Modelling of Simultaneous Reaction and Diffusion in Chemical Reactors with Particle Size Distributions: Application of Ion-exchange Resins in Heterogeneous Catalysis

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A general model and software for simultaneous reaction and diffusion in porous catalysts were developed. The model comprises multiple reactions, diffusion phenomena and catalyst particle size distributions. The applicability of the model was illustrated with two examples originating from green chemistry: hydrolysis of alkyl formate (formic acid process) and perhydrolysis of carboxylic acids (percarboxylic acid process). Cation exchange resins were used as catalysts in both cases. Experiments carried out in batch reactors as well as computations demonstrated in an unequivocal way that the reaction-diffusion model should be used in the application cases. The methodology presented is general, and it can be applied on any heterogeneously catalyzed liquid-phase reaction system.

1. Introduction

The interaction of intrinsic kinetics and mass transfer in porous catalyst particles is a classical topic of chemical engineering since the days of Thiele and Frank-Kamenetskii. The basic theory is well-known and it is nicely summarized in the monumental work of Aris (1975). However, real practical applications of the theory concerning reaction and diffusion in porous media are not that many. The main reason might be that the complex chemical systems appearing in industrial practise require a numerical solution of the catalyst particle model, coupled to the model of the chemical reactor. In this work, we demonstrate the necessity of the reaction-diffusion model in the green synthesis of chemicals through catalyzed liquid-phase reactions. Cation-exchange resins were used as catalysts.

Ion exchange catalysts are frequently used to enhance the rates of numerous chemical processes, such as esterification, ester hydrolysis, etherification and aldolisation reactions. The benefits of ion-exchange resins as catalysts are their well-defined active sites, good reproducibility and good durability.

Many research efforts have been dedicated to the product distribution and kinetic modelling of various reactions on ion-exchange resins, but very few of them comprise mass-transfer effects, namely the interaction between intrinsic kinetics and internal diffusion in porous resin particles (Xu and Chaung, 1999). However, particularly for industrial applications of these catalysts, it is necessary to use particles of the size about 1 mm to keep the pressure drop within a reasonable limit in continuous fixed bed reactors. Furthermore, commercially available ion-exchange resin materials are not monodisperse, but always have a particle size distribution.

2. Modelling Approach

We have developed a very general modelling approach to describe simultaneous chemical reactions and diffusion in porous ion-exchange particles in chemical reactors. The model takes into account the particle size distribution, too. Simultaneous reaction and diffusion in the porous catalyst particles is described by a dynamic model, coupled parabolic partial differential equations,

$$\frac{dC_i}{dt} = \frac{r_i \rho_P}{\varepsilon_P} + r_i + \frac{D_{ei}}{\varepsilon_P R_j^2} \left(\frac{d^2 C_i}{dX^2} + \frac{a\text{-}1}{X} \frac{dC_i}{dX} \right) \tag{1}$$

Consequently, the reaction-diffusion model is solved for each catalyst particle size fraction. Experimentally determined particle size distribution is incorporated in the reactor model; for instance, for a batch reactor, the following model is applied:

$$\frac{dC_i}{dt} = a_p \sum_j y_j N_{ij} x_j^2 \tag{2}$$

The reaction-diffusion model was solved by discretising the space derivatives originating from diffusion in eq. (1) by central difference formula, and thus transforming the PDEs to ODEs, which were solved numerically together with the reactor balance equation (2). Typically 10-20 discretisation points were used in the calculations. A stiff ODE-solver was applied to solve numerically the large initial value problem created.

In general, the following approach was used: The intrinsic kinetics was determined for small particle sizes, in the absence of the internal diffusion limitations. This gave the numerical values of the rate constants. Experiments were performed with different catalyst particle fractions and molecular diffusion coefficients of the compounds were estimated from available correlations, such as Wilke-Chang equation. This information was incorporated in the complete model, eqs (1-2); in which the effective diffusion

coefficients play a central role. The particle porosity-to-tortuosity ratio in the effective diffusion coefficients was adjusted in situ during the simulations by applying non-linear regression analysis. A porosity-to-tortuosity ratio of 0.23 gave a better statistical result.

3. Application Examples

Two application examples were considered: hydrolysis of methyl and ethyl esters as well as perhydrolysis of carboxylic acids. The reaction schemes are displayed below,

$$RCOOR' + H_2O = RCOOH + R'OH$$
$$RCOOH + H_2O_2 = RCOOOH + H_2O$$
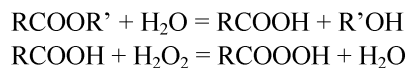
Hydrolysis of formic acid esters is of relevance in the production of formic acid according to the Leonard process and perhydrolysis of carboxylic acids is the dominating reaction route in the production of percarboxylic acids, which are used for bleaching, sanitation purposes and chemical reagents.

The following rate equations were used to describe the intrinsic kinetics.

Hydrolysis :

$$r_{tot} = r_{hom} + r_{het}$$
$$= \left[k_{hom1} + k_{hom2} * [RCOOH] + k_{het} * [-SO_3H]_O \right] *$$
$$\left[[RCOOR'] * [H_2O] - \frac{1}{K^C} * [RCOOH] * [R'OH] \right]$$

Perhydrolysis:

$$r_{tot} = r_{hom} + r_{het}$$
$$= \left[\frac{k_{hom} * \sqrt{K_4^C * [RCO_2H] * [H_2O]}}{[H_2O]} + \frac{k_{het} * [-SO_3H]_O}{1 + K_1^C * ([RCO_2H] + [RCO_3H]) + K_7^C * [H_2O]} \right] *$$
$$\left[[RCO_2H] * [H_2O_2] - \frac{1}{K^C} * [RCO_3H] * [H_2O] \right]$$

where $-SO_3H$ refers to the sulphonic acid sites present in the ion-exchange resin. K_C is the concentration-based equilibrium constant and it is based on the liquid phase concentration, therefore an ideal liquid mixture is assumed and the liquid volume remains constant. The contribution of homogeneous catalysis (r_{hom}) is included in the rate equations, since the hydrolysis and perhydrolysis proceed to some extent also in the absence of an added catalyst.

A thorough analysis of both experimental systems revealed that internal diffusion in the catalyst (resin) particles plays a significant role in practice and thus the modelling approach was applied. Since the particle size range (0.3-1.2 mm) was broad, it was necessary to take the particle size distribution into account in the modelling. The effectiveness factors for the catalyst particles varied within the range of 0.55-1.0 for hydrolysis and 0.76-1.0 for perhydrolysis. Some kinetic curves are displayed in Fig. 1, which nicely illustrate the excellent fit of the kinetic model to the experimental data. The model enables the simulation of the concentration profiles inside the catalyst particle; examples are shown in Figs 2-3, which clearly demonstrate that concentration gradients appear inside the porous catalyst particles and that the concentration profiles and thus also the effectiveness factors strongly depend on the catalyst particle size.
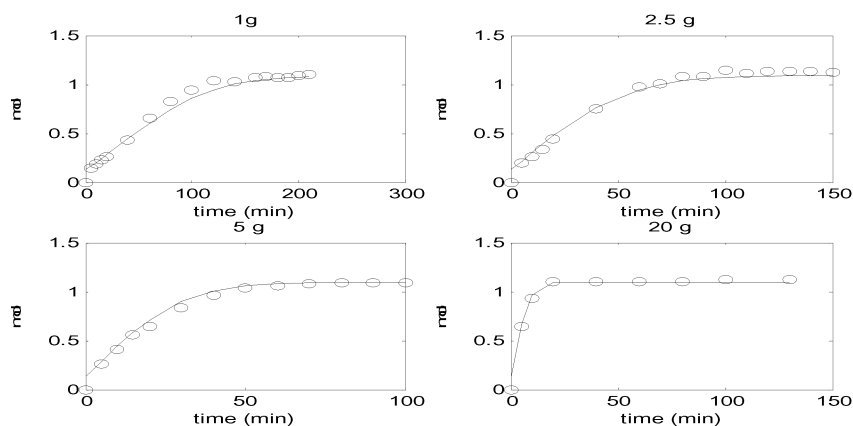

Figure 1. Fit of the model to experimental data (reaction product) for ethyl formate hydrolysis at 60°C and different amounts of the catalyst.
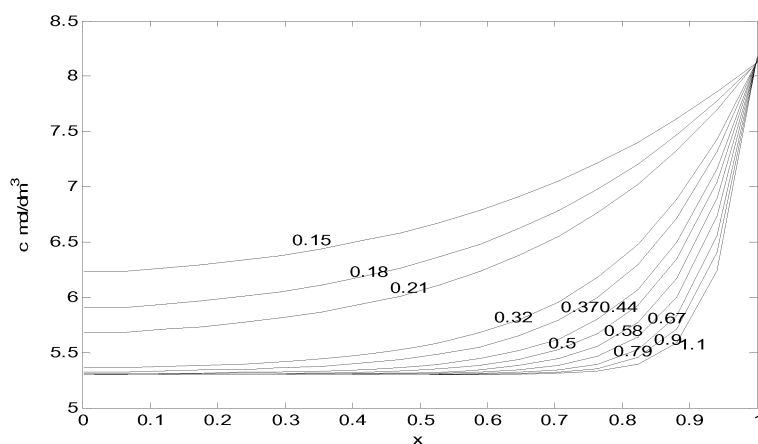

Figure 2. Concentration profiles of ethyl formate inside the catalyst particle at 60°C for different particle sizes (particle diameter in mm) in the beginning of the reaction (x-dimensionless coordinate).
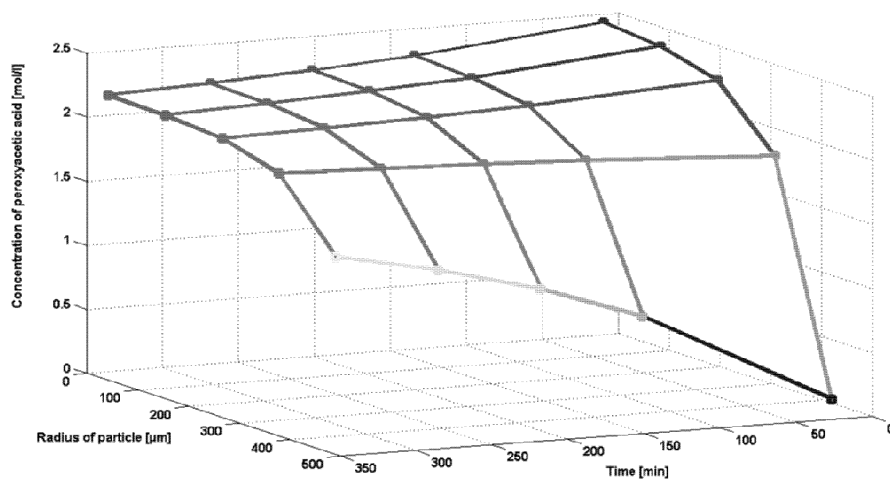
Figure 3. Concentration profile for peroxyacetic acid inside a particle of 898 µm at 30°C.

Conclusions

For a molecular-level understanding of the processes, this kind of approach is necessary. The general methodology proposed by us and the software developed can be used for scale-up purposes, not only for the demonstration examples discussed, but for any heterogeneously catalyzed liquid-phase reaction system, where porous solids and particle size distributions are involved. The modelling and simulation effort was focused on batch reactors; in future, it will be extended to continuous fixed bed reactors

Notation

a	shape factor of a catalyst particle
a_p	outer catalyst particle area-to-liquid volume
C	concentration
D	diffusion coefficient
D_{ei}	effective diffusion coefficient
d_p	particle diameter
het	heterogeneous
hom	homogeneous
K	equilibrium constant
k	rate constant
N	diffusion flux
R_j	particle radius

r_i	generation rate for component i
r	radial coordinate
t	time
X	dimensionless particle coordinate ($X=r/R_j$)
x_j	normalized particle radius ($x_j=R_j/R_{average}$)
y_j	fraction of particles with the radius r_j
ε_p	porosity
ρ_p	density of a catalyst particle
τ_p	tortuosity of a catalyst particle

Acknowledgement

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