



# The concept of selectivity control by simultaneous distribution of the oxygen feed and wall temperature in a microstructured reactor



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## ABSTRACT

This paper explores the feasibility of controlling the selectivity of a partial oxidation reaction by simultaneous modulation of local oxygen concentration and coolant temperature along the length of a reactor. The microstructured membrane reactor (MMR) concept consists of an oxygen-permeable membrane for distributing the oxygen feed with the coolant channel divided into zones of different temperatures. The reactor concept was explored in simulation of the selective oxidation of *o*-xylene to phthalic anhydride (PA). A mathematical model of the reactor was developed and optimization performed with the objective of maximising PA selectivity at the reactor outlet. Dosing of oxygen at uniform wall temperature results in PA selectivity increase by 6.3%, albeit with a reduction in *o*-xylene conversion of about 8% compared to a conventional fixed bed reactor. However, simultaneous modulation of both reactor wall temperatures and local oxygen concentration results in an improved conversion of *o*-xylene without a detrimental effect on selectivity, thus giving maximum yield of PA.

## 1. Introduction

One of the key challenges in many catalytic selective oxidations is poor selectivity of the desired product [1]. Over-oxidation of the desired product as well as total oxidation of the hydrocarbon substrate account for the loss in selectivity, and in most oxidation processes about 10–30% of feed is lost as carbon oxides. For large scale oxidation processes, there is a significant incentive to optimise selectivity, since even a small increase in selectivity can bring significant economic benefits through annual savings in raw material cost as well as the cost of downstream separation and purification of products [2]. Cost savings are hugely important to a petrochemical plant, considering that around 75% of the total production costs are typically allocated to feedstocks [3]. The attendant reduction in CO<sub>x</sub> formation and carbon emissions due to improved selectivity can also make many large-scale commercial oxidation processes more environmentally friendly [4]. In selective oxidations, there is usually a trade-off between product selectivity and conversion of the hydrocarbon; the conditions under which high selectivity can be attained typically correspond to regions of low conversion [5]. Thus, in attempting to improve process selectivity, there is the risk of unavoidable loss of conversion and, consequently, of product yield.

A number of strategies can lead to enhanced selectivity of catalytic

oxidation reactions. The most significant is the development of new catalysts that are more selective for the desired product. However, catalysts on their own rarely determine the overall efficiency of a process, and there are many oxidation reactions for which the desirable catalysts that are highly selective for the target product are still elusive [6]. Furthermore, the selectivity of a catalyst is intimately linked to its activity, productivity and stability, and often a new catalyst which gives a boost in selectivity may suffer from loss of activity and lower lifetime compared to conventional catalysts, thus requiring more frequent regeneration [7]. Thus, further strategies to improve selectivity are developed around engineering of the reaction environment, directed by detailed mechanistic understanding of the reaction pathways.

There is a potential to improve selectivity of oxidation reactions by substituting molecular oxygen with lattice oxygen, in the process known as redox decoupling or “chemical looping” [8]. In this case the selective oxidation of a hydrocarbon substrate is done by lattice oxygen of a metal oxide catalyst, an oxygen carrier, in one reactor while the reduced solid is re-oxidised by contact with air in a separate reactor. The re-oxidised solid is subsequently cycled back to the oxidation reactor, thus the substrate and air are never in direct contact, minimising non-selective homogenous combustion reactions. This strategy has been implemented for example to improve propene selectivity in the oxidative dehydrogenation of propane over V<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> catalyst [9]. The

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**Nomenclature***Latin acronyms and letters*

$A_o$	pre-exponential factor ( $\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1} \text{atm}^{-1.5}$ or $\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1} \text{atm}^{-1.5}$ )
$c$	intercept of axial oxygen permeation function
$C$	products of the total oxidation of <i>o</i> -xylene (CO, CO <sub>2</sub> and MA)
$C_p$	heat capacity of gas ( $\text{J kg}^{-1} \text{K}^{-1}$ )
$d$	diameter (m)
$d_H$	hydraulic diameter of channel (m)
$E_a$	activation energy ( $\text{J mol}^{-1}$ )
$F$	molar flow rate ( $\text{mol min}^{-1}$ )
$G$	superficial mass flow rate ( $\text{kg m}^{-2} \text{s}^{-1}$ )
$h_{gm}$	heat transfer coefficient from gas to membrane ( $\text{W m}^{-2} \text{K}^{-1}$ )
$h_{gw}$	heat transfer coefficient from gas to the walls ( $\text{W m}^{-2} \text{K}^{-1}$ )
$h_{wc}$	heat transfer coefficient from wall to coolant ( $\text{W m}^{-2} \text{K}^{-1}$ )
$\Delta H_r$	enthalpy of reaction ( $\text{kJ mol}^{-1}$ )
$\Delta H_a$	standard enthalpy of adsorption ( $\text{kJ mol}^{-1}$ )
$J_i$	molar flux of species $i$ through the wall ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$k_j$	rate constant of reaction $j$ ( $\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1}$ )
$K_a$	adsorption equilibrium constant $\text{atm}^{-0.5}$ or $\text{atm}^{-1}$
$L$	reactor length (m)
$MA$	maleic anhydride
$n$	$n$ th coolant section i.e. 1, 2, ..., $\aleph$
$N$	total number of reactions
$\aleph$	total number of coolant sections along reactor length
$Nu$	Nusselt number
$oX$	<i>o</i> -xylene
$p$	partial pressure of reaction specie (atm)
$P$	total pressure in reactor (atm)
$PA$	phthalic anhydride
$PH$	phthalide
$r$	radius (m)
$R$	gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$Re_p$	particle Reynolds number
$Q$	volumetric flow rate ( $\text{mL min}^{-1}$ )

$S$	PA selectivity (mol%)
$TA$	<i>o</i> -tolualdehyde
$T$	temperature ( $^{\circ}\text{C}$ )
$U$	overall heat transfer coefficient ( $\text{W m}^{-2} \text{K}^{-1}$ )
$X$	<i>o</i> -xylene conversion (mol%)
$y$	molar fraction
$z$	axial coordinate (m)

*Greek letters*

$\delta$	thickness (m)
$\epsilon_B$	catalyst bed porosity
$\zeta$	parameter of Eq. (15)
$\eta$	catalyst effectiveness factor
$\lambda$	thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ )
$\mu$	viscosity (Pa s)
$\rho$	density ( $\text{kg m}^{-3}$ )
$\rho_B$	catalyst bulk density ( $\text{kg}_{\text{cat}} \text{m}^{-3}$ )
$\tau$	reactor residence time (s)
$\Omega$	optimization variable

*Subscripts*

$c$	coolant
$cat$	catalyst
$g$	gas
$i$	reaction specie
$in$	inlet
$j$	reaction number
$max$	lower bound of optimization variable
$min$	upper bound of optimization variable
$w$	wall (coolant)
$m$	membrane
$p$	catalyst particle
$r$	reactor or catalyst bed
$T$	total

*Superscripts*

$d$	membrane side
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cyclic approach requires development of a new type of a solid catalyst which has a high oxygen-carrying capacity per unit weight. In addition, the solid must have excellent structural stability and high resistant to attrition in multi-cycle operations.

The use of alternative oxidants such as H<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>O and alkylhydroperoxides as substitutes for molecular oxygen has also been investigated for enhancing selectivity in certain reactions, such as the epoxidation of olefins [10] and oxidative dehydrogenation of alkanes to olefins [11]. However, the use of these alternative oxygen sources may be economically unfavourable due to their high cost of production as well as storage and handling issues. Hence, in most commodity chemical processes, oxygen or air is still the preferred oxidant.

Another strategy may involve the use of protective groups that effectively remove the desired products from the reaction medium, thus preventing their over-oxidation. The concept of a protective agent has, for example, been applied in the boron-modified liquid-phase oxidation of alkanes and cycloalkanes into alcohols. In this case a boron compound is used as an esterifying agent to trap the alcohol by forming a borate ester, which is more stable to further oxidation, thus resulting in an improved alcohol selectivity [12,13]. Another example is the direct oxidation of methane to methanol in concentrated sulphuric acid using SO<sub>3</sub> as the oxidant and a Pt(II) complex as catalyst [14,15]. Methane is

converted to methyl bisulphate ester from which methanol is obtained as the final product. In both cases, the desired alcohols are recovered by hydrolyzing the esters with water, with up to 80% final product selectivity.

The development of alternative process chemistry and innovative synthesis routes may also be a successful approach to improve selectivity of certain oxidation reactions. This may involve the use of alternative feedstock that requires fewer number of mechanistic steps and allows oxidation under mild conditions, thus producing less by-products than classical routes [16]. A good example where a change of synthesis route has turned out to be more selective is the production of methyl methacrylate (MMA). Conventional process uses C<sub>4</sub> feedstocks such as isobutylene or *t*-butanol and involves three steps: two high temperature gas-phase catalytic oxidations to methacrolein and methacrylic acid, respectively, followed by esterification of the acid with methanol into MMA [17]. In contrast, a new process developed by Asahi Chemical involves only two steps: isobutylene is first oxidised into methacrolein, followed by direct liquid-phase oxidative esterification into MMA at low temperature with no intermediate formation of methacrylic acid. The new process has better selectivity to MMA, however, it also requires the development of new catalysts [18].

Complementary to developing more selective catalysts and process

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