

Enhancing Ethylene Selectivity via Forced Dynamic Operation of Ethane Oxidative Dehydrogenation on Diffusion Limited Catalytic Pellets

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Highlights

- C₂H₄ selectivity is enhanced during forced dynamic operation compared to steady state operation.
- Dynamic operation mitigates C₂H₄ selectivity losses induced by intrapellet diffusion.
- Dynamic C₂H₄ yields during surpass those achieved via steady state at higher residence times.
- Oscillation frequency mimics changes in reactor residence time further increasing dynamic yields.

1. Introduction

Ethylene is an essential building block used to manufacture higher value products such as ethylene glycol and polymers.¹⁻² Conventional ethylene production relies on ethane steam cracking which is energy intensive due to its endothermicity.¹⁻² Catalytic oxidative dehydrogenation (ODH) of ethane is considered an interesting alternative due to its exothermicity.¹⁻² However, byproduct oxygenate formation and deep oxidation pathways lower ethylene selectivity.³⁻⁴ Desired product selectivity is further exacerbated in industrial scale fixed-bed reactors which require catalyst pellets on the order of 2 mm or larger. As an intermediate product, ethylene is consumed via overoxidation reactions with increasing diffusion length scales resulting in even lower ethylene selectivities. Specifically, ethylene is unable to diffuse out of larger catalyst pellets before it undergoes oxidation to CO_x.

Previous works have shown that forced dynamic operation (FDO) of chemical reactors during selective oxidation processes may increase desired product selectivity compared to steady state operation (SSO).⁴⁻⁵ It is believed that FDO enhancement occurs by limiting interactions between the hydrocarbon to selective catalytically stored lattice oxygen while simultaneously minimizing interactions with unselective gaseous and chemisorbed oxygen species.⁴⁻⁵ In this study we demonstrate how such interactions during FDO can be used to reduce ethylene selectivity losses in the presence of intrapellet diffusion limitations.

2. Methods

Wet impregnation was used to make 3 and 10 wt% VO_x γ-Al₂O₃ catalysts which were tested under SSO and FDO. A feed gas mixture containing a cycle average of 1% C₂H₆ and 10% O₂ with a 50% duty cycle was modulated out of phase over the catalyst (FDO) and compared to SSO at 550°C over a range of residence times. An out of phase 50% duty cycle indicates the reactants were modulated from 0% C₂H₆ and 20% O₂ to 2% C₂H₆ and 0% O₂ such that C₂H₆ and O₂ were not mixed. Reactor effluent was monitored through mass spectrometry (MS) and Fourier transform infrared spectrometry (FTIR) to quantify C₂H₆, O₂, C₂H₄, CO and CO₂ concentrations. A 2-oxygen model utilizing surface bound chemisorbed and lattice oxygen fit to previous experimental data was employed to investigate the roles of selective lattice and unselective chemisorbed oxygen species on ethylene selectivities and yields.⁴

3. Results and Discussion

Catalyst performance during FDO and SSO was assessed by comparing ethylene selectivities as functions of ethane conversion as plotted in Figs. 1(a) and (b) for catalysts under kinetic (0.3 mm) and diffusion (1.9 mm) control, respectively. Fig. 1(a) shows that FDO has no effect on ethylene selectivity

as the values are equivalent to those achieved during SSO. Previous work has shown that FDO selectivity enhancement occurs when unselective reactions have higher oxygen reaction orders than the selective reaction.⁴ Furthermore, it has been shown that all reactions over VO_x are 0th order in oxygen hence the similarities between the kinetically controlled FDO and SSO ethylene selectivities in Fig. 1(a). Fig. 1(b) shows a dramatic decrease in the ethylene yield during SSO with the appearance of diffusion limitations when using 1.9 mm catalyst pellets. The longer diffusion length promotes secondary ethylene overoxidation hence its lower SSO selectivity. For instance, the SSO selectivity at 20% ethane conversion is roughly 68% and 50% for 0.3 and 1.9 mm pellets, respectively. Interestingly, Fig. 1(b) shows that FDO selectivities decrease less rapidly with the introduction of longer diffusion length scales resulting in ethylene selectivities higher than those achievable during SSO. For example, Fig. 1(b) shows an ethylene selectivity of 65% during FDO at 20% ethane conversion. This result is confirmed by the 2-oxygen model fit to previous results as illustrated by the solid and dashed lines in Figs. 1(a) and (b).⁴

While FDO demonstrates higher ethylene selectivities than SSO for the same ethane conversion, it is not without its limitations. For instance, separation of bulk phase ethane and oxygen results in lower rates over the catalyst bed. Therefore a larger FDO reactor, or higher residence time, is needed to achieve the equivalent SSO conversion. Therefore, it is helpful to compare ethylene yield as functions of residence time as illustrated in Fig. 1(c) for a 10 wt% VO_x catalyst under the same experimental conditions as the previous figures. Fig. 1(c) shows that the gains in ethylene selectivity during FDO of 1.9 mm catalysts nearly doubles ethylene yields at residence times above 0.0015 min. Furthermore, Fig. 1(c) shows that decreasing the oscillation frequency from $\frac{1}{2}$ to $\frac{1}{4} \text{ min}^{-1}$ extends the region of enhancement to even higher residence times.

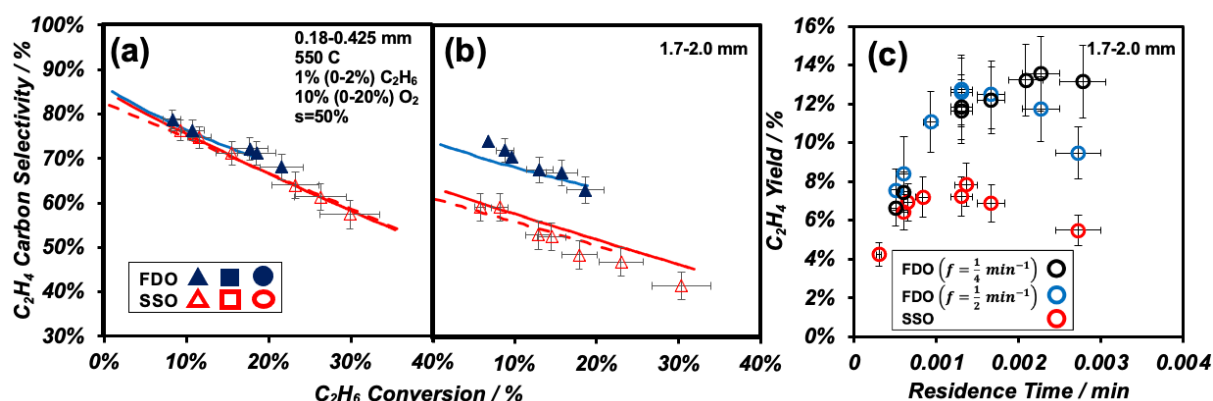


Figure 1. Experimental and model predicted C_2H_4 carbon selectivities versus C_2H_6 conversion obtained for kinetic (0.3 mm) (a) and intrapellet diffusion controlled (1.9 mm) (b) 3 wt% $\text{VO}_x \gamma\text{Al}_2\text{O}_3$ catalyst pellets during FDO and SSO. C_2H_4 yields versus space time during FDO at different oscillation frequencies and SSO using a 10 wt% $\text{VO}_x \gamma\text{Al}_2\text{O}_3$ catalyst (c).

4. Conclusions

These results demonstrate considerable ethylene selectivity and yield gains during ethane ODH utilizing FDO compared to SSO. FDO of chemical reactors can be used to reduce ethylene overoxidation induced by larger intrapellet diffusion length scales. These selectivity gains are enough to outweigh ethane conversion losses during FDO resulting in higher ethylene yields. Dynamic parameters such as frequency can also be used to tune the yield as a function of residence time.

References

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Keywords

Forced Dynamic Operation, Ethane, Oxidative Dehydrogenation, Diffusion