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OPTIMAL POROUS STRUCTURE, GRAIN SHAPE AND SIZE OF CATALYSTS

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Abstract

Optimal porous structure of catalyst is determined as follows: maximal activity per unit volume of catalyst with limitation on selectivity for complex reactions . Activity of catalyst A is determined as observable conversion rate in a porous grain at given pressure and temperature. As the conditions of conversion change along the reactor, optimal porous structure can be different on different stages of the process.

Optimal size of catalyst grains is determined taking into account expenditures for hydraulic resistance and catalyst.

Catalysts of different shapes were checked for hydraulic resistance of layers which resulted in indentical reactor output under different additional conditions: either indentical layer volume, or indentical catalyst mass, or indentical outer sizes of layer elements.

Combination of mathematical and hydrodynamic simulation of the processes in catalyst layer allows the choice of optimal shape and size of catalyst.

Keywords: porous structure of catalysts, grain shape and size of catalysts, catalysts, optimization of catalysts.

Optimization of catalysts is carried out in different stages of their development and on different criteria accordingly as follows:

- chemical composition (the best activity, selectivity);
- inside porous structure (maximum observable activity with limitations on selectivity for complex reactions);
- shape and size of catalyst grains (optimization criterion includes observable activity and selectivity, expenditures for hydraulic resistance and catalyst).

Strictly speaking, optimization is a mathematical procedure. However, not only mathematical methods and criteria have to be used under catalyst optimization. One has to take into account yield requirements, stability of catalyst in working conditions, homogeneity of reactants flow in catalyst layer, etc.

Optimal chemical composition of catalyst is to a great extent a physico-chemical problem. *Optimal porous structure of catalyst* is determined as follows: maximal activity per unit volume of catalyst with limitation on selectivity for complex reactions . Activity of catalyst A is determined as observable conversion rate in a porous grain at given pressure and temperature. As the conditions of conversion change along the reactor, optimal porous structure can be different on different stages of the process.

Observable activity A depends on specific reaction rate W_{sp}, specific inside surface S_{sp} and efficiency of catalyst pores η:

$$A = W_{sp} \times S_{sp} \times \eta.$$

Efficiency $\eta = \operatorname{tg} \varphi / \varphi$ depends on parameters:

$$\varphi = v_p / S_p \sqrt{K_{sp} S_{cp} / D_e}.$$

Effective diffusivity is

$$D_e = \Pi (1/D_b + 1/D_x).$$

Here $\Pi = \Pi' \varepsilon$ is the coefficient of penetration [1], D_b – bulk diffusivity, D_K – Knudsen diffusivity, which depends on pore radius S_{cp}/ε. Here η and φ are given for simple cases-plate catalyst and first order reaction as example. Qualitative results will be the same for more complicated cases.

Optimal porous structure was determined among globular models which represent well real porous structures of catalysts and mathematically described accurately [1]. In particular, S_{sp}, pore radius r and porosity ε are connected by ratio: $S_{sp} = b\ (1 - \varepsilon)/r$, where $b = 1.32 - 1.41$ for different packing of globules. W_{sp} is accepted to be constant.

Increasing of S_{sp} is achieved by decreasing pore size r and porosity ε, but this results in decreasing of catalyst efficiency η. If mass transfer in pores is carried out by molecular diffusion which does not depend on r, enlargement of inside surface increases activity of catalyst (in this case $\eta \sim 1/s^n$, where $n = 0 - 0.5$ depends on whether kinetic or intradiffusional regime is in catalyst grain). With decreasing r, diffusion in pores will be converted to Knudsen's regime (D_K is proportional to n and $\eta \sim 1/S_{sp}$) and does not depend on r, if the process takes place in intradiffusional regime. Porosity of catalyst must be as small as possible. Correlation between A and r_p are given in *Fig. 1*.

In some cases for real porous bodies ε changes with changing S_{sp}, and pore size and porosity are connected described by an empirical relationship [2]: $r \sim [\varepsilon/(1 - \varepsilon)]^n$. That is why functions $A(r)$ will have an extremum.

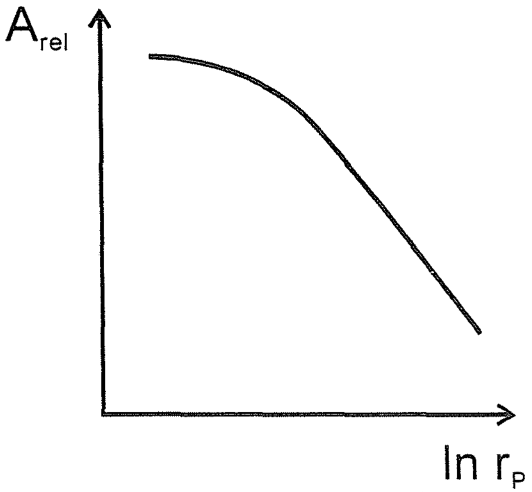

Fig. 1. Correlation between catalyst efficiency A and pore radius r_p

Catalysts of bidispersional structure consist of macroglobules with macropores. Porous macroglobules are formed by microglobules with micropores. It is possible to isolate porosity of macroglobules ε_i and fraction of macropores ε_q. Process effectivity in macroglobules with respect to gas composition near the surface is close to 1 because of small size (usually 1-2 micrometer) even for very active catalysts. Such structure results in a fast transport of components inside grain through large macropores where molecular diffusion dominates and has large S_{sp} which is determined by microglobules. Therefore, optimal structure of bidispersional catalyst is as follows: macropore providing for molecular diffusion and micropores formed by compact packing (minimum possible ε_i) of microglobules with diffusion regime close to Knudsen's.

Correlation of activity of catalyst for monodispersional A_m and for bidispersional A_b optimal structures results in the following relationship:

$$A_b/A_m \sim \sqrt{DT\sqrt{M}/P},$$
$$A_b/A_m = 1.4 \cdot 10^{-4}\sqrt{D_M T\sqrt{M}/PR_i M_b/M_M}.$$

Molecular diffusion coefficient D is inversely proportional to square root of molecular mass M, that is $D_B\sqrt{M} \approx$ const. Transition to bidispersional branched structure is reasonable for processes under low pressure and higher temperature. Calculation of optimal porous structure of catalysts, for example, for oxidation of sulphur dioxide showed that it is necessary to use catalysts of two different structures: in the first layer of reactor, where the process takes place under high temperatures, it is necessary to use bidispersional catalyst; and in further ones where temperature is lower – monodispersional. The best catalysts have such structures.

For complex reactions (particularly for successive ones) intradiffusion decreases the selectivity of processes. If there is a limit on selectivity then there is a limit on η, too. The effectivity determines φ and, therefore, parameters of pore structure – S_{sp}, r_p and ε, that comply with optimum for complex reactions.

Optimal size of catalyst grains is determined taking into account expenditures for hydraulic resistance and catalyst. The amount of catalyst depends on its observable activity which is increasing with decreasing grain size. But this results in increasing pressure drop and, accordingly, energy expenditures. Optimization of common expenditure is a typical engineering task. As far as temperature and composition of reactive mixture changes over catalyst layer, in many cases optimal size of catalyst grains will be different at different stages of process. Distribution of optimal sizes of layers of granules is calculated for processes of sulphur dioxide oxidation [1], ammonia synthesis [3], sour gas scrubbing of natural gas [4], etc. In these cases indentical shapes of grains of different size are expected.

Optimal shape of catalyst grains is chosen from several known structures, usually produced in industry. Tablets, granules, rings (tablet with a hole), multichannel (tablet with many holes or honeycomb) are some of those. Catalysts of different shapes were checked for hydraulic resistance of layers which resulted in indentical reactor output under different additional conditions: either indentical layer volume, or indentical catalyst mass, or indentical outer sizes of layer elements. The most interesting conclusions are as follows.

Multichannel grains of catalysts have advantage over rings for the processes occurring in the range of inside diffusion (methane conversion). In this case multichannel catalysts have outer sizes a little bit larger than granular ones and a big amount of thin holes (*Fig. 2*). Calculations of methane conversion were confirmed by tests of specially prepared catalyst. For the processes occurring in kinetic range it is reasonable to use ring catalysts.

However, in such calculations it is necessary to take into account change of hydrodynamics of flow in layers of complex geometrical shape. Thus, optimization showed advantages of catalyst grains with big amount of thin channels. Flow passes through small channels badly and the surface of such a catalyst is not equally accessible. Just that limits minimum size of channels in such catalysts.

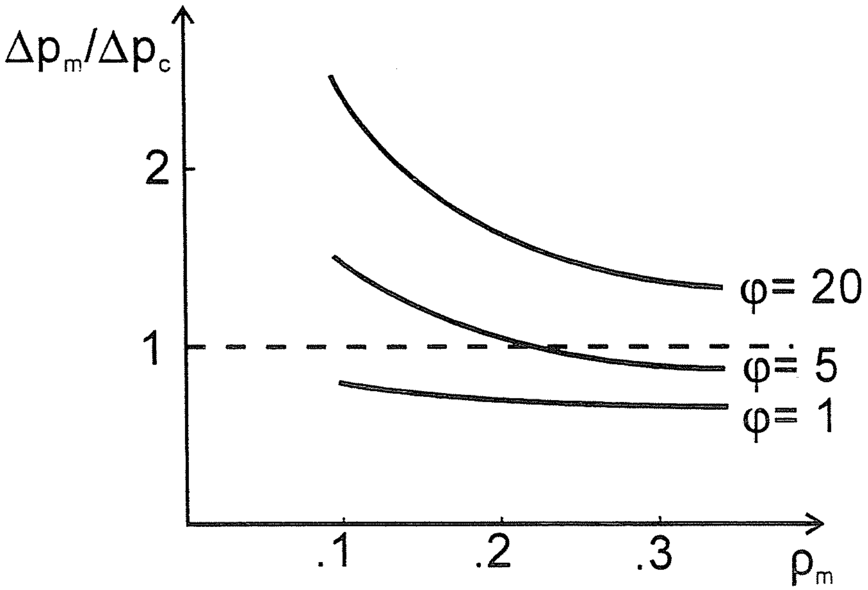

Fig. 2. Influence of relative radius of holes in multichannel catalysts and intradiffusion parameter φ on relation pressure drop in beg of multichannel catalysts (ΔP_m) and (ΔP_r) catalyst

Combination of mathematical and hydrodynamic simulation of the processes in catalyst layer allows the choice of optimal shape and size of catalyst.

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