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Intensification of Catalytic Processes through the Pellet Structuring: Steady-State Properties of a Bifunctional Catalyst Pellet Applied to Generic Chemical Reactions and the Direct Synthesis of DME

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Abstract: Structuring of different types of catalytic active centers at a single-pellet level appears to be a promising and powerful tool for integration and intensification of multistep solid-catalyzed chemical reactions. However, the enhancement in the product yield and selectivity strongly depends on the proper choice of the distribution of different catalysts within the pellet. To demonstrate potential benefits from properly designed catalyst pellet, numerical studies were conducted with the aid of the mathematical model of a single spherical bifunctional catalyst pellet. The analysis was performed both for a system of two generic chemical reactions and for a real process, i.e., direct synthesis of dimethyl ether (DME) from synthesis gas via methanol. Evaluation of the pellet performance was done for three arrangements of the catalytic active sites within the pellet, i.e., a uniform distribution of two types of catalytic active centers in the entire volume of the pellet, and two core–shell structures. It was demonstrated that, especially for the larger pellets typical for fixed-bed applications, the product yield might be significantly improved by selecting proper catalyst arrangements within the pellet.

Keywords: bifunctional catalyst pellet; process integration; direct DME synthesis; steady-state behavior

1. Introduction

Multi- or bifunctional catalyst pellets, also referred to as hybrid pellets, enable integration of more than one functionality in a microscale (Figure 1). The multifunctionality at a pellet level usually consists of the integration of catalytic active sites and adsorbent or two types of catalytic active sites in a single pellet [1,2]. In classical adsorptive reactors, a physical mixture of catalyst and adsorbent particles, bringing the process integration at the entire apparatus level, implements the synergy between chemical reaction and physical adsorption. The application of hybrid pellets may further improve the product yield and selectivity of such multifunctional reactors [3]. Similar benefits may be obtained for multistep solid-catalyzed chemical reactions that require utilization of different types of catalysts [4]. In both cases, the enhancement in the product yield, in comparison to the processes carried out in multifunctional reactors integrating different types of functionalities at the apparatus level (Figure 1) or even carried out in two separate devices, results mainly from the reduction of mass transfer resistances.







Figure 1. Schematic of the structuring of functionalities at reactor level (**a**) and single catalyst pellet level (**b**), where c1-s2 denotes a core–shell structure with catalyst 1 located in the core and catalyst 2 in the shell, and c2-s1 denotes a core–shell structure with catalyst 2 located in the core and catalyst 1 in the shell.

Close integration of different functionalities at the apparatus level is now a well-established approach to the process intensification [1,5]. However, the concept of structuring the functionalities at the pellet level has not been entirely examined yet. Integration of the catalytic and adsorptive functionalities has received recently significant attention [2,6]. Evaluation of the performance of bifunctional pellets integrating catalytic and adsorptive functions applied to the Claus process [2], water-gas shift reaction [2,6] and methane steam reforming [6] has revealed the great influence of the spatial arrangement of different functionalities within the pellet, with non-uniform distributions being very often superior over the uniform. The concept of optimal distribution of a single catalytic activity within the pellet was investigated comprehensively in the past [7], but the number of reports dealing with the influence of the spatial distribution of two or more types of catalytic active sites within the pellet on its performance is very limited, even when considering generic systems of chemical reactions [1].

Now, taking into account both the global energy crisis and the attempts of cost reduction via process integration and intensification, much academic and industrial attention is given to a process of direct synthesis of dimethyl ether (DME) from synthesis gas (syngas) on a bifunctional catalyst [8]. Other examples of solid-catalyzed chemical processes that may be conducted using multifunctional catalyst pellets include conversion of syngas into other liquid hydrocarbons and hydroisomerization of *n*-alkanes [9,10].

Due to high cetane number, relatively low self-ignition temperature and no emission of particulate matter, DME can potentially replace diesel fuel. The properties similar to propane and butane make it also suitable for heating and home cooking [11]. Besides energy application, DME can be used in production of chemicals including propylene and other light olefins [12]. Liquified DME can be applied as a "green" solvent for extraction of lipids, pigments and other high-value products from the biomass [13] or for extraction of spices [14]. Dimethyl ether is also considered as an environment-friendly aerosol and refrigerant [11].

In contrast to the traditional method for the production of DME that consists of two steps, i.e., synthesis of methanol from syngas using a metallic catalyst and its dehydration to DME on an acidic catalyst, the direct synthesis is conducted using bifunctional (hybrid) catalyst pellets containing two types of catalytic active centers. The metallic function used for methanol synthesis is usually composed

of CuO, ZnO and Al₂O₃ or Cr₂O₃, with copper clusters being the active sites for methanol synthesis and water gas shift reaction, and ZnO maintaining the optimal dispersion of copper metal [11]. The acidic catalysts used for the dehydration of methanol to DME are typically γ -Al₂O₃ or zeolites such as H-ZSM-5, HY or SAPO [11,15]. Recently, a ferrite zeolite was also investigated as the acidic functionality, demonstrating superiority over other zeolites in terms of methanol conversion and DME selectivity [16–18]. Due to the very high importance of this technological process, in the last two decades different preparation methods of bifunctional catalyst pellets for DME synthesis were investigated [4,19,20]. Moreover, the integrated and polygeneration systems based on the direct synthesis of DME were proposed and analyzed in terms of the process performance and economical aspects [21,22]. Nevertheless, while the choice of the chemical species of the catalysts and the preparation methods have been analyzed thoroughly, only recently the spatial distribution of different types of catalytic active centers have started to be explored as an additional design parameter [23].

The purpose of this work is to outline the potential of intensification of solid-catalyzed multistep chemical processes using bifunctional catalyst pellets that integrate two types of catalytic active centers. Due to limited literature reports concerning even generic chemical reactions, the influence of the proper choice of intraparticle distribution of the catalysts on the product yield ad selectivity was first analyzed for a system of two elementary reversible chemical reactions:

$$A \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} B \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} C, \tag{1}$$

The main purpose of the analysis of generic chemical reactions catalyzed by two types of arbitrary active centers was to give a general insight on the process performance when using a differently structured pellet with a relatively simple model. Then, in the second part of the work, the numerical analysis was extended to a process of direct synthesis of dimethyl ether from synthesis gas. A scheme consisting of a methanol synthesis step over a CuO/ZnO/Al₂O₃ catalyst [24]:

$$CO + 2H_2 \leftrightarrow CH_3OH$$
, (2)

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$
, (3)

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$
, (4)

followed by the methanol dehydration reaction over an acidic γ -Al₂O₃ catalyst [25]:

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O, \tag{5}$$

was considered when analyzing DME synthesis on a bifunctional catalyst pellet.

2. Results and Discussion

2.1. System of Two Elementary Reversible Chemical Reactions

Three arrangements of catalyst 1 and catalyst 2 within the spherical pellet were examined, including a uniform distribution of the catalysts in the entire volume of the pellet and two non-uniform core–shell distributions. The first non-uniform distribution has catalyst 1 located in the core and catalyst 2 located in the pellet shell, and the second one has inverted arrangement of the catalytic active sites (Figure 2). In all cases, it was assumed that each type of catalyst occupies 0.5 volume fraction of the pellet. Therefore, in the case of the non-uniform core–shell distributions, a dimensionless radius of the pellet core is equal to $\zeta_{core} = 0.7937$.



Figure 2. Radial distribution of catalyst 1 (i.e., the one catalyzing the first step of the process) in the evaluated pellet structures.

It was assumed that for the system of two elementary chemical reactions, the process takes place non-isothermally. The formulation of the model equations and numerical methods used for their resolution are described, respectively, in Sections 3.1 and 3.3, whereas the values of the model parameters employed in the numerical simulations are reported in Table 1. Due to the generic character of the chemical process examined here, some representative values that may be encountered in solid-catalyzed gas phase chemical reactions were selected [26,27]. The analysis was limited to a single pellet; therefore, the bulk gas concentration adopted for reactant A and intermediate product B, i.e., $\beta_{A,bulk} = 1$, $\beta_{B,bulk} = 0$ (Table 1) may be interpreted as the simulation of the pellet located near the inlet of a fixed-bed catalytic reactor.

Parameter	Value	Unit
Bi _m	10	-
Bi_q	0.1	-
D_{eff}	10^{-6}	$m^2 \cdot s^{-1}$
$E_1 = E_2$	5×10^4	kJ·kmol ^{−1}
$k_{01} = k_{02}$	107	s^{-1}
$T_{ref} = T_{bulk}$	500	Κ
R_p	$10^{-4} \div 10^{-2}$	
$\beta_{A,bulk}$	1	-
$\beta_{\mathrm{B},bulk}$	0	-
$\Delta h_1 = \Delta h_2$	-6×10^{4}	kJ·kmol ^{−1}
$\Delta s_1 = \Delta s_2$	-100	kJ∙kmol ^{−1} ∙K ^{−1}
λ_{eff}	10^{-4}	$kW \cdot m^{-1} \cdot K^{-1}$
ϑ_{bulk}	1	-

Table 1. Values of the parameters employed in numerical simulations for a system of two elementary reversible chemical reactions.

Figure 3 reports solution diagrams of the multifunctional catalyst pellet as a function of the pellet radius, R_p , for fixed values of the other parameters of the model. Abbreviations c1-s2 and c2-s1 denote, respectively, a core–shell structure with catalyst 1 in the core and catalyst 2 in the shell, and a core–shell structure with catalyst 2 in the core and catalyst 1 in the shell. Solid lines indicate stable steady states, whereas dashed lines denote unstable states. Variables $\beta_i(0)$, i = A, B and $\vartheta(0)$, and variables $\beta_i(1)$, i = A, B and $\vartheta(1)$ are the dimensionless reactant concentration and temperature at the pellet center ($\zeta = 0$) and at its surface ($\zeta = 1$), respectively. Figure 3b,d,f shows the enlargement of the areas marked, respectively, in Figure 3a,c,e, in which the occurrence of multiple steady-state states for uniform and c2-s1 configuration of the catalysts were observed.

1.0

0.8

0.6

0.4

0.2

0.0

0.8

0.6

0.4

0.2

0.0

 $\beta_{\rm B}(0), \beta_{\rm B}(1)$

10-4

c1-s2

c2-s1

c1-s2

c2-s1

 $\beta_{\rm A}(0), \beta_{\rm A}(1)$





Figure 3. Steady-state solution branches of the state variables, evaluated at the boundaries of the domain, for bifunctional catalyst pellet as a function of the pellet radius, R_p : (**a**,**b**) Dimensionless concentration of reactant A; (c,d) dimensionless concentration of reactant B; (e,f) dimensionless temperature.

The values of the concentration of the reactants and temperature strongly depend not only on the distribution of the catalytic active sites within the pellet, but also on the pellet radius, R_p. However, for the smallest radii, regardless of how the functionalities, i.e., catalyst 1 and catalyst 2, are distributed within the pellet volume, the values of the reactants concentration and temperature at the pellet center and its surface are almost the same, and-additionally-they are almost equal to those corresponding to the bulk gas conditions (Figure 3a,c,e). This result is quite obvious, because it is well known that for very small pellets both external and internal mass and heat transport resistances become negligible. This means that, for such pellets, the radial distribution of both types of active centers has little, if any, influence on the process performance.

As the pellet radius increases, the relevance of transport resistances also increases, except for the internal heat transport resistance—the almost overlapping steady-state branches $\vartheta(0)$ and $\vartheta(1)$ (Figure 3e,f) correspond to a nearly uniform distribution of the temperature within the pellet. However, while the internal resistance to heat diffusion is negligible in the entire interval of R_p , the temperature gradient at the gas–solid interface starts to increase very rapidly as the radius becomes larger than 10^{-3} m (Figure 3e).

Evaluation of the concentration solution branches (Figure 3a–d) confirms the importance of different approaches to catalyst integration at the pellet level. The lowest differences between the concentration at the center and at the surface (Figure 3a,c) are observed for the pellet characterized by c2-s1 distribution of the active centers (for intermediate radii), and by uniform distribution (for larger radii). Because of the very short distance between the individual functionalities, uniform structuring of the pellet offers the highest intensification of intraparticle mass transfer. However, this does not result directly in the highest process performance, the reason being that the reaction $A \leftrightarrow B$ will take place everywhere in the pellet, with significant production of the intermediate product B also near the pellet surface, and this may cause loss of species B to the gas phase for external mass transfer. In this view, a shell containing only active sites for reaction $B \leftrightarrow C$ may function better, in that it may "trap" species B and convert it into the final product C.

To illustrate the influence of different arrangements of two arbitrary catalytic activities on the intraparticle concentration profiles, representative solutions obtained for the pellet radius $R_p = 2 \times 10^{-3}$ m are shown in Figure 4. It is clearly visible that using a different arrangement of the catalytic active centers within the pellet strongly influences the concentration profiles, both qualitatively and quantitatively.



Figure 4. Radial distribution of the reactants concentration for the pellet radius $R_p = 2 \times 10^{-3}$ m: (a) Dimensionless concentration of reactant A, $\beta_A(\zeta)$; (b) dimensionless concentration of reactant B, $\beta_B(\zeta)$.

A preliminary analysis of the concentration profiles could suggest that, due to the higher average concentration of B in the pellet with c1-s2 catalysts arrangement, a higher conversion of the intermediate product B (Figure 4b) towards the desired product C is achieved. However, keeping in mind the spherical shape of the pellet, it may be concluded that, in this case, uniform distribution performs best, since for the c1-s2 arrangement the second chemical reaction $B \leftrightarrow C$ takes place only in the outer shell of the pellet, where the concentration of B is the lowest.

Since it is difficult, and for more complex chemical processes practically impossible, to assess which structure performs best based only on the reactant distribution within the catalyst pellet, it is necessary to define some appropriate quantitative index. The performance of a single catalyst pellet may be measured using various indices including effectiveness factor, selectivity or yield. Under the assumption that production of component C is the objective, the yield of product C with respect to reactant A, Y_{CA} , is employed to assess the pellet performance. Following [7], yield is defined as the ratio between the actual production rate of C and the consumption rate of A in the absence of internal and external transport resistances:

$$Y_{\rm CA} = \frac{3\int\limits_{0}^{1} f_2(\zeta)k_{02}\exp\left(-\frac{\gamma_2}{\vartheta(\zeta)}\right) \left(\beta_{\rm B}(\zeta) - \frac{1}{K_{p2}}\beta_{\rm C}(\zeta)\right) \zeta^2 d\zeta}{k_{01}\exp\left(-\frac{\gamma_1}{\vartheta_{bulk}}\right) \left(\beta_{\rm A,bulk} - \frac{1}{K_{p1}(T_{bulk})}\beta_{\rm B,bulk}\right)}.$$
(6)

Figure 5 reports the yield, Y_{CA} , as a function of the pellet radius R_p , calculated using Equation (6). Figure 5a shows the values of Y_{CA} calculated from the solution presented in Figure 3. Figure 5b,c shows the values of Y_{CA} obtained with one parameter changed with respect to the base case (Table 1), that is the frequency coefficient k_{01} increased from 10^6 s^{-1} to 10^7 s^{-1} (Figure 5b) and the frequency coefficient k_{02} increased from 10^6 s^{-1} to 10^7 s^{-1} (Figure 5b) and the frequency coefficient k_{02} increased from 10^6 s^{-1} to 10^7 s^{-1} (Figure 5b) and the frequency coefficient k_{02} increased from 10^6 s^{-1} to 10^7 s^{-1} (Figure 5b) and the frequency coefficient k_{02} increased from 10^6 s^{-1} to 10^7 s^{-1} (Figure 5c), respectively.



Figure 5. Yield of product C with respect to reactant A, Y_{CA} , as a function of the pellet radius, R_p : (**a**) Y_{CA} for the base-case parameter values (Table 1); (**b**) Y_{CA} for the frequency coefficient k_{01} increased ten times, i.e., $k_{01} = 10^7 \text{ s}^{-1}$; (**c**) Y_{CA} for the frequency coefficient k_{02} increased ten times, i.e., $k_{02} = 10^7 \text{ s}^{-1}$ (Note: The bottom figure is in a different scale).

For the base-case parameters (Figure 5a), a uniform distribution of the two types of catalytic active centers gives the highest values of the yield of the desired product C with respect to A, Y_{CA} , almost in

the whole range of the evaluated pellet radius, R_p . Non-uniform arrangement c2-s1 results perform best in a very narrow region of the solution multiplicity, i.e., for $R_p \approx 1.3 \times 10^{-3}$ m. In the case of the largest pellets, the yield obtained using the c1-s2 structure becomes comparable to the Y_{CA} obtained with uniform distribution.

A tenfold increase of the frequency coefficient of the first chemical reaction, k_{01} , with respect to the base-case value, has two main effects (Figure 5b): For some values of R_p the yield is greater than unity and for larger pellets c1-s2 structure becomes slightly better, in terms of Y_{CA} , than uniform structure. The first one follows from the temperature of the pellet significantly exceeding the bulk gas temperature (Figure 3e,f) and from the fact that in Y_{CA} , defined by Equation (6), the consumption rate of A is evaluated at the bulk gas conditions. The second effect can be explained as follows: When $k_{01} >> k_{02}$ and the pellet radius is, approximately, greater than 2×10^{-3} m, the conversion of A towards B in the pellet core with c1-s2 distribution of catalysts is higher than for $k_{01} = k_{02}$. Then, despite the relatively long distance between the individual functionalities, the intermediate product B is converted efficiently into the desired product C as it diffuses towards the pellet surface through the relatively thick particle shell.

When $k_{01} \ll k_{02}$ (Figure 5c), and with the other model parameters kept unchanged (Table 1), a uniform arrangement, characterized by the most intimate spatial integration of the both functionalities, performs bests. The higher rate of the second chemical reaction could suggest a greater conversion of B towards C during its diffusion through the thick shell when considering c1-s2 structure and large R_p . However, in this case the limiting reactant is the intermediate product B, being produced from A in the pellet core in a much lower amount than it is for the case presented in Figure 5b.

The intraparticle distribution of the catalytic activities influences also the effectiveness factor of the pellet, and thus the product selectivity. Thus, it is also necessary to analyze the pellet performance in terms of the selectivity of reactant A towards the desired product C, defined as [7]:

$$S_{\rm CA} = \frac{\int\limits_{0}^{1} f_2(\zeta) k_{02} \exp\left(-\frac{\gamma_2}{\vartheta(\zeta)}\right) \left(\beta_{\rm B}(\zeta) - \frac{1}{K_{p2}}\beta_{\rm C}(\zeta)\right) \zeta^2 d\zeta}{\int\limits_{0}^{1} f_1(\zeta) k_{01} \exp\left(-\frac{\gamma_1}{\vartheta(\zeta)}\right) \left(\beta_{\rm A}(\zeta) - \frac{1}{K_{p1}}\beta_{\rm B}(\zeta)\right) \zeta^2 d\zeta},\tag{7}$$

Figure 6a reports the selectivity, S_{CA} , determined for the base-case set of parameters (Table 1) as a function of the pellet radius, R_p .



Figure 6. Selectivity of reactant A towards product C, S_{CA} , and observed conversion degree of reactant A, \overline{X}_A , as a function of the pellet radius, R_p , for the base-case parameter values (Table 1): (a) Selectivity, S_{CA} ; (b) conversion degree of A, \overline{X}_A .

As for the Y_{CA} , the worst performance in terms of the selectivity (Figure 6a) is observed for c2-s1 distribution. For medium to large radii the pellet with c1-s2 distribution of the active centers overperforms significantly uniform distribution in terms of S_{CA} , which can be explained by a "trap" function of the second catalyst located in the shell, increasing substantially the selectivity towards product C. However, up to about $R_p \approx 3 \times 10^{-3}$ m the actual conversion degree of reactant A, \overline{X}_A , calculated as mean integral:

$$\overline{X}_{A} = 3 \int_{0}^{1} \left(\frac{\beta_{A,bulk} - \beta_{A}(\zeta)}{\beta_{A,bulk}} \right) \zeta^{2} d\zeta.$$
(8)

for c1-s2 catalyst arrangement is much lower than \overline{X}_A obtained for uniform distribution of active centers (Figure 6b).

2.2. Direct Synthesis of DME from Syngas

The analysis of the performance of a single bifunctional catalyst performed for a generic system of two consecutive chemical reactions demonstrated that a proper pellet structuring permits enhancing the performance of multistep chemical reactions. For this reason, in the second part of the work, the analysis is extended to a real process, i.e., the direct synthesis of dimethyl ether (DME) from synthesis gas (syngas) via methanol.

The model equations and numerical procedure are described in detail in Sections 3.2 and 3.3, whereas the model parameters used in the numerical simulations are reported in Table 2 and Appendix A. Based on the literature reports concerning separately methanol synthesis and methanol dehydration steps [28,29] and to reduce the complexity of the pellet model, it was assumed that the pellet is isothermal. As for the case of the system of two elementary reversible chemical reactions, the influence of three arrangements of catalyst 1 (metallic) and catalyst 2 (acidic) within the pellet on the DME yield was evaluated (Figure 2). Moreover, as before, to limit the number of the model parameters analyzed, it was assumed that the pellet volume fraction occupied by each type of the catalytic active sites was equal to 0.5. The performance analysis of the bifunctional pellet was conducted assuming the bulk gas composition equal to the raw, characterized by high content of nitrogen [30], syngas composition (Table 2). Therefore, again, the simulated case corresponds to the behavior of the pellet located near the inlet of a fixed-bed reactor, or, for smaller diameters, to the behavior of the pellet located in a fluidized-bed reactor being at the start-up phase.

Parameter	Value	Unit
d _{pore}	10 ⁻⁸	m
P	60	bar
T	493, 503	Κ
u_0	1	$m \cdot s^{-1}$
R_p	$10^{-4} \div 10^{-2}$	m
x _{CO}	0.1716	-
$x_{\rm CO_2}$	0.0409	-
$x_{\rm CH_3OH}$	0.003	-
x_{H_2}	0.4225	-
$x_{\rm H_2O}$	0.0002	-
$x_{\rm DME}$	0.0018	-
$x_{\rm CH_4}$	0.044	-
x_{N_2}	0.316	-
ε_p	0.5	-
ρ_p	1775	kg∙m ^{−3}
τ	4	-

Table 2. Values of the parameters employed in numerical simulations for direct synthesis of dimethyl ether (DME) [28–30] (Note: The kinetic parameters are given in Appendix A).

Figure 7 shows representative profiles of the hydrogen and methanol molar fractions obtained for T = 493 K using uniform, c1-s2 and c2-s1 arrangement of the metallic and acidic active centers within the pellet of the radius: $R_p = 2 \times 10^{-4}$ m (Figure 7a,b), $R_p = 10^{-3}$ m (Figure 7c,d) and $R_p = 4 \times 10^{-3}$ m (Figure 7e,f). Computations performed for the smallest of the analyzed radii predict that both hydrogen (Figure 7a) and the intermediate product, i.e., methanol (Figure 7b), are computed as distributed uniformly in the entire volume of the pellet, regardless of the employed arrangements of the catalytic active centers. As the pellet size increases, the catalyst arrangement begins to have an effect on the intraparticle concentration profiles of reactants. Moreover, for the largest radius (Figure 7e,f) the concentration profiles qualitatively resemble those obtained for the system of two elementary chemical reactions (Figure 4). This suggests similar relationships between the values of the product yield that can be achieved using different structures of the pellet.

The yield of the desired product, that is DME, is defined here with respect to the consumption rate of hydrogen as:

$$Y_{\text{DME, H}_{2}} = \frac{3\int\limits_{k=1}^{1} f_{2}(\zeta)r_{4}(\mathbf{K}_{2}, \mathbf{x}(\zeta))\zeta^{2}d\zeta}{\sum\limits_{k=1}^{0} |\nu_{k,\text{H}_{2}}|r_{k}(\mathbf{K}_{1}, \mathbf{x}_{bulk}(\zeta))},$$
(9)

As for the case of the system of generic chemical reactions (Equation (6)), the numerator in Equation (9) denotes the actual production of the final product, whereas the denominator is the consumption rate of hydrogen evaluated in the bulk gas conditions.

Figure 8 shows values of the yield of DME with respect to hydrogen, Y_{DME, H_2} , as a function of particle radius, R_p , calculated for three arrangements of metallic and acidic catalyst and for two values of the process temperature, namely T = 493 K (Figure 8a) and T = 503 K (Figure 8b). The very low values of Y_{DME, H_2} obtained for all three arrangements result from the assumed concentration of the species in the bulk gas conditions. Additionally, Table 3 reports representative values of Y_{DME, H_2} , and the variation in Y_{DME, H_2} determined by treating as a reference value the yield of DME achieved, in the same conditions, using uniform distribution of the functionalities within the pellet.

For the smallest radii $Y_{\text{DME, H}_2}$ curves practically overlap (Figure 8), mainly due to little influence of the pellet structure resulting from the negligible resistance to internal mass transfer. For larger radii, the highest yield of DME is predicted for the c1-s2 arrangement of catalytic active centers. Indeed, the variant c1-s2 appears to perform here much better than the uniform one, meaning that the pellet with acidic shell performing as a "trap" for methanol diffusing towards the surface is the best alternative.

The analysis of the temperature influence on the DME yield indicates that, for small to intermediate pellet radii, i.e., $R_p < 10^{-3}$ m (for which the arrangement of two active centers has no significant impact on the $Y_{\text{DME}, \text{H}_2}$), a temperature increase by 10 K results in a yield enhancement of about 15% (Figure 8a,b). The exothermic character of the methanol synthesis (Equations (2) and (4)) and methanol dehydration (Equation (5)) suggests a decrease in conversion as the temperature increases. However, for the analyzed values of the temperature, the presence of carbon monoxide in a raw syngas may significantly increase the conversion of hydrogen into methanol, even when increasing the process temperature [31].



Figure 7. Radial distribution of hydrogen and methanol molar fraction for T = 493 K and the pellet with different radii: (a) Distribution of x_{H_2} for $R_p = 2 \times 10^{-4}$ m; (b) distribution of x_{CH_3OH} for $R_p = 2 \times 10^{-4}$ m; (c) distribution of x_{H_2} for $R_p = 10^{-3}$ m; (d) distribution of x_{CH_3OH} for $R_p = 10^{-3}$ m; (e) distribution of x_{H_2} for $R_p = 4 \times 10^{-3}$ m; (f) distribution of x_{CH_3OH} for $R_p = 4 \times 10^{-3}$ m.



Figure 8. Yield of DME with respect to hydrogen, Y_{DME, H_2} , as a function of the pellet radius, R_p : (a) Y_{DME, H_2} for the process temperature T = 493 K; (b) Y_{DME, H_2} for the process temperature T = 503 K.

Table 3.	Enhancement in the	DME yield, $Y_{DME,I}$	$_{\rm H_2}$, for c1-s2 and $_{\rm o}$	c2-s1 arrangements	with respect to
$Y_{\text{DME, H}}$	2 obtained for uniform	n distribution of cat	alytic active cente	ers within the pellet	

Catalyst Arrangement	Temperature, K	Particle Radius, m	Yield, Y _{DME,H2}	Yield Enhancement	Selectivity, S _{DME,H2}
Laiform	493	2×10^{-4}	0.0629	-	0.1260
		10^{-3}	0.0474	-	0.1008
		4×10^{-3}	0.0219	-	0.0748
Cimorin	503	2×10^{-4}	0.0731	-	0.1467
		10^{-3}	0.0502	-	0.1091
		4×10^{-3}	0.0247	-	0.1001
c1-s2 -	493	2×10^{-4}	0.0631	+0.32%	0.1263
		10^{-3}	0.0537	+13.34%	0.1232
		4×10^{-3}	0.0345	+57.35%	0.2123
	503	2×10^{-4}	0.0737	+0.79%	0.1480
		10^{-3}	0.0592	+18.03%	0.1432
		4×10^{-3}	0.0400	+62.29%	0.3684
c2-s1		2×10^{-4}	0.0633	+0.68%	0.1273
	493	10^{-3}	0.0473	-0.13%	0.0974
		4×10^{-3}	0.0145	-33.65%	0.0380
	503	2×10^{-4}	0.0736	+0.64%	0.1481
		10^{-3}	0.0478	-4.07%	0.0992
		4×10^{-3}	0.0138	-44.16%	0.0396

Representative values of the yield for uniform, c1-s2 and c2-s1 arrangements, and the yield enhancement, determined for c1-s2 and c2-s1 arrangements of two types of catalytic active centers, and related to uniform distribution being here a reference (Table 3), confirm the superiority of the structured pellets with metallic catalyst distributed in the core and acidic catalyst distributed in the shell (i.e., c1-s2). The selectivity of hydrogen towards DME, S_{DME,H_2} , defined as the ratio of actual production of DME and the actual consumption rate of hydrogen:

$$S_{\text{DME, H}_2} = \frac{\int_{0}^{1} f_2(\zeta) r_4(\mathbf{K}_2, \mathbf{x}(\zeta)) \zeta^2 d\zeta}{\int_{0}^{1} f_1(\zeta) \left(\sum_{k=1}^{3} |\nu_{k, \text{H}_2}| r_k(\mathbf{K}_1, \mathbf{x}(\zeta))\right) \zeta^2 d\zeta}.$$
(10)

also confirms that the structured c1-s2 pellet is the optimal choice. It must be underlined here that the selectivity calculated from Equation (10) strongly depends on the assumed concentration of the species in the bulk gas corresponding to the vicinity of the reactor inlet. For this reason, much higher values of $S_{\text{DME},\text{H}_2}$ are expected when evaluating the performance of bifunctional pellets on the entire reactor level.

3. Materials and Methods

3.1. Mathematical Model of a Single Bifunctional Catalyst Pellet for a System of Two Elementary Reversible Chemical Reactions

Let us consider a system of two elementary chemical reactions given by Equation (1) taking place in a non-isothermal spherical catalyst pellet of radius R_p that integrates two types of active centers. Under the assumption that pore diffusion occurs with the same, concentration independent, effective diffusivity for all components, the pellet mass and energy balances at steady state are [32]:

$$D_{eff}\left(\frac{d^2C_{\rm A}}{dr^2} + \frac{2}{r}\frac{dC_{\rm A}}{dr}\right) - f_1(r)r_1(C_{\rm A}, C_{\rm B}, T) = 0, \tag{11}$$

$$D_{eff}\left(\frac{d^2C_{\rm B}}{dr^2} + \frac{2}{r}\frac{dC_{\rm B}}{dr}\right) + f_1(r)r_1(C_{\rm A}, C_{\rm B}, T) - f_2(r)r_2(C_{\rm B}, C_{\rm C}, T) = 0,$$
(12)

$$\lambda_{eff} \left(\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} \right) + f_1(r) r_1(C_A, C_B, T) (-\Delta h_1) + f_2(r) r_2(C_B, C_C, T) (-\Delta h_2) = 0,$$
(13)

where $f_1(r)$ and $f_2(r) = 1 - f_1(r)$ denote the pellet volume fraction occupied by catalyst 1 (i.e., the one catalyzing the first step of the process) and catalyst 2 (catalyzing the second step), respectively. The reaction rates, r_i are assumed to be of the first order:

$$r_1(C_A, C_B, T) = k_1(T)C_A - k_{-1}(T)C_B = k_{01}\exp\left(-\frac{E_1}{RT}\right)\left(C_A - \frac{1}{K_{p1}(T)}C_B\right),\tag{14}$$

$$r_2(C_{\rm B}, C_{\rm C}, T) = k_2(T)C_{\rm B} - k_{-2}(T)C_{\rm C} = k_{02}\exp\left(-\frac{E_2}{RT}\right)\left(C_{\rm B} - \frac{1}{K_{p2}(T)}C_{\rm C}\right),\tag{15}$$

and K_{pj} is the equilibrium constant for reaction j = 1, 2. Due to generic character of the scheme of chemical reactions analyzed here, the temperature dependence of the equilibrium constants is expressed in the following simplified form [33]:

$$K_{pj}(T) = \exp\left(\frac{\Delta s_j T - \Delta h_j}{RT}\right), \quad j = 1, 2.$$
(16)

Assuming spherical symmetry of the concentration and temperature profiles within the catalyst pellet, the following Neumann boundary conditions are imposed at the pellet center:

$$\left. \frac{dC_i}{dr} \right|_{r=0} = 0, \ i = A, B; \ \left. \frac{dT}{dr} \right|_{r=0} = 0.$$
(17)

Accounting for external resistance to mass and heat transfer and assuming that external mass transfer coefficients are the same for all components, Robin boundary conditions at the pellet surface are written as:

$$D_{eff} \left. \frac{dC_i}{dr} \right|_{r=R_p} = k_m \Big(C_{bulk,i} - C_i(R_p) \Big), \quad i = A, B; \quad \lambda_{eff} \left. \frac{dT}{dr} \right|_{r=R_p} = \alpha_q \Big(T_{bulk} - T(R_p) \Big). \tag{18}$$

After introducing the dimensionless variables:

$$\beta_{\rm A} = \frac{C_{\rm A}}{C_{ref}}, \ \beta_{\rm B} = \frac{C_{\rm B}}{C_{ref}}, \ \vartheta = \frac{T}{T_{ref}}, \ \zeta = \frac{r}{R_p} \in [0, 1],$$
(19)

the pellet model (Equations (11)–(13)) can be recast as:

$$\frac{d^2\beta_{\rm A}}{d\zeta^2} + \frac{2}{\zeta}\frac{d\beta_{\rm A}}{d\zeta} - \Phi_1^2 f_1(\zeta)\frac{\hat{r}_1(\beta_{\rm A},\beta_{\rm B},\vartheta)}{\hat{r}_{1,ref}} = 0,$$
(20)

$$\frac{d^2\beta_{\rm B}}{d\zeta^2} + \frac{2}{\zeta}\frac{d\beta_{\rm B}}{d\zeta} + \Phi_1^2 f_1(\zeta)\frac{\hat{r}_1(\beta_{\rm A},\beta_{\rm B},\vartheta)}{\hat{r}_{1,ref}} - \Phi_2^2 f_2(\zeta)\frac{\hat{r}_2(\beta_{\rm A},\beta_{\rm B},\vartheta)}{\hat{r}_{2,ref}} = 0,$$
(21)

$$\frac{d^2\vartheta}{d\zeta^2} + \frac{2}{\zeta}\frac{d\vartheta}{d\zeta} + \Phi_1^2\delta_1 f_1(\zeta)\frac{\hat{r}_1(\beta_A,\beta_B,\vartheta)}{\hat{r}_{1,ref}} + \Phi_2^2\delta_2 f_2(\zeta)\frac{\hat{r}_2(\beta_A,\beta_B,\vartheta)}{\hat{r}_{2,ref}} = 0.$$
(22)

where:

$$\hat{r}_1(\beta_{\rm A},\beta_{\rm B},\vartheta) = k_{01} \exp\left(-\frac{\gamma_1}{\vartheta}\right) \left(\beta_{\rm A} - \frac{1}{K_{p1}}\beta_{\rm B}\right), \quad \hat{r}_2(\beta_{\rm B},\beta_{\rm C},\vartheta) = k_{02} \exp\left(-\frac{\gamma_2}{\vartheta}\right) \left(\beta_{\rm B} - \frac{1}{K_{p2}}\beta_{\rm C}\right), \tag{23}$$

$$\hat{r}_{j,ref} = k_{0j} \exp(-\gamma_j) \left(1 + \frac{1}{K_{pj}(T_{ref})} \right), \quad \Phi_j^2 = \frac{R_p^2 \hat{r}_{j,ref}}{D_{eff}}, \quad \gamma_j = \frac{E_j}{RT_{ref}}, \quad \delta_j = \frac{D_{eff}(-\Delta h_j) C_{ref}}{\lambda_{eff} T_{ref}}, \quad j = 1, 2.$$

The plus sign in the reference reaction rate, $\hat{r}_{j,ref}$, i.e., the rate evaluated at bulk gas conditions, results from the definition of the Thiele modulus, ϕ , proposed in [32] for reversible chemical reaction. Moreover, considering that the process analyzed here is equimolar, the dimensionless concentration, β_i , is equivalent to molar fraction if $C_{ref} = C_{tot}$.

The boundary conditions (Equations (17) and (18)) associated with the pellet mass and energy balances written in terms of dimensionless variables are:

$$\frac{d\beta_i}{d\zeta}\Big|_{\zeta=0} = 0, \quad \frac{d\beta_i}{d\zeta}\Big|_{\zeta=1} = \operatorname{Bi}_m \left(\beta_{i,bulk} - \beta_i(1)\right), \quad i = A, B,$$
(25)

$$\left. \frac{d\vartheta}{d\zeta} \right|_{\zeta=0} = 0, \quad \left. \frac{d\vartheta}{d\zeta} \right|_{\zeta=1} = \operatorname{Bi}_q(\vartheta_{bulk} - \vartheta(1)), \tag{26}$$

where the mass and heat Biot numbers are defined, respectively, as:

$$\operatorname{Bi}_{m} = \frac{k_{m}R_{p}}{D_{eff}}, \quad \operatorname{Bi}_{q} = \frac{\alpha_{q}R_{p}}{\lambda_{eff}}.$$
(27)

3.2. Mathematical Model of a Single Bifunctional Catalyst Pellet for a Direct Synthesis of DME from Syngas

The kinetic model proposed in [24] describes the methanol synthesis step:

$$r_{1} = \frac{k_{1}K_{CO}\left(p_{CO}p_{H_{2}}^{3/2} - p_{CH_{3}OH} / (p_{H_{2}}^{1/2}K_{p_{1}}^{o})\right)}{\left(1 + K_{CO}p_{CO} + K_{CO_{2}}p_{CO_{2}}\right)\left(p_{H_{2}}^{1/2} + (K_{H_{2}O}/K_{H_{2}}^{1/2})p_{H_{2}O}\right)},$$
(28)

$$r_{2} = \frac{k_{2}K_{\rm CO_{2}}\left(p_{\rm CO_{2}}p_{\rm H_{2}} - p_{\rm H_{2}O}p_{\rm CO}/K_{p2}^{\rm o}\right)}{\left(1 + K_{\rm CO}p_{\rm CO} + K_{\rm CO_{2}}p_{\rm CO_{2}}\right)\left(p_{\rm H_{2}}^{1/2} + (K_{\rm H_{2}O}/K_{\rm H_{2}}^{1/2})p_{\rm H_{2}O}\right)},$$
(29)

$$r_{3} = \frac{k_{3}K_{\rm CO_{2}}\left(p_{\rm CO_{2}}p_{\rm H_{2}}^{3/2} - p_{\rm CH_{3}OH}p_{\rm H_{2}O}/(p_{\rm H_{2}}^{3/2}K_{p3}^{\rm o})\right)}{\left(1 + K_{\rm CO}p_{\rm CO} + K_{\rm CO_{2}}p_{\rm CO_{2}}\right)\left(p_{\rm H_{2}}^{1/2} + (K_{\rm H_{2}O}/K_{\rm H_{2}}^{1/2})p_{\rm H_{2}O}\right)},$$
(30)

whereas the kinetic rate expression selected for methanol dehydration is as follows [25]:

$$r_{4} = \frac{k_{4}K_{\text{CH}_{3}\text{OH}}^{2} \left(C_{\text{CH}_{3}\text{OH}}^{2} - C_{\text{H}_{2}\text{O}}C_{\text{DME}}/K_{p}\right)}{\left(1 + 2\sqrt{K_{\text{CH}_{3}\text{OH}}C_{\text{CH}_{3}\text{OH}}} + K_{\text{H}_{2}\text{O}}C_{\text{H}_{2}\text{O}}\right)^{4}}.$$
(31)

The formulas and parameters used to calculate the kinetic parameters and the equilibrium constants appearing in Equations (28)–(31) are reported in Appendix A.

To reduce the complexity of the pellet model, it is assumed that the process takes place isothermally and that the ideal gas law is obeyed. Following [28,34], the continuity equation and species mass balance for components i = 1, 2, ..., K - 1 are given, respectively, as:

$$\varepsilon_p \frac{\partial C}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u C) = \sum_{i=1}^K S_i,$$
(32)

$$\varepsilon_p \frac{\partial}{\partial t} (Cx_i) + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u Cx_i) = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 J_i) + S_i,$$
(33)

with the source term, S_i , defined as:

$$S_{i} = f_{1}(1 - \varepsilon_{p})\rho_{p}\sum_{k=1}^{3} v_{k,i}r_{i} + f_{2}(1 - \varepsilon_{p})\rho_{p}v_{4,i}r_{4}, \quad i = 1, 2, \dots, K.$$
(34)

where $f_1(r)$ and $f_2(r)$ denote the pellet volume fraction occupied, respectively, by metallic (catalyst 1) and acidic (catalyst 2) catalyst.

Making use of the continuity Equation (32), and assuming steady-state conditions and constant pressure within the pellet (i.e., no viscous flow, thus considering isothermal conditions and also constant concentration), the species mass balance for components i = 1, 2, ..., K - 1 (Equation (33)) can be simplified into the following form:

$$-\frac{1}{r^2}\frac{d}{dr}(r^2J_i) + S_i - \sum_{i=1}^K S_i = 0,$$
(35)

whereas the equation delivering component i = K is simply given by:

$$\sum_{i=1}^{K} x_i = 1.$$
(36)

The molecular diffusion fluxes, *J*_{*i*}:

$$J_i = -CD_{i,eff} \frac{dx_i}{dr}, \ i = 1, 2, \dots, K-1 \text{ and } \sum_{i=1}^K J_i = 0,$$
 (37)

are determined according to Wilke–Bosanquet model for multicomponent mass diffusion that combines bulk and Knudsen flux using the Fickian formulation [35]:

$$\frac{1}{D_i} = \frac{1}{D_{i,W}} + \frac{1}{D_{i,K}},\tag{38}$$

$$D_{i,W} = \frac{1 - x_i}{\sum_{\substack{j \neq i}}^{K} x_j / \mathcal{D}_{i,j}},$$
(39)

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$$D_{i,K} = \frac{97}{2} d_{pore} \sqrt{\frac{T}{M_i}},\tag{40}$$

with binary diffusion coefficients, $\mathcal{D}_{i,j}$ (note that for ideal gas conditions $D_{i,j} = D_{i,j} = D_{i,j}^{o}$), calculated according to the Chapman–Enskog kinetic theory [36]:

$$D_{i,j}^{0} = 1.883 \cdot 10^{-22} \frac{T^{1.5}}{p\sigma_{ij}^2 \Omega_D} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}.$$
(41)

Accounting further for the pores geometry, the effective diffusion coefficient of a component *i* in a multicomponent mixture, $D_{i,eff}$, is calculated as [35]:

$$D_{i,eff} = \frac{\varepsilon_p}{\tau} D_i. \tag{42}$$

The boundary conditions associated with the system of $2 \times (K-1)$ first-order differential equations (Equations (35) and (37)) are:

$$J_i(r=0) = 0, \ i = 1, 2, \dots, K-1,$$
 (43)

$$J_i(r = R_p) = -k_{i,m} \Big(C_{i,bulk} - C x_i(R_p) \Big).$$
(44)

where the mass transfer coefficients, $k_{i,m}$, are calculated from the Sherwood number correlation for a fixed bed [37]:

$$Sh = 2 + 1.8 Re_p^{0.5} Sc^{0.33}.$$
 (45)

Introduction of the expression describing the molecular flux (Equation (37)) into the species mass balance (Equation (35)) enables rewriting the pellet model in a form analogous to Equation (11), namely:

$$C\frac{d}{dr}\left(D_{i,eff}(\mathbf{x})\frac{dx_i}{dr}\right) + CD_{i,eff}(\mathbf{x})\frac{2}{r}\frac{dx_i}{dr} + S_i(\mathbf{x}) - \sum S_i(\mathbf{x}) = 0, \quad i = 1, \dots, K \dots 1,$$
(46)

where $\mathbf{x} = [x_1, \dots, x_K]$. The associated boundary conditions (Equations (43) and (44)) may be rewritten as:

$$\left. \frac{dx_i}{dr} \right|_{r=0} = 0, \quad i = 1, \dots, K-1,$$
(47)

$$CD_{i,eff}(\mathbf{x}) \left. \frac{dx_i}{dr} \right|_{r=R_p} = k_{i,m} \Big(C_{i,bulk} - Cx_i(R_p) \Big).$$
(48)

After introducing the dimensionless radial coordinate, ζ , concentration, β , and the additional dimensionless variables defined as:

$$\hat{D}_{eff} = \frac{D_{eff}}{D_{ref}}, \quad \hat{J} = \frac{JR_p}{D_{ref}C_{ref}}, \quad \hat{S} = \frac{SR_p^2}{D_{ref}C_{ref}}, \tag{49}$$

and assuming $C_{ref} = C = \text{const.}$, Equation (46) can be transformed into the following form:

$$\frac{d}{d\zeta} \left(\hat{D}_{i,eff}(\mathbf{x}) \frac{dx_i}{d\zeta} \right) + \hat{D}_{i,eff}(\mathbf{x}) \frac{2}{\zeta} \frac{dx_i}{d\zeta} + \hat{S}_i(\mathbf{x}) - \sum \hat{S}_i(\mathbf{x}) = 0, \quad i = 1, \dots, K-1.$$
(50)

The boundary conditions (Equations (47) and (48)) written in terms of dimensionless variables are:

$$\frac{dx_i}{d\zeta}\Big|_{\zeta=0} = 0, \quad \frac{dx_i}{d\zeta}\Big|_{\zeta=1} = \operatorname{Bi}_{i,m} \frac{\beta_{i,bulk} - x_i(1)}{\hat{D}_{i,eff}(\mathbf{x}(1))}, \quad i = 1, \dots, K-1,$$
(51)

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where:

$$\operatorname{Bi}_{i,m} = \frac{k_{i,m}R_p}{D_{ref}}.$$
(52)

3.3. Numerical Solution of the Model Equations

A classical strategy based on a finite difference method was used to discretize the pellet model, both in the case of the system of two elementary reversible chemical reactions and the direct synthesis of DME from syngas. Second-order differential Equations (20)–(22) with boundary conditions (Equations (25) and (26)) were transformed into a system of 3N nonlinear algebraic equations by approximation of the derivatives in N = 51 nodes, equally spaced along the particle radius, using central difference schemes [38]:

$$\frac{dy_n}{d\zeta} \approx \frac{y_{n+1} - y_{n-1}}{2\Delta\zeta},\tag{53}$$

$$\frac{d^2 y_n}{d\zeta^2} \approx \frac{y_{n+1} - 2y_n + y_{n-1}}{\Delta\zeta^2}.$$
(54)

where y_n is the value of dependent variable at n^{th} discretization node (n = 1, 2, ..., N) and $\Delta \zeta = 1/(N-1)$ is the distance between adjacent nodes.

In the case of the pellet model for direct synthesis of DME from syngas (Equation (50)), the derivative of the diffusive flux, which can generally be written as:

$$g(\zeta) = D(\mathbf{x}(\zeta)) \frac{dy}{d\zeta'},\tag{55}$$

was approximated using the following scheme [39]:

$$\frac{dg_n}{d\zeta} \approx \frac{g_{n+1/2} - g_{n-1/2}}{\Delta\zeta} = \frac{D_{n+1/2} \frac{y_{n+1} - y_n}{\Delta\zeta} - D_{n-1/2} \frac{y_n - y_{n-1}}{\Delta\zeta}}{\Delta\zeta} = \frac{D_{n+1/2} y_{n+1} - (D_{n+1/2} + D_{n-1/2}) y_n + D_{n-1/2} y_{n-1}}{\Delta\zeta^2}, \tag{56}$$

where:

$$D_{n+1/2} = \frac{D_{n+1} + D_n}{2}$$
 and $D_{n-1/2} = \frac{D_{n-1} + D_n}{2}$. (57)

The system of nonlinear algebraic equations, i.e., 3N equations for elementary chemical reactions and $N \times (K - 1)$ for DME synthesis, resulting from the above approximation, were solved numerically using the MATLAB *fsolve* function. Moreover, due to the detection of multiple solutions for a non-isothermal model of the pellet in which of two elementary chemical reactions take place, the pseudo-arclength continuation method [40] implemented in the AUTO 2007 software [41] was employed for the numerical continuation of the discretized system of Equations (20)–(22).

4. Conclusions

The potential of extending the multifunctionality of catalytic heterogenous chemical reactors down to the single-pellet level was evaluated using mathematical modelling and numerical simulations. Comparative analysis of the performance of three selected bifunctional catalyst pellet structures combining two types of catalytic active centers was conducted for a system of two generic elementary reversible chemical reactions and for the direct synthesis of dimethyl ether (DME) from synthesis gas. It was shown that proper structuring of the bifunctional catalysts is of a great importance, especially for intermediate and large radii of catalyst pellets, typical for fixed-bed reactor applications. Thus, the distribution of the different types of catalytic active centers may be considered as an additional design parameter in the optimization of multifunctional fixed-bed catalytic reactors for multistep process integration.

Based on the system of two generic chemical reactions, it was demonstrated that the superiority of a given catalyst arrangement also strongly depends on the rates of individual steps of the process.

In case of the real process of DME synthesis, the most advantageous was the c1-s2 arrangement with the metallic catalyst for methanol synthesis located in the pellet core and the acidic catalyst for methanol dehydration located in the outer shell. In both cases, the analysis was limited to a constant value of the pellet volume fraction occupied by each type of the catalyst and to fixed bulk gas conditions. However, it is apparent that different shares of the two or more types of catalytic active centers need to be evaluated as an additional design parameter of the pellet and that the very promising results reported here need to be verified with the entire reactor model. Moreover, some additional aspects concerning the direct synthesis of DME that were not considered within this study require further investigations. This includes evaluation of the influence of the pores size distribution on the bifunctional pellet performance, as well as detailed analysis of the impact of significantly different values of the diffusion coefficient of individual species on the process selectivity and, considering the risk of catalyst deactivation due to hot spots, evaluation of the intraparticle temperature distribution. Furthermore, it must be remembered that when the acidic function is mixed with the metallic one, the acidic properties of the former are expected to change, thus it is essential also to evaluate the influence of these changes on the overall performance of the bifunctional catalyst pellet. Finally, considering the growing importance of zeolite-type catalysts in the DME production from methanol, it is necessary to improve the intraparticle mass diffusion model to account also for configurational and surface diffusion.

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Nomenclature

Bi_m , Bi_q	Mass and heat Biot numbers, respectively
С	Total concentration, kmol·m ⁻³
C _i	Concentration of component <i>i</i> , kmol·m ^{-3}
d _{pore}	Pore diameter, m
D_{eff}	Effective diffusion coefficient, $m^2 \cdot s^{-1}$
$D_{i,K}$	Knudsen diffusion coefficient for component i , m ² ·s ⁻¹
$D_{i,W}$	Wilke diffusion coefficient for component <i>i</i> , $m^2 \cdot s^{-1}$
$D^{\mathrm{o}}_{i,j}$	Infinite dilution diffusivity for component <i>i</i> present in trace amount in component <i>j</i> , $m^2 \cdot s^{-1}$
$\mathcal{D}_{i,j}$	Maxwell-Stefan diffusion coefficient, m ² ·s ⁻¹
E_i	Activation energy of the <i>j</i> th chemical reaction, $kJ \cdot kmol^{-1}$
f_i	Volume fraction of the catalyst with active sites enhancing <i>j</i> th chemical reaction
Ĵi	Molecular diffusion flux, kmol·s ⁻¹ ·m ⁻²
Δh_j	Enthalpy of the <i>j</i> th chemical reaction, $kJ \cdot kmol^{-1}$
k_{0j}	Frequency coefficient in the Arrhenius equation for the <i>j</i> th chemical reaction, s^{-1}
k _j	Reaction rate constant for the <i>j</i> th elementary chemical reaction, s^{-1} (note: the units of k_j for
	the process of DME production are given in Appendix A)
k_m	Mass transfer coefficient, $m \cdot s^{-1}$
K_i	Adsorption equilibrium constant for component <i>i</i> (note: the units are given in Appendix A)
K _{pj}	Equilibrium constant for the <i>j</i> th chemical reaction (note: the units of K_{pj} for the methanol
	synthesis step in the DME production are given in Appendix A)
M_i	Molecular weight, kg·kmol ^{−1}
r	Radial coordinate, m
	Rate of the <i>i</i> th chemical reaction based on solid volume within the pellet (for the system of
r_j	elementary chemical reactions) or on the pellet volume (for the process of DME
	synthesis), kmol·m ⁻³ ·s ⁻¹

Р	Pressure, bar
p_i	Partial pressure of component <i>i</i> , bar
R	Universal gas constant, $kJ\cdot kmol^{-1}\cdot K^{-1}$
R_{p}	Catalyst pellet radius, m
Δs_i	Entropy change in the <i>j</i> th chemical reaction, $kJ \cdot kmol^{-1} \cdot K^{-1}$
Si	Molecular source term, $\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$
S _{DME.H2}	Selectivity of H_2 towards DME
Т	Temperature, K
и	Molar average velocity in the catalyst pellet, $m \cdot s^{-1}$
u_0	Superficial gas velocity in the bulk gas, $m \cdot s^{-1}$
x _i	Molar fraction of component <i>i</i>
Y _{CA}	Yield of product C with respect to reactant A
Y _{DME,H2}	Yield of DME with respect to H_2
Greek Letters	
α_q	Heat transfer coefficient, $kW \cdot m^{-2} \cdot K^{-1}$
β_i	Dimensionless concentration of component <i>i</i>
Υi	Dimensionless parameter related to activation energy of the <i>j</i> th chemical reaction
δ_i	Dimensionless parameter related to enthalpy of the <i>j</i> th chemical reaction
ε _p	Porosity of the catalyst pellet
ζ	Dimensionless radial coordinate
θ	Dimensionless temperature
ν	Stoichiometric coefficient
λ_{eff}	Effective heat transfer coefficient within the pellet, $kW \cdot m^{-1} \cdot K^{-1}$
ρ_p	Catalyst pellet density, kg·m ⁻³
σ	Lennard-Jones characteristic length, m
τ	Tortuosity of the catalyst pellet
Фј	Thiele modulus for the <i>j</i> th chemical reaction
Ω_D	Dimensionless collision integral
Subscripts	
bulk	Gas bulk conditions
eff	Effective
р	Pellet
ref	Reference conditions

Appendix A

For the methanol synthesis step (Equations (2)–(4) and (28)–(30)), the following expressions reported for a commercial for the commercial a $CuO/ZnO/Al_2O_3$ catalyst in [24] are used to determine the kinetic parameters:

$$k_1 = 4.89 \times 10^4 \exp\left(\frac{-113000}{RT}\right) \frac{\text{kmol}}{\text{s} \cdot \text{kg} \cdot \text{bar}}, \quad k_2 = 9.64 \times 10^8 \exp\left(\frac{-152900}{RT}\right) \frac{\text{kmol}}{\text{s} \cdot \text{kg} \cdot \text{bar}^{1/2}},$$
(A1)

$$k_{3} = 1.09 \times 10^{2} \exp\left(\frac{-87500}{RT}\right) \frac{\text{kmol}}{\text{s} \cdot \text{kg} \cdot \text{bar}}, \quad K_{\text{CO}} = 2.16 \times 10^{-5} \exp\left(\frac{46800}{RT}\right) \frac{1}{\text{bar}}, \tag{A2}$$

$$K_{\rm CO_2} = 7.05 \times 10^{-7} \exp\left(\frac{61700}{RT}\right) \frac{1}{\rm bar}, \quad K_{\rm H_2O} / K_{\rm H_2}^{1/2} = 6.37 \times 10^{-9} \exp\left(\frac{84000}{RT}\right) \frac{1}{\rm bar^{1/2}}.$$
 (A3)

whereas chemical equilibrium constants are determined using the relationships proposed in [42]:

$$\ln K_{p1}^{0} = \frac{1}{RT} (a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 + a_6T^5 + a_7T\ln T),$$
(A4)

$$\ln K_{p2}^{o} = \frac{1}{RT} (b_1 + b_2 T + b_3 T^2 + b_4 T^3 + b_5 T^4 + b_6 T^5 + b_7 T \ln T),$$
(A5)

$$K_{p3}^{o} = K_{p1}^{o} \cdot K_{p2}^{o} \operatorname{bar}^{-2}, \tag{A6}$$

with the unit for K_{p1}^{0} being bar⁻² and K_{p2}^{0} being dimensionless constant. The parameters in Equations (A4) and (A5) are:

$$a_1 = 7.44140 \times 10^4, \ a_2 = 1.89260 \times 10^2, \ a_3 = 3.2443 \times 10^{-2}, \ a_4 = 7.0432 \times 10^{-6}$$

$$a_5 = -5.6053 \times 10^{-9}, \ a_6 = 1.0344 \times 10^{-12}, \ a_7 = -6.4364 \cdot 10^1,$$
 (A7)

$$b_1 = -3.94121 \times 10^4, \ b_2 = -5.41516 \cdot 10^1, \ b_3 = -5.5642 \times 10^{-2}, \ b_4 = 2.5760 \times 10^{-5}$$

$$b_5 = -7.6594 \times 10^{-9}, \ b_6 = 1.0161 \times 10^{-12}, \ b_7 = 1.8429 \cdot 10^1.$$
 (A8)

The kinetic parameters for the methanol dehydration step (Equations (5) and (31)) are calculated using the following formulas determined for Bayer SAS-350 γ -Al₂O₃ catalyst [25]:

$$k_4 = 1.49 \times 10^{10} \exp\left(\frac{-17280}{T}\right) \frac{\text{kmol}}{\text{s} \cdot \text{kg} \cdot \text{bar}},\tag{A9}$$

$$K_{\rm CH_3OH} = 5.39 \times 10^{-4} \exp\left(\frac{8487}{T}\right) \frac{\rm m^3}{\rm kmol}, \quad K_{\rm H_2O} = 8.47 \times 10^{-2} \exp\left(\frac{5070}{T}\right) \frac{\rm m^3}{\rm kmol}, \tag{A10}$$

whereas the chemical equilibrium constant is calculated as follows [43]:

$$\ln K_p = \frac{c_1}{T} + c_2 \ln T + c_3 T + c_4 T^2 + c_5, \tag{A11}$$

where:

$$c_1 = 2835.2, c_2 = 1.675, c_3 = -2.39 \times 10^{-4}, c_4 = -0.21 \times 10^{-6}, c_5 = -13.360.$$
 (A12)

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