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# Design of a microchannel-based reactor module for thermally coupled reactions: Oxidative coupling and steam reforming of methane



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## ABSTRACT

This study addresses the development of a microchannel-based reactor whereby exothermic oxidative coupling of methane (OCM) and endothermic steam reforming of methane (SRM) reactions were coupled in consecutive catalytic beds to thermally control each bed. A computational fluid dynamics model was developed by combining kinetic rate equations with detailed balance equations, and its effectiveness was corroborated by comparison with experimental data. The temperature of the SRM bed abruptly decreased because the reaction rapidly reached equilibrium, and the large endothermic heat prevented temperature from increasing near the inlet of the OCM bed. Meanwhile, the central region of the bed, which corresponded to the thermodynamically controlled region of the SRM bed, showed a slight temperature increase with a peak temperature observed along the axis. Increasing the linear velocity (by increasing either the amount of N<sub>2</sub> in the feed or the space velocity (SV)) enhanced the heat transfer rate, and the increased amount of endothermic heat could further reduce the peak temperature of the OCM bed. By considering the inert materials near the inlet of the SRM bed, the kinetically controlled region was expanded, reducing the peak temperature of the OCM bed. The height of the OCM bed was increased to obtain a high production rate per unit bed, while the increased exothermic heat could be absorbed by increasing the SV of the SRM bed, even after reducing its height to maintain the size of the entire module.

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## 1. Introduction

Alternative processes and resources for ethylene production should be developed because of the growing demand for ethylene and the rising cost of oil-based feedstocks. Oxidative coupling of methane (OCM), which produces C<sub>2</sub> hydrocarbons by catalyst surface reactions, is a promising alternative process because natural gas shows potential as an economical feedstock [1]. OCM research has focused on developing suitable catalysts and determining appropriate operating conditions [2]; there is a general agreement, despite some ongoing debate, that basic metal oxides promoted by alkali and earth-alkali metals show acceptable performances as OCM catalysts [3].

In addition to developing stable and selective catalysts for the OCM reaction, a detailed thermal-reaction analysis is required to control the operating temperature in the reactor and to improve

the reaction performance in terms of ethylene yield and selectivity. However, the OCM reaction is represented by a combination of several gas-phase and catalyst surface reactions with a strong exothermic behavior; thus, the reactor design is a challenging task for OCM processes [4]. Recently, the concept of coupled reactors, whereby exothermic and endothermic reactions are coupled to effectively control the temperature profiles of highly exothermic reactions, has been introduced. Godini et al. [1,5] suggested a dual-membrane reactor in which dry reforming of methane (DRM) was used to absorb the heat released from the OCM reaction; the CO<sub>2</sub> generated as a by-product of the OCM reaction permeated into the DRM bed and was used as a reactant. This integrated reactor provided a very promising thermal performance by maintaining the temperature peak below 50 °C in the OCM section, with 35% C<sub>2</sub> yield, 40% auto-thermal behavior, 60% total methane conversion, and 90% CO<sub>2</sub> recovery in the OCM process. Farsi et al. [6] combined the OCM reaction and steam reforming of methane (SRM); they modeled the effects of feed composition, temperature, portion of catalyst, and SV on the conversion, selectivity, yield, and temperature profile along the length of the reactor. Tiemersma

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## Nomenclature

$C_p$	heat capacity, J/(kg·K)	$R_i$	reaction rate of species $i$ , mol/(m <sup>3</sup> ·s)
$D_i^m$	mixture-averaged diffusion coefficient of species $i$ , m <sup>2</sup> /s	$T$	temperature, °C
$D_i^T$	thermal diffusion coefficient of species $i$ , kg/(m·s)	$\mathbf{u}$	velocity vector, m/s
$D_{ik}$	multicomponent Maxwell-Stefan diffusivities of species $i$ and $k$ , m <sup>2</sup> /s	$x_i$	mole fraction of species $i$ , dimensionless
$\mathbf{F}$	volume force, N/m <sup>3</sup>	<i>Greek letters</i>	
$\mathbf{I}$	identity matrix	$\varepsilon_p$	porosity, dimensionless
$\mathbf{j}_i$	mass flux of species $i$ , kg/(m <sup>2</sup> ·s)	$\kappa$	thermal conductivity, W/(m·K)
$M_{AB}^{1/2}$	harmonic mean of molar mass of species A and B, kg/mol	$\kappa_{br}$	permeability of the porous medium, m <sup>2</sup>
$M_n$	mean molar mass, kg/mol	$\mu$	dynamic viscosity, Pa·s
$P$	pressure, Pa	$\rho$	fluid density, kg/m <sup>3</sup>
$P_i$	partial pressure of species $i$ , Pa	$v_i$	diffusion volume of species $i$
$Q$	heat source term, W/m <sup>3</sup>	$\omega_i$	mass fraction of species $i$ , dimensionless
$Q_{br}$	mass source term, kg/(m <sup>3</sup> ·s)		

et al. [7] also suggested combining OCM and SRM; packed-bed reverse flow membrane reactor tubes for the OCM reaction were submerged into a fluidized bed for the SRM reaction, and the reactor effluents from the OCM beds were fed to the SRM section after C<sub>2</sub> was separated. Their simulation results showed that the cyclic steady state can provide up to a 30% yield of C<sub>2</sub> at full methane conversion.

One of the most important factors in the design of exo- and endothermic coupled reactors is the heat transfer rate; therefore, microchannel-based reactors have been intensely studied because they guarantee a high productivity, compactness, and thermal stability because of the high heat transfer capacity [8]. For example, the specific surface area of microchannel-based reactors is higher than that of conventional reactors (twice as high as that of shell & tube reactors and 320 times higher than that of jacketed batch reactors), and its volumetric heat transfer coefficient is six times higher than that of a shell & tube metallic reactor [9]. Understanding the operational performance of microreactors or reactors with microchannel-based heat exchangers and its dependence on structural parameters (either from experiments or simulations) is important because the performance strongly depends on the channel design, wall properties, and interplay between adjacent channels for either exothermic or endothermic reactions [10].

In this study, computational fluid dynamics (CFD) was used to demonstrate the effectiveness of a microchannel-based reactor by evaluating the effects of the operating conditions and structural parameters on the thermal stability and reaction performances. A strategy to combine OCM (highly exothermic) with SRM (highly endothermic) using a microchannel-based reactor was suggested to control thermal behaviors of the catalytic beds for OCM. Because the characteristics of the two reactions are different, the CFD approach is used to find the appropriate operating conditions to maximize thermal interactions between the reactions over the entire heat transfer area. In addition, the model was further used to provide useful information on determining the heights of the catalytic beds for each reaction while maintaining the thermal stability.

## 2. Experimental and modeling methods

### 2.1. Catalyst preparation

The Na<sub>2</sub>WO<sub>4</sub>/Mn/SiO<sub>2</sub> catalyst was prepared using the two-step incipient wetness impregnation method. A silica gel support (Davisol 635, 60–100 mesh, 60 Å pore size) was impregnated with aqueous solutions containing Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, dried at 110 °C for

12 h, and calcined at 500 °C for 5 h. Subsequently, the sample was impregnated by an aqueous solution of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, dried at 110 °C for 12 h, and calcined in air at 800 °C for 5 h. Finally, the catalyst was obtained with 5 wt% Na<sub>2</sub>WO<sub>4</sub> and 2 wt% Mn.

The Ni/Mg-Al catalyst (12 wt%) was prepared for SRM using a wetness impregnation method. Commercial hydrotalcite (Sasol, PURAL MG30) was used as a precursor of the catalyst support. First, the hydrotalcite was calcined at 600 °C for 6 h. Then, the calcined support was pelletized and crushed, and it was sieved to obtain particles of 300–500 μm. The support (50 g) was impregnated using an aqueous solution containing 33.8 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, dried at 110 °C for 12 h, and calcined at 800 °C for 6 h.

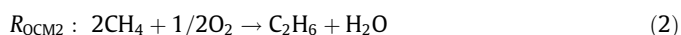
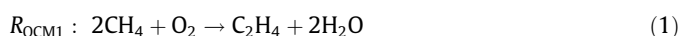
### 2.2. Setup of the coupled reactor

Schemes of the experimental setup and configuration of the coupled reactor are provided in Fig. 1. Three layers of OCM catalytic beds were located between four layers of SRM catalytic beds, and five temperature detectors were installed in the middle OCM bed. One detector was fixed at the center of the bed (red dot surrounded by a red circle in the photograph in Fig. 1b), while the temperatures were measured at four points along the axis (numbers in the photograph in Fig. 1b) by changing the location of a movable resistance temperature detector. Experimental conditions, such as the inlet temperature, SV, and feed compositions, are listed in Table 1. The oven temperature was set at the same temperature as the inlet.

### 2.3. Kinetic modeling

The overall reaction mechanisms considered for the OCM and SRM reactions are provided in Eqs. (1)–(4) and Eqs. (5)–(7), respectively. In the OCM reactions,  $R_{OCM1}$  and  $R_{OCM2}$  represent the catalytic surface reactions that produce ethylene and ethane, respectively, while  $R_{OCM3}$  and  $R_{OCM4}$  correspond to the gas-phase reactions to produce CO and CO<sub>2</sub> by-products, respectively. In the SRM reactions, the steam reforming reaction ( $R_{SRM1}$ ), side reaction of SRM ( $R_{SRM2}$ ), and water-gas-shift reaction ( $R_{SRM3}$ ) were considered.

Overall OCM reaction mechanisms:



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