Dual Bed Membrane Reactor for the Oxidation of Propane to Acrolein

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Introduction

Partially oxygenated hydrocarbons provide the building blocks for plastics and synthetic fibers as well as precursors for specialty chemicals. However, the oxidation of hydrocarbons with O_2 also results in the thermodynamically favored (in)complete combustion to CO and CO_2 which reduces the selectivity of the partial oxidation (POx) products. POx of hydrocarbons has seen significant interest in distributive membrane reactors (MRs) [1-3]. These works demonstrate the ability of MRs to inhibit full oxidation products and promote POx products. Acrolein is a POx products of interest as it is a precursor to a number of polymers and an intermediate for various specialty chemicals. This work focuses on producing acrolein from propane using consecutive catalytic beds for (1) the oxidative dehydrogenation (ODH) of propane to propylene and (2) the partial oxidation of propylene to acrolein (POA). Prior theoretical work has shown the dual bed reactor to be successful for this reaction [4].

Materials and Methods

All reactions are conducted using a quartz glass reactor (OD 3/4in) with either one or two catalyst beds. Each bed in the reactor can be converted for use as a membrane reactor through the insertion of a porous alumina tube (US Filter, 3/8in) from either end of the quartz reactor. Propane, propylene, oxygen, and helium (Mittler) are supplied to the reactor through mass flow controllers. The reactor effluent is analyzed using online gas chromatography (HP 5890 Series II) with HayeSep Q (6ft, 1/8in, 80/100 mesh) and Carboxen 1000 (15ft, 1/8in, 60/80 mesh) columns being used in both series and parallel. Catalysts are prepared in our lab for use in each reaction (VMgO for ODH of propane and BiMo oxide for POA reaction).

Results and Discussion

The desired ODH and POA reactions are generally first order in the hydrocarbon and zero order in oxygen while the competing combustion reactions are first order in both reactants. The membrane reactor design is ideal for taking advantage of this difference in reaction order as it maintains a low partial pressure of oxygen throughout the catalyst bed. Table 1 shows how the FBR and MR effect conversion and selectivity for both the ODH of propane and POA reaction. The two reactor types show very little difference in conversion of the hydrocarbon with the MR conversion is only a few percent lower than the FBR. Selectivity is where the most significant differences between the two reactors can be seen. The MR not only increases the selectivity to the desired product but it also decreases the selectivity to CO_2. These improvements in the selectivity support the use of a MR over a FBR for the ODH and POA reactions.

With the improvements seen for each reaction in the single bed MR it is interesting to look at the effect of the reactor type for a dual bed reactor. Figure 1 shows the effect of the reactor type on conversion and selectivity in the production of acrolein from propane. The inclusion of a single MR increases the selectivity toward acrolein and a dual MR further enhances this formation. Simultaneously, the CO_2 selectivity is reduced. As shown, the overall selectivity to acrolein is low, however work to optimize the conditions to increase the yield is underway.

Table 1. Conversion and selectivity of FBR versus MR for ODH and POA reactions

Reaction	Reactor Type	Temp. (°C)	Conversion	Selectivity		
				Propylene	Acrolein	CO_2
ODH	FBR	500	33	27	--	42
ODH	MR	500	30	33	--	36
POA	FBR	425	38	--	50	26
POA	MR	425	36	--	66	22

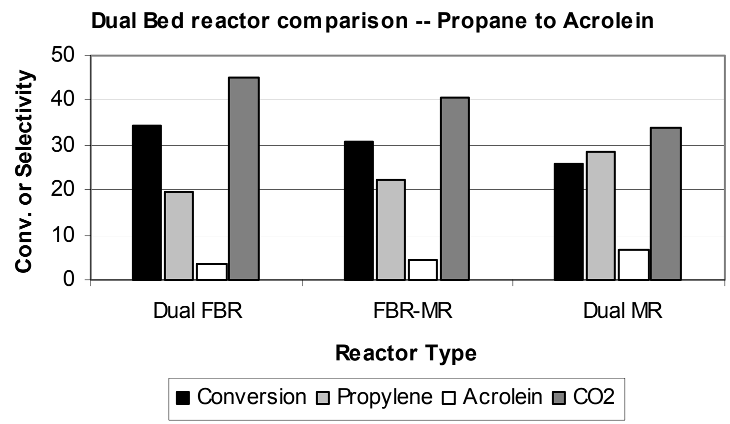

Figure 1. Conversion and selectivity data for three unique configurations of the dual bed reactor in the oxidation of propane to acrolein

Significance

Improving selectivity in partial oxidation of hydrocarbons by reducing the formation of waste CO and CO_2 is essential for a more efficient process. By improving reactor designs, the selectivity of a catalyst can be further enhanced to increase product yields.

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References

1. Capannelli, G., Carosi, E. et.al. *Chem Eng Sci.* 51, 1817 (1996).
2. Ramos, R., Menendez, M. et.al. *Catalysis Today* 56, 239 (2000).
3. Sanchez, J. and Tsotsis, T. in "Fundamentals of Inorganic Membrane Science and Technology" (A.J. Burggraaf and L. Cot, Eds.) Vol. 4 p. 529 Elsevier, Amsterdam, 1996.
4. O'Neill, C. and Wolf, E. *Ind. Eng. Chem. Res.* 45, 2697 (2006).