



# Mass transfer limitations in a monolithic reactor for the catalytic oxidation of ethanol



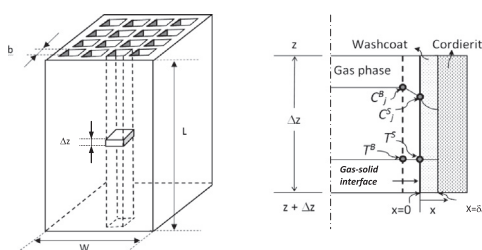
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## HIGHLIGHTS

- Catalytic oxidation of ethanol in a monolithic ceramic reactor is modelled.
- Significant diffusional resistances at low operating temperatures are found.
- Process rate is reduced by internal mass transfer resistances at high VOC conversions.
- Poor interfacial areas lead to significant external mass transfer resistances.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A theoretical study of a monolithic reactor for the catalytic oxidation of Volatile Organic Compounds (VOC) over manganese–copper mixed oxide catalysts is presented. An isothermal one-dimensional heterogeneous model is selected to account for the external (gas–solid) and internal (washcoat) mass transport limitations.

The results reveal that under certain operating conditions, e.g. thick washcoats and high conversions of VOCs (high temperatures), the overall process rate is reduced by internal diffusion inside the catalyst. At high temperatures and/or monoliths with poor interfacial areas, the overall process rate is limited by external mass transfer resistance to the catalyst. Proper quantification of both internal and external mass transfer resistances by means of a heterogeneous model can result in avoiding situations of incomplete VOC abatement under conditions of high VOC dilution.

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## 1. Introduction

The pollutant emission control such as Volatile Organic Compounds is one of the priorities of environmental catalysis (Everaert and Baeyens, 2004; Heck et al., 2009; Khan and Ghoshal, 2000). Increasingly tighter and more precise global standards exist towards controlling the emissions of these dangerous pollutants (Air Quality Guidelines – WHO, 2005; The Clean Air Act – EPA, 2004). The European Commission (<http://ec.europa.eu/environment/air/legis.htm>) sets an emission limit value of 20 mg/Nm<sup>3</sup> in the stream discharged into the atmosphere.

VOCs emissions affect the climate change, plants growth and decay and human beings and animal's health. Despite their undeniable danger, their use is widely spread because of their degreasing/solvent properties. VOCs are emitted by both, industries that synthesise them and industries that generate them as by-products or use them in their processes.

Technology to reduce VOC emissions is selected according to the temperature and composition of the VOC contained by the stream, the volumetric flow rate of the emission, the available site for the installation and operating costs. VOC concentrations in the air streams are often in the 50–2000 ppm range and flow rates in the 1000–10,000 scfm (1700–17,000 m<sup>3</sup>/h) range are common (Wang et al., 2001). Catalytic oxidation as a removal method is a particularly suitable technology for treating emissions at low VOC

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concentrations since the total oxidation of diluted fuels occurs at relatively low temperatures leading to low emissions of  $\text{NO}_x$  and unburned fuels (Everaert and Baeyens, 2004; Mitsui et al., 2009).

Thus, not only a suitable catalyst is important but also an appropriate reactor configuration to process large volumes of air+VOC emissions with low pressure drops.

Due to the diverse nature of VOCs, as well as the volume and composition of the industrial emissions, the monolithic reactors become particularly attractive to perform the catalytic removal. The major advantages of this design are low pressure drop under high fluid throughputs leading to an energy-efficient operation, short diffusion path in the catalyst and high external surface area, among others (Avila et al., 2005; Chen et al., 2008; Heck et al., 2001; Tomasic and Jovic, 2006).

Considerable effort has been directed towards obtaining suitable catalysts for catalytic oxidation (Choudhary et al., 2002; Ertl et al., 2008). The Mn–Cu mixed oxide catalyst formulated by Morales et al. (2008) demonstrated to be highly active at moderate temperatures for the catalytic oxidation of a wide number of VOCs. This catalyst has been successfully deposited by impregnation on ceramic monoliths (Agüero et al., 2013), setting the most appropriate features to perform the VOC catalytic combustion process in a single device.

Ethyl acetate and ethanol are the predominant VOC in the printing industry. These processes generally present temporal VOC emission patterns. When VOC concentration decreases to a few hundred part per millions (ppm), the heat generation caused by the evolution of oxidation reactions is very low and may lead to a non-effective pollutant removal.

Detailed modelling and simulation of monolith reactors contribute to understand the complexity of interactions between various physical and chemical processes that occur within the channels and inside the channel coating (Chen et al., 2008) playing a significant role in the design of these systems. The correct interpretation of the mass transfer phenomena occurring in the process is essential to define operating and design conditions to achieve a complete removal of VOCs (Hayes and Kolaczowski, 1997).

In previous researches, for washcoat thickness less than 50  $\mu\text{m}$ , diffusion resistances were assumed to be negligible. However, more recent studies have shown that this may not be so (Gonzo, 2008; Hayes et al., 2004). Hayes and Kolaczowski (1994) found that when temperature is high ( $> 700$  °C), internal diffusion limitations could be significant even with a very thin washcoat thickness. Metkar et al. (2011) observed washcoat diffusion limitations for the standard SCR reaction ( $\text{NH}_3 + \text{NO} + \text{O}_2$ ) on a Cu-zeolite catalyst at low temperatures starting at 250 °C. It was also found that the contribution of external mass transfer was significant under certain conditions.

The Mn–Cu mixed oxide powder catalyst (particle size: 500–841  $\mu\text{m}$ ) presents a strong influence of intraparticle mass transfer at temperatures between 217 and 229 °C. Thus, the effectiveness factor for ethanol combustion varies between 0.013 and 0.220 along the reactor (Campesi et al., 2011).

In the present article, a theoretical study of a monolithic reactor for the catalytic oxidation of ethanol over Mn–Cu mixed oxide catalysts is presented. The effect of the interphase and intraphase mass transport limitations at high VOC dilution is analysed by means of a 1D heterogeneous model. The influence of the main operating variables on the reactor performance is also studied.

## 2. Mathematical model

### 2.1. Model equations

Fig. 1 shows the schematic representation of the design under study. A stream of ethanol diluted in air enters the ceramic monolithic reactor. The channels of a ceramic monolith of square section are covered by the Mn–Cu mixed oxide catalyst with an atomic ratio of 9:1 (Agüero et al., 2013).

The reaction scheme considered in this work is shown in Table 1. A system of two reactions in series is considered, which includes the partial oxidation of ethanol to acetaldehyde (Reaction 1) and the total oxidation of acetaldehyde (Reaction 2). The kinetic expressions and the kinetic parameters given by Campesi et al. (2011) for the Mn–Cu catalyst are adopted and presented in Tables 1 and 2, respectively.

A one-dimensional heterogeneous model to represent the steady-state operation of the monolithic reactor is proposed. It is assumed that the gas-phase temperature, composition and velocity are uniform across the monolith cross-section. The following additional hypotheses are adopted:

- Isobaric conditions: a total developed laminar flow is assumed through the channels, leading to a low pressure drop.
- Isothermal conditions: the high dilution of the VOC in the inlet stream supports this hypothesis. Estimations of the temperature drop over the film were calculated according to the guidelines of Froment and Bischoff (1990). The overall temperature gradients in the gas diffusion layer are lower than 1.5 °C for all the explored operating conditions.
- Axial dispersion of mass is neglected: longitudinal mass Peclet number ( $Pe$ )  $\gg 2$  demonstrates that the flow behaviour of the gas phase is plug flow type (Hessel et al., 2005).
- Unidirectional flow inside the monolith channel is assumed.
- The catalytic material accumulation in the corners of the square channels is negligible.
- A single channel is considered as representative of the entire reactor: size and shape of the channels, catalyst activity and gas flow distribution between the channels are assumed uniform (Hayes and Kolaczowski, 1997).
- Ideal gas is assumed.

Based on these assumptions, the reactor is represented by the following equations:

Gas phase  
Mass balances

$$\frac{dC_{Et}}{dz} = -\frac{1}{u} \frac{V_w}{V_g} \eta_1 r_1^s \quad (3)$$

$$\frac{dC_{Ac}}{dz} = \frac{1}{u} \frac{V_w}{V_g} (\eta_1 r_1^s - \eta_2 r_2^s) \quad (4)$$

where

$$\eta_i = \frac{\int_0^{V_w} r_i(C_{s,j}) dV_w}{V_w r_i(C_{s,j}^s)} = \frac{r_i^{eff}}{r_i^s} \quad \text{with } i = 1, 2 \quad (5)$$

Initial conditions:

$$\text{At } z = 0 : C_j = C_{0j} \quad (6)$$

Solid phase (washcoat)  
Mass balances

$$D_{e,Et} \frac{d^2 C_{s,Et}}{dx^2} = -\rho_w r_1(C_{s,j}) \quad (7)$$

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