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*Chemical Engineering Science* Vol 35 pp 2351-2352  
 Pergamon Press Ltd, 1980 Printed in Great Britain

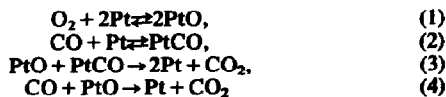
## Macroscopic clusters induced by diffusion in catalytic oxidation reactions

(Received 20 December 1979, accepted 4 February 1980)

Ordered state of catalysts surface layers has been recently proposed for various oxidation reactions [1,2]. It is known that simultaneous occurrence of a non-linear chemical reaction and diffusion may produce periodic structures ("dissipative structures" by Prigozhin [3]). These phenomena have been analyzed in more detail by Barelko *et al* (see, e.g. [4]). The objective of this study is to explain the appearance of these structures for the catalytic reaction oxidation of CO on Pt.

### MODEL

We consider the following reaction mechanism (see, e.g. [5]):



Assume that (i) diffusion of adsorbed CO molecules on the surface is due to "jumps" onto the neighbouring vacancies, (ii) the temperature interval is such that oxygen adsorption is localized and oxygen diffusion on Pt surface may be neglected.

Then the model which describes the process in the chemisorbed layer will be as follows:

$$\begin{aligned} x &= 2k_1 p_{\text{O}_2} z^2 - 2k_{-1} x^2 - k_3 xy - k_4 p_{\text{CO}} x, & (1) \\ y &= k_2 p_{\text{CO}} z - k_{-2} y - k_3 xy + D(z\Delta y - y\Delta z), \end{aligned}$$

where

$$\begin{aligned} x &= [\text{PtO}], \quad y = [\text{PtCO}], \\ z &= 1 - x - y = [\text{Pt}] \end{aligned}$$

Using the balance considerations we can easily receive eqn (1). The diffusion term in eqn (1) is not generally accepted. The details will be presented in our next article.

Consider now one-dimensional stationary problem

$$\Delta = \frac{\partial^2}{\partial \xi^2}, \quad x = y = 0,$$

i.e.

$$2k_1 p_{\text{O}_2} (1-x-y)^2 - 2k_{-1} x^2 - k_3 xy - k_4 p_{\text{CO}} x = 0, \quad (2)$$

$$D \left( (1-x) \frac{d^2 y}{d\xi^2} + y \frac{d^2 x}{d\xi^2} \right) + k_2 p_{\text{CO}} (1-x-y) - k_{-2} y - k_3 xy = 0 \quad (3)$$

### Main properties of the system

(1) Equation (2) determines a single-valued dependence (provided that  $x \geq 0$ ,  $y \geq 0$ ,  $x + y \leq 1$ )

$$x(y) = \frac{b - \sqrt{(b^2 - 4ac)}}{2a},$$

where

$$\begin{aligned} a &= 2k_1 p_{\text{O}_2} - 2k_{-1}, \\ b &= 4k_1 p_{\text{O}_2} (1-y) + k_3 y + k_4 p_{\text{CO}}, \\ c &= 2k_1 p_{\text{O}_2} (1-y)^2 \end{aligned}$$

$x(y)$  is differentiable function, therefore, eqn (3) may be reduced to

$$a_2(y) \frac{d^2 y}{d\xi^2} + a_1(y) \left( \frac{dy}{d\xi} \right)^2 + a_0(y) = 0, \quad (4)$$

where

$$\begin{aligned} a_2(y) &= D \left( 1 - x(y) + y \frac{dx}{dy} \right), \\ a_1(y) &= Dy \frac{d^2 x}{dy^2}, \\ a_0(y) &= k_2 p_{\text{CO}} (1 - x(y) - y) - k_{-2} - k_3 x(y)y \end{aligned}$$

(2) At higher derivative the coefficients in eqn (4) are not equal to zero where the function  $x(y)$  is determined. It holds true for such  $y$  that  $x(y) \leq 1$ . Equation (4) may be integrated in the explicit form. By substituting

$$\rho(y) = \frac{dy}{d\xi}$$

we arrive at

$$\rho^2(y) = \left( 2A - 2 \int_0^y f(u) \exp \left( 2 \int_0^u r(v) dv \right) du \right) \exp \left( - \int_0^y r(u) du \right), \quad (5)$$

where  $A$  is an arbitrary constant,

$$f(y) = \frac{a_0(y)}{a_2(y)},$$

$$r(y) = \frac{a_1(y)}{a_2(y)}$$

(3) An inspection of (5) indicates that  $\sqrt{(\rho(y))}$  (accurate to within

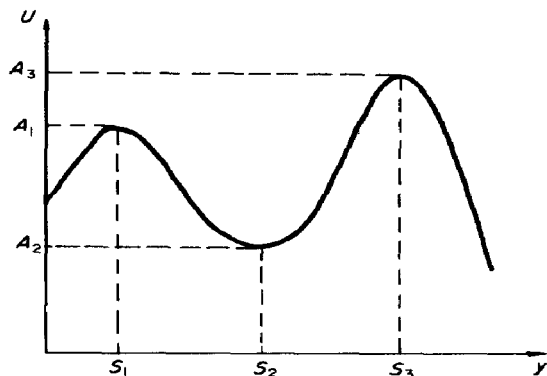


Fig 1

non-zero multiplier) is coincident with the rate of motion of the unit body with energy  $A$  in the field of potential energy

$$U(y) = \int_0^y f(u) \exp\left(2 \int_0^u r(v) dv\right) du$$

(3) If a lumped system described in terms of mechanism (1)–(4) has three steady states (which are possible in a wide range of temperatures and pressures [6, 7]), then the shape of the function  $U(y)$  is similar to that shown in Fig 1. Here  $S_1, S_3$  stand for stable steady states,  $S_2$  is an unstable steady state. If in (5)

$$A_2 < A < \min\{A_1, A_3\}$$

then we obtain a periodic solution of eqn (4) which represents the searched "dissipative structure". Even more interesting case is observed when

$$A = \min\{A_1, A_3\}$$

We deal with the object well-known in the theory of non-linear waves, namely, so called solitary wave (soliton) [8, 9]. This solution corresponds to the case when at  $\xi \rightarrow \pm\infty$  one of the stable steady states exists on the surface and in a certain region the state approaches another steady state (not reaching it) (Fig 2).

#### CONCLUSION

Existence of the above properties of system (2), (3) indicates that at simultaneous occurrence of a complex catalytic reaction and surface diffusion the appearance of ordered structures, spots, clusters, etc. is possible. They may be of pure macroscopic origin. The problem of stability of these formations is beyond the scope of this study.

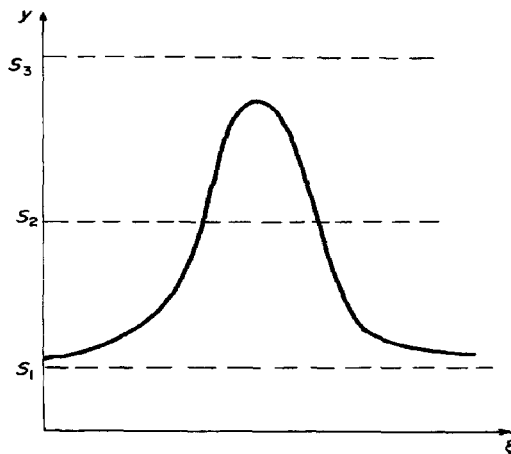


Fig 2

Computing Center, Siberian Branch  
U S S R Academy of Sciences  
Krasnoyarsk 660049, U S S R

A N GORBAN  
V I BYKOV

Institute of Catalysis  
Siberian Branch  
U S S R Academy of Sciences  
Novosibirsk 630090, U S S R

G S YABLONSKII

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### Bubble growth in a viscous Newtonian liquid

(Accepted 5 March 1980)

The problem of diffusion-fed gas bubble growth in a liquid is of interest in many areas of engineering. The particular case of such growth in a highly viscous fluid has application in polymer foam formation. One method of foam formation involves growth of bubbles by diffusion of blowing agent from an oversaturated solution of the blowing agent in the liquid surrounding the bubbles. The oversaturation may be achieved by a lowering of the system pressure, or by some other means.

A large body of literature exists on the subject of phase

growth. Detailed bibliographies may be found in the works of Scriven [1], Street *et al* [2] and Rosner and Epstein [3]. Diffusion-fed phase growth in viscous liquids has been treated by Barlow and Langlois [4], Street *et al* [2] and Szekely and Martins [5]. Barlow and Langlois and Szekely and Martins treated phase growth in Newtonian liquids while Street *et al* considered growth in an Ostwald-de-Waele power law liquid. The analysis of Street *et al* is further complicated by considering the liquid surrounding the bubble to be finite, the liquid viscosity to vary