Open-cell foams as catalysts support

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Open-cell foams as catalysts support: A systematic analysis of the mass transfer limitations

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**HIGHLIGHTS**

- Systematic analysis of the mass transfer limitation in wash-coated open-cell foams.
- CFD simulations on Kelvin’s cell by DNS.
- Mass transfer correlation for low Reynolds number.
- Practical criteria in terms of dimensionless numbers for rate limiting regimes.

**ARTICLE INFO**

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Direct Numerical Simulations  
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**ABSTRACT**

In this work, the analysis of the mass transfer phenomena in catalytic open-cell foams is carried out through the combination of computational fluid dynamics (CFD) simulations and experiments, using the CO oxidation on Pt (1%)/γ-Al\textsubscript{2}O\textsubscript{3}/foam as a model reaction. The influence of the local hydrodynamic effects on the diffusion-reaction phenomena occurring at the gas-solid interface of the open-cell solid foams are investigated by Direct Numerical Simulations assuming an infinitely fast reaction. A correlation for the Sherwood number as function of Reynolds -for low Re- is proposed. To validate this experimentally, aluminum foams coated with Pt(1%)/γ-Al\textsubscript{2}O\textsubscript{3} are tested at different reaction conditions for the CO oxidation. The obtained reaction rates and apparent activation energy show the presence of external mass transfer limitations. An analysis of the diffusion-reaction phenomena taking place in the wash-coated layer is presented in terms of dimensionless numbers. A practical criterion is developed in terms of the Thiele modulus (Φ\textsubscript{w}) and the Biot number (B\textsubscript{im}) for the identification of the reaction regimes: kinetic control (<Φ\textsubscript{w}/B\textsubscript{im} > 0.1), internal and/or external mass transfer limitations (0.1 < Φ\textsubscript{w}/B\textsubscript{im} < 10), and full mass transfer control (>Φ\textsubscript{w}/B\textsubscript{im} > 10).

1. Introduction

Open-cell foams are one of the most promising structured catalysts for process intensification, combining a large surface area and high void fraction [1]. These characteristics, with respect to packed bed reactors, lead to enhanced mass transfer properties and lower pressure drop. Compared to honeycombs, it was shown that the overall performance of foams is better for certain applications [2]. Foam catalysts were applied for Fischer-Tropsch synthesis [3,4], volatile organic compounds oxidation [5], water disinfection by photocatalytic process [6,7], catalytic wet peroxide oxidation [8], preferential oxidation of CO (CO-PROX) [9], partial oxidation of methanol [10], among others. While foam catalysts have proven successful for numerous applications, a fundamental understanding and first-principle quantification of the contribution of transport phenomena (momentum, heat and mass) to the performance of open-cell foams is lacking.

In the last few years, several research groups have made an effort to study and quantify the mass transport in open-cell foams by means of experiments [2,11–14] and numerical simulations [15–27]. Richardson et al. [11] investigated the mass and heat transport properties for a ceramic foam coated with Pt/γ-Al\textsubscript{2}O\textsubscript{3}. The authors studied the CO oxidation operating in the external mass transfer controlling regime,
and obtained correlations for the mass and radial heat transfer coefficients as a function of the Reynolds number. Later, Tronconi et al. [12] characterized the mass transfer in a Pd/Al2O3 wash-coated metal foams during the CO oxidation and obtained a dimensionless correlation for mass transfer coefficients which closely resembles semi-theoretical correlations. They further extended their work to ceramic foams with higher relative densities [13], and proposed a more generalized correlation. Similarly, Incera Garrido et al. [2,14] studied the mass transfer during the CO oxidation and obtained a dimensionless correlation for the mass and radial heat transfer coefficients as a function of the Reynolds number. Later, Tronconi et al. [12] characterized the mass transfer in a Pd/Al2O3 wash-coated metal foams during the CO oxidation and obtained a dimensionless correlation for mass transfer coefficients which closely resembles semi-theoretical correlations. They further extended their work to ceramic foams with higher relative densities [13], and proposed a more generalized correlation. Similarly, Incera Garrido et al. [2,14] studied the mass transfer during the CO oxidation and obtained a dimensionless correlation for the mass and radial heat transfer coefficients as a function of the Reynolds number. Later, Tronconi et al. [12] characterized the mass transfer in a Pd/Al2O3 wash-coated metal foams during the CO oxidation and obtained a dimensionless correlation for mass transfer coefficients which closely resembles semi-theoretical correlations. They further extended their work to ceramic foams with higher relative densities [13], and proposed a more generalized correlation. Similarly, Incera Garrido et al. [2,14] studied the mass transfer during the CO oxidation and obtained a dimensionless correlation for the mass and radial heat transfer coefficients as a function of the Reynolds number. Later, Tronconi et al. [12] characterized the mass transfer in a Pd/Al2O3 wash-coated metal foams during the CO oxidation and obtained a dimensionless correlation for mass transfer coefficients which closely resembles semi-theoretical correlations. They further extended their work to ceramic foams with higher relative densities [13], and proposed a more generalized correlation. Similarly, Incera Garrido et al. [2,14] studied the mass transfer during the CO oxidation and obtained a dimensionless correlation for the mass and radial heat transfer coefficients as a function of the Reynolds number. Later, Tronconi et al. [12] characterized the mass transfer in a Pd/Al2O3 wash-coated metal foams during the CO oxidation and obtained a dimensionless correlation for mass transfer coefficients which closely resembles semi-theoretical correlations. They further extended their work to ceramic foams with higher relative densities [13], and proposed a more generalized correlation. Similarly, Incera Garrido et al. [2,14] studied the mass transfer during the CO oxidation and obtained a dimensionless correlation for the mass and radial heat transfer coefficients as a function of the Reynolds number. Later, Tronconi et al. [12] characterized the mass transfer in a Pd/Al2O3 wash-coated metal foams during the CO oxidation and obtained a dimensionless correlation for mass transfer coefficients which closely resembles semi-theoretical correlations. They further extended their work to ceramic foams with higher relative densities [13], and proposed a more generalized correlation. Similarly, Incera Garrido et al. [2,14] studied the mass transfer during the CO oxidation and obtained a dimensionless correlation for the mass and radial heat transfer coefficients as a function of the Reynolds number. Later, Tronconi et al. [12] characterized the mass transfer in a Pd/Al2O3 wash-coated metal foams during the CO oxidation and obtained a dimensionless correlation for mass transfer coefficients which closely resembles semi-theoretical correlations. They further extended their work to ceramic foams with higher relative densities [13], and proposed a more generalized correlation. Similarly, Incera Garrido et al. [2,14] studied the mass transfer during the CO oxidation and obtained a dimensionless correlation for the mass and radial heat transfer coefficients as a function of the Reynolds number. Later, Tronconi et al. [12] characterized the mass transfer in a Pd/Al2O3 wash-coated metal foams during the CO oxidation and obtained a dimensionless correlation for mass transfer coefficients which closely resembles semi-theoretical correlations. They further extended their work to ceramic foams with higher relative densities [13], and proposed a more generalized correlation. Similarly, Incera Garrido et al. [2,14] studied the mass transfer during the CO oxidation and obtained a dimensionless correlation for the mass and radial heat transfer coefficients as a function of the Reynolds number.

When performing numerical studies, the effect of intrinsic kinetics on the determination of the mass transfer coefficient can be avoided as one may impose a pre-determined rate value. Over the last few years, some research groups have studied the mass and heat transport, as well as the hydrodynamics, in foams by CFD simulations and numerical calculations [15–27]. Lucchi et al. [16] used CFD calculations with so-called Kelvin cell structures to estimate the mass transfer coefficient. They obtained Sherwood correlation as a function of the dimensionless pressure drop, comparing the analysis to honeycombs and to experimental results [17]. Della Torre et al. [18] presented a CFD model for the simulation of the fluid-dynamics coupled with the reactions occurring on the surface of foams. The model could describe the conversion under kinetic control and diffusion control regime, and was able to predict the light-off curve for the CO oxidation. In a recent work [19], CFD calculations for fundamental investigation of the fluid–solid mass transfer properties of foams using virtually generated structures were performed and correlations of Sherwood vs Reynolds numbers were proposed taking into account the geometry parameters of the foams (porosity, strut diameter, etc.). However, in these works [17–20] the mass transfer coefficient was obtained at relatively high Re numbers and no asymptotic value of the mass transfer coefficient in the absence of convection was calculated. Furthermore, in the reported experimental [2,11–14] and simulation works [16–19], Sherwood numbers were calculated assuming full external mass-transfer limitations and measuring the conversion at the exit of the reactor. Then, the mass transfer coefficient was calculated by:

$$k_{\text{inj}} = -\frac{\ln(1 - X_{\text{CO}})}{S_{\text{geo}} W V / Q}$$  

(1)

where $X_{\text{CO}}$ is the CO conversion, $S_{\text{geo}}$ the geometrical specific surface area, $V$ the volume of the foam and $Q$ the volumetric flow rate. Equation (1) is derived by neglecting the hydrodynamic dispersion mechanism and assuming a uniform and constant mass transfer coefficient. Nevertheless, the foams may not be oriented in a uniform manner and the local mass transport could vary considerably depending on the local velocity profile [29], thus influencing the mass transfer coefficient as well. It was shown by some of us [29] that at low Reynolds numbers dispersion may not be negligible and thus a more rigorous approach to calculate the mass transfer coefficient such as the one used in this work must be used.

For all the presented reasons, a systematic analysis on the effects of internal and external mass transport in open-cell foams, including a more accurate determination of the mass transfer coefficient, is of crucial importance. Ideally, this should result in an easy-to-use practical criterion able to identify the controlling regime in terms of dimensionless numbers, thus facilitating the future study and development of open-cell foams for real applications.

For the first time, this work describes a systematic evaluation of transport effects on catalytic performance using open-cell foams, specifically addressing the to-date unresolved question of the relative importance of external and internal diffusion limitations. To this end, we use a combined numerical and experimental approach. The CO oxidation as a model reaction is studied using aluminum foams of different ppi with wash-coatings of Pt(1%)/γ-Al2O3. The experimental work is
complemented by pore-scale Direct Numerical Simulations of flow and mass transport in idealized open-cell foams represented by the Kelvin’s unit cell. The simulations are performed by applying periodic boundary conditions whereby, the Sherwood number is dependent only on the fully-developed local velocity field. Finally, a systematic analysis of a first order reaction in a slab coupled with the fluid–solid mass transfer is performed and a criterion for determining the presence/absence of mass transfer limitation in open-cell foams in terms of dimensionless numbers is developed. The criteria is essential for develop open-cell foams for applications beyond this study.

2. Experimental

2.1. Foam preparation and characterization

Aluminum foams (Duocel®, Alloy AA6101) of 10, 20 and 40 ppi and 6–8% of relative density were coated with layers of Pt(1%)/γ-Al2O3 of thickness from 15 to 50 µm following a wash-coating methodology earlier developed in our group [30,31].

Briefly, the foams were cut in cylinders of 20 mm length and 10 mm diameter and anodized in order to increase the adherence of the wash-coating layer. A layer of γ-Al2O3, previously ball-milled, was deposited on the foams by wash-coating. The textural and physical properties (SBET, pore volume, pore size, particle size) of the aluminum oxide before and after ball-milling are shown in Table S.I. 1. A suspension containing γ-Al2O3, boehmite as binder and citric acid for pH regulation was prepared. The foams were dipped in the suspension, later dried and calcined at 550 °C for 4 h. The Pt was deposited on the wash-coated foams by wet impregnation using a solution of [Pt(NH3)4](NO3)2 (Sigma-Aldrich), with a final Pt loading of 1 wt%. Afterwards, the foams were washed with deionized water and dried in oven. Then, the foams were oxidized at 400 °C for 4 h, reduced at 400 °C for 4 h in pure hydrogen, and finally passivated. The wash-coated foams were characterized by SEM and a stability test. More details of the preparation procedure and materials utilized can be found in the Supplementary Information (S.I.).

2.2. Activity tests

The prepared foams were tested at different reaction conditions for the CO oxidation: 1 bar, 135–185 °C, and CO/O2 = 1/2. The conditions were chosen in order to have differential conditions, i.e. conversion less than 10%. The foams were placed in a 10 mm diameter reactor between two pieces of 10 mm length bare foams (i.e. without wash-coating) to ensure a developed velocity profile through the active foam. The reactor was filled with SiC previous to the foams to pre-heat the gases (Fig. 1). The reactor was placed in an oven and the temperature was measured with two thermocouples inserted in the reactor, one at the inlet in the SiC bed, and the second one close to the reactor exit. Before the experiments, the catalysts were reduced in-situ by flowing 40 mL/min of pure H2 (5 °C/min, 250 °C, 2 h), and then cooling down to the reaction temperature (135 °C) flowing N2. The reaction was studied in the range of 135–185 °C at intervals of 10 °C, fixed for 30 min to reach steady-state at each temperature. The exit of the reactor was connected to a mass spectrometer for the quantification of the reactants/products.

2.3. Simulations

Fully resolved simulations were performed using the Immersed Boundary Method developed by Deen et al. [32], which employs a uniform three-dimensional Cartesian mesh. The computational domain is a cubic box that contains both the fluid and solid phases, where the solid phase is the idealized construction of open-cell foams represented by the spatially periodic Kelvin unit cell. The quantitative measurement of the fluid-solid heat transfer coefficient for realistic computationally generated open-cell foams by Das et al. [23] showed very little deviation against the periodic foam samples [39]. Thus, justifying the using of the periodic Kelvin cells. The details of the geometry and construction process of the Kelvin cell may be found in Das et al. [33]. The Kelvin cell used in the simulations has a porosity of 0.92 consistent with the experiments performed here. It is assumed that an infinitely fast reaction occurs over the surface of the Kelvin’s cell and the influence of varying flow rates on the external mass transfer coefficient is studied. The species balance equation is solved along with the momentum balance equations and the fluid-solid interface mass transfer coefficient is calculated to perform an analysis of the external mass transport limitations. The momentum and mass transport equations governing the fluid phase is given by:

\[ \nabla \cdot \mathbf{v} = 0 \]  
\[ \rho \frac{D\mathbf{v}}{Dt} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \nabla \left[ \mu \left( \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right) \right] \]  
\[ \frac{Dc}{Dt} + \mathbf{v} \cdot \nabla c = D_m V^2 c \]

where \( \mathbf{v} \) is the velocity, \( \rho \) is the density, \( c \) is the molar concentration and \( D_m \) is the diffusion coefficient. The following boundary conditions are enforced using the Immersed Boundary Method [33] along the entire fluid-solid interface within the computational domain where the no-slip boundary condition is used for the velocity field and an infinitely fast fluid–solid heat transfer is enforced.

![Fig. 1. Schematic representation of the reactor.](image-url)
reaction for concentration given by:

\[ \bar{v} = 0 \quad (5) \]

\[ c = 0 \quad (6) \]

As the medium is modeled as spatially periodic, the following self-similarity constraints given by the periodic boundary conditions are used to simulate the fully-developed profile. This ensures that the closures obtained are free of inlet, outlet or wall effects, which generally influence the heat and mass transfer coefficients obtained experimentally in small-scale laboratory experiments. The physical reasoning and justifications for the employed boundary conditions may be found in Das et al. [33].

\[ \bar{v}(x, y, z) = \bar{v}(x + L, y, z), \bar{v}(x, y, z) = \bar{v}(x, y + L, z), \bar{v}(x, y, z) = \bar{v}(x, y, z + L), \quad (7) \]

\[ \frac{c(x, y, z)}{c_v(x)} = \frac{c(x + L, y, z)}{c_v(x + L)}, \quad (8) \]

where L refers to the length of the Kelvin’s cell and \( c_v \) refers to the velocity averaged concentration across any axial plane within the computational domain given by \( c_v(x) = \frac{\iint \text{D} c \text{d}l}{\iint \text{d}S} \). The details of the numerical procedure to solve the above system of equations may be found in Deen et al. [32] and Das et al. [33].

3. Results and discussion

3.1. Foams characterization

SEM images (Fig. S.I. 1) were obtained after the anodization process for studying the effect on the surface of the foams. The anodization process produces a non-uniform pattern of holes, and the whole surface is covered by irregular grooves. The overall process increases the adherence of the aluminum oxide layer. Details of the results can be found in the S.I. Similar results were obtained by Sanz et al. [34], using comparable anodization conditions.

A series of foams were wash-coated with γ-Al2O3 and characterized by SEM (Fig. S.I. 2), showing that the obtained oxide layers are uniform. Also, several scratched were made in order to measure the thickness of the layer and correlate it with the mass deposited. In order to test the satisability of the wash-coated layer, some foams where placed in an ultrasonic-bath and sonicating during 30 min. In all cases the mass loss was less than 5%. Table 1 shows the properties of the wash-coated foams used in this work for the CO oxidation.

3.2. Carbon monoxide oxidation

The foams were tested in a tubular reactor with the conditions shown in Table 2. The reaction rates per mass of wash-coated catalyst vs. the temperature are plotted in Fig. 2A-C. The CO conversion is shown in Fig. S1. If the reaction is in kinetic control regime, the reaction rate should be independent of the external surface area, or other geometrical factor. However, it can be seen that the activity of the 40 ppi foam is higher than that of the other foams under all experimental conditions, following the trend of 40 > 20 > 10. Furthermore, when the reaction rates are normalized by the external surface area (Sgeo) the curves come together, stronger indicating an effect of the external mass transport on the observed reaction rate. In Fig. 2D-E the reaction rate per mass of catalyst is normalized by the product \( k_{fl} S_{geo} \) where the mass transfer coefficient \( k_{fl} \) was calculated using the correlation obtained in this work (Eq. 11, section 3.3).

In order to further analyze the effects of the mass transfer limitations effect, the apparent activation energy (E_{app}) was calculated using the Arrhenius plot in Fig. 3A-C. Table 2 shows the E_{app} obtained for the different foams and conditions. If the reaction was fully mass-transfer limited, one would expect an E_{app} close to zero [35], which is not the case in this study. Here, the E_{app} changes with the flow rates between 110 and 70 kJ/mol, still suggesting the presence of (external) mass transfer limitations. Fig. 3D-E shows the Arrhenius plot, were the reaction rate was normalized by the product \( k_{fl} S_{geo} \). It can be clearly seen that the slope of the curves for the three foams are similar for each flow rate condition, but different for different flow rates, showing the effect of the flow rate on the E_{app}. Thus, the results in Figs. 2 and 3 indicate the presence of external mass transfer limitations, and consequently, it becomes necessary to quantify the effect of the internal and external mass transfer resistances.

In section 3.4, a systematic analysis of the influence of the internal and external mass transfer limitation in a slab is consider and a criterion is established for quantifying the relative importance of the transport phenomena. In order to calculate the mass transfer coefficient, direct numerical simulations (DNS) are performed in section 3.3.

3.3. Direct numeric simulation

DNS was performed to study the influence of flow-rate on the mass transfer coefficient. The flow-rate (characterized by the Reynolds number Re) is varied by varying the pressure gradient applied along the length of the periodic unit cell. All analyses is performed at low Re (non-dimensionalized by the superficial velocity, U) within the Kelvin cell in accordance with the experiments and the mass transfer coefficients are evaluated as explained below. The dimensionless concentration contour plots for various Reynolds numbers are presented in Fig. 4 which depicts how the reactant spreads across the Kelvin cell. It is observed that at low Reynolds numbers the concentration is spread uniformly across the Kelvin cell with the external film boundary almost absent. As the Reynolds number is increased, the concentration boundary layers are visibly prominent with sharp gradients along the surface of the catalyst. Much of the reactants are trapped within the inertial core of the Kelvin cell inhibited from reaching the active catalytic surface of the foams. This is due to the existence of a continuous jet which flows right through the periodic Kelvin cell [33].

The mass flux through the interface of the Kelvin cell within the computational domain is calculated as follows:

\[ j = \frac{\iint \text{D} c \text{vc} \text{nd}S}{\iint \text{d}S} \quad (9) \]

The local mass transfer coefficient is calculated using

\[ k_{fl} = \frac{j}{(c)^f - c_0} \quad (10) \]

Here \((c)^f\) refers to the intrinsically averaged (fluid phase volume averaged) concentration and \( c_0 \) is the averaged surface concentration being 0 in this case. The dimensionless Sherwood number, \( Sh = \frac{k_{fl} \text{Re}^{1/2}}{D} \) is plotted against the Reynolds number for varying flow-rates in Fig. 5. A non-linear regression fit is used to obtain the expression for the Sherwood number of the form:

\[ Sh = A + B \cdot Re^{0.5} \cdot Sc^{1/3} \quad (11) \]

where B is a function of the porosity and geometrical structure of the foams.

### Table 1

Geometrical properties of the foams utilized in the experiments.

<table>
<thead>
<tr>
<th>Foam ppi</th>
<th>Geometrical surface area (m²/m³)</th>
<th>Wash-coated mass (mg)</th>
<th>Thickness (µm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1663</td>
<td>87.6</td>
<td>20</td>
</tr>
<tr>
<td>20</td>
<td>1240</td>
<td>84.1</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>758</td>
<td>79.3</td>
<td>39</td>
</tr>
</tbody>
</table>

*Measured with SEM.
Table 2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Total flow (mL/min)</th>
<th>ηC</th>
<th>ηO2</th>
<th>Apparent activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 ppi</td>
<td>20 ppi</td>
<td>10 ppi</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>36</td>
<td>0.05</td>
<td>0.1</td>
<td>75.2</td>
</tr>
<tr>
<td>2</td>
<td>73</td>
<td>0.05</td>
<td>0.1</td>
<td>84.1</td>
</tr>
<tr>
<td>3</td>
<td>65</td>
<td>0.025</td>
<td>0.05</td>
<td>86.2</td>
</tr>
</tbody>
</table>

studied foam sample and m characterizes the non-linear dependency of the Sherwood number on the magnitude of velocity. A is the asymptotic value of the Sherwood number in the absence of convection, obtained when a fast reaction occurs along the surface of the Kelvin cell immersed in an unbounded stagnant pool of fluid saturated with the reactant. For spheres, A is 2.0 and for the Kelvin cell of porosity 0.92 considered here, it was found to be 1.94. The correlation for the Sherwood number obtained through DNS indicated an exponential dependency against the Reynolds number of 0.53. The Sherwood number dependency on the Schmidt number is assumed to follow the classical 1/3 dependency as obtained from boundary layer theory. The curve-fit analysis yields the expression:

\[ \text{Sh} = 1.94 + 0.41 \text{Re}^{0.3} \text{Sc}^{0.33} \]  

(12)

The correlations reported in the literature calculated by experiments [12-14], as well as the calculated by simulations [19], have the form of: \( \text{Sh} = B \text{Re}^m \text{Sc}^{1/k} \). Since these correlations were obtained at relative high Re values (Re > 10), no asymptotic value was obtained. Thus, the Sh number, for low Re, calculated with our correlation is slightly higher than the reported ones (See Fig. 7). Nevertheless, the correlation gives similar Sh for high Re.

Equation 12 may be compared against a more conventional one, such as the Gunn [40] correlation which was proposed for spherical particle systems. In the dilute limit, the Gunn correlation shows a strong dependency with the Reynolds number with a scaling of 0.7 indicating that mass transfer is significantly enhanced when the flow-rate is increased. Correlations for the Sherwood number for foams [12-15], including equation 12, all indicate a weaker dependency on the Schmidt number when compared to unconsolidated systems where the solid phase is a discrete medium.

3.4. Analysis of the mass transfer limitations in a slab

In this section, the influence of the internal and the external mass transfer limitations is analyzed. Fig. 6 shows the concentration profile in and around a catalyst slab considering a first-order reaction taking place in the wash-coat layer.

The dimensionless mass balance equation for the A species in steady-state in the layer is [35]:

\[ \frac{\partial C_A^{*}}{\partial z^*} = \phi_w - \phi_{w2} \]  

(13)

where \( \phi_w = \frac{k_w}{k_L} \) is the Thiele modulus in the wash-coat layer, \( C_A^{*} = C_A/C_A^\infty \) is the dimensionless concentration, \( b^* = z/b \) is the dimensionless z direction, \( k_w \) is the volumetric reaction constant rate and \( D_{\text{eff}} \) is the effective diffusion coefficient. The boundary conditions are:

\[ B_{\text{lin}}(1 - C_A^\infty) = \frac{\partial C_A^\infty}{\partial b^*} = 1 \]  

(14)

\[ \frac{\partial C_A^\infty}{\partial b^*} = 0 \]  

(15)

where \( B_{\text{lin}} = \frac{k_{\text{lin}}}{D_{\text{eff}}} \) is the Biot number, \( k_{\text{lin}} \) is the mass transfer coefficient, \( C_A^\infty \) is the concentration at the solid/fluid interface (\( z = b \)). The solution for Eq. 13–15 is giving by:

\[ C_A^* = \frac{\cosh(\phi_w b^*)}{\cosh(\phi_w) \Phi} \]  

(16)

where \( \Phi = \frac{\tanh(\phi_w)}{\Phi_{\text{lin}}} + 1 \). Through Eq. 19 the concentration profile in the slab as function of the Thieles modulus and the Biot number can be calculated. Furthermore, the importance of the internal and external mass transfer limitations can be studied in terms of the internal (\( \eta \)) and global effectiveness factor (\( \eta_{G} \)) [35]:

\[ \eta = \frac{\tanh(\phi_w)}{\phi_w} \]  

(17)

\[ \frac{1}{\eta_G} = \frac{1}{\eta} + \frac{\phi_w^2}{B_{\text{lin}}} \]  

(18)

Eq. 21 shows the resistance additivity for a first-order reaction. At this point, the aim of the study is to develop a criterion for evaluating the presence/absence of internal and external mass transfer limitations. Analyzing the case for low Thiele modulus values (\( \phi_w \to 0 \)), that is neglecting the internal diffusion limitations, Eq. 19 becomes:

\[ \frac{1}{\eta_G} = 1 + \frac{\phi_w^2}{B_{\text{lin}}} \]  

(19)

For neglecting any effect of mass transfer, i.e. for kinetic control regime, \( \eta_G \) must be higher than, for example, 0.9. Then, the ratio \( \frac{\phi_w^2}{B_{\text{lin}}} \) should be smaller than 0.1.

Now, for the extreme case of a very large Thiele modulus (\( \phi_w \to \infty \) and \( \phi_w > B_{\text{lin}} \)), that is strong internal diffusion limitations, Eq. 19 becomes [35]:

\[ \frac{1}{\eta_G} = 1 + \frac{\phi_w^2}{B_{\text{lin}}} \]  

(20)

In this case, the influence of the external mass transfer limitations can be bounded, by setting that the reaction is fully mass transfer limited when \( \eta_G \) is lower than 0.1. In other words, when the ratio \( \frac{\phi_w^2}{B_{\text{lin}}} \) is larger than 10. It is worth noticing that the ratio \( \frac{\phi_w^2}{B_{\text{lin}}} \) is called usually the Damköhler number \( D_{\text{a}} = \frac{b_{\text{lin}}}{b} \).

The limits for external and internal mass transfer limitations have been established. Still, the Biot number is a derived dimensionless number and can be expressed in terms of the Reynolds number. The ratio \( \frac{\phi_w^2}{B_{\text{lin}}} \) can be re-written in terms of the Sherwood number:

\[ \frac{\phi_w^2}{B_{\text{lin}}} = \frac{\phi_w^2}{\text{Sh}} \left( \frac{1}{\text{b}} \right) \left( \frac{D_{\text{d}}}{D_{\text{eff}}} \right) \]  

(21)

The correlations for the Sherwood number as function of the Reynolds reported in bibliography [12,13] and obtained in this work follow Eq. 11. By combining Eq. 21 and Eq. 11, it is possible to plot \( \phi_w^2 \) vs. Re and identify the governing regime zones (Fig. 7): the limits for full-mass transfer limited reaction \( \phi_w \to \infty; \frac{\phi_w^2}{B_{\text{lin}}} > 10 \) and kinetic control regime \( \phi_w \to 0; \frac{\phi_w^2}{B_{\text{lin}}} < 0.1 \), as well as the intermediate regions. The internal mass transfer limitations can be neglected for a value of \( \frac{\phi_w^2}{B_{\text{lin}}} < 0.1 \).

Using Fig. 7, it is possible to distinguish the working regions with experimental results by calculating the Thieles modulus and the Reynolds number. Moreover, this figure helps to clarify the debate around the importance of the internal and external mass transfer limitations in foams.

For example, the shaded areas were obtained based on the reaction rates or conversion and the Re numbers reported in the literature [11–14,28]. As can be seen in the figure, the results presented in this work (see section 3.5) are in the limit of kinetic control and influence of external mass transfer limitations, confirming our previous conclusions.
Richardson et al. [11] used higher values of Re, but their results are also in the same region. The data reported in the works of Tronconi et al. [12,13] are above the line of full mass-transfer limitations, and some points are just below the line. In the work of von Rickenbach et al. [28], relatively high values of mass transfer coefficients were used for the simulations; and therefore, an influence of the internal mass transfer limitation and the intrinsic kinetic can be observed, even for high Thiele modulus values.

Fig. 2. Activity plots. Reaction rate per catalyst mass vs. temperature, for conditions 1 (A), 2 (B) and 3 (C). Reaction rate per catalyst mass normalized by $k_w S_p$ vs. temperature, for conditions 1 (D), 2 (E) and 3 (F). See Table 2 for the conditions details.

Richardson et al. [11] used higher values of Re, but their results are also in the same region. The data reported in the works of Tronconi et al. [12,13] are above the line of full mass-transfer limitations, and some points are just below the line. In the work of von Rickenbach et al. [28], relatively high values of mass transfer coefficients were used for the simulations; and therefore, an influence of the internal mass transfer limitation and the intrinsic kinetic can be observed, even for high Thiele modulus values.

From Fig. 7, it is possible to conclude that, when the reaction rate increases, e.g. by increasing the temperature, external mass transfer limitations arises before the internal diffusion limitations. This is opposite to the traditional case of spherical catalyst particles [35]. The reason is that in foams $b \ll l_d$; and therefore, the region dominated by internal mass transfer does not arise. Note that in foams the thickness and the external surface area can be selected/tuned independently; but for spheres the relation of the characteristic diffusion length (diameter) and external surface area ($6/diameter$) is fixed.
3.5. Verification of the proposed criteria for the case of CO oxidation

3.5.1. First order reaction assumption

In order to verify the proposed criteria, the representative dimensionless numbers for the experimental results of section 3.2 were calculated, and the effect of the mass transfer limitations was quantified. The estimation of internal mass transfer limitations can be analyzed using the Weisz-Prater criterion:

\[ \eta = \frac{\phi R_s C_{w}}{D_{sg} C_b} \]

(22)

where \( C_b \) is the concentration of CO at the solid/gas interface and is unknown. Combining Eq 16, 18 and 22, the criteria can be written as:

\[ \eta = \frac{\eta \phi^2}{\phi^2 + \left( \frac{\phi^2}{D_{sg} C_b} \right)} \]

(23)

where the right part of the equation is calculated from measured values and the \( B_{\text{int}} \) was estimated with the correlation obtained in this work (Eq. 12). Then, using Eq. 23 and 17, it is possible to determine the Thiele modulus and the effectiveness factor for each experimental point. For all cases, \( \eta \) was higher than 0.99, indicating the absence of mass transfer limitations.

Fig. 3. Arrhenius plot: ln(R CO) vs 1/T, for conditions 1 (A), 2 (B) and 3 (C). The reaction rate per catalyst mass is normalized by kmSgeo for conditions 1 (D), 2 (E) and 3 (F). The dots are the experimental points and the lines the best fit of the data, for calculating the \( E_{\text{app}} \). See Table 2 for the conditions details.
internal mass transfer limitations. Additionally, the global effectiveness factor was calculated with Eq. 18 for each experimental point and plotted in Fig. 8. As can be seen in the figure, for low temperatures (i.e. $T < 440 \text{ K}$) the global effectiveness factor is higher than 0.9, indicating absence of mass transfer limitations. However, as the temperature, and thus the reaction rate, increase the effect of external diffusion limitations becomes important.

The distinction of a clear regime region is not possible, and the results suggest that the global reaction rate is influenced by both, the intrinsic kinetics and the external mass transfer. It is also possible to neglect the effect of the internal mass transfer by diffusion in the catalyst layer. However, heterogeneities in the film and the difficulty to measure $D_e$ experimentally make us use this claim with caution.

Finally, the obtained results were used to plot the “working window” in Fig. 7.

### 3.5.2. Non first order reaction

The CO oxidation on Pt and Pd-based catalyst is in fact, not a first order reaction. It presents a negative reaction order with respect to CO for high CO coverages [36,37]:

$$r_{\text{CO}} = k\frac{C_{\text{CO}}}{1 + k_{\text{CO}}C_{\text{CO}}}$$

Therefore, it makes sense to question if the criterion developed in the previous sections, as well as the graphic in Fig. 7, are still meaningful for this kinetics. Here, the analysis of the internal and external mass transfer is extended for a reaction with the kinetic of Eq. 24.

If $K_{\text{CO}} \gg 1$, that is high coverage of CO and considering an excess of O$_2$, the reaction rate can be written as:

$$r_{\text{CO}} = k'\text{C}_{\text{CO}}^{-1}\text{K}_{\text{CO}}\text{C}_{\text{CO}} > > 1$$

The overall effective factor for a reaction with order $-1$ is given by [38]:

---

**Fig. 4.** Concentration contour plots for various Reynolds numbers (A) $Re = 2.0$ (B) $Re = 5.0$ (C) $Re = 10.0$ (D) $Re = 20.0$.

**Fig. 5.** Sherwood number vs. Reynolds number. Dots stand for the simulation results and the line is the best fit using Eq. 11.

**Fig. 6.** Schematic representation of a wash-coated layer on a metallic foam.
where the Thiele modulus now is 

\[ \phi_w = \frac{b}{\eta} \left( 1 - \eta \right) \]  

Please note that, for a reaction with negative order the global and the internal effectiveness factor are always higher than 1. Analyzing the extreme case for a low Thiele modulus value \( \phi_w \rightarrow 0, \eta \rightarrow 1, \frac{\phi_w^2}{B_l} \rightarrow 1 \), that is neglecting the internal diffusion limitations, Eq. 26 becomes:

\[ \frac{1}{\eta_G} = 1 - \frac{\phi_w^2}{B_{lm}} \]  

In order to neglecting any effect of mass transfer, i.e. in kinetic control regime, \( \eta_G \) must be smaller than, for example, 1.1 (this value represents a deviation of 10% from the kinetic control regime). Then, the ratio \( \frac{\phi_w^2}{B_{lm}} \) should be smaller than 0.1, as settled in the previous section for a reaction order +1.

In the case of low CO coverages, i.e. high temperatures and/or high conversions, the kinetic for the CO oxidation (Eq. 27) follows a first order reaction:

\[ r_{CO} = k_{CO} k_{CO}C_{CO}C_{CO} < 1 \]  

Therefore, the analysis for a very large Thiele modulus \( \phi_w \rightarrow \infty \), that is strong internal diffusion limitations, becomes the same as that of a first order reaction. Thus, it is possible to conclude that, when the ratio \( \frac{\phi_w^2}{B_{lm}} \) is larger than 10, the condition of full-mass transfer limitations is achieved. In summary, the limits established in Fig. 7 are still valid for the kinetic expression in Eq. 24.

In order to further prove this claim, the global effectiveness factor assuming the kinetic of Eq. 24 was calculated for all the experiments. The Weisz-Prater criterion (Eq. 23) combined with Eq. 26 leads to:

\[ \frac{1}{\eta_G} = \frac{1}{\eta} - \frac{\phi_w^2}{B_{lm}} \]  

where the Thiele modulus now is \( \phi_w = \frac{b}{\eta} \left( 1 - \eta \right) \). Please note that, for a

Table 3

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Foams</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>410</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>440</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>460</td>
</tr>
</tbody>
</table>

Kinetics for the CO oxidation on Pt(1%)/γ-Al₂O₃/Foam.

<table>
<thead>
<tr>
<th>( k_{CO} ) (mol bar⁻¹ s⁻¹)</th>
<th>( E_r ) (kJ mol⁻¹)</th>
<th>( K_{CO} ) (bar⁻¹)</th>
<th>( \Delta H ) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.42 x 10⁶</td>
<td>91.48</td>
<td>4.06</td>
<td>3.06</td>
</tr>
</tbody>
</table>

Fig. 7. Operating regimes in a wash-coat foam represented in a Thiele modulus-Reynolds diagram. Eq. 23 was used with Eq. 11 for the Sherwood number. In this case \( l_w/b = 2 \times 10^2; D_{ef}/D_m = 0.1 \).

Fig. 8. Global effectiveness factor as function of the temperature. The colors indicate the foams: 40 ppi (black), 20 ppi (red) and 10 ppi (blue); and the symbols stands for the experimental condition 1 (squares), 2 (circles) and 3 (triangles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
1.01, indicating the absence of internal mass transfer limitations. Additionally, the global effectiveness factor for each experimental point are plotted in Fig. S.1. 5. This figure is analogous to Fig. 8, and the same conclusion can be drawn. For low temperatures, the global effectiveness factor is lower than 1.1, indicating absence of external mass transfer limitations. When the temperature increases, the effect of external diffusion limitations becomes important.

3.5.3. Kinetic constant calculations

In the previous sections, it was shown that the internal global effectiveness factor was $\eta \approx 1$, and the global effectiveness factor was plot for each reaction point in Fig. 8. In order to calculate the kinetic parameters of Eq. 24, the reaction rate was corrected by the global effectiveness factor and the results was fitted considering equations 30–32:

$$ R_{CO} = \frac{k_{f CO}}{(1 + K_{CO}P_{CO})^\eta} $$

(30)

$$ k = k_{f,exp} \left( \frac{-E_f}{RT} \right) $$

(31)

$$ K_{CO} = K_{CO,exp} \left( \frac{\Delta H}{RT} \right) $$

(32)

Table 3 shows the values for the kinetic parameters calculated and Fig S.I. 6 shows the error of the fitting. The fitting results are in close agreement with the values reported in the literature [37], showing the consistency of the procedure followed during this publication.

4. Conclusions

Owing to its reportedly excellent transport properties, open-cell foams are prominent structured catalysts for process intensification. However, the exact impact of mass transfer limitations on the catalytic performance remained unresolved. This work reports, for the first time, a systematic study of the mass transfer limitations combining numerical simulations, experiments and a theoretical analysis, showing the relative importance of the external and internal mass transfer limitations. In particular, DNS were performed to derive a concentration of Sh vs. Re, also valid at low Re numbers. This correlation was found comparable with those in the literature for higher Reynolds, supporting that the absence of convection. This is crucial, since it allows us to evaluate the foams performance also at low velocities, where mass transfer limitations are more likely to occur. The experimental results of the CO oxidation were combined with a theoretical analysis of the diffusion–reaction equation for settling a criterion for the absence of mass transfer limitations. Combining the developed criteria and the numerically obtained correlation, the reaction regimes were plotted in a Thiele modulus vs. Reynolds graph. This graph serves as a practical guide to determine the controlling regime beyond the scope of this study. This is particularly important to further study and develop open-cell foams in real applications. Remarkably, for low Re and a high $l_{ps}/b$ ratio, the external mass transfer limitations become important before the influence of internal mass transfer limitations for a first order reaction. This is opposite to the case of a typical sphere catalyst pellet, where the external transport limitations will never arise until internal diffusion limitations are also present. Thus, the large specific surface area of the open-cell foams ensures that external mass transport remains the determining factor only for $Re < 10^2$. However, the effect of internal mass transfer limitations becomes important for high Re numbers ($Re > 10^3$) and low $D_{eff}/D_m$ ratio, even at high reaction rates.

These new insights into the limits of controlling regimes with open-cell foams will be crucial to prevent the underestimation of the role of internal diffusion on overall reaction rates, as well as to further develop and scale-up these structures as catalyst support in real applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


