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# Kinetic Modeling of Dimethyl Ether Synthesis in a Single Step on a CuO–ZnO–Al<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> Catalyst

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A kinetic model has been proposed for the synthesis of dimethyl ether in a single reaction step from (H<sub>2</sub> + CO) and (H<sub>2</sub> + CO<sub>2</sub>), and the kinetic parameters have been calculated for a CuO–ZnO–Al<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> bifunctional catalyst. The kinetic model suitably fits the experimental results obtained in an isothermal fixed bed reactor within a wide range of operating conditions: 225–325 °C; 10–40 bar; space time, 1.6–57.0 (g of catalyst) h (mol H<sub>2</sub>)<sup>−1</sup>. The crucial steps for modeling are the synthesis of methanol from (H<sub>2</sub> + CO)—synthesis from (H<sub>2</sub> + CO<sub>2</sub>) is not important—methanol dehydration (very fast), and the water-shift reaction (in equilibrium). The inhibiting effect of water is also taken into account in the synthesis of methanol and the formation of hydrocarbons. The advantage of carrying out methanol dehydration *in situ* is noteworthy, given that it allows for attaining yields higher than 60% of carbon converted into DME and 5% into methanol, when (H<sub>2</sub> + CO) is fed at 30 bar and 275 °C. At higher temperatures, hydrocarbons (mainly methane) are produced.

## 1. Introduction

Dimethyl ether (DME) has been used as a propellant and coolant, but great interest has currently been aroused regarding its use as a fuel, either for diesel engines or as a substitute for liquified petroleum gas (LPG) used as a household fuel in rural areas.<sup>1–4</sup> Easy transportation and handling make it a suitable hydrogen source for fuel cells.<sup>5</sup> This interest in DME is enhanced by the technological development of its production from oil alternative raw materials (coal, natural gas, and biomass) via synthesis gas,<sup>6–9</sup> which explains that the industrial implementation of DME synthesis is a priority in those geographic areas without oil sources but with coal or natural gas sources.<sup>7,10</sup> In such areas, in addition to its use as fuel, DME is contemplated as an alternative raw material to methanol for obtaining olefins (methanol to olefins (MTO) process).<sup>11</sup>

There are two strategies for the production of DME from synthesis gas: (i) a two-step process (methanol synthesis on a metallic catalyst and subsequent dehydration of methanol on an acid catalyst); (ii) a single step using a bifunctional catalyst. It is noteworthy that the steps in strategy i have been studied separately with the aim of attaining either methanol synthesis<sup>12</sup> or the production of DME, although in the latter case methanol dehydration is considered an intermediate step in the transformation of methanol into hydrocarbons.<sup>13–16</sup> The interest in CO<sub>2</sub> capture justifies the present efforts for its incorporation in methanol synthesis, given that it is a process involving high pressure requirements.<sup>17</sup> The selective transformation of methanol into DME has become an important objective, due to the aforementioned interest in DME.<sup>18,19</sup>

The main advantage of DME synthesis in a single step on a bifunctional catalyst is the lower thermodynamic limitation than methanol synthesis (due to the low concentration of methanol in the reaction medium, which shifts the thermodynamic equilibrium of methanol synthesis) and the fact that it can be carried out at higher temperature and lower pressure.<sup>20,21</sup> Consequently, CO<sub>2</sub> incorporation in the feed is more feasible than in the synthesis of methanol, given that it requires lower pressure.<sup>22,23</sup>

Contributions to the study of the integrated process of DME synthesis have been aimed at discriminating catalysts and gaining knowledge on the effect of operating conditions.<sup>24–29</sup> It has been proven that the selective dehydration of methanol is conditioned by the properties of the acid function of the bifunctional catalyst. Thus, a significant concentration of acid sites is required, but they should have a moderate strength in order to avoid the subsequent transformation of DME into C<sub>2</sub>–C<sub>4</sub> olefins and hydrocarbons of higher molecular weight.<sup>30–35</sup>

Studies focusing on the design of the reactor for single-step DME synthesis, either in a fixed bed<sup>36,37</sup> or fluidized bed,<sup>38</sup> have been carried out by combining literature kinetic models,<sup>39</sup> which have been proposed for methanol synthesis,<sup>40</sup> and for dehydration of the latter to DME.<sup>14,15</sup> The drawback of this approach is the use of kinetic models proposed for specific commercial catalysts (in the case of methanol synthesis, the process is commercially well-established) and certain given conditions specified for each one of the individual steps, which are different from those for the integrated process of DME synthesis.

In this paper, an original kinetic model is proposed for single-step DME synthesis based on experimental results obtained on a CuO–ZnO–Al<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst prepared for attaining high DME activity and selectivity.<sup>25,26,41</sup> Simple kinetic models with a clear physical meaning have been chosen for the single-step DME synthesis, and the thermodynamic equilibrium constants of the individual steps have been incorporated. Moreover, relevant aspects concerning process conditions of great significance in the kinetic modeling have been considered, as are the following: the inhibiting effect of water in the kinetic steps and the formation of hydrocarbons from synthesis gas. These peculiar circumstances of DME synthesis in a single step and especially the synergetic effect of *in situ* methanol transformation justify the need for a specific kinetic model for this process. Furthermore, the simplicity of the kinetic model for zero time on stream is an interesting objective, given that this model is to be the basis for establishing the kinetic model by coke deactivation in future papers. This model is essential for the design of the reactor and for establishing an optimum reaction-regeneration strategy that will condition the viability of the process at industrial scale.

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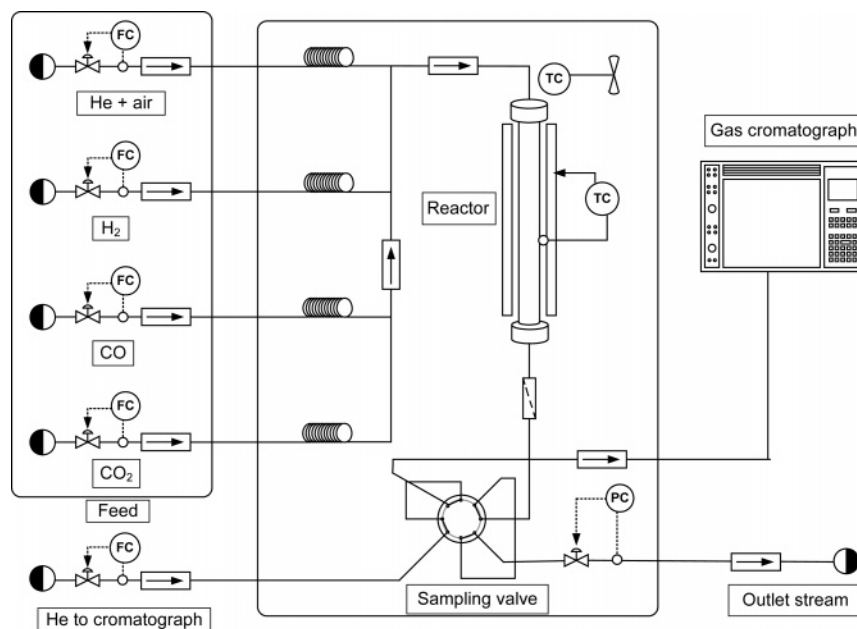


Figure 1. Reaction equipment.

Table 1. Properties of the Individual Functions of the Catalyst

catalyst	BET surface (m <sup>2</sup> g <sup>-1</sup> )	pore volume (cm <sup>3</sup> g <sup>-1</sup> )	average pore diameter (Å)
CuO–ZnO–Al <sub>2</sub> O <sub>3</sub>	90.8	0.54	172.2
γ-Al <sub>2</sub> O <sub>3</sub>	395.5	0.44	40.6

## 2. Experimental Section

**2.1. Catalysts.** CuO–ZnO–Al<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> bifunctional catalyst has been chosen because it has been extensively used in this process.<sup>42–44</sup> Furthermore, it is made up of metallic and acid functions, which perform well in the individual steps. Thus, CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> function has been widely used in the synthesis of methanol (in both fixed bed and slurry reactor)<sup>12,45</sup> and in the water–gas shift reaction.<sup>46</sup> The catalyst γ-Al<sub>2</sub>O<sub>3</sub> is the standard one in the selective dehydration of methanol to DME.<sup>18,47–50</sup>

The CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> metallic function has been prepared by coprecipitation at pH 7.0 of the corresponding nitrates with Na<sub>2</sub>CO<sub>3</sub>. The γ-Al<sub>2</sub>O<sub>3</sub> acid function has been prepared by precipitation of 0.5 M NaAlO<sub>2</sub> solution with 2 M HCl under well-established conditions in the literature.<sup>42</sup> Table 1 sets out the physical properties of the metallic function and of the acidic function of the catalyst determined by nitrogen adsorption–desorption (Micromeritics ASAP 2000).

The bifunctional catalyst has been prepared by mixing the dry metallic function and the acidic function in aqueous suspension. This suspension is filtered, and the solid is washed, dried (in two steps, at 20 and 120 °C, for 12 h each), and calcined (300 °C, 6 h). A mass ratio of 2:1 has been chosen between the metallic function and the acid one, which is appropriate for ensuring that the limiting step is methanol synthesis.<sup>25</sup> Maximum synergism is thus attained, given that methanol is totally transformed into DME. The catalyst has an acidity of 0.03 (mmol of NH<sub>3</sub>) g<sup>-1</sup>, determined by temperature-programmed desorption (TPD) of NH<sub>3</sub> at 150 °C. The atomic ratio Cu:Zn:Al = 2.1:1.0:2.9 has been determined by X-ray fluorescence (Philips Minipal PW4025).

Prior to use, the bifunctional catalyst has been subjected to an equilibration treatment by oxidation–reduction in the reactor itself, which consists of successively exposing it to different

streams: (a) a H<sub>2</sub> stream diluted in He (at 10%) at 200 °C for 14 h and (b) a H<sub>2</sub> stream diluted in He (20%) at 300 °C for 1 h.

**2.2. Equipment and Reaction Conditions.** The reaction equipment used (Figure 1) is provided with an Autoclave Engineers BTRS Jr. reactor, which has been conditioned for operating up to 100 bar and 650 °C.<sup>25,26</sup> The reactor is a vertical hollow cylinder of 6.4 mm internal diameter and 152.4 mm length with a volume of 5 cm<sup>3</sup> for the catalyst. It is placed within a stainless steel chamber heated by an electric resistance, and the inside is clad with a 9 mm thick thermal insulator. The equipment is provided with a temperature controller (Eurotherm 847) that actuates on the catalyst bed and on the wall of the reactor. The molar flowrate of the reactants (H<sub>2</sub>, CO, and CO<sub>2</sub>) is controlled by Brooks 5850 mass flow meters. The reaction mixture is passed through several purifiers to eliminate possible traces of oxygen, water, and iron carbonyl that may deactivate the catalyst.

In order to carry out kinetic modeling, runs have been carried out under the following reaction conditions: 225–325 °C; 10–40 bar; space time, 1.6–57.0 (g of catalyst) h (mol H<sub>2</sub>)<sup>-1</sup>; time on stream, 6 h, which is sufficiently short for deactivation to be insignificant; (H<sub>2</sub> + CO) and (H<sub>2</sub> + CO<sub>2</sub>) feeds, both with a 4:1 molar ratio between the components. These ranges have been established subsequent to a detailed study of the effect of operating conditions.<sup>25,26</sup>

**2.3. Product Analysis.** The reaction equipment is connected on-line to a Micro-GC Varian CP-4900 gas chromatograph provided with a thermal conductivity detector (TCD) and a Porapak Q (PPQ, 10 m) column, where the lighter reaction products (H<sub>2</sub>, CO, CO<sub>2</sub>, methane, ethane, propane, methanol, DME, and water) are separated. Both detector and column are placed in the oven and operate within the 0–150 °C range.

The identification of the reaction products has involved gas chromatography/mass spectrometry (Hewlett-Packard 5890 II/MS-engine) and the injection of pure standards. These techniques have allowed most of the components of the gaseous product stream to be identified.

### 3. Results

The results quantified are the yields of methanol, DME, and hydrocarbons. The yields of methanol ( $Y_{\text{MeOH}}$ ) and DME ( $Y_{\text{DME}}$ ) have been calculated as the percentage of carbon atoms that convert to methanol or DME from CO or  $\text{CO}_2$  in the feed:

$$Y_{\text{MeOH}} = \frac{n_{\text{MeOH}}}{(n_{\text{CO}} + n_{\text{CO}_2})_0} 100 \quad (1)$$

$$Y_{\text{DME}} = \frac{2n_{\text{DME}}}{(n_{\text{CO}} + n_{\text{CO}_2})_0} 100 \quad (2)$$

where  $n_{\text{MeOH}}$  and  $n_{\text{DME}}$  are the molar flowrates of methanol in the product stream and  $(n_{\text{CO}} + n_{\text{CO}_2})_0$  is the sum of CO or  $\text{CO}_2$  molar flowrates in the feed.

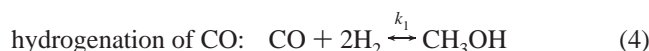
Similarly, the yield of hydrocarbons obtained as byproducts ( $Y_{\text{HC}}$ ) has been calculated as the quotient between the moles of organic carbon present in the hydrocarbons and the moles of inorganic carbon in the reactor feed:

$$Y_{\text{HC}} = \frac{\sum_i n_{\text{Ci}} n_i}{(n_{\text{CO}} + n_{\text{CO}_2})_0} 100 \quad (3)$$

where  $n_{\text{Ci}}$  is the number of carbon atoms in each one of the hydrocarbons and  $n_i$  is their molar flowrate.

**3.1. Kinetic Scheme and Thermodynamic Study.** The results of this study allow for quantifying the synergism between the steps involved in DME synthesis for justifying the integrated process. Furthermore, in order to establish the kinetic model, the values of the equilibrium constants for each step and the corresponding values of component yields are required.

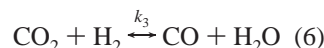
A scheme with the following reactions has been considered:



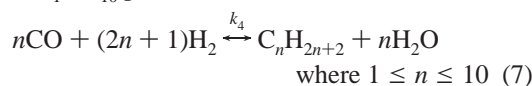
dehydration of methanol to DME:



reverse water–gas shift reaction:



formation of  $\text{C}_1$ – $\text{C}_{10}$  paraffins:



hydrogenation of  $\text{CO}_2$ :



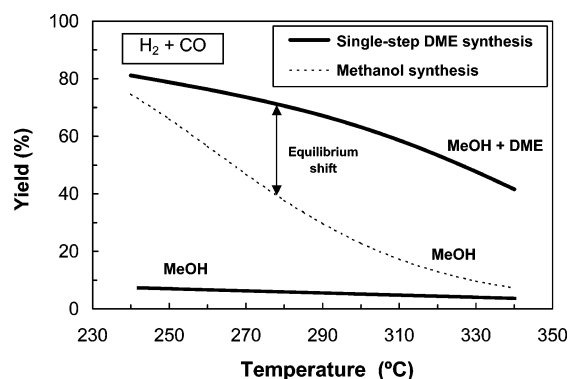
The calculation of thermodynamic equilibrium or reaction extent has been carried out by considering the equilibrium constant for each independent reaction. Consequently, the reaction of methanol formation from  $\text{CO}_2$  and  $\text{H}_2$  (eq 8) has not been considered, given that it is a linear combination of the reactions in eqs 4 and 6, and consequently, the equilibrium constant in eq 8 has been calculated as the product of those corresponding to eqs 4 and 6.<sup>51</sup>

The consideration of paraffin formation (eq 7) is justified by the synthesis capacity of the metallic function at the high

**Table 2.** Coefficients  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ , and  $f$  in the Equilibrium Constant (Equation 9) for the Reactions in Equations 4–7

eq	equilibrium constant coefficients, eq 9					
	$a$	$b \cdot 10^{-3}$	$c$	$d \cdot 10^4$	$e \cdot 10^8$	$f \cdot 10^{-3}$
4	21.84	9.04	−7.66	54.07	−57.50	−6.75
5	−9.76	3.20	1.07	−6.57	4.90	6.05
6	18.01	−5.87	−1.86	2.70	0	58.20
7*	24.90	22.78	−7.95	43.54	−36.07	−4.85

\* Corresponds to  $n = 1$  (reverse reaction to that of methane steam reforming). Methane is the main paraffin formed.



**Figure 2.** Effect of temperature on the yield of oxygenates at equilibrium, at 40 bar: feed ( $\text{H}_2 + \text{CO}$ ).

pressure of the process. In order to verify this hypothesis, runs have been carried out by feeding methanol and DME, and they have proven that hydrocarbon formation is insignificant for these feeds. Consequently, hydrocarbon formation is not produced by either of the other two possible mechanisms on the acid function: (i) thermal decomposition of DME and (ii) transformation of methanol and DME into olefins (which would undergo hydrogenation to paraffins on the metallic function).

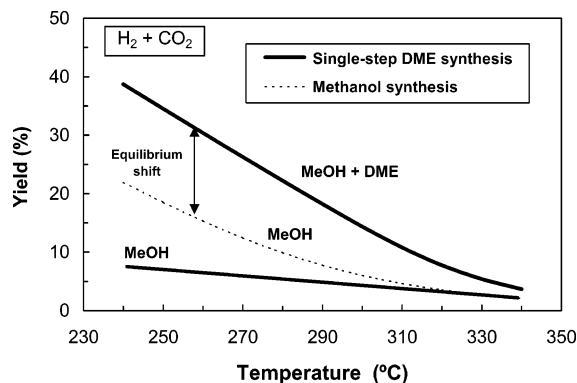
The equilibrium constant for each individual reaction has been related to temperature by means of the following expression:

$$K_j = \exp\left(a + \frac{b}{T} + c \log T + dT + eT^2 + \frac{f}{T^2}\right) \quad (9)$$

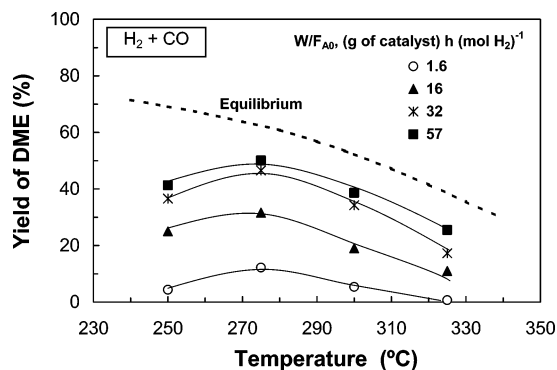
A calculation program has been developed in Matlab to determine the values of the  $a$ – $f$  coefficients in the equilibrium constants for each reaction (Table 2), the composition of the system, and the yields of methanol, DME, and hydrocarbons in the equilibrium. The method is the one established in the literature for determining the equilibrium constants from the standard values of formation enthalpies and entropies for the components of each individual reaction.<sup>52</sup> The study has been carried out in a wide range of pressures (10–80 bar) and temperatures (240–340 °C) and for binary mixtures, ( $\text{H}_2 + \text{CO}$ ) and ( $\text{H}_2 + \text{CO}_2$ ), both with a 4:1 molar ratio.

The main conclusions of the thermodynamic study are the following: (a) Methanol and DME yields in the equilibrium rise as pressure is increased and temperature is decreased, due to the decrease in the number of moles in the reaction and to its exothermic nature, respectively. (b) A feed of ( $\text{H}_2 + \text{CO}_2$ ) gives way to much lower yields of methanol and DME in the equilibrium than those corresponding to ( $\text{H}_2 + \text{CO}$ ). (c) The yield of hydrocarbons in the thermodynamic equilibrium is very high for ( $\text{H}_2 + \text{CO}$ ) and ( $\text{H}_2 + \text{CO}_2$ ) feeds.

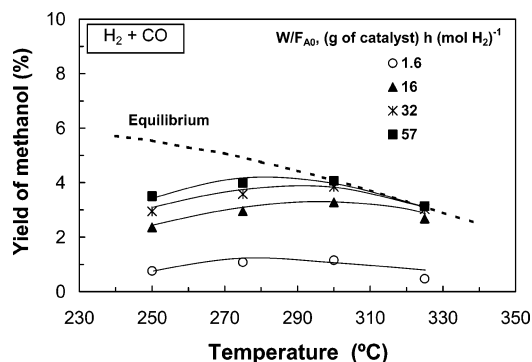
Figures 2 and 3, corresponding to the ( $\text{H}_2 + \text{CO}$ ) and ( $\text{H}_2 + \text{CO}_2$ ) feeds, respectively, compare the yield of oxygenates ( $Y_{\text{MeOH}} + Y_{\text{DME}}$ ) in the integrated process for the production of DME in a single step with the yield of methanol in the synthesis of this oxygenate. The results correspond to a pressure of 40



**Figure 3.** Effect of temperature on the yield of oxygenates at equilibrium, at 40 bar: feed ( $\text{H}_2 + \text{CO}_2$ ).



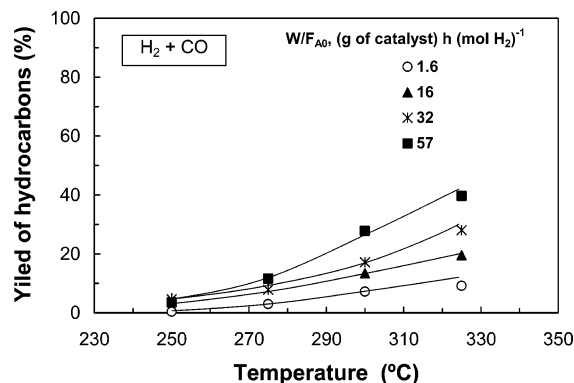
**Figure 4.** Results for DME yield at different temperatures and space times, under 30 bar: feed ( $\text{H}_2 + \text{CO}$ ). Points represent experimental results. Lines represent calculated results with kinetic model 2.



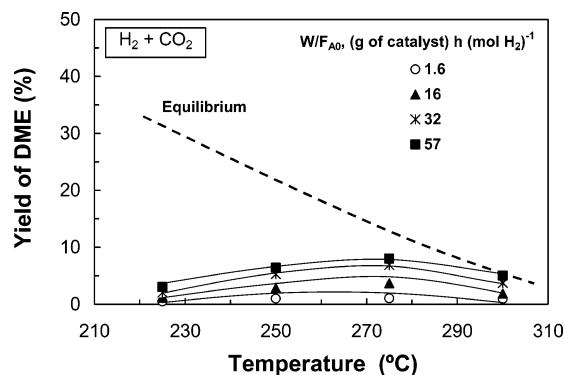
**Figure 5.** Results for methanol yield at different temperatures and space times, under 30 bar: feed ( $\text{H}_2 + \text{CO}$ ). Points represent experimental results. Lines represent calculated results with kinetic model 2.

bar. As is observed, the integrated process shifts the thermodynamic equilibrium (because methanol is transformed in situ), and consequently, the yield of oxygenates is significantly higher than that corresponding to the synthesis of methanol under the same pressure and temperature conditions. As is observed, the yield of methanol in the single-step DME synthesis is low. Equilibrium shift is also observed under other pressures, and the thermodynamic results are consistent with those recorded by Ng et al.<sup>39</sup> and Jia et al.<sup>51</sup>

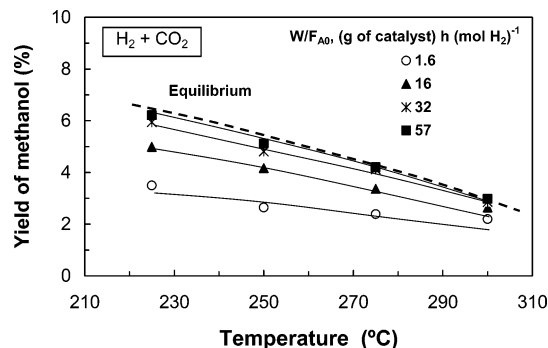
**3.2. Experimental Kinetic Results.** Figures 4–6 show the effect of temperature and space time on the yields of DME, methanol, and hydrocarbons, respectively. The experimental results (points in Figures 4–6) correspond to the ( $\text{H}_2 + \text{CO}$ ) feed, with a  $\text{H}_2/\text{CO}$  molar ratio of 4:1 and 30 bar. In view of the results, the following may be concluded: (i) The yield of DME reaches a maximum value at 275 °C. (ii) The yield of methanol is low (lower than 5%), with the maximum value in



**Figure 6.** Results for hydrocarbon yield at different temperatures and space times, under 30 bar: feed ( $\text{H}_2 + \text{CO}$ ). Points represent experimental results. Lines represent calculated results with kinetic model 2.



**Figure 7.** Results for DME yield at different temperatures and space times, under 30 bar: feed ( $\text{H}_2 + \text{CO}_2$ ). Points represent experimental results. Lines represent calculated results with kinetic model 2.

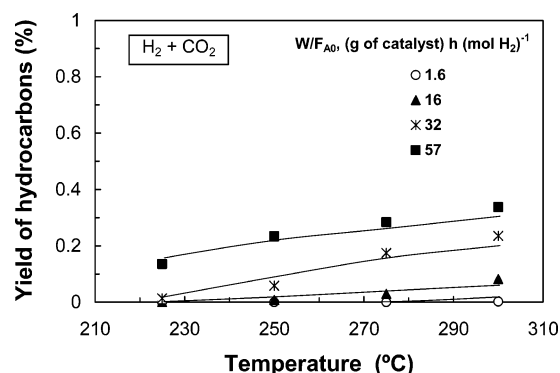


**Figure 8.** Results for methanol yield at different temperatures and space times, under 30 bar: feed ( $\text{H}_2 + \text{CO}_2$ ). Points represent experimental results. Lines represent calculated results with kinetic model 2.

the 275–300 °C range, depending on the operating conditions. (iii) The yield of hydrocarbons (made up of mainly  $\text{C}_1$ – $\text{C}_4$  paraffins) increases with temperature, pressure, and space time. These results and those corresponding to other pressures show that operation must be carried out below 275 °C in order to selectively produce oxygenates.

The results in Figures 7–9 correspond to ( $\text{H}_2 + \text{CO}_2$ ) feed, with a  $\text{H}_2/\text{CO}_2$  molar ratio of 4:1 and 30 bar. The points correspond to experimental results, and the following is noteworthy: (i) The yield of DME is much lower than that corresponding to ( $\text{H}_2 + \text{CO}$ ) feed under the same operating conditions. This result is consistent with that obtained in the literature and justified by the lower formation of methanol.<sup>21</sup> (ii) As for ( $\text{H}_2 + \text{CO}$ ) feed, the maximum yield of DME is obtained at 275 °C. (iii) The yield of methanol decreases progressively as temperature is increased. This result is different from the aforementioned for ( $\text{H}_2 + \text{CO}$ ) feed, in which the





**Figure 9.** Results for hydrocarbon yield at different temperatures and space times, under 30 bar: feed ( $\text{H}_2 + \text{CO}_2$ ). Points represent experimental results. Lines represent calculated results with kinetic model 2.

maximum value was attained in the 275–300 °C range. (iv) As opposed to the result for ( $\text{H}_2 + \text{CO}$ ) feed, the presence of hydrocarbons in the product stream is insignificant.

**3.3. Kinetic Modeling.** The three kinetic models studied are described forthwith. They are ordered by increasing complexity. Model 1 considers the following reaction rates for the individual reactions of the kinetic scheme:

formation of methanol by CO hydrogenation (eq 4):

$$r_{\text{MeOH}} = k_1 \left[ f_{\text{CO}} f_{\text{H}_2}^2 - \frac{f_{\text{CH}_3\text{OH}}}{K_1} \right] \quad (10)$$

formation of DME (eq 5):

$$r_{\text{DME}} = k_2 \left[ f_{\text{CH}_3\text{OH}}^2 - \frac{f_{\text{CH}_3\text{OCH}_3} f_{\text{H}_2\text{O}}}{K_2} \right] \quad (11)$$

formation of  $\text{CO}_2$  (water–gas shift) (reverse of eq 6):

$$r_{\text{CO}_2} = k_3 \left[ f_{\text{CO}} f_{\text{H}_2\text{O}} - \frac{f_{\text{CO}_2} f_{\text{H}_2}}{K_3} \right] \quad (12)$$

formation of hydrocarbons (HC) (eq 7):

$$r_{\text{HC}} = k_4 \left[ f_{\text{CO}} f_{\text{H}_2}^3 - \frac{f_{\text{HC}} f_{\text{H}_2\text{O}}}{K_4} \right] \quad (13)$$

where  $f_i$  is the fugacity of  $i$  component and  $k_j$  and  $K_j$  are the kinetic constant and the equilibrium constant for  $j$  reaction. The reaction rate,  $r_j$ , has been defined in eqs 10–13 as the moles of  $i$  species formed per mole of  $\text{H}_2$  in the feed and per time unit and catalyst mass unit.

As is observed in eqs 10–13, the reactions have been considered as elemental. The stoichiometry of hydrocarbon (HC) formation corresponds to that of methane formation. It must be pointed out that eq 13 has been proposed based on the experimental fact that hydrocarbons are formed from ( $\text{H}_2 + \text{CO}$ ) feed. Thus, runs carried out by feeding methanol show that the presence of hydrocarbons is insignificant in the whole range of operating conditions. This result shows that, due to its weak acid sites,  $\gamma\text{-Al}_2\text{O}_3$  is a suitable acid function for avoiding the transformation of methanol and DME (more reactive in these processes) into  $\text{C}_2\text{--C}_4$  olefins or into heavier hydrocarbons. These secondary reactions are important when the acid function sites are very strong, as happens with the HZSM-5 zeolite fully in its acid form.<sup>16,26</sup>

**Table 3.** Weighting Factors Used for Each Compound in the Kinetic Modeling

compound	weighting factor
$\text{H}_2$	1.30
CO	13.98
$\text{CO}_2$	10.15
$\text{H}_2\text{O}$	34.89
methanol	265.50
DME	106.40
hydrocarbons	159.60

Model 2 is a modification of model 1. It consists of eqs 11 and 12, and the kinetic equations for the formation of methanol (eq 10) and hydrocarbons (eq 13) are modified by incorporating a term ( $\theta$ ) that quantifies the attenuation in the rate of these steps by adsorption of water on the catalyst. Thus, these expressions are as follows in model 2:

$$r_{\text{MeOH}} = k_1 \left[ f_{\text{CO}} f_{\text{H}_2}^2 - \frac{f_{\text{CH}_3\text{OH}}}{K_1} \right] \theta \quad (14)$$

$$r_{\text{HC}} = k_4 \left[ f_{\text{CO}} f_{\text{H}_2}^3 - \frac{f_{\text{HC}} f_{\text{H}_2\text{O}}}{K_4} \right] \theta \quad (15)$$

where

$$\theta = \frac{1}{1 + K_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}}} \quad (16)$$

and  $K_{\text{H}_2\text{O}}$  is a parameter that quantifies the capacity of catalyst for water adsorption:

$$K_{\text{H}_2\text{O}} = K_{\text{H}_2\text{O}}^* \exp \left[ \frac{\Delta H_{\text{H}_2\text{O}}}{R} \left( \frac{1}{T} - \frac{1}{548} \right) \right] \quad (17)$$

The term  $\theta$  has not been considered in the dehydration of methanol because, with the metallic function/acid function ratio of 2/1 used for the kinetic study, the limiting step is the methanol synthesis and the acid function is in excess. The inhibition of the reaction steps by the presence of water in the reaction medium has been experimentally proven in this process and has also been proven in other reactions, such as methanol to gasoline (MTG) and MTO processes.<sup>53,54</sup> The adsorption of water on the support of the metallic phase ( $\text{Al}_2\text{O}_3$ ) will probably have consequences on the bifunctional catalyst. It has been proven that the mathematical expression adopted for quantifying the inhibiting effect of water (eq 16) has a better fitting than other empirical expressions of potential or exponential type.

Model 3 consists of the equations of model 2 (eqs 11 and 12 and eqs 14–17) and it also considers the kinetics for methanol formation by  $\text{CO}_2$  hydrogenation (eq 8):

$$r_{\text{MeOH}_{\text{CO}_2}} = k_5 \left[ f_{\text{CO}_2} f_{\text{H}_2}^3 - \frac{f_{\text{CH}_3\text{OH}} f_{\text{H}_2\text{O}}}{K_5} \right] \theta \quad (18)$$

In the three models described, the water–gas shift reaction (eq 6) has been assumed to be in equilibrium, which is consistent with the results obtained in the thermodynamic study and is also supported in the literature.<sup>40,46</sup>

A fourth-order Runge–Kutta method was used to integrate the ordinary differential equations of the kinetic model. The

**Table 4.** Kinetic Parameters of the Best Fitting, Residual Sum of Squares ( $\Phi$ ) and Residual Variance ( $\sigma^2$ ) for Models 1, 2, and 3<sup>a</sup>

kinetic and statistical parameters	model 1	model 2	model 3
$k_1^*$ , mol <sub>MeOH</sub> (mol <sub>H<sub>2</sub></sub> ) <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> bar <sup>-3</sup>	$(1.91 \pm 0.05) \times 10^{-6}$	$(3.37 \pm 0.04) \times 10^{-6}$	$(3.03 \pm 0.08) \times 10^{-6}$
$k_2^*$ , mol <sub>DME</sub> (mol <sub>H<sub>2</sub></sub> ) <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> bar <sup>-2</sup>	$1.44 \pm 0.04$	$1.57 \pm 0.09$	$1.48 \pm 0.03$
$k_4^*$ , mol <sub>HC</sub> (mol <sub>H<sub>2</sub></sub> ) <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> bar <sup>-4</sup>	$(2.04 \pm 0.10) \times 10^{-7}$	$(2.81 \pm 0.09) \times 10^{-7}$	$(2.69 \pm 0.12) \times 10^{-7}$
$k_5^*$ , mol <sub>MeOH</sub> (mol <sub>H<sub>2</sub></sub> ) <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> bar <sup>-4</sup>			$(1.02 \pm 0.04) \times 10^{-10}$
$E_1$ , kcal mol <sup>-1</sup>	$11.30 \pm 0.56$	$26.95 \pm 0.64$	$23.46 \pm 0.79$
$E_2$ , kcal mol <sup>-1</sup>	$80.64 \pm 2.09$	$84.14 \pm 1.88$	$85.12 \pm 2.27$
$E_4$ , kcal mol <sup>-1</sup>	$15.92 \pm 0.48$	$54.32 \pm 1.72$	$49.08 \pm 1.45$
$E_5$ , kcal mol <sup>-1</sup>			$1.04 \pm 0.02$
$K_{H_2O}$ , bar <sup>-1</sup>		$1.04 \pm 0.05$	$0.91 \pm 0.05$
$\Delta H_{H_2O}$ , kcal mol <sup>-1</sup>		$65.99 \pm 2.85$	$61.38 \pm 2.11$
$\Phi$	6.25	4.49	4.56
$\sigma^2$	$2.71 \times 10^{-2}$	$2.01 \times 10^{-2}$	$1.96 \times 10^{-2}$
$F$ test	$F_{12} = 1.39$	$F_{23} = 0.99$	

<sup>a</sup> The superscript \* indicates the value at 275 °C.

calculation of the kinetic parameters has been carried out by nonlinear regression using a program written in Matlab. The parameters to be optimized are the kinetic constants at a reference temperature (275 °C) and the activation energies, with the objective function being the sum of square residuals:

$$\Phi = \sum_{i=1}^{n_y} w_i \phi_i = \sum_{i=1}^{n_y} w_i (y_i^* - y_i)^2 \quad (19)$$

where  $w_i$  and  $\phi_i$  are, respectively, the distribution weighting factor and the sum of square residuals for each  $i$  dependent variable,  $n_y$  is the number of dependent variables of the model to be fitted,  $y_i^*$  is the vector of experimental molar fraction values for  $i$ , and  $y_i$  is the vector of molar fraction values calculated by solving the mass balance in the reactor. The quality of the chromatographic analyses is noteworthy, which has allowed for obtaining a mass balance closure above 98% in all the runs used for the kinetic study.

In order to reduce the correlation between the estimated values of frequency factor and activation energy (both parameters are related by means of the Arrhenius equation), reparameterization has been carried out. Accordingly, the initial estimation of the reaction parameters is less critical and the time required for the program to reach the minimum value of the objective function is less. Furthermore, the assumption of eq 6 at equilibrium conditions in the calculation program is carried out by establishing a high value of the kinetic constant for the direct reaction.

The low concentration of certain products (especially methanol) in the reactor outlet stream hinders the fitting, and weighting factors must be used for each component in the kinetic equations. These factors are set to be inversely proportional to their mean squares (Table 3).

The values shown in Table 2 have been used for the coefficients in the equilibrium constants. The kinetic parameter values, and those for the 95% confidence interval calculated for the three models are set out in Table 4.

Model discrimination has been carried out by hypothesis testing based on the value of the  $F$  (Fisher) sampling distribution, which consists of comparing the value of the statistic  $F_{ij}$ , corresponding to the ratio of mean squares for the  $i$  and  $j$  models, with the critical value  $F_c$ , corresponding to the degrees of freedom used for calculating the mean squares for these models (in this case  $F_c = 1.08$ ), with a 95% confidence interval.<sup>55</sup> Table 4 also shows the values of  $F_{ij}$  corresponding to the comparisons of models 1–2 and models 2–3.

The fitting of model 2 (which considers the inhibiting effect of water adsorption on the catalyst) is considerably better than that of model 1 and is only slightly bettered by model 3 (a

slightly lower residual mean square). Consequently, the consideration of methanol formation by CO<sub>2</sub> hydrogenation (eq 18), model 3, is not interesting, as it makes the model more difficult to solve and subsequently use in the reactor design. This result is confirmed by the  $F$  test, which clearly shows that the addition of new kinetic parameters, eq 18, does not give way to a significant improvement in the fitting.

Consequently, model 2 is the one with the best balance concerning simplicity and fitting to experimental results. This simplicity is interesting for future studies in which this model is combined with a kinetic equation for catalyst deactivation, which occurs by coke deposition on the Al<sub>2</sub>O<sub>3</sub> support of the metallic function (under conditions of acid function excess in the catalyst used).<sup>41</sup> A comparison is carried out in Figures 4–6, corresponding to (H<sub>2</sub> + CO) feed, between the values for the yields of DME (Figure 4), methanol (Figure 5), and hydrocarbons (Figure 6) calculated using model 2 and those corresponding to experimental results (points). The adequate fitting of this model to the experimental results is also shown in Figures 7–9, in which the same comparison is carried out for the results corresponding to the (H<sub>2</sub> + CO<sub>2</sub>) feed.

Figure 10 shows the fitting corresponding to all the experimental values and those calculated for the molar fraction of each compound using model 2.

When the activation energies calculated using the different kinetic models (Table 4) are analyzed, the values for  $E_2$  (corresponding to methanol dehydration) are similar, whereas the values for  $E_1$  and  $E_4$  (corresponding to methanol formation by CO hydrogenation and to formation of hydrocarbons) for models 2 and 3 are of the same order as those common to catalytic processes, which is an indication of the higher consistency of these models.

The simplicity of the kinetic equations in the model proposed is noteworthy. For the methanol synthesis step, mechanistic kinetic equations developed in the literature have not been used.<sup>56–63</sup> Although these equations faithfully describe this reaction step, their complexity is not required to quantify this integrated process, in which overall kinetics is conditioned by the synergism between both steps. Furthermore, more complex expressions than those used would mask the study of relevant phenomena in the integrated process, such as the restriction of water adsorption on the catalyst.

Furthermore, as noted above and due to the composition established for the bifunctional catalyst, the limiting step of the process is methanol synthesis, in order to favor a synergetic effect and, consequently, achieve the complete transformation of methanol into DME. Consequently, there is an excess acid function under reaction conditions, which explains that mech-

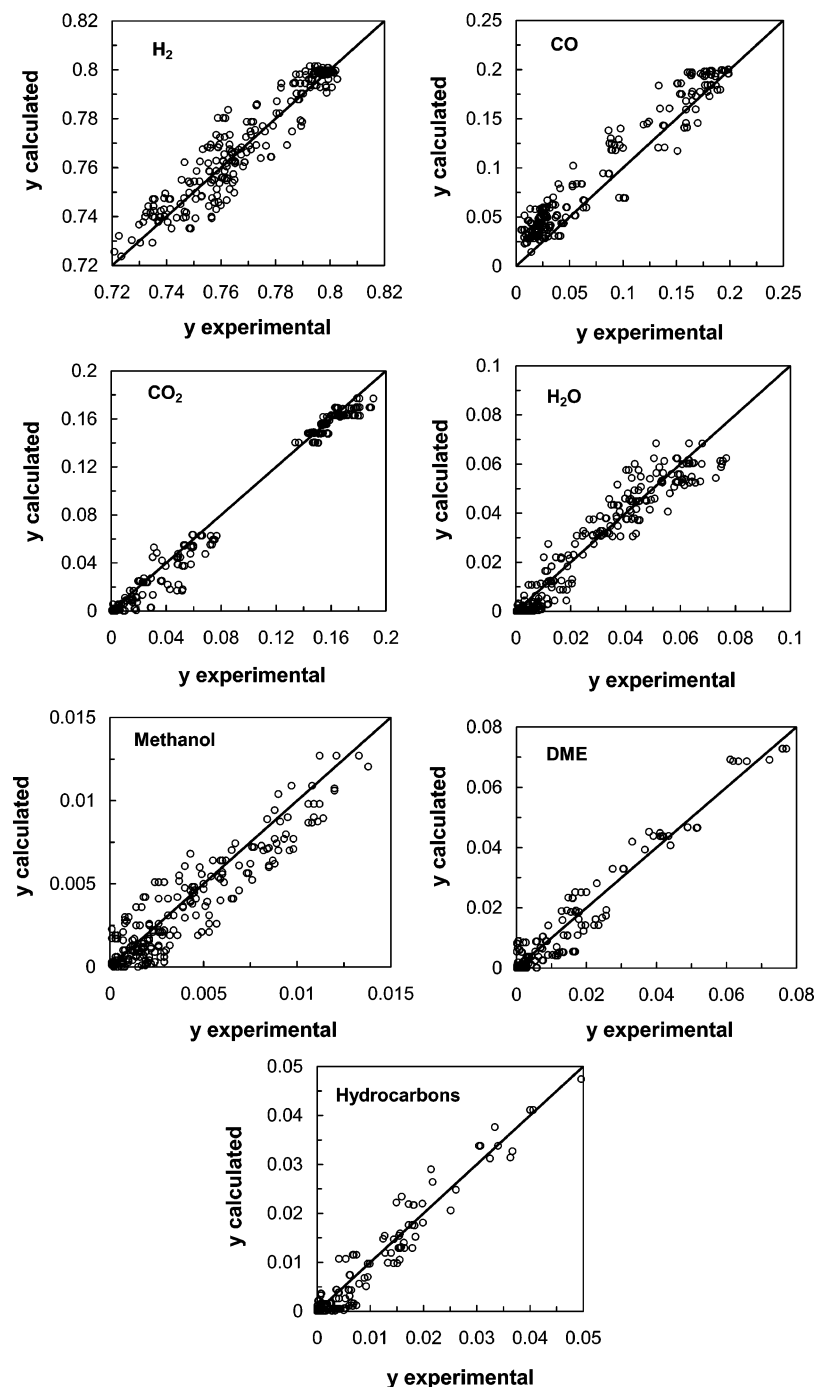


Figure 10. Fitting between the experimental values of molar fraction of components and the values calculated with kinetic model 2.

anisms with intervention of acid sites are not required in the dehydration kinetics and that the results are consistent with a model based on elemental reactions.

#### 4. Conclusions

DME synthesis in a single reaction step from synthesis gas or ( $\text{H}_2 + \text{CO}_2$ ) has important thermodynamic advantages over the two-step process and over methanol synthesis, given that it gives way to a considerable increase in the yield of oxygenates (methanol and DME). The single-step reaction provides good perspectives for incorporating  $\text{CO}_2$  in the feed together with synthesis gas.

The operation using a  $\text{CuO-ZnO-Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  bifunctional catalyst allows for reaching yields higher than 60%

for carbon converted to DME and 5% to methanol when feeding ( $\text{H}_2 + \text{CO}$ ) at 30 bar and 275 °C. At higher temperatures, production of hydrocarbons (mainly methane) is significant.

The yield of DME in the conversion of ( $\text{H}_2 + \text{CO}_2$ ) requires very high space times in order to overcome a value of 10%, at temperatures in the 275–300 °C range, with a yield of methanol around 5% and with hardly any hydrocarbon formation.

A kinetic model has been proposed for the reactions involved in the synthesis of methanol, dehydration of DME, the water–gas shift reaction, and hydrocarbon formation. This model suitably fits the concentrations of the individual components in the reaction medium in a wide range of experimental conditions (225–325 °C, 10–40 bar), for feeds of synthesis



gas and ( $\text{H}_2 + \text{CO}_2$ ) and under conditions of metallic function/acid function ratio in the catalyst, where methanol synthesis is the controlling step of the overall process. The model contemplates the role of water in the reaction medium, given that it has a relevant effect as an inhibitor in the steps of methanol synthesis and formation of hydrocarbons. The step of direct synthesis of methanol by  $\text{CO}_2$  hydrogenation has been proven to be of minor significance in the kinetic model.

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## Notation

$a-f$  = equilibrium constant coefficients, eq 9

DME = dimethyl ether

$E_j$  = activation energy of  $j$  reaction,  $\text{kcal mol}^{-1}$

$F_{ij}$  = ratio of mean squares for  $i$  and  $j$  models

$F_c$  = critical value of Fisher sampling distribution

$f_i$  = fugacity of  $i$  component, bar

HC = hydrocarbons

$K_{\text{H}_2\text{O}}$ ,  $K_{\text{H}_2\text{O}}^*$  = parameter that quantifies the capacity of a catalyst for water adsorption and its value for the reference temperature (275 °C), eq 17

$K_j$  = equilibrium constant for  $j$  reaction, defined in eq 9

$k_j$ ,  $k_j^*$  = kinetic constant for  $j$  reaction and its value for the reference temperature (275 °C)

LPG = liquefied petroleum gas

MTG = methanol to gasoline process

MTO = methanol to olefins process

$n_{\text{Ci}}$  = number of carbon atoms in each hydrocarbons

$n_{\text{CO},0}$ ,  $n_{\text{CO}_2,0}$  = molar flowrate of CO and of  $\text{CO}_2$  in the feed,  $\text{mol s}^{-1}$

$n_{\text{DME}}$ ,  $n_{\text{HC}}$ ,  $n_{\text{MeOH}}$  = molar flowrate of dimethyl ether, hydrocarbons, and methanol in the product stream, respectively,  $\text{mol s}^{-1}$

$n_v$  = number of dependent variables for the model to be fitted

$r_{\text{CO}_2}$  = reaction rate for the formation of  $\text{CO}_2$  from the water–gas shift reaction, eq 12

$r_{\text{DME}}$  = reaction rate for the formation of DME from dehydration of methanol, eq 11

$r_{\text{HC}}$  = reaction rate for the formation of hydrocarbons, eq 13

$r_{\text{MeOH}}$  = reaction rate for the formation of methanol from hydrogenation of CO, eq 10

$r_{\text{MeOH},\text{CO}_2}$  = reaction rate for the formation of methanol from hydrogenation of  $\text{CO}_2$ , eq 18

TCD = thermal conductivity detector

$w_i$  = distribution weighting factors for the  $i$  dependent variables

$Y_{\text{DME}}$ ,  $Y_{\text{HC}}$ ,  $Y_{\text{MeOH}}$  = yield of dimethyl ether, hydrocarbons, and methanol, respectively

$y_i$  = vector of molar fraction values for the  $i$  components, calculated by solving the mass balance in the reactor

$y_i^*$  = vector of experimental molar fraction values for the  $i$  components

## Greek Letters

$\Delta H_{\text{H}_2\text{O}}$  = coefficient in eq 17,  $\text{kcal mol}^{-1}$

$\Phi$  = sum of square residuals, defined in eq 19

$\phi_i$  = sum of square residuals for the  $i$  dependent variables

$\theta$  = term that quantifies the attenuation in the rate by adsorption of water on the catalyst, eq 16

$\sigma$  = residual variance

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