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UDC 66.097+541.136

In the past year, we have been able to achieve a gas-liquid phase heterogeneous reaction which takes place in a layer of granulated catalyst, through which gaseous and liquid reagents are transmitted by direct or reverse flow [1, 2]. This method of maintaining gas-liquid phase heterogeneous reactions has a number of advantages over the use of a suspension reactor [3]. Therefore, it can be expected that reactors with a stationary layer will be used as information becomes available about their operating characteristics. The productivity of these reactors depends to a great extent on the mass transfer processes which take place within the layer and the catalyst granule. This paper proposes a catalyst together with improved feed of the gaseous reagent through the granule into the reaction zone.

Let us consider the processes which go on in the usual catalyst granule. Inasmuch as the catalyst, whether on a carrier or carrier-free, is usually well saturated with liquid reagents, then, in its stationary state, the catalyst granule is completely flooded by the original liquid reagents and the reaction products. In order to take part in the reaction, the gas should diffuse in the dissolved state through the saturated granule pores to the active surface. Because the concentration of dissolved gaseous reagents is 10^6 to 10^2 times as small as the concentration of the liquid reagents, and the diffusion coefficient of the gas dissolved in the liquid is quite small (about 10^{-5} cm²/sec at room temperature), the process itself, restricted as it is to the use of an internal catalyst system (and also the decrease in catalyst productivity which accompanies the reaction) both cause the diffusion of the dissolved gas within the porous granule to slow down. In this way, the macrokinetics of gas-liquid phase reactions on the usual hydrophilic catalysts is analogous to the macrokinetics of liquid phase reactions. Hence, the efficiency of using the internal surface of a catalyst for an irreversible isothermal first-order reaction [4, 5] is determined by the equation

$$h = \frac{1}{L} \frac{\Psi}{\Psi_0} \quad (1)$$

where $\Psi = L\sqrt{k/D}$ is the Thiele modulus, L is the maximum diffusion path for the gas dissolved in the liquid, equal in this case to one-half the depth (L) of the pelleted catalyst, k is the reaction velocity constant. Thus, as L decreases, the value of h and, therefore, the catalyst productivity increase very strongly in proportion to the value of $1/L$ for fast reactions. However, one cannot decrease the thickness of the granule to less than a few millimeters due to the increase in hydrodynamic resistance of the catalyst layers. As a result, the yield (h) of these catalysts can be low [1, 2]. In fact, in this case, only the outside surface of the catalyst granule takes part in the reaction.

If the catalyst granule does not contain lyophilic (i. e., liquid-wettable) components of catalyst or carrier, it will contain a lyophobic (i. e., a nonwettable) component. Then the pores formed with this component will already have been filled with gas, not liquid. In this way, part of the porous volume will be filled with liquid and part with gas, as shown schematically in Fig. 1. The diffusion coefficient in the gas phase is 10^4 to 10^5 times as great as in the liquid phase. Moreover, when an essentially one-component reagent is present in the gas phase, its migration into the gaseous pores will take place because of filtration transfer rather than by diffusion, with an even further gain in speed. The result is that gas phase transfer cannot limit the reaction velocity. At the same time, the migra-

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. (Presented by Academician Ya. M. Kolotyrkin January 31, 1977.) Translated from Doklady Akademii Nauk SSSR, Vol. 234, No. 2, pp. 403-406, May, 1977. Original article submitted December 29, 1976.

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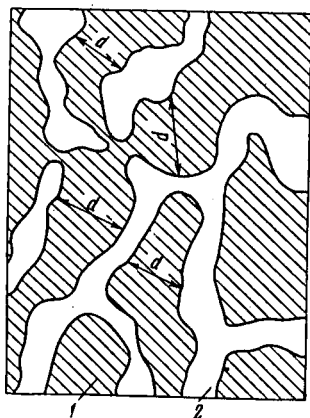


Fig. 1

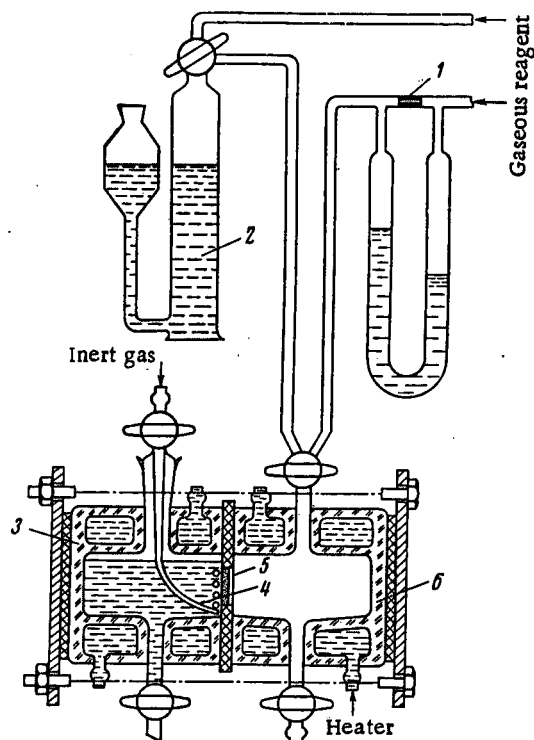


Fig. 2

Fig. 1. Schematic depiction of the lyophobic catalyst structure: 1) catalyst+liquid, 2) lyophobicizer+gas.

Fig. 2. Device for measuring gas-liquid phase reaction velocity on pelleted catalyst. 1) Capillary, 2) gas flow-rate measuring device, 3) liquid reagent reaction chamber, 4) purging device for inert gas, 5) porous water seal, 6) gaseous reagent reaction chamber.

tion of the dissolved gas to the catalyst surface is also greatly speeded up, as indicated by Eq. (1), in the form of a sharp decrease of a few orders of magnitude in the maximum diffusion path l of the dissolved gas. In this case, $l \sim (1/2)d$, where d is the mean shortest distance between neighboring gas pores, measured across the liquid pores (see Fig. 1). The value of d can be about 10^{-5} to 10^{-3} cm, while L is about 0.1 to 1 cm. Thus, the introduction of a lyophobic agent should significantly increase the extent to which a catalyst can be utilized as well as its productivity in rapid gas-liquid reactions. Such hydrophobizing catalyst pellets are analogous to hydrophobized gas diffusion electrodes, which are used in hydrogen-oxygen fuel cells for accelerating gas-liquid phase electrochemical (electrocatalytic) reactions [6].

Figure 2 shows the apparatus used to verify these conclusions experimentally. The reaction velocity was determined from the flow rate of the gaseous reagent. The gas flow was measured by its pressure drop through the capillary (designated 1 on Fig. 2) or from the decrease in its volume in a unit time at its exit from a confined volume (2). The reaction chamber was made of glass and consisted of two halves, one for liquid reagents, products, and solvents (3) and the other for gaseous reagents (6). To reduce the surface diffusion resistance to a minimum along the input and output lines for the liquid reagents and products, the liquid phase was stirred by the inert gas exhaust (4). Pellets made of a platinum catalyst of two types were compared: 1) a hydrophilic pellet containing 0.8 g of compressed platinum black with a surface of about $20 \text{ cm}^2/\text{g}$, and 2) a hydrophobized pellet compressed from a mixture of the same quantity of platinum black with a suspension of fluoroplast [polytetrafluoroethylene] FP-4D (15 wt. % of dry plastic). The tablet diameter was 20 mm, its thickness about 1 mm. A porous layer (5) of fluoroplast-4 was prepressed to one side of each pellet. This layer acted as a liquid seal, blocking the ingress of liquid into the gaseous half of the cell, as can be seen in Fig. 2. The presence of this highly porous hydro-

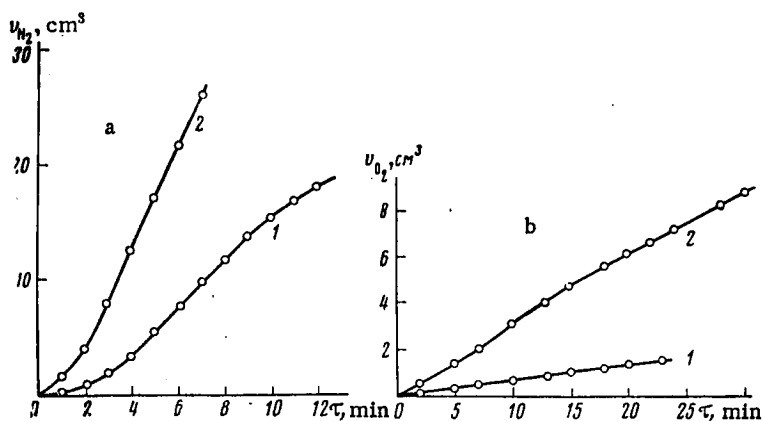


Fig. 3. Volume of gas reagent consumed: hydrogen for reduction of Ce^{4+} (a), and oxygen for oxidation of Fe^{2+} (b), with hydrophilic (1) and hydrophobized pellets (2).

phobic layer (lyophobic in the general case) brings the surface diffusion resistance to the input of gas to a constant and minimal level, and renders the experimental results unambiguous.

Both pellets were used in reduction reactions of Ce^{4+} to Ce^{3+} by hydrogen in a water solution of $4 \text{ N Ce}(\text{SO}_4)_2 + 1 \text{ NH}_2\text{SO}_4$ and oxidation of Fe^{2+} to Fe^{3+} by oxygen in a water solution of $3 \text{ N FeSO}_4 + 1 \text{ NH}_2\text{SO}_4$ at 25°C . The results are shown in Fig. 3 in terms of the volume of gas consumed (v) as a function of time (τ) for the hydrophilic (curve 1) and hydrophobized pellets (curve 2). The reaction velocity was taken from the slope of the curves. In the case of Fe^{2+} oxidation, the reaction velocity for the hydrophobized and hydrophilic pellets was $0.315 \text{ cm}^3/\text{min}$ and $0.06 \text{ cm}^3/\text{min}$, respectively; for Ce^{4+} reduction $4.65 \text{ cm}^3/\text{min}$ and $1.83 \text{ cm}^3/\text{min}$. As is evident, in both cases the velocity with the hydrophobized pellets was significantly higher than that with the hydrophilic pellets, 5.3 times as fast in the case of Fe^{2+} oxidation, and 2.5 times for Ce^{4+} reduction. It should be pointed out that the same value was obtained for reaction velocity by measuring the hydrogen flow on the basis of capillary pressure drop or by using the confined gas volume.

In addition, it should be observed that, in the course of the Ce^{4+} reduction, whose velocity constant in this experiment was at least 30 times higher than for Fe^{2+} oxidation, the reaction velocity on the hydrophobized pellet was limited by surface diffusion restrictions at the pellet surface where the reagent soluble in the liquid phase enters, and not by internal diffusion. On removing these restrictions (for example, with more intensive agitation, which could not be strong enough in this particular reaction vessel) the reaction velocity should be still higher, but the effect of catalyst hydrophobization should be even greater in the case of Fe^{2+} oxidation, according to Eq. (1).

Thus, we feel that the experimental results confirm the conclusion that gas-liquid phase reactions can be speeded up by selective lyophobicization of a granulated catalyst.

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