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DIFFUSION MODEL OF SOLID-STATE CATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS. THE INFLUENCE OF THE SIZE OF METAL CRYSTALLITES.

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Abstract The kinetics of the reaction was experimentally studied in the platinum black/thymine system. It was shown that the data obtained and the kinetic data of reference[2] could be interpreted by the diffusion model and not by the available models of catalyst poisoning. The diffusion model was developed for reactions on dispersed metals. We calculated the dependence of both the reaction zone specific volume and the maximum compound/catalyst ratio ensuring complete conversion of the initial reagent on the radius of the catalyst metal crystallites for a series of values of the process parameter.

INTRODUCTION

The possibility of catalytic hydrogenation of organic solids has been demonstrated[1]. A number of specific features - which offer new possibilities for the production of tritium labeled compounds[1] and for performing assymetric synthesis[2] are typical of solid-state catalytic hydrogenation (SSCH) reactions.

It was shown in[2,3,4] that the mechanism of SSCH is based on hydrogen spillover: the migration of activated hydrogen from the surface of the catalyst metal into the organic compound layer. Further investigation of the SSCH mechanism is an important task. It is necessary to find out which processes account for the kinetics of these reactions, such as the reaction stops before the initial reagent has been completely converted into the product. The phenomenon was observed for a certain thickness of the compound layer in the palladium membrane/organic compound system[3,4], and for any compound/catalyst ratio in the supported catalyst/organic com-

pound system[1,2]. SSCH models suggesting catalyst poisoning[3,4] and a diffusion model of the reaction[4] have been proposed. In this study, the reaction kinetics was experimentally studied in the platinum black/thymine system. It was shown the data obtained and the kinetic data of reference[2] could be interpreted in terms of the diffusion model and not of the available models of catalyst poisoning. The diffusion model was developed for reactions on dispersed metals. We calculate the dependence of both the reaction zone specific volume and the maximum compound/catalyst ratio ensuring complete conversion of the initial reagent on the radius of the catalyst metal crystallites for a series of values of the process parameter.

EXPERIMENTAL

Platinum black was obtained following the procedure described[8]. The mixture of Pt black and thymine (1:1 g/g) was prepared by drying the Pt black suspension in thymine solution in a vacuum rotor evaporator. This was reacted with hydrogen-tritium (1000:1) mixture at 293 K at a gas pressure of 60 torr. Labile radioactivity was removed by isotope exchange with water with subsequent lyophilization. Non-labile radioactivity was measured on a liquid scintillation counter. The standard relative deviation of measurements was 13%. Fig.1 shows the dependence of the products total radioactivity (Ci/mmol of the initial thymine) on the reaction time. It is easily demonstrated by the radioactivity of the products that less than 2% of initial thymine is involved in the reaction in all experiments.

RESULTS AND DISCUSSION

In studies[3,4] SSCH models are proposed that suggest catalyst poisoning. Two possible equations for kinetics of product accumulation are offered:

$$C = b\ th(at) \qquad (I)$$

$$C = b\ (1-\exp(-at)) \qquad (II)$$

where t is the reaction time, a and b are the parameteres, C is the concentration or the quantity (depending on the b parameter dimension) of the product, th denotes hyperbolic tangent. A diffusion model has been proposed[4] according to which the SSCH kinetics is determined by the spillover hydrogen concentration gradient in the organic phase. The model is based on the following assumptions:

- the activated hydrogen particles participating in spillover are hydrogen atoms;
- the spillover hydrogen (H) concentration gradient in the organic phase is determined by the diffusion and disappearance of H in a two-stage reaction of hydrogen exchange with groups containing labile hydrogen (OH, NH, NH_2, SH):

$$RH + H \longrightarrow R^{\cdot} + H_2 \qquad (i)$$

$$R^{\cdot} + H \longrightarrow RH \qquad (ii)$$

- the gradient of concentration is instantaneously set up, and hydrogenation reactions proceed in a stable gradient.

The diffusion model for the plane catalyst/compound interface case results in the following kinetic equation for the product concentration C:

$$C = b \int_0^1 (1 - \exp(-aty))\, y^{-1}\, dy \qquad (III)$$

Which of the three available equations can be used to describe the experimental kinetic data? The Table 1 shows regression results of the data from this study and from study[2]. It is clear from the table that both sets of data can be described only by the diffusion model equation, since the r.s.r.d. for this equation is much less compared to the other equations. In Fig.1 the results are graphically depicted of the regression of experimentally obtained data by the diffusion model equation.

The equation (III) is inferred assuming that the catalyst/compound interface radius considerably exceeds the reaction layer thickness. The

TABLE 1 Regression results of the data from this study and from study[2].

equation	b Ci/mol	a min^{-1}	r.s.r.d. %	s.d. %	b cm^3	a $hour^{-1}$	r.s.r.d. %	s.d. %
I	0.326	0.0374	39.4		0.529	40.9	12.4	
II	0.329	0.0388	35.3	13%	0.593	42.2	9.77	?
III	0.0546	0.325	15.9		11.2	2.95	6.76	
	this study data				data from[2]			

r.s.r.d. - relative standard regression deviation

s.d. - standard deviation of measurements

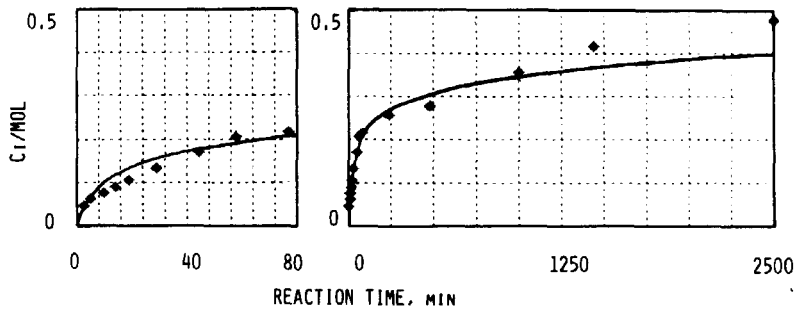

FIGURE 1. Reaction in the platinum black/thymine/hydrogen:tritium (1,000:1) system. The kinetics of radioactivity incorporation in the organic phase. The points are experimental, the curve is the graph of the function (III) with parameters taken from Table 1.

assumption is probably true for platinum black for it consists of particles of several tens of nanometers in size adhering in aggregates of some 1,000 nm. However, for metal zoles or supported catalysts with far smaller metal particles the assumption seems to be unlikely.

We shall infer some useful ratios within the diffusion model for SSCH

reactions on catalysts consisting of metal spheres comparable in size to the reaction layer thickness.

Let the metal crystallites have the same radius r_0 and be distributed at equal distances from each other in infinite crystals of organic compound. Assuming that the (i) stage determines the (i)+(ii) reaction rate, we shall obtain an equation for the tritium atom concentration C for a steady state:

$$D\Delta C = kC ,$$

$k=k'[RH]$, k' is the (i) reaction rate constant, D is a diffusion coefficient, [RH] is the organic compound concentration. Solving the equation for the spherical symmetry case with the boundary condition $DC'(r_0)=-I$ (I is the spillover-hydrogen flow intensity through the metal/organic compound interface) we obtain :

$$C(r) = Ir_0^2\exp(\sqrt{k/D}(r_0-r))/(Dr(1+r_0\sqrt{k/D})) \qquad (1)$$

r_0 is the radius of the metal crystallite, r is the distance from the crystallite centre.

It is easy to obtain the expression for the concentration of reaction products [P] for time T at point r:

$$[P] = [RH]_0(1-\exp(-k_1C(r)t)) , \qquad (2)$$

where $[RH]_0$ is the compound's initial concentration, k_1 is the rate constant of the reaction between H atoms and the organic compound, giving product P. If several reactions are possible, k_1 equals the sum of all reaction rate constants.

To obtain an expression for the radius of the reaction zone around the metal crystallite, we introduce into consideration the value z, which is determined as follows:

$$k_1 C(z)t=1 \qquad (3)$$

that is, z is the point at which the initial compound concentration is decreased by a factor of (e-1)/e at time t.

The reaction practically stops at time t_1. This may be determined from the condition:

$$\frac{4}{3}\pi(z^3(t_1/2) - r_0^3) = 0.9\frac{4}{3}\pi(z^3(t_1)-r_0^3) \qquad (4)$$

therefore, $z(t_1)=q$ is the reaction zone radius. Using (4),(3) and (1) we

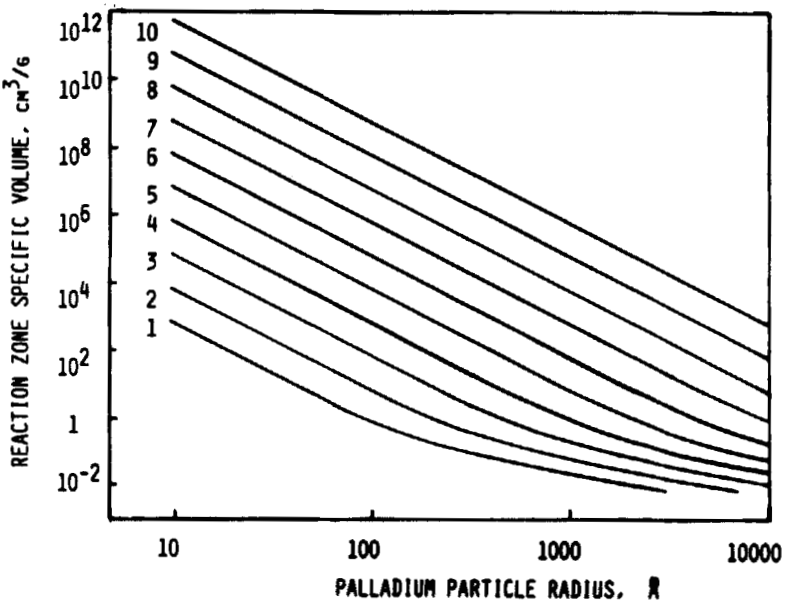

FIGURE 2. Dependence of the reaction zone specific volume on the palladium particle radius for different values of $\sqrt{k/D}$: 1 - 10^{-1}, 2 - $10^{-1.33}$, 3 - $10^{-1.67}$, 4 - 10^{-2}, 5 - $10^{-2.33}$, 6 - $10^{-2.67}$, 7 - 10^{-3}, 8 - $10^{-3.33}$, 9 - $10^{-3.67}$, 10 - 10^{-4} $Å^{-1}$.

obtain the equation for q:

$$q(0.9q^3+0.1r_0^3)^{-1/3}\exp(\sqrt{k/D}(q-(0.9q^3+0.1r_0^3)^{1/3})) = 2 \qquad (5)$$

Fig.2 shows the dependence of the reaction zone specific volume per 1 g of the metal-catalyst, ($V=(q^3/r_0^3-1)\rho_m$, (ρ_m is the metal density)), on the metal crystallite radius r_0 for the $\sqrt{k/D}$ range of 10^{-1}-10^{-4} Å^{-1}. In[4] it was shown that $\sqrt{k/D}$ is of the order of 10^{-2} Å^{-1} for a number of organic compounds.

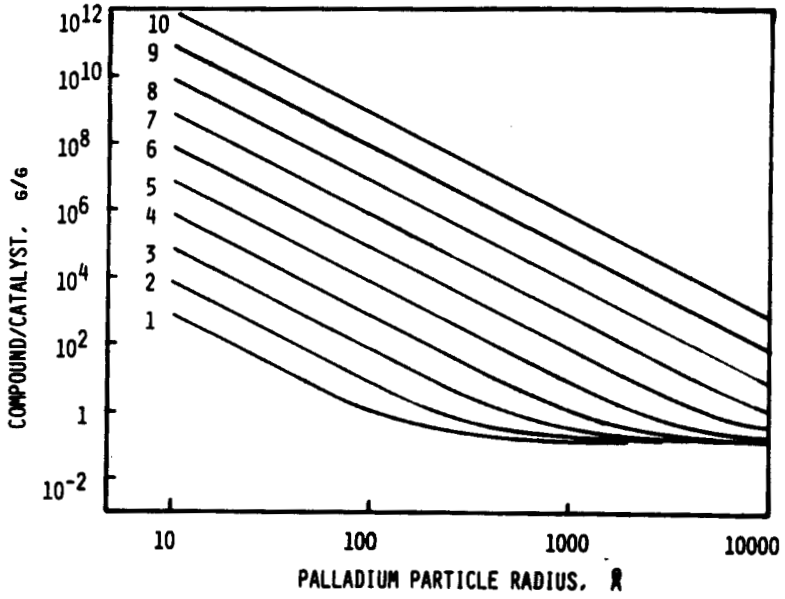

FIGURE 3. Dependence of the reaction mixture composition M on the palladium particle radius for different values of $\sqrt{k/D}$: 1 - 10^{-1}, 2 - $10^{-1.33}$, 3 - $10^{-1.67}$, 4 - 10^{-2}, 5 - $10^{-2.33}$, 6 - $10^{-2.67}$, 7 - 10^{-3}, 8 - $10^{-3.33}$, 9 - $10^{-3.67}$, 10 - 10^{-4} Å^{-1}.

Evidently, the initial reagent conversion is about 100% if the metal crystallites are $<q\sqrt{2}$ distant. This corresponds to the reaction mixture composition:

$$M = \text{compound/catalyst} = \rho_c/\rho_m(3q^3/\sqrt{2}\pi r_0^3-1) \quad , \quad g/g \quad ,$$

ρ_c is the compound density. Fig.3 shows the dependence of M on r_0 for the $\sqrt{k/D}$ range of 10^{-1}-10^{-4} $Å^{-1}$, ρ_m=12.02 (palladium) and ρ_c=1 g/cm^3.

If the reaction kinetics is determined by the catalyst poisoning then the initial reagent conversion (and consequently, the specific reaction volume, which may be defined as the reaction product volume per 1 g of the catalyst) is evidently inversively proportional to r_0, whereas the compound/catalyst ratio, ensuring the initial reagent conversion close to 100%, is directly proportional to r_0. Fig.2 and 3 show that functions V and M still more sharply depend on r_0 in the r_0 value range less than $10\sqrt{D/k}$ by an order of magnitude. This fact makes it possible to distinguish experimentally between the reactions with catalyst poisoning and the reactions for which the diffusion model is true.

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