High Propylene Oxidative Dehydrogenation Selectivity Using Consecutive Propane Addition and a Novel Fluidizable Catalyst: Kinetic Modelling

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Highlights

- A 7.5V/ZrO$_2$-γAl$_2$O$_3$ propane oxidative dehydrogenation (PODH) catalyst was implemented.
- Lattice oxygen was the only source of oxygen contributing to the 94% propylene selectivity.
- Runs were developed at 500-550°C, 10-20 seconds and at a 44.0 catalyst/propane weight ratio.
- A kinetic model was established using a Langmuir-Hinshelwood rate equation.

1. Introduction

Propylene is one of the major building blocks in the chemical industries. The oxidative dehydrogenation (ODH) process is a low-temperature process offering potentially high olefin yields and extended catalyst life given the low coke deposition [1]. The present investigation considers the kinetics of propane ODH using a fluidizable VO$_x$/ZrO$_2$-γAl$_2$O$_3$ catalyst with high propylene selectivity and operating in the absence of molecular oxygen gas. This valuable kinetics has not been reported before. It provides critical information for the scale up of continuous circulating fluidized bed downer and riser units.

2. Methods and PODH Kinetic Model

A catalyst was synthesized by a wet saturation impregnation technique. Details of the catalyst preparation and characterizations (BET, XRD, H$_2$-TPR, NH$_3$-TPD, pyridine FTIR, Laser Raman Spectroscopy and X-ray photoelectron spectroscopy) together with various reaction procedures in the CREC Riser Simulator are described in a previous work. [2]

PODH involves a network of consecutive and parallel reactions: the ODH of propane, the combustion of propane feed and the combustion of a propylene product. These reactions can be represented as follows by using a Hinshelwood model:

$$r_1 = \frac{k_1 K_{C3H8} p_{C3H8}}{(1 + K_{C3H8} p_{C3H8} + K_{C3H6} p_{C3H6} + K_{COx} p_{COx})} \exp[-\lambda(X_{C3H8})] \dots (1)$$

$$r_2 = \frac{k_2 K_{C3H8} p_{C3H8}}{(1 + K_{C3H8} p_{C3H8} + K_{C3H6} p_{C3H6} + K_{COx} p_{COx})} \exp[-\lambda(X_{C3H8})] \dots (2)$$

$$r_3 = \frac{k_3 K_{C3H6} p_{C3H6}}{(1 + K_{C3H8} p_{C3H8} + K_{C3H6} p_{C3H6} + K_{COx} p_{COx})} \exp[-\lambda(X_{C3H8})] \dots (3)$$

Where, r_i= reaction rate (mol.g$_{cat}^{-1}$s^{-1}), K_i= adsorption constants of species "i" (atm^{-1}), k_i= reaction rate constant (mol.g$_{cat}^{-1}$s^{-1}) =$k_i^0 \exp\left[\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right]$, k_i^0= pre-exponential factor, E_i= activation energy (kJ.mol^{-1}), p_i=partial pressure (atm), T_m= average temperature (K), λ= decay constant and X_{C3H8}= propane conversion.

3. Results and discussion

Runs in the CREC Riser Simulator show that propane conversion increases from 13 to 22%, with propylene selectivity slightly increasing from 92-94% and CO$_x$ selectivity decreasing from 4% to 2% (Figure 1). Given the lack of activity decay after injection 3, the λ decay parameter was set to zero.
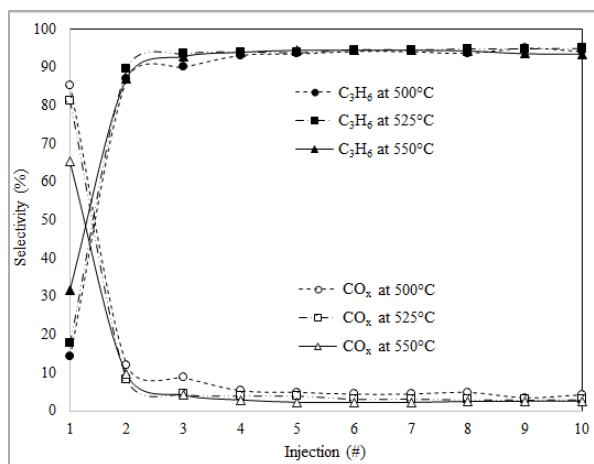
Figure 1: Propylene and CO_x Selectivities with Feed Injections. Reported points correspond to at least three repeats.
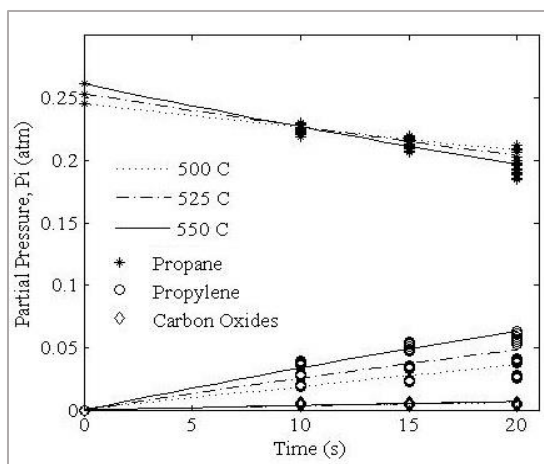

Figure 2: Experimental Results and Model Predictions at Different Temperatures. Every reported data point is the average of 190 runs.

On the basis of these data, one can calculate the propane, the propylene and the CO_x rates as:

$$\frac{dp_{C3H8}}{dt} = -\frac{W_c RT}{V_R}(r_1 + r_2); \quad \frac{dp_{C3H6}}{dt} = \frac{W_c RT}{V_R}(r_1 - r_3); \quad \frac{dp_{COx}}{dt} = \frac{W_c RT}{V_R}(6r_2 + 6r_3)$$

In this scenario, adsorption constants were independently evaluated [3]. Thus, using equations (1-3), a DOF=184 and a MATLAB "lsqnonlin" nonlinear least-square regression algorithm, 6 kinetic parameters were estimated with 95% confidence intervals and low cross correlation coefficients. Table 1 reports 28-106 kJ/mole energies of activation of moderate magnitude with $E_1 > E_2$. Applicability of the proposed model is shown in Figures 2 and 3.

Table 1: ODH Kinetic Parameters for a VO_x/ZrO_2-γAl_2O_3 Catalyst.
(DOF=Data points-parameters=184)

Parameters	Value (95% CI)	Parameters	Value (95% CI)
k_1^{0a}	$2.92 \times 10^{-5} \pm 9.32 \times 10^{-7}$	E_1^b	78.89 ± 7.08
k_2^0	$6.58 \times 10^{-7} \pm 6.47 \times 10^{-8}$	E_2	28.05 ± 2.30
k_3^0	$5.03 \times 10^{-8} \pm 1.42 \times 10^{-9}$	E_3	106.48 ± 8.10

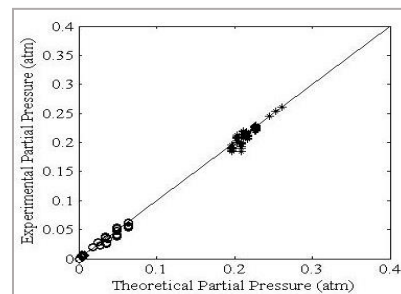^{a}mol.$g_{cat}^{-1}s^{-1}$; ^{b}kJ.mol^{-1}

Figure 3: Overall Comparison between Experiments and Model Data. Every reported data is the average of 190 runs.

4. Conclusions

This study reports a kinetic model for a highly performing ODH catalyst operating under an oxygen free atmosphere. This catalyst displays the highest propylene selectivity of all the ODH catalysts developed by our research group [1]. The proposed kinetics is valuable for ODH implementation at the industrial scale.

References

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Keywords
Oxidative Dehydrogenation; Propane; Selectivity; Kinetic Modelling.