catalyst. This inhibitory effect is reversible and temperature-sensitive: at 270°C was not observed, so this temperature is the most adequate to carry out the reaction. Higher temperatures could not be tested because they lead to irreversible deactivation due to Cu sintering.

The catalyst also exhibited long-term deactivation caused by deposition of two types of carbonaceous species. This decrease on activity was found to be affected by the concentration of oxygenate compounds (methanol and dimethyl ether) and water, rather than temperature.

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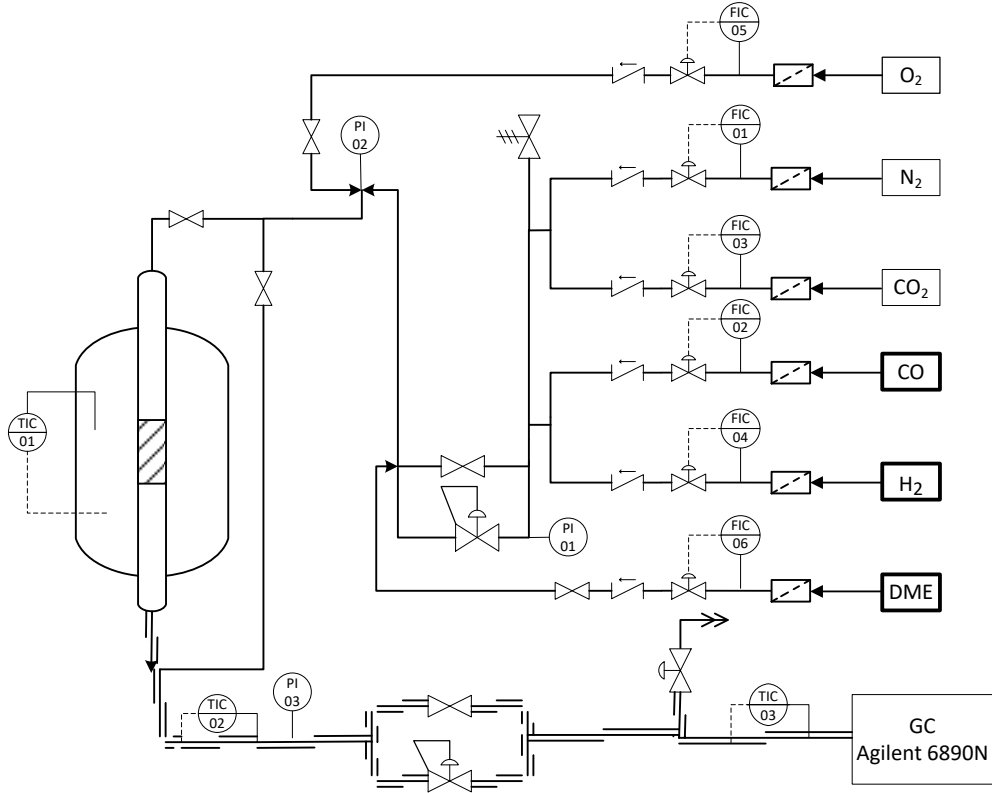
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Figures

a)



b)

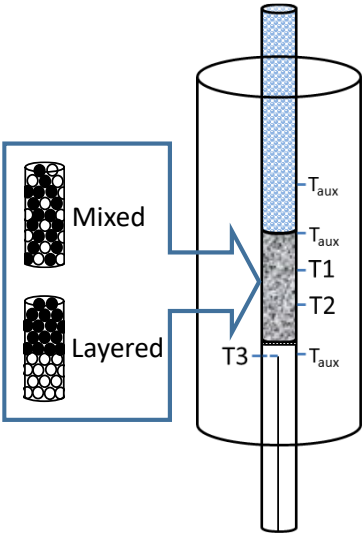
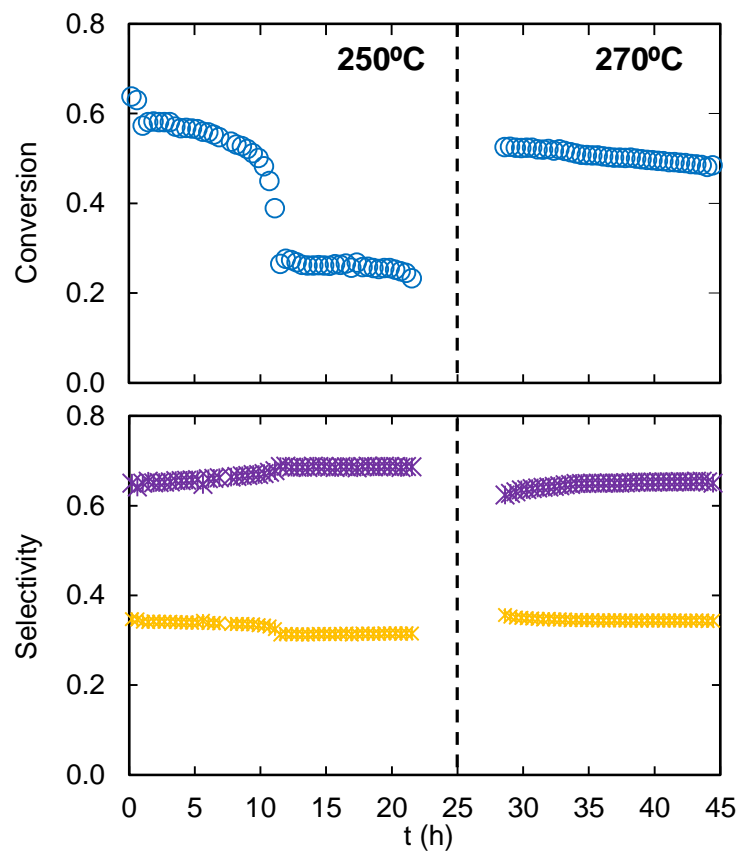


Figure 1. Flowsheet of the experimental device: a) Global diagram, b) Reactor detail with thermocouples position and catalytic bed configurations.

a)



b)

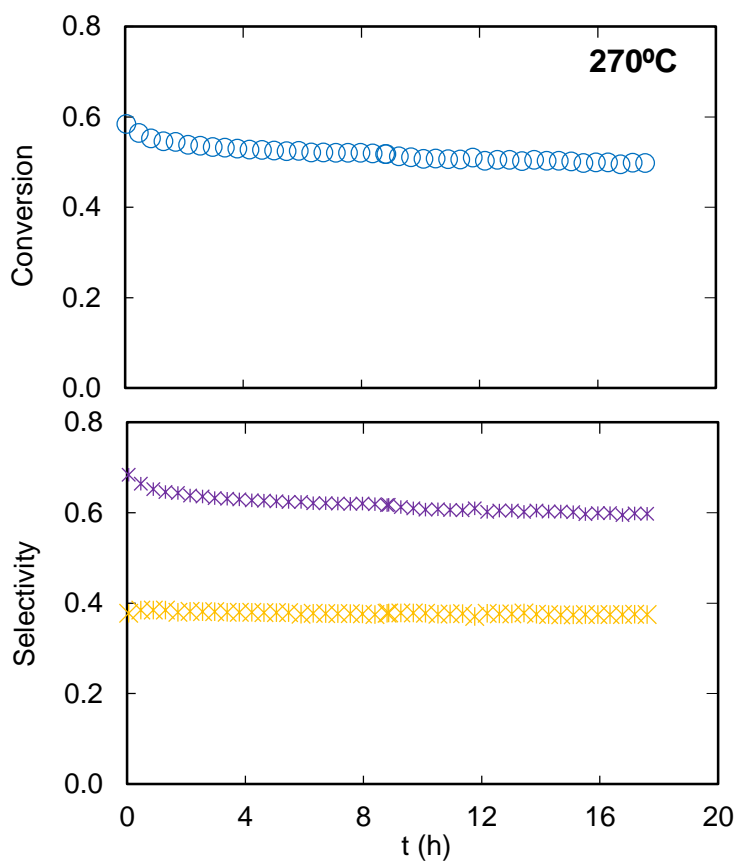
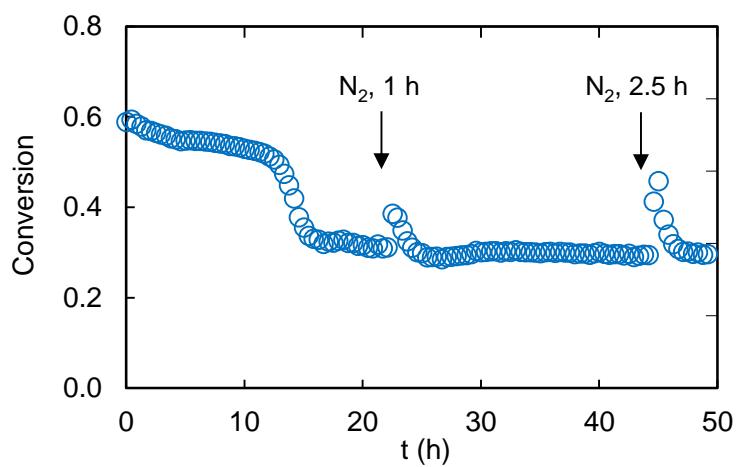


Figure 2. Initial stabilization of the CuO/ZnO/Al₂O₃ catalyst in the direct synthesis of dimethyl ether at different temperatures (CO conversion (○) and selectivities to DME (✱) and CO₂ (✱)): a) 250°C, then increasing to 270°C, and b) 270°C. Operating conditions: 30 bar, H₂/CO = 1.5, 0.20 kg_{cat} h/Nm³ (70 wt.% of CuO/ZnO/Al₂O₃).

a)



b)

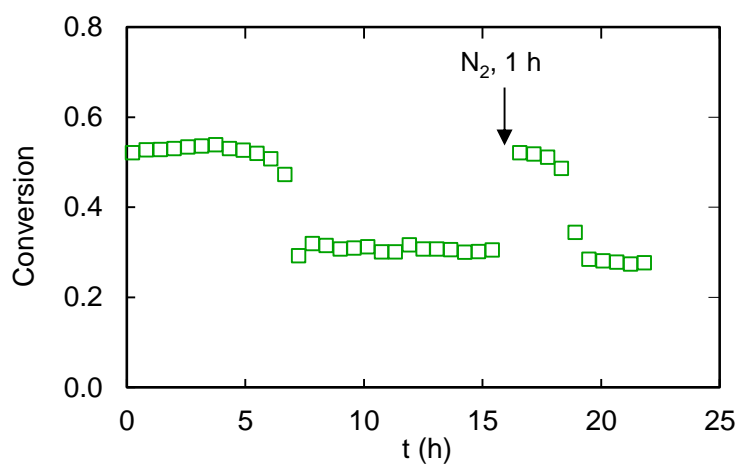
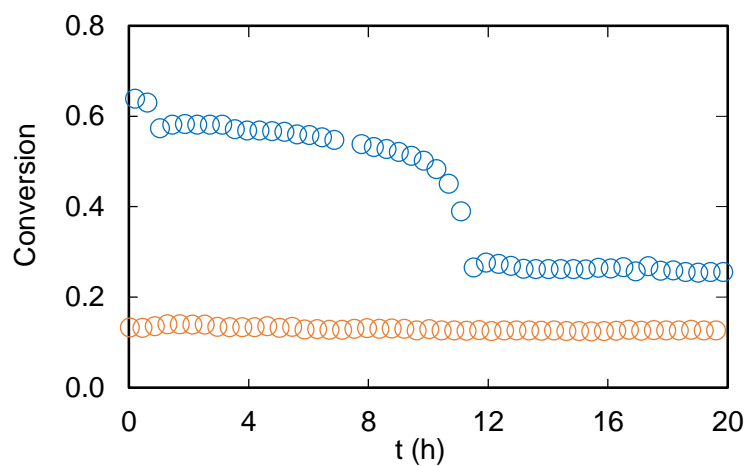


Figure 3. Water desorption cycles with N_2 for the catalyst mixtures of reactions performed at 30 bar, 250°C, H_2/CO molar ratio: 1.5, and a space time with respect to $CuO/ZnO/Al_2O_3$ of $0.14 \text{ kg}_{\text{cat}} \text{ h}/\text{Nm}^3$. Fraction of $CuO/ZnO/Al_2O_3$ in the mixture: a) 70% (\circ), b) 92.5% (\square).

a)



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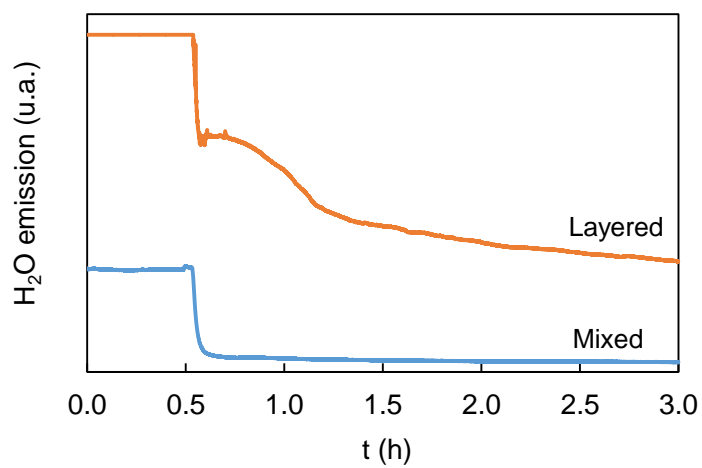
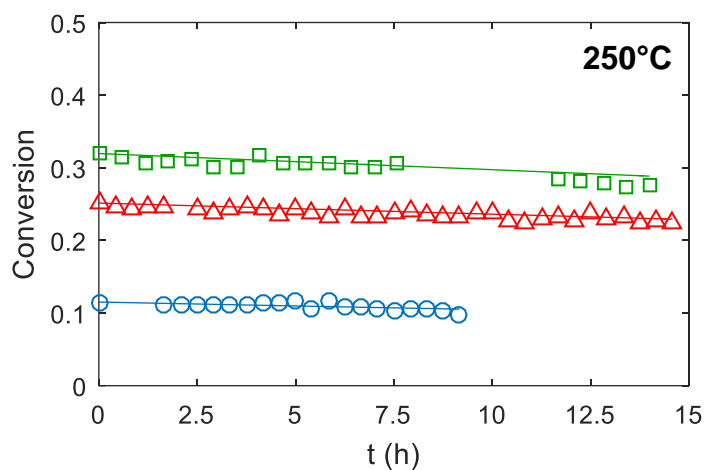


Figure 4. a) Conversion profile for initial catalyst stabilization in the mixed (○) and layered (○) reactors, b) MS signal for water desorption cycles with N₂ for the same reactors. Operating conditions: 30 bar, 250°C, H₂/CO molar ratio: 1.5, and a space time 0.20 kg_{cat} h/Nm³ (70% fraction of CuO/ZnO/Al₂O₃).

a)



b)

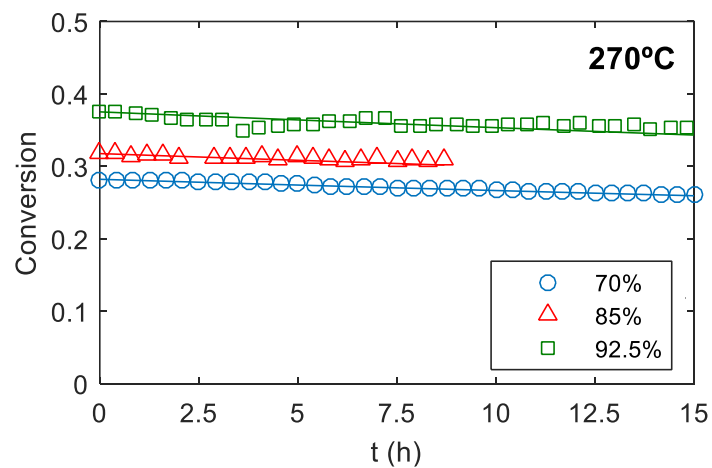


Figure 5. Stability of the CuO/ZnO/Al₂O₃ catalyst in the direct synthesis of dimethyl ether. Operating conditions: 30 bar, 60% H₂, 40% CO and space time with respect to CuO/ZnO/Al₂O₃ of 0.14 kg_{cat} h/Nm³. Fraction of CuO/ZnO/Al₂O₃ in the mixture: 70% (○), 85% (△) and 92.5% (□). Temperature: a) 250°C, b) 270°C. Symbols: experiments. Lines: model fitting.

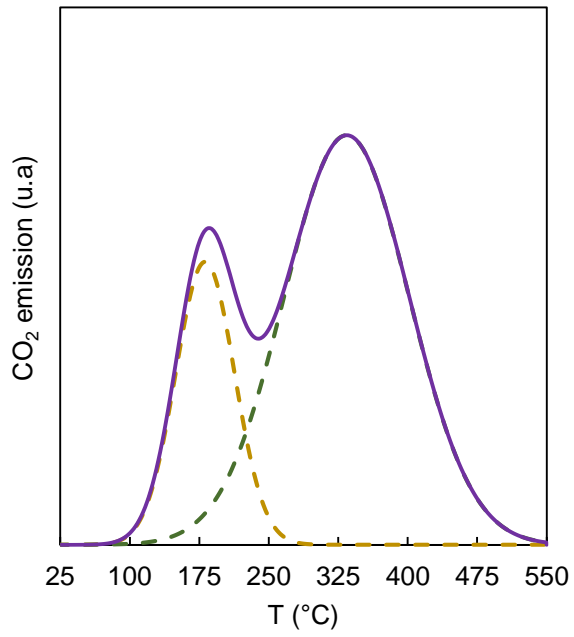


Figure 6. TPO analysis of the catalyst after being used in the reaction. Reaction conditions: 70% wt. of CuO/ZnO/Al₂O₃ catalyst; 250-270°C; 30 bar; H₂/CO molar ratio: 1.5; space time: 0.20 kg_{cat} h/Nm³; time on stream: 110 h.

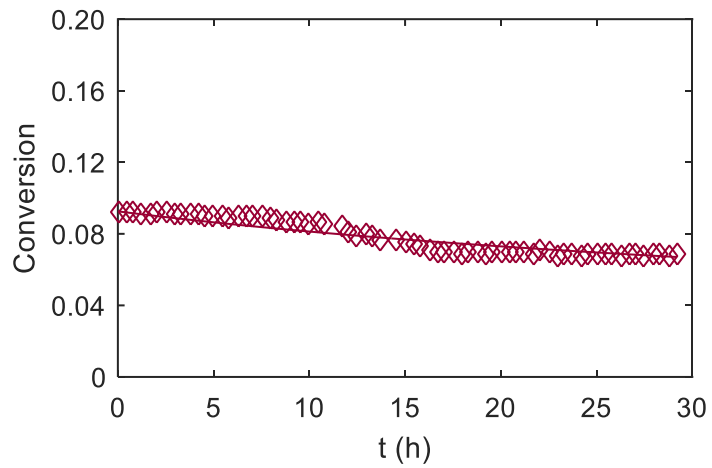


Figure 7. Stability of the CuO/ZnO/Al₂O₃ catalyst in methanol synthesis. Reaction conditions: 250°C; 30 bar; H₂/CO molar ratio: 1.5; space time with respect to CuO/ZnO/Al₂O₃: 0.14 kg_{cat} h/Nm³. Symbols: experiments. Line: model fitting.

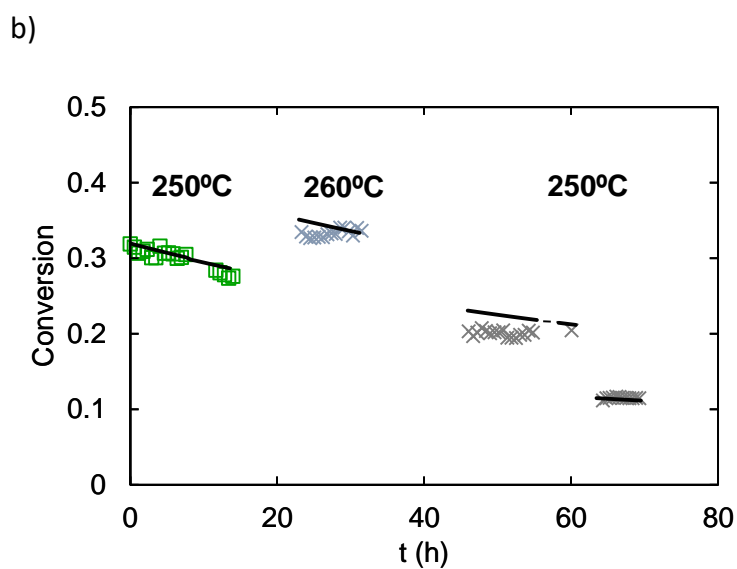
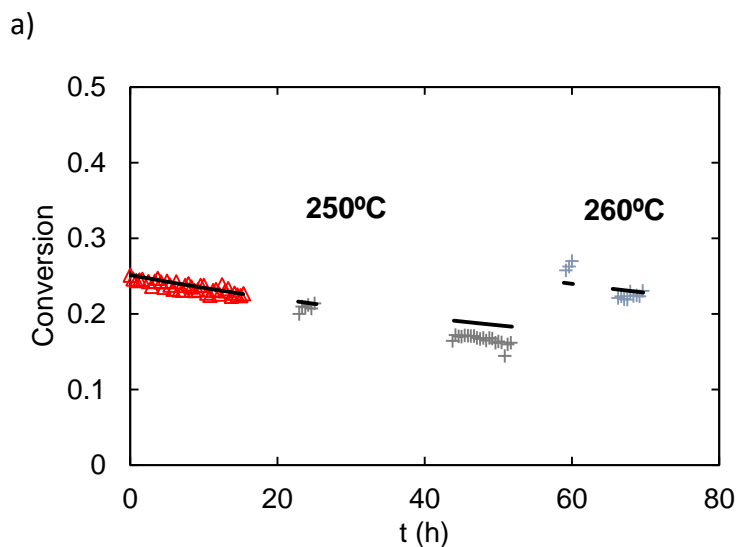


Figure 8. Catalyst loss of activity for long times of reaction. Reaction conditions: 250-260°C; 30 bar; H₂/CO molar ratio: 1.5; space time with respect to CuO/ZnO/Al₂O₃: 0.14 kg_{cat} h/Nm³. Fraction of CuO/ZnO/Al₂O₃ in the mixture: a) 85% (\triangle : data used in the fitting of the model, \dagger : data for the validation of the model); and b) 92.5% (\square : data used in the fitting of the model, \times : data for the validation of the model). Symbols: experiments. Lines: model fitting.