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PREDICTION OF INDUSTRIAL CATALYSTS DEACTIVATION RATE USING FIRST PRINCIPLE MODEL AND OPERATING DATA

(Ramalan Kadar Penyahaktifan Mangkin Industri Menggunakan Model Prinsip Pertama dan Data Operasi)

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Abstract

Catalyst deactivation is the loss of catalytic activity and /or selectivity over the course of time. Catalyst deactivation is a considerable and enduring problem in the operation of industrial catalytic processes. It is very costly in terms of catalyst replacement and process shutdown. The deactivation phenomenon not only affects the final product quality but also negatively influences the efficiency of the downstream processes. Therefore, a practical method which can accurately predict the deactivation rate can be a quite advantage to the industrial processes. In this paper, the deactivation rate of the industrial catalyst is predicted using operating data and catalyst specifications. The first principle model (FPM) is employed to predict the catalysts deactivation rate. The devised model is implemented into an industrial catalyst, which is palladium supported on carbon (Pd/C) utilized for the purification process of terephthalic acid, to show its applicability. The whole programs to obtain the rate of catalyst deactivation have been coded into Matlab R2013a environment. The model validated against industrial data. For the proposed catalyst, the catalyst sintering order is calculated with less that 3 percent error, and the pre-exponential values and the activation energy for the deactivation were calculated 0.00092 h^{-1} and 5279 J mol^{-1}. Moreover, the catalyst is deactivated after around 360 days of operation. The methods, which are devised in this study, can be applied to any industrial catalyst to calculate the rate of deactivation.

Keywords*: catalyst, deactivation rate, first principle model, sintering*

Abstrak

Penyahaktifan mangkin adalah kehilangan aktiviti mangkin dan / atau kepilihan mangkin yang berkadaran dengan masa. Penyahaktifan mangkin adalah masalah besar yang sering berlaku dalam proses pemangkinan di industri. Ini kerana penggantian mangkin memakan kos yang tinggi dan boleh menyebabkan penutupan proses. Fenomena penyahaktifan tidak hanya memberi kesan kepada kualiti akhir produk tetapi juga mempengaruhi kecekapan proses hiliran. Oleh itu, satu kaedah praktikal yang mampu meramal dengan tepat kadar penyahaktifan boleh menjadi satu kelebihan untuk proses industri. Dalam penyelidikan ini, kadar penyahaktifan pemangkin industri diramalkan menggunakan operasi data dan spesifikasi mangkin. Model prinsip pertama (FPM) digunakan untuk meramalkan kadar penyahaktifan mangkin itu. Model yang dihasilkan ini digunakan sebagai mangkin di industri, iaitu palladium disokong pada karbon (Pd/C) digunakan untuk proses penulenan asid tereftalik, untuk membuktikan keterterapannya. Keseluruhan pengaturcaraan untuk mendapatkan kadar penyahaktifan mangkin telah dikodkan ke dalam perisian Matlab R2013a. Model ini telah disahkan terhadap data industri. Bagi mangkin yang dicadangkan, urutan pensinteran mangkin dikira dengan ralat kurang daripada 3 peratus, dan nilai pra-eksponen serta tenaga pengaktifan untuk penyahaktifan

yang dikira adalan 0.00092 h^{-1} and 5279 J mol^{-1}. Selain itu, mangkin telah dinyahaktif selepas sekitar 360 hari operasi. Kaedah-kaedah yang direka dalam kajian ini boleh diaplikasikan untuk segala jenis mangkin industri bagi mengira kadar penyahaktifan.

Kata kunci: mangkin, kadar penyahaktifan, prinsip model pertama, pensinteran

Introduction

Catalyst deactivation, the loss over time of catalytic activity or selectivity, is a considerable economical concern in the operation of industrial catalytic processes. Catalyst deactivation is referred to the interaction between the impurities and the catalyst in the process which the catalyst is utilized. Any physical or chemical interaction that declines the catalyst activity or selectivity is categorized as catalyst deactivation phenomena. Deactivation results in a shortened lifetime of the catalyst, and the replacement of the deactivated catalyst with a fresh one is required to maintain the product quality and the efficiency of the catalytic process. Deactivation of the industrial catalyst can vary from several seconds to several months. Shorter catalyst lifetime has a significantly adverse influence on the process economics. Therefore, to increase the catalyst lifetime can be considered as a great success in a catalytic process [1].

Catalyst deactivation is significantly related to the catalyst application and scientifically it has numerous challenges. Figure 1 displays the deactivation time for some processes in the refining and petrochemical industries. The deactivation time refers to the time after which a catalyst has lost so much of its initial activity that it must be replaced or regenerated. Regeneration is usually possible, but there is a limit. At the end of the cycle life the catalyst is recycled or, when this is more economical, disposed. It is clear that disposal should be postponed as long as possible and that recycling is becoming more and more important. In accordance to Figure 1, the deactivation time fluctuates prominently for the different processes. Depending on the process used the catalyst cycle life may vary from a few seconds, as in fluid catalytic cracking (FCC), to several years, as in for instance ammonia synthesis. Deactivation of a hydrodesulphurisation (HDS) catalyst is much slower, depending on the feed, in the order of months or a year [2].
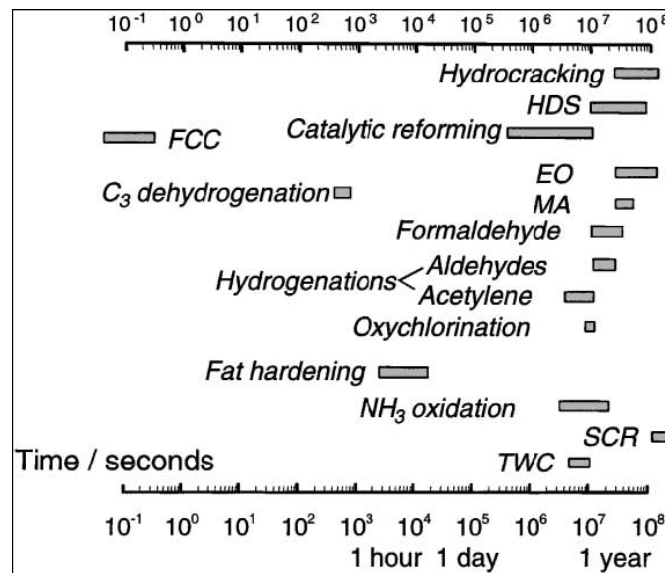

Figure 1. Time scale of deactivation of different catalytic processes

Modeling and simulation is an effective tool to analyse the process engineering systems. It is employed to improve the process efficiency and predict the process performance under different operating conditions. The accuracy of

the modeling effort is strongly related to the parameters involved into the developed model. The two most important parameters which are very influential on the model outputs precision are the rate of reactions and deactivation rate [3, 4]. The latter is considered when the catalytic process suffers from the deactivation phenomenon. Note that most of the industrial catalytic processes deal with the deactivation of the catalyst. Thus, to employ a suitable method which is able to accurately predict the rate of deactivation can improve the accuracy of the mathematical model considered for the catalytic process.

The reasons for catalyst deactivation can be divided into five categories as poisoning, fouling, sintering, mechanical deactivation through attrition or erosion, and corrosion/leaching by the reaction mixture [2, 5]. Therefore, the cause of the catalyst deactivation might originate from different reasons. Moreover, any catalysts depending on the type of process might encounter different mechanisms through the way of deactivation. Thus, to devise a model which ignores the complicated mechanisms of the deactivation and can be employed for the prediction of any catalysts utilized in the catalytic processes is a real and great advantage to the area of the modeling of such processes [6, 7].

Thermally induced catalyst deactivation is a major concern in high temperature catalytic processes. Thermal deactivation might take place due to different reasons. They might be loss of catalytic surface area, loss of support area, reactions/transformations of catalytic phases to non-catalytic phases, and loss of active material. The first two reasons are usually considered as sintering. Sintering phenomenon usually occurs at high temperature reactions, and its rates rely on temperature, reaction atmosphere, and catalyst formulation. Sintering is one of the significant reasons for the deactivation of supported metals catalysts. These precious metal catalysts are widely employed in the industries of petrochemicals, refineries, polymer, chemicals, and pharmaceuticals [8].

There are many studies carried out on the catalytic systems for the derivation of catalyst deactivation rate. Pellegrini et al. [9] did an extensive study on the several aged 0.5 wt.% palladium supported on carbon (Pd/C) catalysts taken from different purified terephthalic acid (PTA) production plants. The results verified that all catalysts experienced Pd sintering regardless of the nature and amount of contaminants. Li et al. [10] studied the positive effect of silica on the stability and activity of Ni/alumina catalyst. The results revealed that the addition of silica efficiently restricted the hydration of alumina support, and inhibited the deactivation of Ni/alumina catalyst. Salmi et al. [11] devised a model and applied it to a batch-wise hydrogenation of sitosterol to sitostanol on a platinum catalyst in the presence of a sulphurous poison. The model was able to determine the behaviour of the system based on the adsorption-reaction-poisoning idea. Sørensen [12] developed a methodology to estimate the deactivation models for industrial catalysts. The model employed the movement of the determined axial temperature profile to obtain the information on the deactivating phenomena. In this model, the temperature profile change determines the deactivation trend. The goal is to cover the calculated progress of the temperature profile through the reactor and deactivation models, estimating the deactivation model by means of non-linear least square. Keyvanloo et al. [13] investigated the impacts of carbon monoxide and hydrogen partial pressures on the deactivation by carbon of a CoPt/AlSi Fischer-Tropsch catalyst.

The objective of this paper is to predict the deactivation rate of industrial catalysts encountering sintering phenomenon utilizing first principle model and the process data. The operating data including the catalytic process information and catalyst specifications are used to devise the relevant model. In the developed model, the operational variables are incorporated into the model, and the catalyst deactivation rate is calculated considering the effects of the variables simultaneously.

Purified terephthalic acid (PTA) is the ninth largest industrial chemical, which is utilized as a raw material for the production of polyester, especially polyethylene terephthalate. Terephthalic acid (TA) is produced via the transition metal-catalyzed oxidation of p-xylene (PX) in acetic acid (AA), which is one of the largest industrial-scale applications of homogeneous catalysis. Co, Mn, and Br are the components of the catalyst [14]. Following reaction shows the PX oxidation:

$$H_3C - C_6H_4 - CH_3 \xrightarrow{Air/(Co-Mn-Br)} HOOC - C_6H_4 - COOH \tag{1}$$
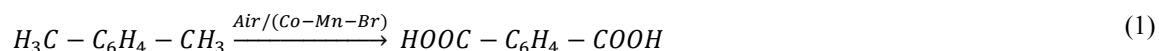
The crude terephthalic acid (CTA) produced from PX oxidation consists of 4-carboxybenzaldehyde (4-CBA), which results in the discoloration of CTA. The purification of CTA is carried out in a fixed-bed reactor (FBR) contained Pd/C catalyst through the hydrogenation of 4-CBA to para-toluic acid (pta) in the water. The hydropurification reaction can be summarized as follows [9]:

$$OHC - C_6H_4 - COOH \xrightarrow{H_2/(Pd/C)} H_3C - C_6H_4 - COOH \tag{2}$$
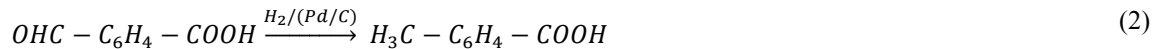
Pd/C catalyst bears sintering of Pd particles, which is an inevitable reason for the catalyst deactivation. Sintering phenomenon is one the most commonly reasons for the industrial catalysts deactivation [9].

Materials and Methods

In order to devise the model, the data of the catalyst and operation are required. The following sections deal with the data acquisition of industrial Pd/C catalyst and the hydropurification process.

Materials: Catalyst and characterization

Samples of deactivated 0.5 wt. % Pd/C catalyst were gathered from different PTA production plants. Inductively coupled plasma (ICP), x-ray powder diffraction (XRPD), extended x-ray absorption fine structure (EXFAS) spectroscopy, transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), CO chemisorption, and catalyst activity methods were carried out to analyse the deactivation phenomenon of Pd/C catalyst [9].

Pd surface area

The Pd surface area considerably decreases when the temperature increases. Industrial 0.5 wt. % Pd/C catalyst was used for the Pd surface area measurement. A chemisorption stoichiometry of Pd/CO equal to 2 and a surface Pd atomic density of 1.27×10^{19} atoms/m^2 were taken into account to estimate the Pd surface area [15].

Powder analysis

The PTA powder analysis was done in the industrial plant. Samples of the PTA powder were taken at the end of the dryer at certain times of the daily operation. The samples were analysed using the HPLC machine [16].

Operating data

The operating data including the hydropurification system and the catalyst specifications are required. The operating data can usually be found in the process flow diagram, and the catalyst specifications are included into the operating manual.

Methods

In this section, the methodology employed for the perdition of the deactivation rate is explained. Figure 2 shows the methodology used for this study.

The operating data including the catalyst specifications are used to calculate the deactivation rate parameter using the following mass balance for the different components, which their values are analysed for each particular-time:

$$C_{i,in} - C_{i,out} + (r_k)\, \rho_B\, \tau\, a(t)\, \eta_k = 0 \tag{3}$$

where C is the component concentration, r is the rate of reaction, ρ_B is the bulk density, τ is the residence time of the component, a is the deactivation rate parameter, and η is the effectiveness factor. For the hydrogenation of 4-CBA, three reactions are considered as depicted in Figure 3 [17].
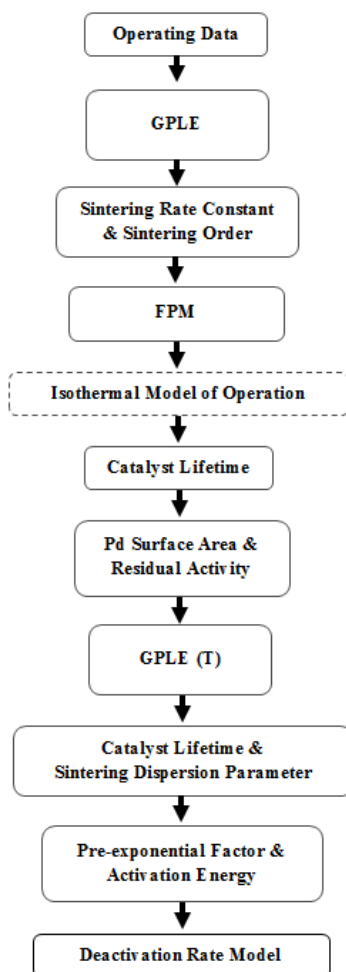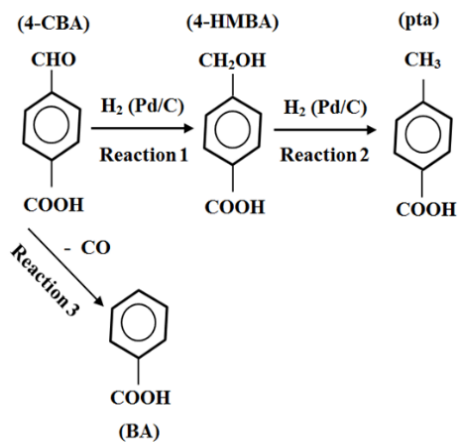
Figure 2. Flowchart for methodology

Figure 3. Hydrogenation reactions of 4-CBA

The calculated parameter is incorporated into the general power law expression (GPLE), which is usually used for the presentation of sintering phenomenon for the catalyst. The following equation shows the GPLE [5]:

$$-r_d = -\frac{da}{dt} = k_d a^m = k_{do} \exp\left(\frac{-E_d}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right)\left(\frac{S}{S_o} - \frac{S_{eq}}{S_o}\right)^m \tag{4}$$

where k_{do} is the pre-exponential factor; a is the metallic sintering dispersion parameter; m is the sintering order; k_d is the sintering rate constant; S is the active surface of the catalyst; S_o is the initial active surface of the catalyst; E_d is the activation energy; T_R is the reference temperature; and the ratio of S_{eq} to S_o is the residual active surface of the catalyst.

The calculated sintering rate constant and sintering order via writing a code into Matlab2013a environment using nonlinear technique are emerged into a simple deactivation rate model. The preliminary simple model is incorporated into first principle model (FPM) consisting of mass balances of the catalytic process at isothermal condition to predict the catalyst lifetime.

Then, the measured Pd surface area and the residual activity of the catalyst, which is different for different types of catalyst, are incorporated into GPLE to finally derive the catalyst lifetime and sintering dispersion parameter under different operating conditions. Using the obtained values, the pre-exponential factor and activation energy for deactivation are computed, which results in the derivation of the catalyst deactivation rate model.

The whole program was coded into Matlab 2013a environment. First, the partial differential equations were transformed into ordinary differential equation using backward difference method. The resulted equations were solved using *ode45* and *optimset* commands with the tolerance less than 10^{-8}.

Results and Discussion

The experimental and modeling results are analysed in this section. To implement the devised strategy, the data of the operation and catalyst are required. The study on the deactivated industrial Pd/C catalyst reveals that the most part of Pd particles are segregated. Moreover, Pd/C catalyst is aged owing to the sintering of Pd and the reduction of Pd active surface area [9]. Figure 4 shows a deactivated Pd/C catalyst. Regarding the measurement of Pd surface area, Pd/C catalyst was thermally treated at different temperatures up to 800 °C. The results showed that Pd experiences the sintering phenomenon. The relation between Pd surface area with the temperature can be found in Pernicone et al. [15]. Regarding the residual activity of the aged catalyst, Table 1 signifies the values of residual activity for different samples of Pd/C catalyst taken from different PTA production plants [9].
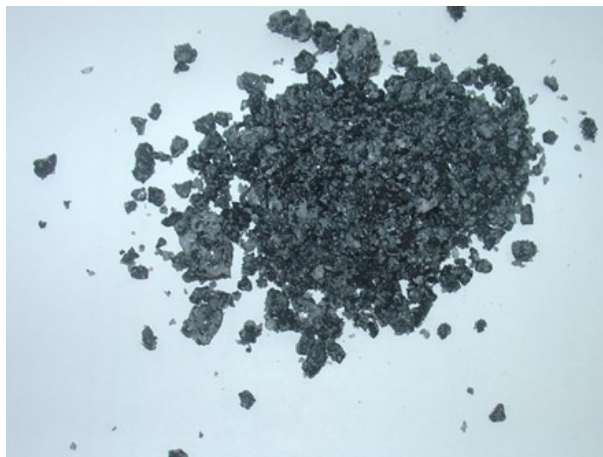

Figure 4. Deactivated Pd/C catalyst taken from the bottom of the reactor

Table 1. Residual activity of different Pd/C catalysts

Catalyst Sample	Residual Activity (-)
A	0.11
B	0.09
C	0.1

In this study, the average residual activity was considered as 0.1. PTA powder analysis was done in the PTA plant laboratory, and the results were reported at Azarpour et al. [18]. The operating data and the Pd/C catalyst specifications are shown in Table 2 [16].

Table 2. Operating data of the hydropurification process and Pd/C catalyst specifications

Item	Value
Pressure (barg)	73.5
Temperature (°C)	285
Feed flowrate (t h^{-1})	196
Hydrogen flowrate (kg h^{-1})	13.2
TA concentration (wt.%)	23
Catalyst bed length (m)	7.4
Catalyst bed diameter (m)	2.8
Particle diameter (mm)	3.53
Bulk density (kg m^{-3})	475
Bed void fraction (-)	0.44
Particle porosity (-)	0.61

Table 3 includes the modeling outputs for different sintering orders along with the model error values. The pre-exponential values and the activation energy for the deactivation were calculated 0.00092 h^{-1} and 5279 J mol^{-1}. Table 4 incorporates the trend of the catalyst deactivation through the operation days. It implies that the catalyst is totally deactivated after 360 days of operation. More information on the modeling and the derivation of the deactivation rate of Pd/C catalyst are available in the published papers [19, 20].

Table 3. Sintering order values and the relevant percent relative errors

Sintering Order	Percent Relative Error (%)
1	12.9
1.4	8.3
1.8	3.7
1.9	3.0
2.0	2.6
2.1	2.4
2.2	2.6
2.6	6.1
3.0	9.9

Table 4. Pd/C catalyst deactivation trend over the days of operation

Operation Days	Deactivation Trend (%)
30	17
60	27
90	37
120	46
150	55
180	64
210	73
240	82
270	90
300	95
330	98
360	100

Conclusion

A methodology to derive the deactivation rate of the industrial catalysts was given. It is used for the catalysts encountering sintering phenomenon, which is one of the commonest reasons for the industrial catalysts deactivation. The model considers the operating data, catalyst specifications, functionality of catalyst surface area on temperature, and residual activity to structure the model. The study was applied to the industrial Pd/C catalyst, which is used for the hydropurification process in PTA production plant.   The model validated against industrial data. For the proposed catalyst, the catalyst sintering order is calculated with less that 3 percent error, and the pre-exponential values and the activation energy for the deactivation were calculated 0.00092 h^{-1} and 5279 J mol^{-1}. Moreover, the catalyst is deactivated after around 360 days of operation. The model can be used for the industrial catalysts suffering from sintering phenomenon.

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