Indo-German Workshop - Advances in Reaction and Separation processes
February 18th-20th, 2008 in Chennai India

Analysis of single- and multi-stage membrane reactors for the selective oxidation of short-chain alkanes – simulation study and pilot scale experiments

C. Hamel[1], E. Tsotsas[2], A. Seidel-Morgenstern[1,2]

[1]*Max-Planck-Institut für Dynamik komplexer technischer Systeme, D-39106 Magdeburg, Germany*
[2]*Otto-von-Guericke-Universität, Institut für Verfahrenstechnik, D-39106 Magdeburg, Germany*

1. Summary

Based on an optimal distributed dosing of reactants and the resulting concentration and residence time effects the product spectrum can differ in a membrane reactor compared to a conventional fixed-bed reactor. In case of low oxygen concentrations the selectivity of the desired product ethylene can be increased significantly compared to the conventional fixed-bed reactor. The obtained results for the ODH of propane are similar even though the increase of the propylene selectivity is not so distinctive compared to ethylene. This reactor principle can be further enhanced using a multi stage reactant feeding with an increasing dosing profile (O_2 concentration and total volumetric flow rate). The developed detailed 2D models allow a good mathematical description of the exothermal reactions taking place in the membrane reactor.

Keywords: Membrane reactors, pilot plant, selectivity enhancement, propane, ethane

2. Extended Abstract

In the field of chemical reaction engineering intensive research is devoted to develop new processes in order to improve selectivity and yields of intermediate products. Important example reactions are catalytic partial oxidations or selective hydro-genations [1]. For such reactions improved integral reactor performance can be achieved by optimised stage-wise dosing of one or several reactants [2]. Adjusted dosing profiles can be realised e.g. by feeding reactants separately through permeable reactor walls, e.g. through tubular membranes. Additionally, various types of stage-wise temperature profiles in combination with characteristic dosing and/or residence time profiles can be realised. The concept allows to improve significantly the selectivity and yield with respect to a desired intermediate product .
This contribution intends to provide insight into various aspects of multi-stage dosing concepts based on an experimental and model based analysis. For this aim the partial oxidations of ethane to ethylene and propane to propylene on a VO_x/Al_2O_3 catalyst

were considered as model reactions. For the experimental study, a pilot scale set-up has been constructed with a single stage packed bed membrane reactor and a three stage membrane reactor cascade. The inner/outer diameters were 21/35 mm, the effective membrane length 104mm, of the investigated asymmetric alumina and sinter metal membranes. A comparison with a conventional fixed-bed reactor operation was possible using the conventional co-feed-mode. Based on a preliminary theoretical analysis, a large set of experimental studies was carried out in a temperature range between 520/630 °C (ethane) and 350/500 °C (propane). The molar O_2/C_nH_m ratio was varied between 0.5 and 8. In the three-stage membrane reactor different dosing profiles could be realised, e.g. increasing (10/30/60%), uniform (33/33/33%) and decreasing (60/30/10%) profiles.
Due to the separated and distributed feeding of the reactants, the resulting concentration and residence time profiles and the corresponding product spectra are distinctly different in membrane reactors compared to fixed-bed reactors. The analysis performed reveals for the investigated operation conditions a higher ethylene/-propylene selectivity and simultaneously a higher conversion in membrane reactors (see figure 1 for different WHSV). In the presentation will be shown that improved performance could be achieved by combining optimised stage-wise temperatures profile with a stage-wise dosing of one or several of the reactants, respectively.

Reduced simple 1D and more detailed 2D models have been used to identify optimal operation parameters and to describe the concentration and temperature profiles, respectively.

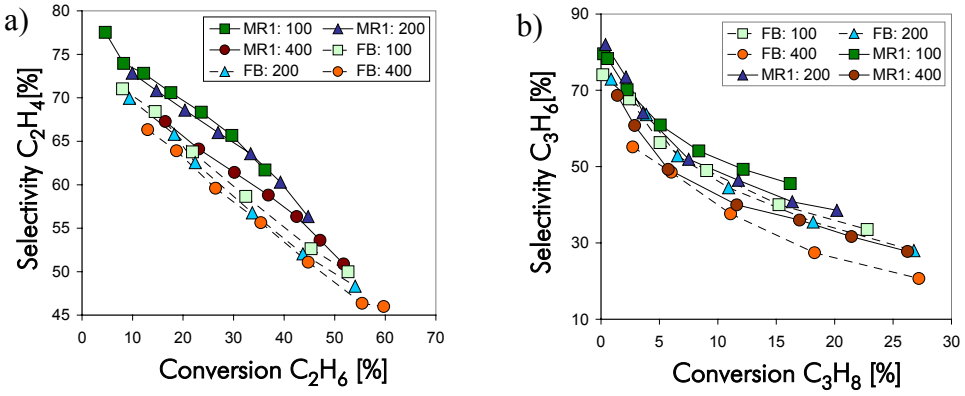

Figure 1: a) selectivity ethylene vs. conversion, b) selectivity propylene vs. conversion: $C_2H_6^{in}$ = 1,5%, $C_3H_8^{in}$ = 1%, O_2/C_nH_m = 1, WHSV = 100-400kgs/m³, catalyst: VO_X/γ-Al_2O_3, (V: 1.4%), BET: 157m²/g, particle: d_P =1.0 mm

References

[1] Dixon, A.G., Int. J. Chem. React. Eng., Vol. 1, 2003, R6, 1-35
[2] Hamel C., Thomas S., Schädlich K., Seidel-Morgenstern A., Chem. Eng. Sci., 58, 2003, 4483-4492