

Kinetic investigations of the catalytic propene epoxidation in the vapour phase using nitrous oxide as oxidant

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The present study focuses on the reaction network and kinetics of the direct epoxidation of propene using nitrous oxide (N₂O) on silica supported FeOx catalysts promoted with caesium oxide. The main objective is to quantify the effect of the reaction conditions by an appropriate kinetic model, which enables reactor simulations.

Propylene oxide (PO) is an important intermediate for the chemical industry with an annual worldwide production capacity of more than 5 megatons. Nevertheless, PO production technology is dominated by disadvantageous, liquid phase processes containing multiple reaction steps. Particularly in the last ten years, different approaches led to progress concerning a direct epoxidation of propene, but a direct, vapour phase route seems to be far from realisation. Limited PO selectivities and space-time-yields are the major drawbacks, so far. However, such a process is still in the focus of research because of a simpler reactor technology, higher production rates, absence of mass transfer limitations and more convenient catalyst handling. One promising alternative is the use of nitrous oxide as oxidant, which was firstly demonstrated by Duma and Hönicke [1]. Our further development of the catalyst led to a promising silica supported iron oxide system, which provides a PO selectivity of ~ 75% at propene conversion of ~ 10 %. Not only higher iron contents than previously reported, but also the use of caesium oxides instead of sodium oxides permit space-time yields of ~ 25 g PO/ kg_{Catalyt}/h [2].

Experimental investigations were done in a fixed bed reactor with plug-flow characteristics. Inlet concentrations and temperatures were varied in a range of space velocities of 1 - 10 l(N)·(g(Cat.)·h)⁻¹. PO and propanal as major products were added to the reactor feed to isolate their reaction pathways and to quantify the kinetics of their consumption.

The reaction network was mainly derived from the trends of product selectivities as function of propene conversion under different conditions. Besides of PO, propanal and acetone are the major products. Since the PO selectivities steeply decrease with increasing propene conversion, the reactions of PO consumption are much faster than the PO formation. The most important consecutive reactions of PO are isomerisation reactions to propanal and acetone which was proved by the addition of PO to the reactor feed. The total oxidation plays a minor role in the reaction network. The PO formation rate must be modelled with an approach accounting for inhibition by propene. This fact reflects the stronger interaction of propene compared to N₂O with the catalyst. Therefore, high rates of PO formation over this catalyst can only be obtained with an adequate surplus of nitrous oxide versus propene in the feed.€

[1] V. Duma, D. Hönicke, J. Catal. 191 (2000) 93.

[2] E. Ananieva, A. Reitzmann, Chem. Eng. Sci. 59 (2004) 5509.