

# Paradox of Catalyst Deactivation: How to Extend the Catalyst Life Intensifying the Catalytic Cycle.

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## Highlights

- A new conceptual framework for transient behaviour of catalytic systems accompanied by deactivation.
- Insights into the intrinsic characteristics of the deactivation process and the main catalytic process.
- A recipe for extending catalyst life for regimes with small concentrations of active sites.

## 1. Introduction

Dynamic behavior of complex catalytic ‘gas-solid’ reactions accompanied by catalyst deactivation, both self-regeneration and ageing, was studied. Quasi-steady-state (QSS) behavior of intermediates of the catalytic cycle is determined by two small parameters: 1) the small parameter caused by the difference in magnitude between the number of catalyst active sites and the number of gaseous molecules; 2) the small parameter caused by the difference between the deactivation parameters and the parameters of the main catalytic cycle.

## 2. Background

In one of the typical cases, the irreversible catalytic cycle accompanied by irreversible deactivation under QSS conditions, the deactivation equation can be written as follows [1, 2],

$$\frac{d\Theta_p}{dt} = \frac{R_0}{k_j N_S} k_p (1 - \Theta_p), \quad (1)$$

where  $R_0$  is the QSS reaction rate of the fresh catalyst [ $\text{mol m}^{-2} \text{s}^{-1}$ ],  $N_S$  is the total number of active catalytic sites per square meter [ $\text{mol m}^{-2}$ ], and  $k_j$  and  $k_p$  are apparent kinetic constants of the reaction of the catalytic cycle and deactivation reaction [ $\text{s}^{-1}$ ], respectively. The ratio  $\frac{R_0}{k_j N_S} = \Theta_{\text{fresh}}$  is the QSS concentration of the catalytic intermediate that deactivates [-]. Using Equation (1), for the single-route catalytic reaction accompanied by both reversible and irreversible deactivation, the semi-phenomenological three-factor equation [3] was obtained,

$$R(t) = R_0 \varphi_{\text{rev}}(R_0, c, t; T) \varphi_{\text{irr}}(R_0, c, t; T), \quad (2)$$

where  $\varphi_{\text{rev}}(R_0, c, t; T)$  and  $\varphi_{\text{irr}}(R_0, c, t; T)$  are factors related to the reversible and irreversible deactivation [-], respectively,  $c$  is the set of reactant and product concentrations [ $\text{mol m}^{-3}$ ],  $t$  is the time [s] and  $T$  is the temperature [K]. Equation (2) was used for the description of catalytic dehydration of acetaldehyde and crotonaldehyde dehydrogenation.

## 3. Results and Discussion

For irreversible deactivation, Equation (2) can be represented as,

$$\begin{aligned}
 R(t) &= R_0 \exp(-k_p \Theta_{\text{fresh}} t), \\
 &= R_0 \exp\left(-\frac{k_p R_0}{k_j N_S} t\right).
 \end{aligned}
 \tag{3}$$

The relationship for the single-route complex catalytic reaction over the deactivated catalyst was found,

$$A_{\text{lim}} = \lim_{t \rightarrow \infty} A(t) = N_S \left(1 - \frac{Q}{K}\right) \frac{k_j}{k_p},
 \tag{4}$$

where  $A(t)$  is the integral reactant consumption/product release per catalyst unit [ $\text{mol cm}_{\text{cat}}^{-2}$  or  $\text{mol g}_{\text{cat}}^{-1}$ ] at time  $t$ ,  $A_{\text{lim}}$  is the total reactant consumption/product release per catalyst unit [ $\text{mol cm}_{\text{cat}}^{-2}$  or  $\text{mol g}_{\text{cat}}^{-1}$ ] of the fresh catalyst,  $Q$  and  $K$  are the quotient and the equilibrium constant of the overall catalytic reaction [-], respectively.

Within the presented approach, the total (integral) reactant consumption/ product release over time,  $A(t)$ , and its possible limit,  $A_{\text{lim}}$ , have been distinguished as resources of informative data [4]. Experimental and computational values of  $A(t)$  and  $A_{\text{lim}}$  as functions of catalyst pretreatment and regime parameters have been analysed using the literature data [5].

As the main result, it is shown that the catalyst lifetime can be enhanced by decreasing the steady-state (QSS) concentration of free active sites. This can be achieved by increasing the steady-state (QSS) reaction rate over the catalyst. This conclusion can be presented conceptually as follows: under some conditions, an elevated catalyst activity protects the catalyst from deactivation. Obviously this result can be applied as a recipe for extending catalyst life for catalytic systems accompanied by catalyst deactivation. These theoretical results are illustrated by computer simulations. Moreover, this idea was previously announced by Kagan et al. [6], based on experimental data in studies of the hydroformylation reaction of olefins, however with no theoretical explanation.

## References

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## Keywords

Catalytic cycle; Catalyst deactivation; Extending catalyst life.