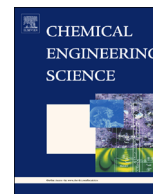




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# Integrated modelling of reaction and catalyst deactivation kinetics—Hydrogenation of sitosterol to sitostanol over a palladium catalyst

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## HIGHLIGHTS

- Modelling of a catalytic reaction  $A \rightarrow R$  along with surface poisoning  $P+^* \rightarrow P^*$ .
- Simple semi-analytical model solutions.
- Model behaviour in the parameter space revealed through numerical simulations.
- Analysis of hydrogenation of sitosterol to sitostanol on Pt in the presence of S.
- Successful description of experimental data.

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## ABSTRACT

Catalyst deactivation is traditionally described with semi-empirical models involving separable kinetics and time-dependent activity factors, but the rational approach is to treat catalyst deactivation as a chemisorption process among other surface processes. The catalytic process  $A \rightarrow R$  along with surface poisoning  $P+^* \rightarrow P^*$  (\* is an active site) was modelled for batch and continuous reactors. Simple semi-analytical mathematical solutions were obtained, which avoid the use of surface coverage in computations. Numerical simulations revealed the behaviour of the model in the parameter space. For batch reactors, the approach to a limit conversion as well as the increase of the apparent reaction order due to catalyst poisoning was illustrated. The model was applied to batchwise hydrogenation of sitosterol to sitostanol on a dispersed platinum catalyst and in the presence of a sulphurous poison. The behaviour of the system was successfully described with a simple, mechanistic model based on the adsorption-reaction-poisoning concept.

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## 1. Introduction

Catalyst deactivation is one of the most important issues in the industrial application of heterogeneously catalysed processes. In some processes, such as ammonia synthesis and water-gas shift reaction, the catalyst lifetime is long, up to several months and years. For some other processes, on the other hand, the catalyst is deactivated in few seconds and a rapid regeneration of the catalyst is accomplished with fluidized bed reactors coupled to catalyst regeneration units. A typical example of this is catalytic cracking of hydrocarbons. The critical issue is not only the development of new and more durable catalysts but also the very precise description of the catalyst deactivation kinetics. Such a model can then be used to predict the catalyst activity and selectivity in any reactor.

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Behind catalyst deactivation is always a physical and/or chemical mechanism. For supported metal catalysts, *sintering* is a typical deactivation mechanism, if the catalyst is exposed to too high temperatures: metal nanoparticles agglomerate and the surface area declines leading to impaired catalyst performance. For catalysis in the liquid phase, the active component can be *leached* out from the catalyst surface. *Fouling* is a typical mechanism appearing, for instance, in the treatment of hydrocarbons: the reactant molecule adsorbs strongly on the catalyst surface and transforms to undesired compounds, which mainly remain on the catalyst surface, thus blocking the active sites. Catalyst *poisoning* takes place when a component, for example, a sulphurous component is present in the feed stream occupying the sites by irreversible adsorption. In many cases, catalyst deactivation is strongly coupled to the mass transfer effects in the catalyst pores. Extensive descriptions of catalyst deactivation mechanisms and mathematical modelling in the presence and absence of mass transfer limitations are provided by textbooks, e.g. [Froment and Bischoff \(1990\)](#), [Butt \(2000\)](#) as well as [Levenspiel \(1999\)](#).

The engineering tradition of catalyst deactivation kinetics is to use lumped models and separable deactivation kinetics, in which the catalyst activity decline is described by a time-dependent activity factor,  $a=f(t)$  (Levenspiel, 1999). In fact, the activity factor is a function of temperature, pressure and the feed composition. Here is the weakness of the approach: the relation of the activity factor to the evident parameters mentioned above remains mostly empirical and thus the model has a very weak predictive power. Detailed models for the coupling of catalyst deactivation and diffusion in porous media are presented, for instance, by Hughes (1984) as well as by Butt and Petersen (1988). The majority of work has concerned modelling of catalyst deactivation in fixed beds, for which empirical equations for catalyst deactivation have been used in order to predict the reactor performance.

Empirical equations have been proposed for catalyst deactivation by poisoning by several authors (e.g. Froment and Bischoff, 1961, Butt and Petersen, 1988, Castano et al., 2009). The activity functions are either linear ( $a/a_0=1-\alpha'c_p$ ), exponential ( $a/a_0=\exp(-\alpha'c_p)$ ) or hyperbolic ( $a/a_0=1/(1-\alpha'c_p)$ ), in which  $c_p$  is the poison (e.g. sulphurous compound) concentration,  $\alpha'$  is an adjustable parameter and  $a/a_0$  denotes the deactivation function. Thereafter, these models have been applied to several catalytic reactions. For instance, an exponential activity decay has been applied to methanol synthesis (Radovic and Vannice, 1987), catalytic hydrogenation of  $\alpha$ -methylstyrene (Phiong et al., 2008), in nitrite reduction (Pintar et al., 1998), to liquid-phase metathesis of 1-alkenes (Spronk et al., 1992), whereas the reciprocal model has been used for liquid-phase hydrogenation of biphenyl (Castano et al., 2009) and phenolysis of ethyl 2-bromoisobutyrate (Yang et al., 2000).

A pioneering work on the mechanistic modelling of catalyst deactivation was carried out by Pozzi and Rase (1958), who considered the formation of irreversibly adsorbed species on a nickel catalyst in a continuous fixed bed reactor during the hydrogenation of isobutene. The deactivation mechanism was assumed to be fouling, formation of a dimer species from the reactant molecule, isobutene. The breakthrough of this work was the consideration of the catalyst deactivation as a part of the mechanism on the surface, not by empirical functions for the activity decline.

Corella and Asua (1982a) present several equations based on reaction mechanisms for catalyst coking and Beeckman and Froment (1982) described the interactions of coking kinetics and mass transfer. Comparative studies between different models have been made (Castano et al., 2009). The reaction order for deactivation and number of active sites, which control the deactivation can also be taken into account. This approach has been used in studying the activity decline of the catalyst in a continuous differential reactor in isobutene oxidation in gas phase (Corella and Asua, 1982b) and in catalytic cracking (Corella, 2004) by relating the initial activity to the activity function. In addition, residual non-zero steady state activity was considered in kinetic modelling when studying the thiotolerance of naphta reforming using cyclohexane dehydrogenation as a gas-phase model reaction (Borgna et al., 1994). The extent of catalyst deactivation caused by different species was considered by deriving rate equations for each species separately so that their part in the severity of catalyst deactivation has been taken into account (Mier et al., 2011). The model reaction in this case was gas-phase olefin production over zeolite catalysts (Mier et al., 2011). Furthermore, several specific concepts have been derived for modelling catalyst deactivation. One example was the case, in which the catalyst deactivation term in the rate equation was divided into reversible and irreversible deactivation in hydrogen peroxide synthesis via anthraquinone (Santacesaria et al., 1994) and in tritium removal (Sohn and Lee, 2006). In the work of Agorreta et al. (1991) a catalyst activation–deactivation model was considered. The work was based on the dynamics of active sites on the catalyst surface.

Catalyst poisoning is typically a chemisorption phenomenon and the crucial step is the reversible or irreversible adsorption of the poison molecule on the active surface site. Thus poisoning should not be treated as a separate effect, but it is coupled to all the adsorption processes on the surface. This approach was taken by Sandelin et al. (2006), who showed numerical simulations for cases, where the catalyst deactivation was incorporated among the elementary steps. The work concerned mainly skeletal isomerization of 1-butene. Sulphur is known to be a strong catalyst poison: Radovic and Vannice (1987) studied the sulphur tolerance of a methanol synthesis catalyst in a continuous fixed bed and described the process successfully by the Szepe-Levenspiel (1971) approach modified by a generalization proposed by Fuentes and Figueras (1978). The crucial issue in the modelling of catalyst deactivation is: can the concept of separable surface reaction kinetics and catalyst deactivation be used, as has been proposed by many authors, or should deactivation be treated as an integrated part of the surface reaction mechanism. This issue was considered by Lynch and Emig (1989), who developed criteria for the use of the separability approach for some reaction mechanisms. The main conclusion of the work was that the separability approach can be used for limited cases involving a strongly rate-determining step in the reaction mechanism.

In recent years, the surface analysis techniques, such as XPS, Auger and EXAFS and temperature-programmed techniques, such as TPD, TPO, TPR and TPSR have advanced very much and they can reveal the chemical and physical reasons for deactivation. The kinetic model for deactivation should be based on this kind of fundamental information. This implies that the catalyst deactivation steps, such as poisoning, fouling and sintering can be incorporated among the other elementary steps proceeding on the solid surface.

The current trend is to use renewable feedstock for the production of fuels and chemicals. For the multifunctional molecules originating from nature, the issue of catalyst deactivation is even more severe than for molecules originating from crude oil or natural gas. Furthermore, the interest in fine and specialty chemicals, including health-promoting components available in biomass is steadily growing. For this kind of components, the use of batch reactor technology is common, since the production volumes are small and the reaction times are long.

Although a lot of research work has been focused on catalyst deactivation caused by sintering, leaching, fouling and poisoning, the quantitative treatment of catalyst deactivation in batch reactors has not been considered to a great extent. However, several processes related to fine and specialty chemicals are carried out in batch or semibatch reactors. Typical examples are processes related to biomass conversion, such as catalytic hydrogenation, oxidation and isomerization of sugar molecules and terpenes. Finely dispersed catalysts (particle diameter < 0.1 mm) in liquid phase are used, and the detection and modelling of catalyst deactivation often become tricky. In continuous reactors, it is easy to recognize the activity decline by monitoring the reactant conversion at the reactor outlet, but in batch reactors, deactivation becomes clearly visible only comparing the performances of successive batch experiments with recycled catalysts. Misleading conclusions can easily be drawn concerning the reaction order and the thermodynamic equilibrium when considering an individual batch experiment, since catalyst deactivation can obscure fundamental information.

In the present paper, we were concerned with a deactivation model for catalyst poisoning in batch and continuous reactors to reveal how the operation mode of the reactor influences the reaction kinetics including poisoning. The practical application is the double-bond hydrogenation in a health-promoting component, sitosterol, which is one of the phytosterols obtainable in

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