Catalysis Letters 9 (1991) 369–376

KINETICS OF THE CATALYTIC DEACTIVATION BY SITE COVERAGE AND PORE BLOCKAGE: APPLICATION OF PERCOLATION THEORY

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Received 10 April 1991; accepted 22 April 1991

The kinetics of the catalyst deactivation by site coverage is analyzed using percolation theory. The pore space is treated as a lattice of voids interconnected by necks in a three-dimensional network. The deactivation is assumed to occur under kinetic control and to be primarily caused by blockage of necks. The effect of various factors (such as pore-size distribution, a mean coordination number, the rate constant of disappearance of active sites, and the kinetics of blockage of separate necks) on the deactivation process is demonstrated and discussed.

Keywords: Catalyst deactivation, kinetic control, percolation theory, pore space, voids, necks, pore-size distribution

1. Introduction

Many catalytic processes are accompanied by side reactions (for example, by coke formation) that decreases the catalyst activity. The deactivation of pore catalysts by coke formation is a complex phenomenon that includes coverage of active sites, simultaneously with coke growth and pore blockage [1–5]. An analysis of the deactivation kinetics is difficult because, in order to obtain quantitative information about pore blockage, it is necessary to take into account interconnection of various pores. The pore space can generally be treated as a lattice of voids interconnected by necks in a three-dimensional network. The effect of the pore-space topology on the deactivation kinetics can be considered in the framework of percolation theory. In particular, a percolation model of catalyst deactivation has been presented by Sahimi and Tsotsis [4]. The pore blockage was assumed to be caused by coke deposition in voids. In this paper, we analyze the opposite case: the pore blockage is assumed to be primarily caused by blockage of necks.

2. Percolation theory

A comprehensive review of the theory of percolation is presented by Shante and Kirkpatrick [6]. In this brief section, we reproduce some aspects of this

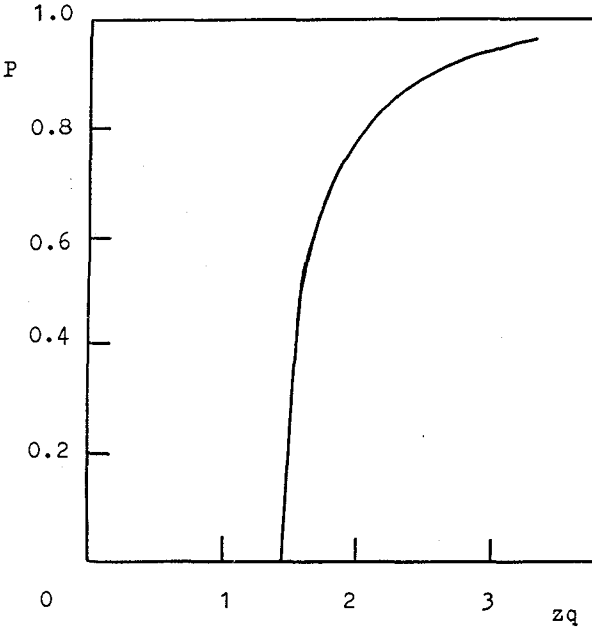

Fig. 1. Percolation probability [8].

theory which are important for the following discussion. In the framework of percolation theory, the medium is defined as an infinite set of sites interconnected by bonds. The coordination number, z, of any regular medium is defined to be the number of bonds leaving each site. The bond percolation problem is of interest for us. In this case, the random characteristic of the medium is introduced by blocking some of its bonds at random such that any bond, independently of all other bonds, has a fixed probability q of being unblocked. The percolation probability, P, is defined as the probability that a single site is connected with infinitely many other sites by unblocked bonds. Fortunately, the percolation probability for regular and disordered media may be considered as a universal function dependent on one parameter zq (fig. 1).

3. General equations

For the analysis of the deactivation kinetics, we use the following assumptions:

(a) The pore space is treated as a lattice of voids interconnected by necks in a three-dimensional network. The pore volume and surface are assumed to be concentrated in voids, whereas necks do not possess their own volume. Active sites are uniformly distributed on the catalyst surface.

(b) The deactivation of a catalyst by coverage of active sites and pore blockage occurs under kinetic control. The conditions at the catalyst-fluid interface do not change with time. The process is isothermal.

(c) The rate of disappearance of active sites is described by the first order law

$$\mathrm{d}c_s/\mathrm{d}t = -kc_s, \tag{1}$$

where c_s is concentration of sites, and k is the deactivation rate constant.

(d) The pore blockage is assumed to be primarily caused by blockage of necks. The latter process is described by the time-dependent critical radius, $r_c(t)$. At time t, any neck with $r < r_c(t)$ is assumed to be completely blocked (by coke deposition on this neck or in other necks with $r < r_c(t)$), and necks with $r > r_c(t)$ are blocked only partly. The time dependence of the critical radius is described phenomenologically as

$$r_c(t) = vt, \tag{2}$$

or

$$r_c(t) = w\sqrt{t}. \tag{3}$$

The former equation is applicable, for example, to the coke growth through a polymerization process, the rate of which is independent of the degree of polymerization. The latter equation is correct, e.g., if coke formation is limited by diffusion of reactants through the coke coverage. The rate constants k and v (or w) may be, in principle, interconnected if the disappearance of active sites is caused by formation of the coke precursor. However, we do not take into consideration any interconnection between these rate constants.

Percolation theory can be applied to describe the deactivation process via identification of network sites with voids and bonds with necks. A bond is considered to be unblocked if the neck radius is of $r > r_c$.

Generally speaking, a strict description of the deactivation process demands the solution of more complicated problems than those that have been solved in the modern percolation theory, since in the case of real porous materials the coordination number is not constant and voids are not equivalent. Besides, the size distributions of voids and necks can be overlapping. For a rather large group of porous materials, however, a suitable description of the deactivation process can, apparently, be obtained on the basis of the available percolation theory data using the mean coordination number and applying percolation theory to the voids which can be unblocked at a given value of the critical radius in principle, i.e., to those with the radius $r > \lambda r_c(t)$ ($\lambda \geqslant 1.0$ is the empirical coefficient taking into account that a void with the radius r has necks with radii lower than r/λ).

The deactivation of a catalyst by site coverage and pore blockage can be expressed in terms of a relative activity, R, which is the ratio of the rate of the catalytic reaction at time t to the rate at time zero. Using assumptions (a)–(d), we have

$$R = P(zq)F(\lambda r_c)\exp(-kt), \tag{4}$$

where z, q and $P(zq)$ are the mean coordination number, the fraction of unblocked necks and the percolation probability for voids with $r > \lambda r_c$, and $F(\lambda r_c)$ is the fraction of the pore surface belonging to these voids. The latter value is defined by

$$F(\lambda r_c) = \int_{\lambda r_c}^{\infty} r^2 f(r)\, \mathrm{d}r \Big/ \int_0^{\infty} r^2 f(r)\, \mathrm{d}r, \tag{5}$$

where $f(r)$ is the size distribution of voids.

To use eq. (4), we should calculate the parameter zq for voids with $r > \lambda r_c$. This problem has been solved in refs. [7–9], where percolation theory is applied to analyze a desorption branch of the capillary condensation hysteresis [7,8] and mercury penetration into porous solids [9]. Using eq. (7) from ref. [6] or eq. (11) from ref. [8], we have

$$zq = 2\int_{r_c}^{\infty} \varphi(r)\, \mathrm{d}r \Big/ \int_{\lambda r_c}^{\infty} f(r)\, \mathrm{d}r, \tag{6}$$

where $\varphi(r)$ is the size distribution of necks, defined so that $\varphi(r)\, \mathrm{d}r$ is the number of necks with the radius from r to $r + \mathrm{d}r$ per unit volume (or mass) of the catalyst. The distribution function for voids, $f(r)$, is normalized analogously.

Equations (2)–(6) permit one to calculate a time dependence of the relative activity.

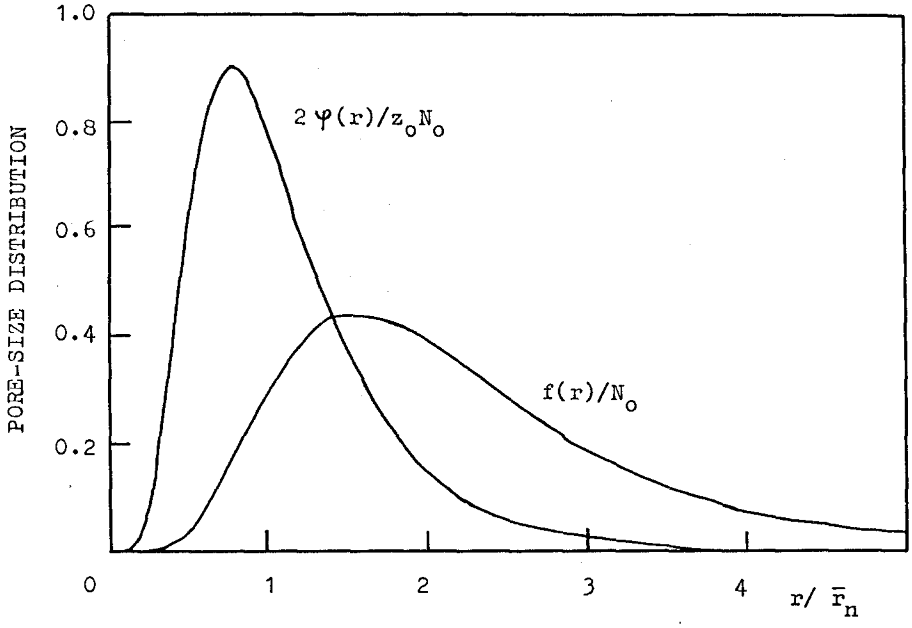

Fig. 2. Lognormal size distribution of necks and voids at $\bar{r}_v/\bar{r}_n = 2$ and $\sigma = 0.5$

4. Results and discussion

To demonstrate the effect of various parameters on the deactivation kinetics, we have used a lognormal size distribution (fig. 2) of necks

$$\varphi(r) = (z_0 N_0/2)\ \exp\left[-\left(\ln(r/\bar{r}_n)\right)^2/2\sigma_n^2\right]/\left[r\sigma_n(2\pi)^{1/2}\right]$$

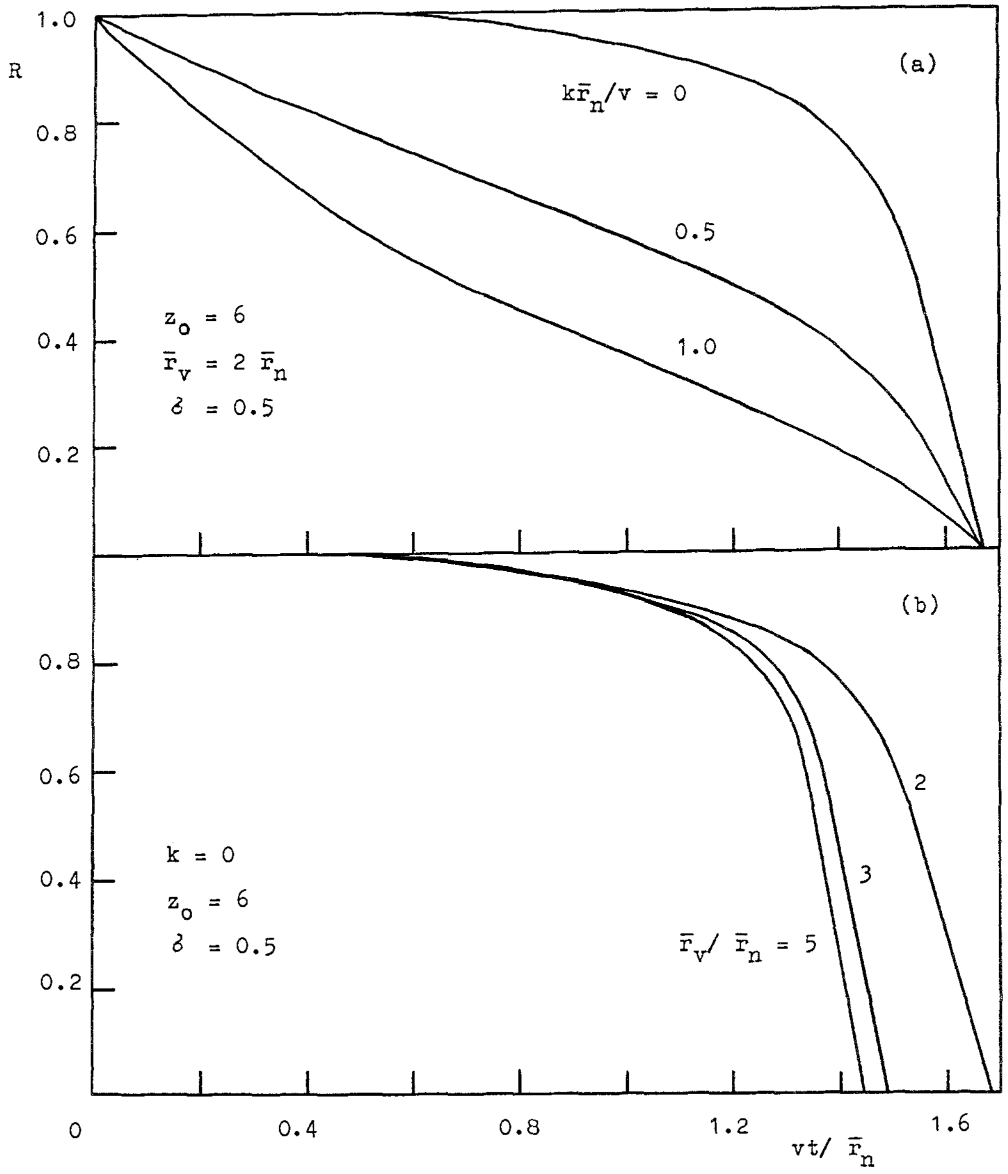

Fig. 3. Relative activity as a function of time at various values of the deactivation rate constant (*a*) and at various values of the mean void radius (*b*). The time dependence of the critical radius is described by eq. (2).

and voids

$$f(r) = N_0 \exp\left[-\left(\ln(r/\bar{r}_v)\right)^2/2\sigma_v^2\right]/\left[r\sigma_v(2\pi)^{1/2}\right],$$

where $\bar{r}$ and σ are the median and dispersion, z_0 is the coordination number for all voids, and N_0 is the number of voids per unit volume (or mass) of the catalyst. Besides, we have assumed that $\sigma_n = \sigma_v = \sigma$ and $\lambda = 1.0$.

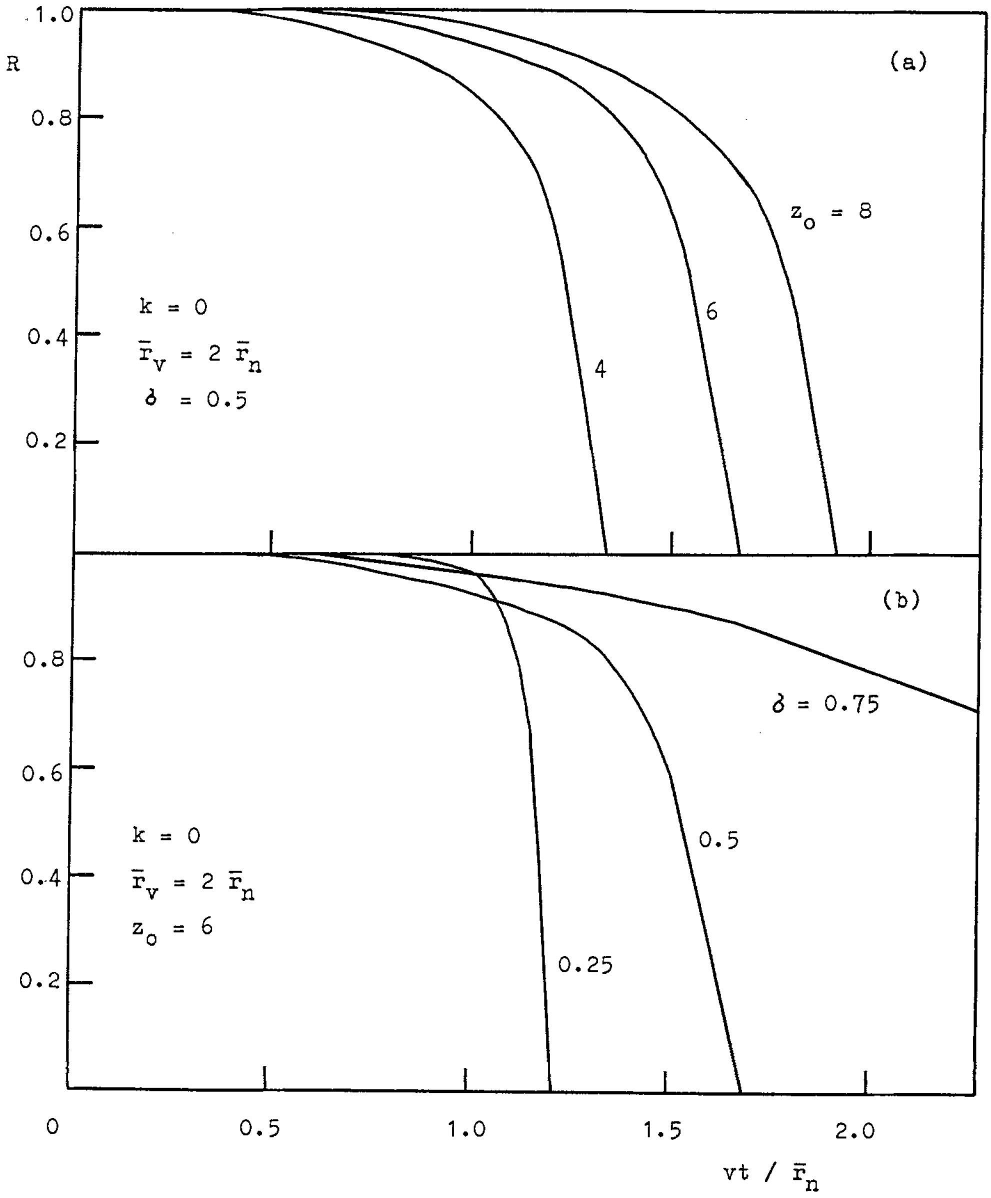

Fig. 4. Relative activity as a function of time at various values of the mean coordination number (a) and at various values of dispersion of pore-size distribution. The time dependence of the critical radius is described by eq. (2).

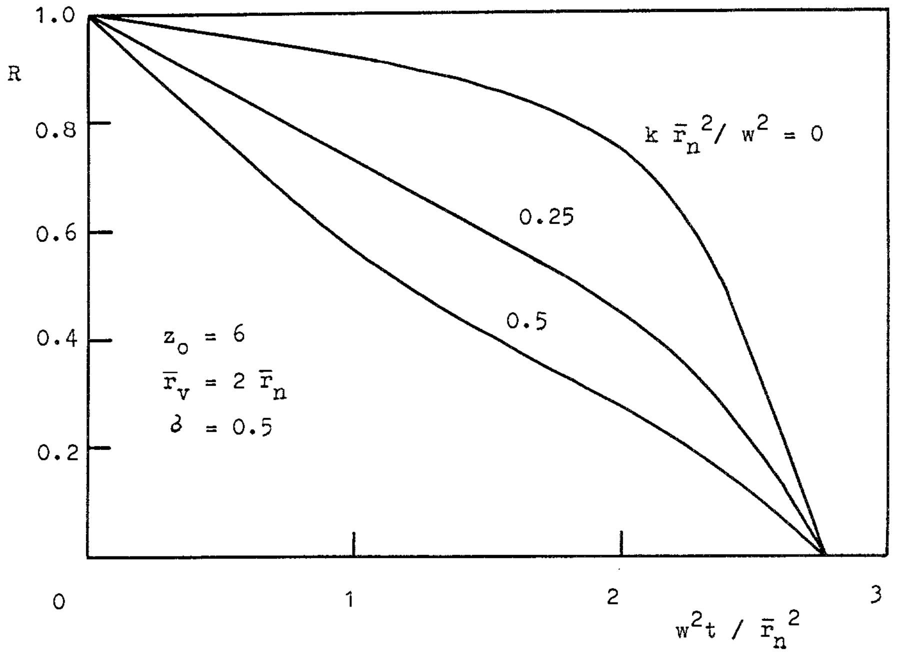

Fig. 5. Relative activity as a function of time at various values of the deactivation rate constant. The time dependence of the critical radius is described by eq. (3).

The deactivation kinetics for a linear dependence of the critical radius on time (eq. (2)) is presented in figs. 3 and 4. In particular, fig. 3a that disappearance of active sites makes a dominant contribution to the deactivation process at $k\bar{r}_n/v >$ 0.5. To stress the effect of pore blockage on the deactivation kinetics, we assume further that the contribution of disappearance of active site to the catalyst deactivation is negligible and set that $k\bar{r}_n/v = 0$.

Fig. 3b shows the influence of the mean void radius on the deactivation process. An increase in the mean void radius results in a sharper threshold below which the network loses its global connectivity. The effect of the mean coordination number on the deactivation kinetics is shown in fig. 4a. An increase of the coordination number leads, of course, to a delay of pore blockage. The deactivation process is delayed also by an increase in dispersion of pore-size distribution (fig. 4b).

If the time-dependence of the critical radius is described by eq. (3), the deactivation kinetics is not so sharp as in the case of eq. (2) (cf. figs. 3a and 5). However, the effect of various parameters on the deactivation process is qualitatively the same in both cases.

References

[1] R.A. Buyanov, *Coking in Catalysts* (Nauka, Novosibirsk, 1983) (in Russian).
[2] R. Hughes, *Deactivation of Catalysts* (Academic Press, London, 1984).

[3] *Catalyst Deactivation*, eds. B. Delmon and G.F. Froment (Elsevier, Amsterdam, 1987).
[4] M. Sahimi and T.T. Tsotsis, J. Catal. 96 (1985) 552.
[5] G.B. Marin, J.W. Beeckman and G.F. Froment, J. Catal. 97 (1986) 416.
[6] V.K.S. Shante and S. Kirkpatrick, Adv. Phys. 20 (1971) 325.
[7] V.P. Zhdanov, V.B. Fenelonov and D.K. Efremov, React. Kinet. Catal. Lett. 32 (1986) 185.
[8] V.P. Zhdanov, V.B. Fenelonov and D.K. Efremov, J. Colloid Interface Sci. 120 (1987) 218.
[9] V.P. Zhdanov and V.B. Fenelonov, React. Kinet. Catal. Lett. 33 (1987) 337.