

# MODELING OF SUPPORTED-LIQUID-PHASE CATALYSTS BY PERCOLATION THEORY

Frerich J. KEIL, Hans-Peter DETERING and Andreas KLEIN

Technische Universität Hamburg-Harburg  
Chemische Reaktionstechnik  
Eißendorfer Str. 38, 21071 Hamburg, Germany

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## Abstract

The program developed is a useful tool for detailed examination of different influences on the behavior of SLP-catalysts. Up to now, not all of the possible parameter variations have been studied. The program can be a useful support of modeling SLP-catalysts by comparing measurable values to computed results effected by particular parameters.

*Keywords:* supported-liquid-phase catalysts.

## 1. Introduction

Despite the fact that in 1939 MORAVEC, SCHELLING and OLDERSHAW [1] and CIAPETTA [2] reported about supported sulfuric acid within porous media for the polymerization of olefin-paraffin mixtures, the first systematic investigations concerning supported liquid-phase catalysis (SLPC) were carried out by RONY in 1968 [3], who performed a theoretical analysis describing the diffusion and reaction kinetics within this type of catalyst.

In general SLP catalysts consist of a solid porous support and a low-volatile liquid phase which fills a part of the pore space. The catalytic active component is dissolved in the liquid. The SLP-catalysis shows its high advantages especially for reactions in which both reactants and products are in gaseous or vapor form at reaction conditions. In comparison with the classical homogeneous process, such as the reaction in a bubble column, the area of gas-liquid interface is larger, the diffusional resistance in the liquid phase is less, the difficulties in separating the product off the catalyst are reduced to a minimum. The advantages of homogeneous catalysts such as higher stability, product selectivity and milder operating conditions are retained.

A process involving SLP catalysts can be described by the following simplified steps: The gaseous reactants diffuse from the bulk gas phase through the pores to the gas-liquid interface. They are absorbed into the liquid, undergo homogeneous reaction at the active component, and the

volatile products are then desorbed again into the pore gas phase and diffuse back out of the SLP-pellet into the reactor bulk gas stream.

It is obvious that the reaction rate depends strongly on the so-called liquid loading  $q$  which is the fraction of the pore space occupied by the liquid phase. With low saturation of the pore space ( $q \ll 1$ ) and also if the pore space is almost completely filled ( $q \approx 1$ ) the effective reaction rate is low. In the first case the concentration of the active component is low, in the latter case the gas-liquid interface is of the same order of magnitude as the outer pellet surface. In many cases one gets the maximum of conversion in the region of  $q = 0.5$  [3, 4].

Not only the amount of liquid, but also the shape of the interior gas-liquid interface has an important influence on the performance of the SLP catalyst. Therefore, many attempts have been made to model the liquid distribution in porous media. Some authors propose a uniform film on the pore's surface [5]. This seems not to be a very realistic model, and there is no experimental evidence for this assumption. An extension of the film model, the ideal macropore model, has been proposed by RONY [3]. In this model the micropores are considered to be completely filled with liquid, whereas the macropores are divided into two sections. One is filled in form of a liquid plug and the residual part of the pore wall is wetted by a film with a certain thickness. Separate inclusions of the liquid which are distributed all over the pore space of the support are proposed by ABED and RINKER [6]. VILLADSEN *et al* [7] related the type of liquid distribution to physical properties of the liquid and structural parameters of the support. One of the basic problems in modeling SLP catalysts is the difficulty to prove the proposed assumptions concerning the liquid distributions within the catalyst pellet. The global distribution can easily be checked by dissolving a dye [8] or a metal salt in the penetrating liquid. The liquid-loaded pellets are then broken open, and by visual observation one can investigate the distribution of liquid within the pellet. Unfortunately, it is much more difficult to get information about the local distribution of liquid.

The purpose of our investigations is to find out the influence of the distribution of pore radii, pore lengths, the connectivity and the mode of pore filling with liquids on the BET-surface, average pore radii, and especially the gas-liquid interfaces that are accessible for gases from the outer pellet surface.

## 2. Description of the Program

### 2.1. *The Random Pore Network*

The pore structure is represented by a system of cylindrical capillaries with given radii and length distribution. These pores (bonds) are the connections between the intersection points of the pore network. The intersections (sites) are nodes of a certain number of pores (bonds). Each site is characterized by three indices which indicate its location in the network. Each bond is characterized by the site from where it starts and an additional number  $l$  which specifies this bond. The maximum connectivity is an input integer variable. With the given input variables a random three-dimensional network is generated. The number of sites in each direction may be set.

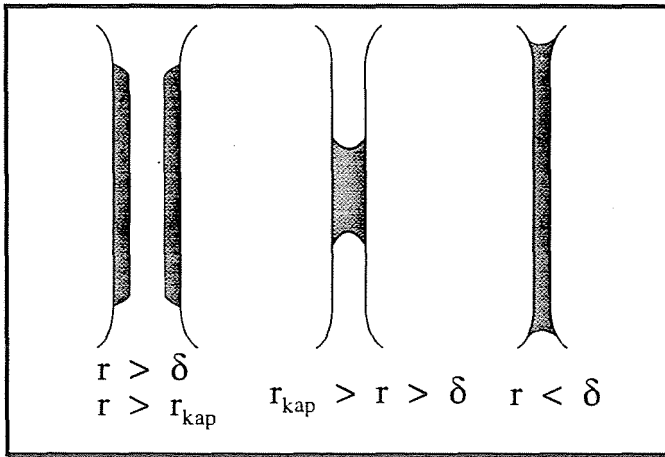
Generating the network each site and each bond is set permeable or nonpermeable (in other words: existing or not existing) with a certain probability. The permeability of the whole network is thus depending on the probability of existence of sites and bonds. In the language of percolation theory we have a combination of bond- and site-percolation in this case. Optionally a network of macropores passing through the pellet may be defined.

### 2.2. *The Pore Filling Algorithm*

A random walker starts at a randomly chosen site on the outer surface of the network. If the site is existent, he will pick one of the existent bonds, walk to the next site, randomly choose the next bond starting from the actual site and so on. Wherever he walks, he fills up the pores according to given pore filling rules. The local liquid distribution is defined by parameters of the pore (i. e. length, radius) and other user defined parameters (see below). Back steps of the random walker are only allowed if there is no more feasible forward step. Totally filled pores are impenetrable for the walker. An input parameter controls the penetration depth of the walker. If this value is low, the walker will generate only in a thin impregnated shell. As an alternative of the random walk method the pellet might be wetted starting from the center. This is not in agreement with the experimental impregnation procedure but in certain cases reorganization of the fluid after the impregnation might lead to this kind of a central liquid cluster.

## Parameters defining the local liquid distribution:

filled pore length:	fraction of length filled with liquid
limiting radius $r_{kap}$ :	for radii $\leq r_{kap}$ capillary forces are active
wetting fraction:	ratio of wetted to wettable area
film thickness $\delta$ :	thickness of the wetting film (if existent)



*Fig. 1.* Local distribution of liquid

### 2.3. Analysis of the Generated SLP-Catalyst Pellet

First of all, those sites which are connected by gas-phase paths, were labeled with an individual cluster number by the Hoshen-Kopelman Algorithm [9]. Clusters are defined as isolated regions of unfilled pore space. Some of these clusters have contact to the outer bulk gas phase. Only these clusters are significant for the catalysts performance. The program evaluates i. e. residual pore radii, gas-liquid interfaces for all as well as for the outside-clusters only, BET-surface (from outside accessible gas-liquid plus gas-solid interface) and percolation threshold as a function of liquid loading.

### 3. Results and Conclusion

The following example demonstrates the influence of the global liquid distribution on experimentally measurable values like catalyst activity and

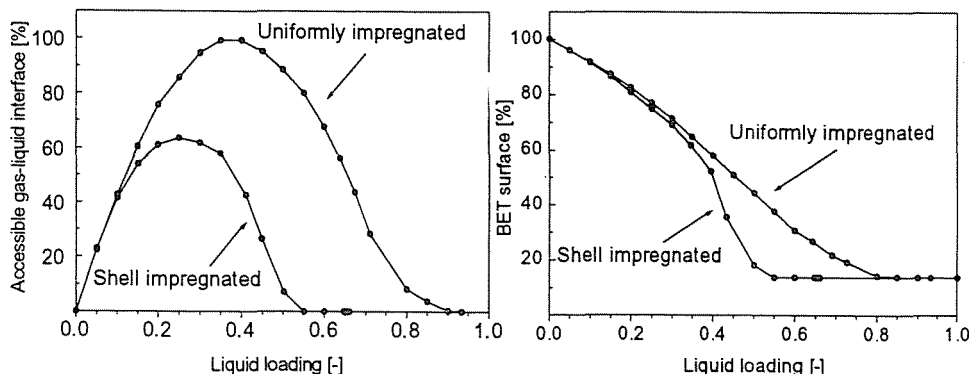


Fig. 2. Influence of global liquid distribution on accessible gas-liquid interface and BET surface

BET-surface. The computed curves are in good agreement with experimental results. In case of 'shell-impregnated' catalysts, the maximum activity is lower and is reached at lower liquid loading than in case of uniformly distributed liquid within the pellet. The decrease of BET-surface to zero (the percolation threshold) lies also at lower values of liquid loading  $q$ .

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