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# Hexagonal boron nitride catalyst in a fixed-bed reactor for exothermic propane oxidation dehydrogenation

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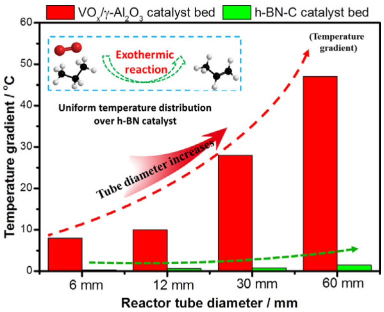
## HIGHLIGHTS

- h-BN is an effective catalyst for exothermic propane ODH in a fixed-bed reactor.
- Temperature profile in catalyst bed for propane ODH was studied using CFD.
- Nearly isothermal operation can be maintained using h-BN for industrial propane ODH.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Hexagonal boron nitride (h-BN) with high thermal conductivity is potentially an effective catalyst for highly exothermic propane oxidative dehydrogenation (ODH) reaction. Here, we report our experimental and theoretical studies of such a catalyst for propane ODH in a fixed-bed reactor. Based on the computational fluid dynamics calculation (CFD) results, the catalyst bed temperature increases by less than 1 °C in the h-BN catalyst bed which is much smaller than that (8 °C) in the $VO_x/\gamma\text{-}Al_2O_3$ catalyst bed at a similar propane conversion (25%) using a micro-tubular reactor with a diameter of 6 mm. Even in an industrially relevant reactor with an inner diameter of 60 mm, a uniform temperature profile can still be maintained using the h-BN catalyst bed due to its excellent thermal conductivity as opposed to a temperature gradient of 47 °C in the $VO_x/\gamma\text{-}Al_2O_3$ catalyst bed. The results reported here provide useful information for potential application of h-BN catalyst in propane ODH.

## 1. Introduction

Non-oxidative propane dehydrogenation process has been extensively practiced in the chemical industry (Otroshchenko et al., 2015; Liu et al., 2016). However, this reaction is limited by thermodynamic equilibrium and is favored at high temperature due to its endothermic nature (Ayandiran et al., 2016). Propane oxidative dehydrogenation (ODH) reaction, on the other hand, offers remarkable advantages, including no thermodynamic constraint, alleviating the coking of catalysts and readily providing heat owing to its exothermic nature (Shylesh and Singh, 2004; Wu and Lin, 2008). However, the hotspots are unavoidably present in the catalyst bed due to the highly exothermic nature of propane ODH, which can significantly accelerate the undesired

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over-oxidation of propene, leading to decreased propene selectivity and catalyst deactivation (Schwarz et al., 2009; Steinfeldt et al., 2001). Therefore, it is highly desired to efficiently remove the reaction heat in ODH of propane (Frank et al., 2007). The heat of reaction in the ODH of propane and associated reactions is shown as follows:

$$C_3H_8 + 0.5O_2 \rightarrow C_3H_6 + H_2O \quad \Delta rH_1 = -118\ \text{kJ mol}^{-1} \tag{1}$$

$$C_3H_6 + 3O_2 \rightarrow 3CO + 3H_2O \quad \Delta rH_2 = -1077\ \text{kJ mol}^{-1} \tag{2}$$

$$C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O \quad \Delta rH_3 = -1926\ \text{kJ mol}^{-1} \tag{3}$$

To prevent the formation of hotspots in the catalyst bed, efforts have been made by either diluting the feed with an inert gas or catalyst bed with thermally conducting materials. In addition, microchannel reactors (Schwarz et al., 2009; Cao et al., 2009; Baier and Kolb, 2007), structured catalysts (metal foam or fiber), etc. (Li et al., 2015; Zhao et al., 2011; Palma et al., 2018), and fluidized-bed reactors (Lu et al., 2004; Elbadawi et al., 2016) have also been attempted. Thermal conductivity of the catalysts is a key to removing the heat of the exothermic ODH reaction. Unfortunately, traditional refractory metal oxide-supported catalysts, such as $VO_x/\gamma$-$Al_2O_3$, have poor thermal conductivity (less than 0.5 W/K m), which inevitably causes the hotspots in the catalyst bed (Li et al., 2015), resulting in undesired over-oxidation of propene to $CO_x$ (CO and $CO_2$) (Löfberg et al., 2011) and catalyst deactivation.

Hexagonal boron nitride (h-BN), a highly promising material with its unique physicochemical properties (Wu et al., 2016, 2016), especially high thermal conductivity (33 W/K m) (Li et al., 2016; Zhi, 2009), has been recently reported with unique and hitherto unanticipated catalytic performances for ODH reaction (Shi et al., 2017; Grant et al., 2016). For example, Hermans's group reported that h-BN exhibits high selectivity to propylene (79%) and ethylene (12%) at 14% propane conversion (Grant et al., 2016). Besides, Lu's group also found that the hydroxylated edge of h-BN can efficiently catalyze propane ODH to propene with a superior selectivity (80.2%) but with only negligible $CO_2$ formation (0.5%) at a given propane conversion of 20.6% (Shi et al., 2017). Based on the above results, h-BN is expected to effectively suppress the over-oxidation of propene to $CO_x$ in the ODH reactions, which is a key benefit for ODH of alkanes to olefins. To evaluate the potential application of h-BN in a fixed-bed reactor for industrial ODH process, the heat transfer and the temperature profile in the fixed-bed reactor using h-BN as catalyst were studied in this work, which is crucial to the commercial application of h-BN (Zaynali and Alaviamleshi, 2017).

In this article, the temperature profiles in the h-BN catalyst bed for propane ODH were studied using the computational fluid dynamics calculation (CFD), which shows visual temperature profile in the catalyst bed (Li et al., 2015; Tran et al., 2017). The temperature profile was simulated along the axis and radial directions in the h-BN catalyst bed for propane ODH. A comparison was also made with using $VO_x/\gamma$-$Al_2O_3$ catalyst in a micro-tubular reactor with an inner diameter of 6 mm. An industrial-scale fixed-bed reactor with an inner diameter of 60 mm was further simulated and the results generated can offer useful information for the potential commercialization of propane ODH process using h-BN as a catalyst in a fixed-bed reactor.

## 2. Experimental section

### 2.1. Preparation of the catalysts

h-BN was commercially obtained from Qinhuangdao Eno High-Tech Material Development CO., LTD with the purity >99%, which is named as h-BN-C. The sample was used as provided without further chemical or thermal treatment. The h-BN-C catalyst before the reaction is named as h-BN-C fresh and the h-BN-C after the reaction is named as h-BN-C spent.

As a comparison, 5 wt%$VO_x/\gamma$-$Al_2O_3$ catalyst was prepared by wet impregnation (Frank et al., 2007). 1 g $\gamma$-$Al_2O_3$ support was impregnated with 5.7 mL 0.1 M $NH_4VO_3$ solution and the resultant slurry was stirred at room temperature for 12 h. After the impregnation, the catalyst was dried at 90 °C overnight and then calcined at 600 °C for 4 h. 5 wt% $VO_x/\gamma$-$Al_2O_3$ was denoted as $VO_x/\gamma$-$Al_2O_3$.

### 2.2. Characterizations

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer (Rigaku, Japan). Cu $K_\alpha$ radiation (40 kV and 30 mA) was used as the X-ray source. For each sample, Bragg's angles ($2\theta$) between 10° and 60° were scanned at a rate of 10°/min. Specific surface areas of catalysts were measured by the Brunauer-Emmett-Teller (BET) method, using a Micromeritics Tristar 3020 surface area and porosimetry analyzer. Prior to the measurement, all samples were degassed at 150 °C for 6 h. Thermal gravimetric analyzer (TGA; TG 209F1 Netzsch Germany) was used to investigate the carbon deposition of the spent catalysts. The samples were preheated at 80 °C and then heated to 970 °C at a rate of 10 °C/min in air (20 mL/min). Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 spectrometer (Thermo Fischer Scientific). The FT-IR spectra of the samples were recorded in the range of 650–4000 $cm^{-1}$.

### 2.3. Catalytic test

The $VO_x/\gamma$-$Al_2O_3$ and h-BN-C (80–100 mesh) were tested without dilution to provide a direct comparison with the CFD results. Propane (99.9%) and a gas mixture ($O_2$:$N_2$:He = 1:8:1) were individually controlled using two mass flow controllers (Sevenstar) to provide a reaction gas feed of $C_3H_8$:$O_2$:$N_2$:He = 1:1:8:1. The reactor wall temperatures were set from 510 °C to 590 °C. The reaction products were analyzed by using a gas chromatography (GC2060, Shanghai Ruimin GC Instruments, Inc) which has a flame ionization detector (equipped with KB-$Al_2O_3$/$Na_2SO_4$ column) for hydrocarbon ($C_xH_y$) analysis and a thermal conductivity detector (equipped with TDX-01 column) for CO and $CO_2$ analysis. Control experiments with quartz show that there is negligible propane conversion without the catalyst. In all tests, carbon mass balances exceed 95%. The $C_3H_8$ conversion (X) and product selectivity (S)

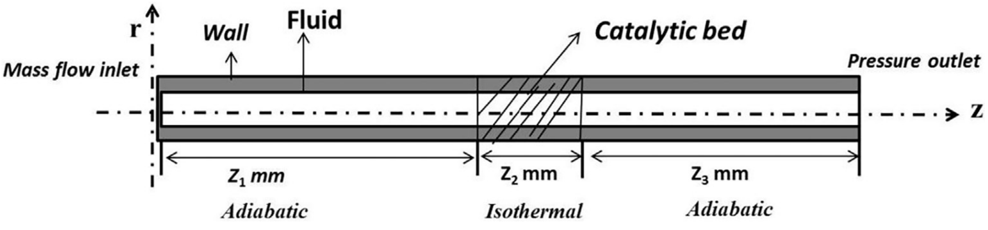

**Fig. 1.** Schematic diagram of the system modeled by "FLUENT"