OPTIMIZING CHEMICAL REACTOR PERFORMANCE BY EXPLOITING THE INTERPLAY BETWEEN HETEROGENEOUSLY CATALYZED AND HOMOGENEOUS REACTIONS

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Abstract

The relative contributions of heterogeneously catalyzed and homogeneous bulk phase reactions have been assessed via 1D reactor simulations for a consecutive, reversible reaction network. Heterogeneous products can be obtained with high yields in fixed bed reactors, especially at high catalyst bed densities as encountered in industrial trickle bed reactors. Homogeneous product yields are higher in slurry batch reactors, often implemented as an ejector loop reactor. Component adsorption enthalpies are determining factors in the interplay of heterogeneously catalyzed and homogeneous reactions as increasing adsorption strength of a reactive intermediate shifts the selectivity towards the corresponding product while simultaneously decreasing the yield of other products as a consequence of competitive adsorption.

Keywords

Heterogeneous catalysis, Homogeneous reactions, Chemical reactor selection, Simulations

Introduction

Various heterogeneously catalyzed reactions exist in which also homogeneous bulk phase reactions play a significant role. The latter may either contribute positively to the overall reaction, such as in oxidative coupling of methane (Lunsford et al., 1995), or negatively such as in the hydrogenation of nitriles to primary amines (Gomez et al., 2002). A theoretical analysis of the contribution of heterogeneously catalyzed and homogeneous reactions to the overall reactor behavior will provide strategic guidelines for adequate reactor selection and design.

Procedures

The interplay between heterogeneously catalyzed reactions and homogeneous bulk phase reactions is investigated for three reaction schemes of increasing complexity, see Figure 1. All schemes consider a 'heterogeneous' product D and a 'homogeneous' product E. In the most simple, parallel, scheme, D and E are formed via 2 parallel reactions from a reactant A whereas in the more complex, consecutive schemes this reactant A is first converted into an intermediate B via a homogeneous reaction. This intermediate B is either heterogeneously converted into D, or homogeneously into another intermediate C. The latter is then heterogeneously converted into product E. The scheme of intermediate complexity considers irreversible reactions whereas the most complex one, which corresponds to an industrial application, considers reversibility, particularly for the homogeneous reactions.

Figure 1: Reaction schemes used for assessing the interplay between heterogeneously catalyzed reactions (dashed lines) and homogeneous bulk phase reactions (full lines)

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Equations (1) and (2) illustrate how homogeneous and heterogeneous reaction rates are calculated for the most complex scheme:

$$r_1 = (k_1 C_A - k_{-1} C_B) \quad [\text{mol m}^{-3}_L \text{ s}^{-1}] \quad (1)$$

$$r_2 = \frac{K_{ads,B} k_2 C_B C_{tot}}{1 + K_{ads,B} C_B + K_{ads,C} C_C} \cdot \frac{w_{cat}/V}{\varepsilon} \quad [\text{mol m}^{-3}_L \text{ s}^{-1}] \quad (2)$$

All simulations have been performed at a conversion of A of 50%. By diluting with an inert of the same size as the catalyst particles the free bulk is volume unaffected, i.e. ε is fixed, while maintaining the reactor volume, both for the 2.5 m^3 reactor and the 1 m^3 slurry batch reactor.

Results and discussion

As evident from Eqs. (1) and (2), the relative contributions of homogeneous reactions decrease and those of heterogeneously catalyzed ones increase with the catalyst amount w_{cat}/V. As a result, yields of D are the highest in a continuous fixed bed reactor, while E dominates in a slurry batch reactor. The molar product yields in the slurry batch reactor correspond to those observed in a continuous fixed bed reactor with a very low catalyst bed density.

Parallel Reaction Scheme

In this simple scheme the main effect corresponds to changes in surface coverage of the intermediate leading to D. A 10 fold lower adsorption equilibrium coefficient for reactant A and correspondingly 50% lower surface coverages result in a 26% lower heterogeneous product D selectivity.

Consecutive, Irreversible Reaction Scheme

In the consecutive reaction scheme the intermediates B and C competitively adsorb on the catalyst surface. As shown in Figure 2, for all catalyst amounts, the heterogeneous product yield increases only slightly with increasing adsorption equilibrium coefficient for B.

The corresponding decrease of E is far more pronounced and results in an enhancement of the yield of its corresponding intermediate C, i.e., from 0.8% to 18% when $K_{ads,B}$ increases from 0.1 to 10 m^3 mol^{-1} at ρ_{bed} of 1000 kg$_{cat}$ m^{-3}. The latter is mainly an effect of the surface coverage of B which increases from 87 to 96% and inhibits any C adsorption.
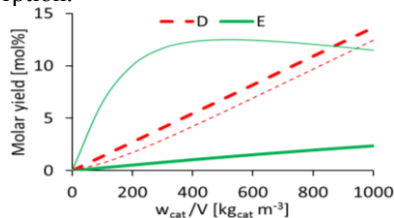
Figure 2: Molar heterogeneous (D) and homogeneous (E) product yields as a function of the catalyst amount, $K_{ads,C} = 1$ m^3 mol^{-1}. Thick lines: $K_{ads,B} = 10$ m^3 mol^{-1}, thin lines: $K_{ads,B} = 0.1$ m^3 mol^{-1}. $k_1 = k_3 = 10^{-5} \cdot k_2 = 10^{-6} \cdot k_4 = 3 \cdot 10^{-3}$ s^{-1}

Consecutive, Reversible Reaction Scheme

As shown in Figure 3 (left) a low K_1 results in high final product yields and a distinct shift from E to D at a higher catalyst amount compared to higher K_1. Variations in equilibrium coefficient between B and C, K_3, result in less pronounced variations as evidenced Figure 3 (right). Interestingly, an optimum of the E yield is observed as a function of the catalyst amount. Increasing the latter enhances the conversion of B to D rather than the conversion of B to C. Up to the maximum sufficient C is present to result in enhanced E yields as the catalyst amount increases.
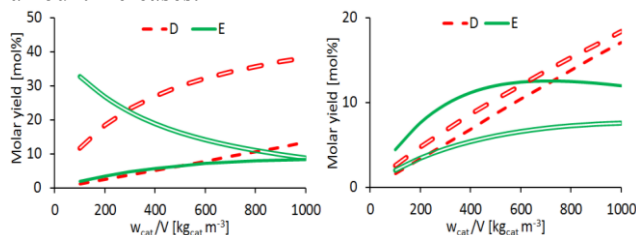
Figure 3: Molar yields of the reaction products as a function of the catalyst amount for varying K_1 (left, $K_3 = 1$, closed lines $K_1 = 10$, open lines $K_1 = 0.1$) and K_3 (right, $K_1 = 1$, closed lines $K_3 = 10$, open lines $K_3 = 0.1$) with $K_{ads,B} = K_{ads,C} = 1$ m^3 mol^{-1}. $k_1 = k_3 = 10^{-5} \cdot k_2 = 10^{-6} \cdot k_4 = 3 \cdot 10^{-3}$ s^{-1}

Conclusions

The higher catalyst bed density in a fixed bed reactor compared to a slurry batch reactor results in high heterogeneous product yields in the former. Competitive adsorption between intermediates plays a dominant role in the product distribution. Depending on the reaction scheme, the latter can show a counter intuitive maximum when varying the relative amounts of catalyst and homogeneous bulk phase. This holds in particular for bulk phase components which are formed via a contribution of heterogeneously catalyzed and homogeneous reversible reactions.

Acknowledgements

References

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