

Microkinetic Modelling of the Oxidative Coupling of Methane (OCM) in a Membrane Reactor: Influencing Selectivity by Modulating Oxygen Permeation

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Highlights

- Modulating O₂ permeation across membrane length can enhance C₂ selectivity.
- Gas phase reactions play significant role in determining C₂ selectivity.
- Radial concentration gradients need to be minimised to further enhance yield.

1. Introduction

Ethylene is the most widely produced organic commodity in the chemical industry with an annual global demand of over 140×10^6 tons and a growth rate of 3.5% per year. Being produced via steam cracking of naphtha or ethane, its availability is directly dependent on the fast diminishing crude oil resources, whereas its demand is expected to only increase due the ever-increasing need of our society for plastics, among others. For many years, the Oxidative Coupling of Methane (OCM) has been considered as a promising process to obtain ethylene. However, this homogeneous-heterogeneous process is a typical reaction where the desired C₂ products (Ethane and Ethylene) are not the most thermodynamically or kinetically favoured ones. Till now, C₂ yield per pass achieved has never been above techno-economically accepted limits [1].

Strategies to improve C₂ yield have ranged from catalyst to process design. Catalysis, even though considered as the most effective method of achieving this and despite extensive research, has not resulted in obtaining acceptable yields. The recently developed nanowire catalysts by Siluria Technologies, as mentioned in [2], are a promising exception that has brought closer the commercial realization of OCM. Reactor engineering, guided by the detailed mechanistic understanding of the OCM reaction, can further contribute to overcoming the C₂ yield limitations. Various strategies that can achieve the latter have been highlighted alongside with their limitations [3]. Generally, most of these methods are aimed at minimising the deep oxidation of the desired C₂ products in the reactor.

In this work, a packed bed membrane reactor concept for OCM is presented, wherein O₂ permeation along the reactor length is modulated, aiming at the maximisation of C₂ selectivity. The performance of this reactor is compared to that of a conventional packed bed membrane reactor (PBMR), paying particular attention to the effect of the gas phase reaction network on products selectivity within the proposed reactor concept. The work reveals that selectivity gains can be achieved, following an optimisation of the O₂ flux profile.

2. Methods

A 10-step Langmuir-Hinshelwood kinetic model is adopted from Stanch et al. [4] to describe the heterogeneous catalytic chemistry over a La₂O₃/CaO catalyst. A multi-step gas-phase microkinetic model described in the work of Chen et al. [5] is further superimposed on the catalytic kinetic model to account for the effect of homogeneous reactions of participating molecules and radicals. 1D and 2D pseudo-homogeneous reactor models are implemented to investigate the effect of radial concentration gradients of radicals and molecules that arise from the distribution of O₂ through the membrane in the performance of the MR. As a proof of concept of the proposed reactor design approach, the O₂ permeation modulation into the MR is achieved by considering a linear increase of the membrane thickness along the reactor length. The partial differential equations describing the mass and heat balances are discretized in the radial dimension with a central finite difference scheme and solved using the Athena Visual Studio software.

3. Results and discussion

The kinetic model implementation was first validated against the fixed bed reactor OCM experiments reported in [4]. Further analysis using the validated kinetic model in membrane reactor models showed that, in all configurations studied, the 2D model predicts a lower CH₄ conversion in comparison to the 1D (Table 1). In the 2D models, the consumption of O₂ that permeates takes place mostly close to the membrane, while slower radial mass transport by diffusion results in unutilized O₂ compared to the 1D model. C₂ products are similarly formed at the boundary where most of the O₂ exists, slowly diffusing to the centre. This uneven distribution also results in loss of C₂ selectivity in 2D implementations. Including the effect of gas-phase reactions shows that the highly reactive radicals produced near the membrane boundary further consume the produced C₂, leading to additional selectivity loss. The proposed reactor concept achieves higher C₂ selectivity, at all space times studied (Figure 1) in comparison to the conventional MR. Through the regulation and modulation of the amount of O₂ that permeates across the membrane, the rate of unselective reactions is reduced progressively as methane reacts, resulting in an overall decrease in C₂ selectivity losses.

Table 1. Comparison of the performance of conventional PBMR and PBMR with modulated O₂ considering different gas phase reaction networks in 1D and 2D reactor models. Conditions: 1073K and 1 bar shell and tube pressure.

Reactor configuration/Gas phase reaction network (L_m is the thickness of the membrane)	CH ₄ Conversion, %		O ₂ Conversion, %		C ₂ Selectivity, %	
	2D	1D	2D	1D	2D	1D
	PBMR/Single reaction from [4], L_m constant = $L_{m,0}$	26.41	33.30	91.43	97.75	68.85
PBMR/Detailed microkinetics from [5], L_m constant = $L_{m,0}$	26.11	32.65	94.51	98.98	57.58	62.18
Proposed PBMR/Detailed microkinetics from [5], L_m increases linearly to $2 \times L_{m,0}$	26.09	31.31	97.06	99.29	60.43	65.04
PBMR/No gas-phase reactions considered, L_m constant = $L_{m,0}$	26.58	33.55	92.05	98.16	72.43	78.62

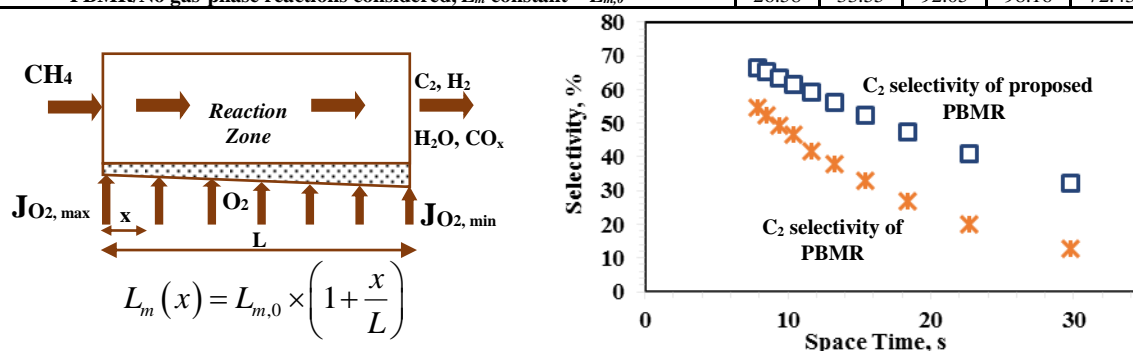


Figure 1. [Left] Scheme of membrane reactor concept proposed, $L_m(x)$ is the membrane thickness at axial position x of the proposed reactor. [Right] C₂ selectivity of PBMR and proposed PBMR at different space times at 1073K and 1 bar tube and shell pressure.

4. Conclusions

The loss in C₂ selectivity attributed to unselective oxidation reactions, particularly evident when detailed gas-phase microkinetics are accounted for, and the uneven distribution of O₂ and C₂ versus CH₄ when radial concentration gradients are important, was minimized by the proposed reactor concept, where a linear increase in the membrane thickness was considered. Future work will address the implementation of heterogeneous catalytic microkinetics and the optimisation of the O₂ permeation profile.

References

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Keywords

Membrane Reactor; C₂ Selectivity; Gas Phase Reactions; Oxidative Coupling of Methane