

Optimum water/syngas molar ratio in the feed for minimizing deactivation by coke in the single step synthesis of DME

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Optimum water/syngas molar ratio in the feed for minimizing deactivation by coke in the single step synthesis of DME

I. Sierra, J. Ereña, A. T. Aguayo, J. M. Arandes, M. Olazar, J. Bilbao

Departamento de Ingeniería Química, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain. Phone: +34-94-6015363, Fax: +34-94-6013500, e-mail: javier.arena@ehu.es

Abstract

This paper deals with the one-step synthesis of dimethyl ether (DME) from mixtures of H₂ and CO in a fixed bed reactor over CuO-ZnO-Al₂O₃/γ-Al₂O₃ bifunctional catalysts. Deactivation by coke deposition, which is severe in this process, leads to a pronounced decrease in DME yield and selectivity with time on stream. Coke formation may be limited by using the strategy of co-feeding water with syngas. Nevertheless, water in the feed has an unfavourable effect in the initial yield of DME, due to the thermodynamics of the overall reaction and to the water adsorption capacity of the acidic function γ-Al₂O₃. Taking this effect into account, a serie of experiments with different water/syngas molar ratios in the feed has been carried out. It has been found that a water/syngas molar ratio of 0.20 effectively reduces deactivation by coke without a significant decrease in the initial activity of the catalyst.

Keywords: dimethyl ether, syngas, catalyst deactivation, coke

1. Introduction

Considerable attention is being paid in the literature to the synthesis of dimethyl ether (DME) due to its potential use as multi-purpose fuel. DME is considered to be one of the clean fuels with greater potential for being used in the medium term, in order to reduce the dependency on petroleum and to use alternative sources to oil, such as natural gas, coal and biomass (Semelsberger et al., 2006). DME is an alternative clean fuel for diesel engines, due to its high cetane number and much lower NO_x emission, near-zero smoke production and less engine noise compared to conventional diesel fuels (Arkharov et al., 2003; Bo et al., 2006). Moreover, DME is easily liquefied (can be stored and distributed using LPG handling technology) and it is an strategic raw material that may be a substitute for methanol in obtaining olefins and for the

production of H₂ for fuel cells by hydrolysis and reforming (Adachi et al., 2000; Galvita et al. 2001; Semelsberger et al., 2005; Yu et al., 2005).

Three reactions take place in the syngas-to-DME process:

Methanol synthesis from CO and H₂:



Methanol dehydration reaction:



Water gas shift reaction:



There are two different ways for the transformation of syngas to DME: (a) in two reaction steps, firstly, synthesis of methanol over a metallic function (composed of oxides such as CuO, ZnO, Al₂O₃ and Cr₂O₃) and, subsequently, dehydration of methanol to DME over an acidic function (such as γ -Al₂O₃, NaHZSM-5 and HY zeolites or SAPOs) and (b) synthesis in one reaction step, over a bifunctional catalyst provided with the two functions. The synthesis of DME in one reaction step improves the DME yield over the two-step process (the dehydration of methanol displaces the equilibrium of methanol synthesis reaction, due to its continuous removal by the dehydration reaction) and has better perspectives for CO₂ incorporation in the feed (Ng et al., 1999; Takeguchi et al., 2000; Kim et al., 2004).

There are several studies in the literature concerning the effect of operating conditions in the synthesis of DME over bifunctional catalysts. Peng et al. (1999) reported that the optimum H₂/CO ratio for the synthesis of methanol is 2/1, while for the synthesis of DME the optimum ratio is between 1/1 and 2/1, depending on the operating conditions and the catalyst. Consequently, the synthesis of DME allows for a more flexible operation regarding H₂ requirement, and, since a higher concentration of CO can be used, makes it possible an easier integration of the processes of synthesis gas production by methane reforming and coal gasification.

In recent works, the effect of feed composition in the synthesis of DME from mixtures of (H₂+CO), (H₂+CO₂) and (H₂+CO+CO₂) has been studied, using CuO-ZnO-Al₂O₃/ γ -Al₂O₃ and CuO-ZnO-Al₂O₃/NaHZSM-5 bifunctional catalysts (Ereña et al., 2005a,b). The results show the good performance of the catalyst based on γ -Al₂O₃ for the synthesis of DME from (H₂+CO) and the advantages of the acidic function NaHZSM-5 from mixtures of (H₂+CO₂) and, in general, when water concentration in the reaction medium is high, as this acidic function is not affected by water adsorption. Conversion is total at 275 °C and 40 bar, with a selectivity to DME of 80 % and a yield of DME of 78 %, for a space time of 67 (g of catalyst) h (mol of reactants)⁻¹ and for a feed made up of H₂/CO= 2/1.

Despite the interest of the DME synthesis process in one reaction step over bifunctional catalysts, its industrial implementation requires the optimization of the

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operating conditions and a more accurate design of the reactor, using a kinetic model which takes into account the deactivation of the catalyst. Aguayo et al. (2007), using an extensive experimental database, have proposed a kinetic model at zero time on stream for the synthesis of DME over a CuO-ZnO-Al₂O₃/γ-Al₂O₃ bifunctional catalyst.

There are few studies in the literature concerning the deactivation of the catalyst in the one-step synthesis of DME. The loss of activity of the catalyst due to coke deposition is severe in this process, which gives way to a pronounced decrease in the yield of DME with time on stream. In addition to the deposition of coke, there are other possible ways of deactivation: (a) sintering of the CuO of the metallic function, which limits the operating and the regeneration (by coke combustion) temperature at values below 300 °C (Kung, 1992) and (b) the irreversible adsorption of water on the acid sites of γ-Al₂O₃ (Gayubo et al., 2002).

This paper approaches the viability of co-feeding water with the syngas as an efficient strategy for minimizing deactivation by coke. However, this strategy of co-feeding water has the inconvenience of reducing the initial DME yield, due to the thermodynamic limitations of the reaction and to the adsorption of water in the acidic function (Aguayo et al., 2005). Thus, the main objective of this paper is to find the optimum water/syngas molar ratio in the reactor feed.

In this work, a tapered element oscillating microbalance (TEOM) has been used to measure the coke content in deactivated catalysts, in order to investigate the origin of their loss of properties with time on stream. TEOM results have been compared to those obtained by the conventional TGA technique.

2. Experimental

The hybrid catalyst is composed of a metallic function to carry out the hydrogenation of CO to produce methanol (CuO-ZnO-Al₂O₃) and an acidic function for the dehydration of methanol to DME (γ-Al₂O₃).

The metallic function has been prepared by coprecipitation of the corresponding metallic nitrates with a solution of Na₂CO₃ at pH= 7.0, following the method proposed by Garoña (2006). The γ-Al₂O₃ acidic function has been prepared by the coprecipitation of a NaAlO₂ suspension with HCl at 70 °C until pH reaches a value of 9.0. The following steps are the aging of the catalyst at 70 °C during 1 h, filtering, washing, drying (at 20 °C and at 120 °C during 12 h each step) and calcination (550 °C, 2 h). This function has low acid strength, in order to minimize the production of light olefins and heavy hydrocarbons.

The bifunctional catalyst has been prepared by mixing the dry metallic function and the acidic function in an aqueous solution at a ratio of 2/1 by mass, which is the ratio that provides the best performance of the catalyst. This preparation method provides the highest values of CO conversion and DME selectivity and yield (Aguayo et al.,

2005; Ereña et al. 2005a,b). According to this preparation method, subsequent to the mixing of the metallic and acidic functions, the suspension is filtered and the solid is washed, dried (in two steps, at 20 °C and 120 °C for 12 h each step) and calcined (300 °C, 6 h). Prior to use, the bifunctional catalyst is subjected to an equilibration treatment by oxidation-reduction in the reactor itself, which consists of exposing it to a stream of hydrogen diluted in helium at 200 °C for 14 h.

The reaction equipment used, PID Eng. & Tech. Microactivity-Reference, is provided with a fixed bed and allows for operating at high temperatures and pressures. The on-line analysis of the reaction products has been carried out by means of a Varian CP-4900 gas micro-chromatograph.

Runs have been carried out at a temperature of 275 °C (low enough to avoid CuO sintering), under 30 bar (not too high, in order to limit water adsorption on the acidic function), feeding a mixture of (H₂+CO) with a molar ratio of 3/1, with a small amount of water at different concentrations. Four different feeds have been used: feed A: (H₂+CO), without water; feed B: (H₂+CO), with a water/syngas molar ratio of 0.08; feed C: (H₂+CO), with a water/syngas molar ratio of 0.20; feed D: (H₂+CO), with a water/syngas molar ratio of 0.60. The space time is 12.8 (g of catalyst) h (mol of reactants)⁻¹.

Coke content has been measured by means of an Agilent 3000A gas micro-chromatograph coupled to a tapered element oscillating microbalance (TEOM Series 1500 Pulse Mass Analyzer from Rupprecht & Patashnick Co.). TEOM is an inertial thermobalance in which mass changes are calculated by measuring the natural resonance frequency of a tapered quartz element containing the sample. TEOM microbalance has some advantages over the conventional thermogravimetric techniques: (i) a well-defined flow-through profile, avoiding bypass problems and possible heat and mass transfer resistance phenomena, in contrast to flow around and over the sample crucible in conventional microbalances, (ii) a very fast response time resolution (0.1 s), allowing the study of processes with fast kinetics, (iii) a high mass resolution (1×10^{-6} g) across the entire range of pressure and temperature, and (iv) the measurement of changes in inertia rather than weight allows for avoiding the influence of flow patterns of gas streams, buoyancy and other aerodynamic factors on the obtained data.

Although the TEOM was initially developed for measuring the concentration of particles in a gas (Patashnick and Rupprecht, 1991), it has been used for studying many processes in catalysis with great accuracy and reproducibility. This technique has been applied to different studies, including coking (Chen et al., 1996; Chen et al., 2000; Armor and Martenak, 2001; Lemonidou et al., 2004; Pérez-Ramírez et al., 2004; Christensen et al., 2006; Olafsen et al., 2006; Teschner et al., 2006), adsorption (Zhu et al., 1998; Giaya and Thompson, 2002; Smith et al., 2003; Lee et al., 2004a,b; Jalani et al., 2005), thermal decomposition (Pérez-Ramírez and Abelló, 2006) and redox processes (Urasaki et al., 2005). Nevertheless, works in which temperature-programmed oxidation (TPO) has been carried out by means of this novel technique to measure coke content are scarce.

The TEOM is loaded with 30-40 mg of sample, using quartz wool to keep the particles firmly packed. After sweeping with helium at 300 °C during 30 min (to remove physically adsorbed components), the temperature is increased from 100 to 600 °C at a heating rate of 3 °C/min. A flowrate of purge gas (He) and reaction gas (air) of 40 cm³/min (20 cm³/min each gas) has been used. The data of CO₂ formed during the combustion has been used to calculate carbon amount in coke, which practically corresponds to the total amount of coke in the catalyst.

Coke content has also been measured by means of EM Thermostar mass spectrometer (Balzers Instruments) coupled to SDT 2960 thermobalance (T.A. Instruments). Coke amount has also been determined from the evolution of the signal of CO₂. The physical properties of the fresh and deactivated catalysts have been measured by nitrogen adsorption-desorption in a Micromeritics ASAP 2000.

3. Results and discussion

The yield of organic compounds (Y_{OC} , by mass unit of carbon) has been defined as the sum of carbon contents corresponding to the organic products in the reactor outlet stream divided by the sum of molar flowrate of CO in the feed, $(n_{CO})_0$:

$$Y_{OC} = \frac{\sum_i n_{C_i} n_i + 2n_{DME} + n_{MeOH}}{(n_{CO})_0} 100 \quad (4)$$

where n_{C_i} is the number of carbon atoms for each of the hydrocarbons, n_i is the molar flowrate of these hydrocarbons and n_{DME} and n_{MeOH} are the molar flowrates of DME and of methanol in the outlet stream.

The DME yield (Y_{DME}) is calculated as the percentage of inorganic carbon fed in CO that converts to organic carbon in the product DME:

$$Y_{DME} = \frac{2n_{DME}}{(n_{CO})_0} 100 \quad (5)$$

The selectivity to DME (S_{DME}) is determined as the ratio (expressed in %) between the content of organic carbon in the product DME and the sum of organic carbon content present in the reactor outlet stream:

$$S_{DME} = \frac{2n_{DME}}{\sum_i n_{C_i} n_i + 2n_{DME} + n_{MeOH}} 100 \quad (6)$$

Figures 1 and 2 show the effect of feed composition on the evolution with time on stream of DME yield and selectivity. It is observed that when there is no water in the feed (feed A) or when its content in the reaction medium is low (feed B, water/syngas

molar ratio= 0.08), DME yield and selectivity decrease considerably with time on stream. This means that the bifunctional catalyst (especially the metallic function) is affected by coke deposition, which leads to a higher concentration of hydrocarbons (mainly in the C₁-C₇ range) in the reactor outlet stream.

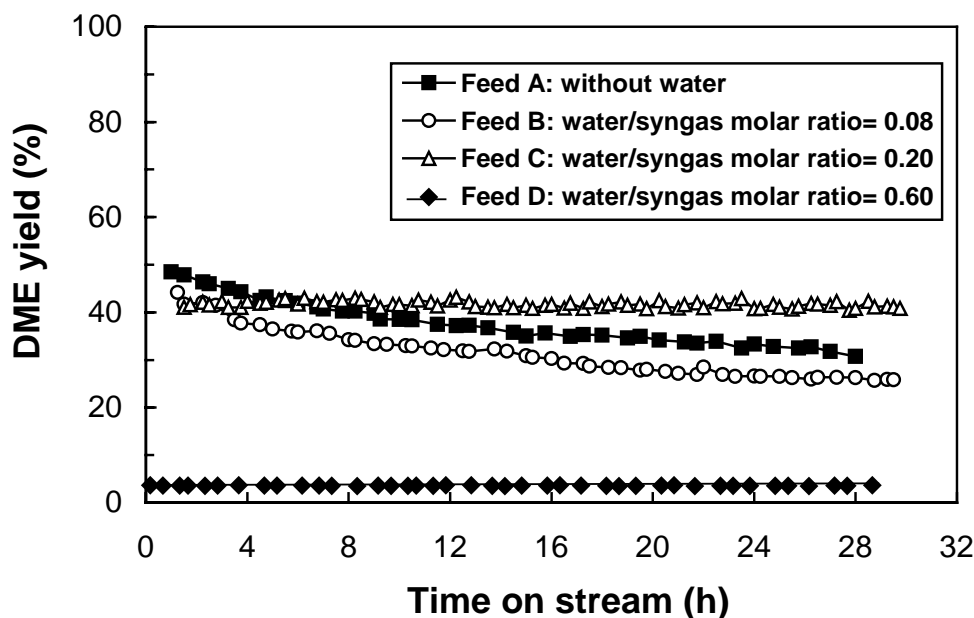


Figure 1. Evolution with time on stream of DME yield for different water/syngas molar ratios in the feed.

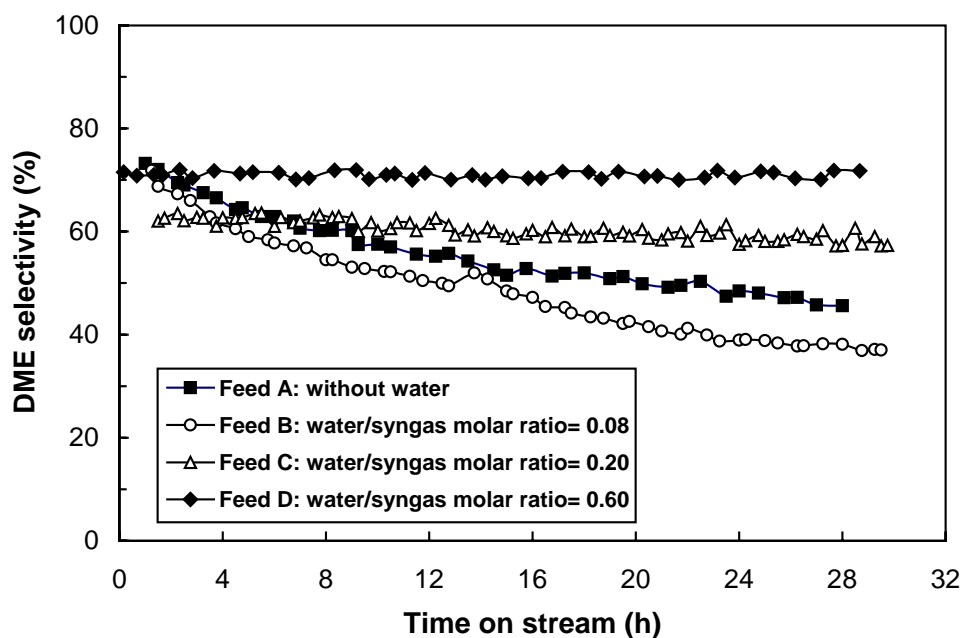


Figure 2. Evolution with time on stream of DME selectivity for different water/syngas molar ratios in the feed.

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A water/syngas molar ratio of 0.20 (feed C, corresponding to a water flowrate of 0.005 ml/min) effectively limits the loss of DME selectivity, as coking rate is considerably reduced. In this case, the decrease in the initial yield of DME due to the adsorption of water in the Lewis sites of the γ -Al₂O₃ is not significant.

A higher water/syngas molar ratio (Figures 1 and 2 show, as an example, the results for a ratio of 0.60, feed D) is not advisable, as the initial DME yield is severely affected. This is a consequence of the low yield of organic compounds for this feed, due mainly to the overall thermodynamics, unfavourably affected by such a high water concentration in the reaction medium. Nevertheless, for feed D DME selectivity has the highest values of all the feeds studied, which makes it clear that water adsorption at 30 bar is not so important as not to allow the small amount of methanol formed to be converted into DME, even for this high concentration of water.

These results are confirmed in Table 1, where the values of coke content on the catalyst for different feeds into the reactor are shown. Coke contents correspond to the average value between the measures in the TEOM and in the thermobalance. It is evident that coke deposition has a direct effect on the loss of properties of the bifunctional catalyst. Coke content is greatly reduced for feed C (due to the appropriate amount of water in the feed) and it is negligible for feed D.

Table 1: Effect of feed composition on the coke content on the catalyst (wt.%).

	Feed A	Feed B	Feed C	Feed D
Coke content (wt.%)	5.5	4.2	1.3	0.1

Figures 3 and 4 show the TPO profiles obtained in the TEOM and in the thermobalance for different feeds into the reactor. Coke content in the catalyst, as well as the shape of the TPO curves, are similar for both techniques.

The TPO profiles of deactivated catalysts consist of two peaks, which is in good agreement with the results in the literature for catalysts containing metals (Larsson et al., 1996; Pieck et al., 1997; Querini, 2000; Ma et al., 2002; Pieck et al., 2005). The low temperature peak (225-260 °C) is attributed to carbonaceous material deposited in the metal and its neighbourhood, whose combustion is assisted by the metal (copper, in this case). The second peak (310-370 °C) corresponds to the removal of coke deposited far from the metallic sites (on the Al₂O₃ support or on the acidic sites), which requires higher temperatures to be carried out.

For feed C two peaks of similar size are observed. When coke content increases (feed B), the peak associated with coke deposited near metallic sites increases to a greater extent than the high-temperature peak. Finally, for the maximum amount of coke (feed A), the size of the low-temperature peak is similar to that of feed B, while the second peak increases, leading to a pair of peaks of similar size. Taking these effects into account, it seems that the reactions which lead to the formation of coke take place more probably near the metallic sites of the catalyst. Nevertheless, there is also a part of the carbonaceous material located far from the metal. When coke content in the catalyst increases, a higher amount of this material is spread over the Al₂O₃ support,

leading to a higher proportion of the high-temperature coke, whose combustion is not favoured by metallic copper.

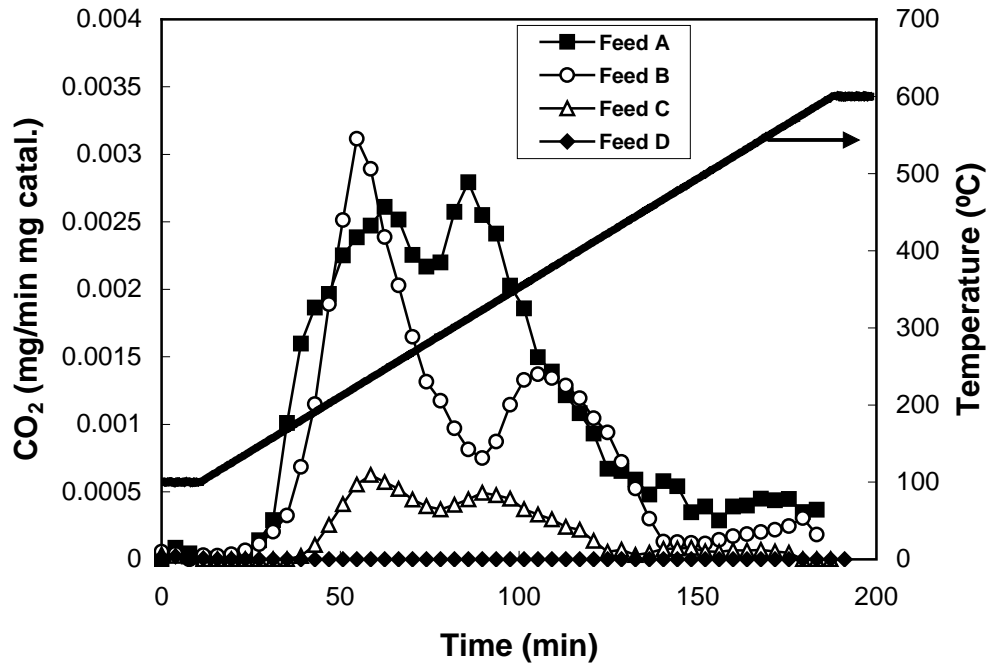


Figure 3. TPO profiles obtained in the TEOM for different feeds into the reactor.

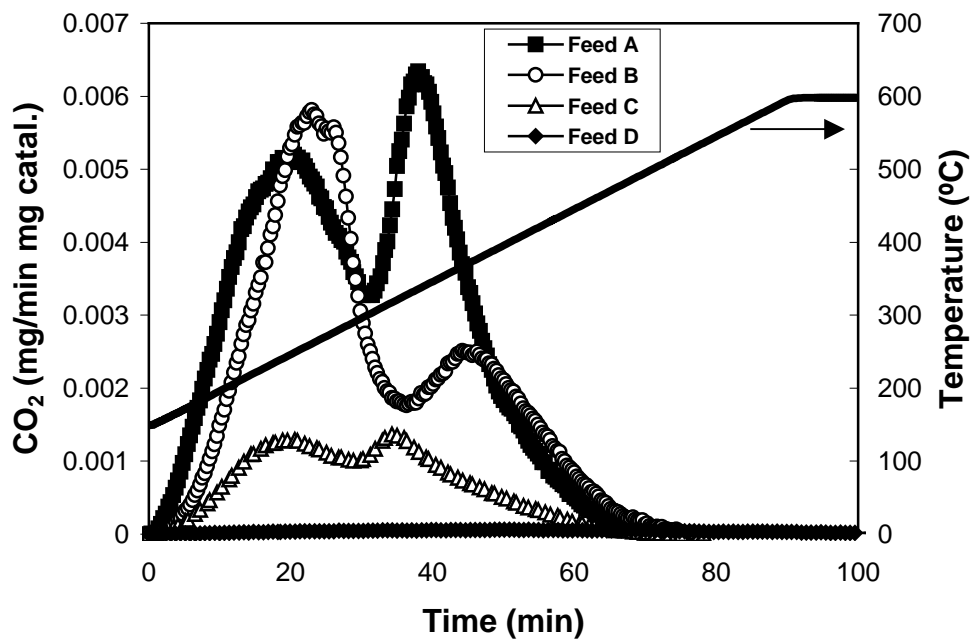


Figure 4. TPO profiles obtained in the conventional thermobalance for different feeds to the reactor.

Table 2 shows the physical properties of fresh and deactivated catalysts (after 30 h of time on stream). It is clear that an increase in the amount of carbonaceous deposits leads to a slight decrease on the BET surface area of the catalyst. On the other hand, an increase in water amount in the reaction medium has the effect of increasing the pore volume, due to the expansion of the pores.

Table 2: Effect of coke content on the physical properties of deactivated catalysts.

	Coke content (wt. %)	BET surface (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å)
Feed A	5.5	95.1	0.234	82.2
Feed B	4.2	97.4	0.257	85.1
Feed C	1.3	100.2	0.273	94.7
Feed D	0.1	104.2	0.294	109.3
Fresh catalyst	---	125.3	0.227	74.5

4. Conclusions

A water/syngas molar ratio of 0.20 (corresponding to a water flowrate of 0.005 ml/min) effectively reduces the deactivation by coke of the bifunctional catalyst (the DME yield hardly decreases with time on stream), without a significant decrease in the initial yield of DME. A higher water/syngas molar ratio is not advisable, as the initial DME yield is severely affected by the overall thermodynamics and water adsorption on the Lewis sites of the γ -Al₂O₃. Water/syngas molar ratios lower than 0.20 (e.g. 0.08) do not lead to an acceptable limitation of deactivation by coke. Coke deposition may be associated with methanol synthesis step and takes place, to a larger extent, over the metallic function of the catalyst.

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