



Deactivation Kinetics Model of Pt/C Catalyst for Hydrogenation of Nitrobenzene to *p*-Aminophenol

GUANG-XUE LI^{1,2,*}, JIAN-HUA MA², XIN-HUA PENG¹ and CHUN-XU LV¹

¹Department of Fine Chemicals, Nanjing University of Science and Technology, Nanjing 210094, P.R. China

²Department of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, P.R. China

*Corresponding author: Tel: +86 554 6668563; E-mail: gxli@aust.edu.cn

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The deactivation kinetics of Pt/C catalyst for hydrogenation of nitrobenzene in acid medium to *p*-aminophenol (PAP), with aniline as a by product, was investigated in a batch reactor. Caused by carbonaceous fouling and poisoning in the nitrobenzene phase, deactivation of Pt/C catalyst is regarded as independent deactivation. Based on experimental results, a simple power law expression (SPLE) model for the deactivation kinetics is proposed. The kinetic parameters for the deactivation were determined by theoretical analysis and data fittings and the following

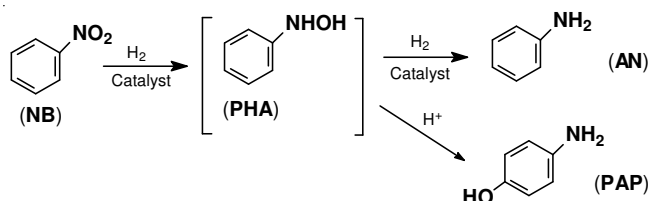
model for the system progressing with time-on-stream is obtained: $r_{\text{PAP}} = (-r_{\text{PAP}})_0 \cdot a$, $-\frac{da}{dt} = k_{d_0} \exp\left(-\frac{E_d}{RT}\right) a^m = 2.614 \exp\left(-\frac{25.57}{RT}\right) a^{0.0198}$.

The kinetic parameters evaluated from a batch reactor model were found to represent the observed experimental data very well. That is the deactivation order $m = 0.0198$, $k_{d_0} = 2.614$, the apparent activation energy for the deactivation $E_d = 25.57$ KJ/mol. Regarding the deactivation as a pore mouth fouling/poisoning model, the selectivity for *p*-aminophenol to aniline can be explained.

Key Words: Deactivation kinetics, SPLE model, Pt/C catalyst, Nitrobenzene, Hydrogenation, *p*-Aminophenol.

INTRODUCTION

Henke and Vaughen¹ were first to disclose the process for the manufacture of *p*-aminophenol (PAP), which was obtained by direct hydrogenation of nitrobenzene (NB) in the presence of platinum supported on charcoal (Pt/C) catalyst and a mineral acid. Rylander *et al.*² and Ternary³ postulated that the hydrogenation of nitrobenzene (NB) to *N*-phenylhydroxylamine (PHA) was followed by *in situ* a Bamberger rearrangement to *p*-aminophenol in the presence of an acid and the formation of aniline was the main competing side reaction in this process (Scheme-I).



Scheme-I: Hydrogenation reaction of nitrobenzene to *p*-aminophenol

Among various supported catalysts such as Pd^{1,10}, Ni¹¹ and sulfides of Mo and W¹, Pt^{1,2,4-9} have advantages of good selectivity for *p*-aminophenol, anticorrosive to acid and low

hydrogen pressure. The addition of morpholine, phosphorous acid¹² and dimethyl sulfoxide^{2,4,8,9} favoured the formation of *N*-phenylhydroxylamine successively to *p*-aminophenol.

However, the rapid kinetics and exothermicity of nitrobenzene hydrogenation makes a detailed kinetic discussion difficult. Juang *et al.*¹³ found that the rate-determining step for the catalytic hydrogenation of nitrobenzene to *p*-aminophenol was the process involving hydrogen atom adsorption on to the metal surface, suggested a kinetic equation as in formula (1):

$$-\frac{d[\text{PhNO}_2]}{dt} = k[\text{H}_2]^{1/2} \quad (1)$$

Rode *et al.*¹⁴ suggested a kinetic equation as in formula (2), giving an overall reaction rate in a four-phase system reactor with mass transfer effect. R_A , which is present on both sides of the equation, is a coupling or implicit function.

$$R_A = wk_1 + wk_2 \left[\frac{\frac{A_{\text{NB}}^* - R_A}{k_L a_B}}{1 + K_A \left(\frac{A_{\text{NB}}^* - R_A}{k_L a_B} \right)} \right] \quad (2)$$

It is found that the activity, life-span or deactivation rate and selectivity of Pt/C catalyst made a great difference from each other in present experiment, even according to the same

procedure from patent or literature. For the complexity of the process factor and technology secrecy, few papers¹⁶⁻²⁰ refer to the life-span of catalyst, deactivation and influence factor, such as refination of sulfuric acid and nitrobenzene¹⁵, seal off from air and protection by nitrogen¹⁰.

Deactivation and its kinetics: "Deactivation" is the activity loss of the heterogeneous catalyst with time-on-stream. Deactivation of catalysts is one of the most investigated problems in industrial catalysis due to its negative impact on both economy and environment. Deactivation is inevitable, but it can be slowed or prevented and some of its consequences can be avoided. Catalyst improvement is often achieved through identification of sources for its deactivation, with the final goal of preventing deactivation and increasing long-term catalyst activity, selectivity and stability.

The causes of deactivation are basically three-fold: chemical, mechanical and thermal. Intrinsic mechanisms of catalyst deactivation can be classified into six distinct types²¹ as in Table-1.

Carbonaceous deposits (referred as coke) are formed from the reaction mixture through polymerization and condensation complex polynuclear aromatic structures²². Coke deposits may amount to 15 or even 20 % (w/w) of the catalyst and they may deactivate the catalyst selectively or non-selectively-covering the active sites, respectively, causing the pore and surface blockage²³.

Poisoning²³ is the loss of activity due to the strong chemisorption on the active sites of impurities present in the feed stream. The surface metal atoms active in the catalytic reactions can be depicted as involved in the chemisorption of the reactants (and of poisons as well) *via* their "dangling orbitals". Accordingly, any chemical species having a "proper electronic configuration" (*e.g.*, unoccupied orbitals or unshared electron) or multiple bonds (*e.g.*, CO, olefins, acetylenes, *etc.*) can be considered as potential poisons. Poisoned catalyst can hardly be regenerated and therefore the best method to reduce poisoning is to decrease to acceptable levels the poison content of the feed. Another approach to prevent poisoning is to choose proper catalyst formulations and design.

Minachev *et al.*^{24,25} and Seoane *et al.*²⁶ have used poison's negative impact on long-term catalyst activity, an extremely small amount of catalyst poison (sulfur-containing organic compounds, such as thiophene) for the reversible poisoning for the suppression of the activity of catalysts, particularly those containing group VIII metals, such as Pt/C, higher sulfur resistance that gave a long life-time.

Sahimi *et al.*²⁷ were the first who identified catalyst deactivation as a percolation-type process. A schematic picture²³ representing three poison and/or fouling model is shown in Fig. 1, that so called core poisoning model, pore mouth poisoning model and uniform poisoning model.

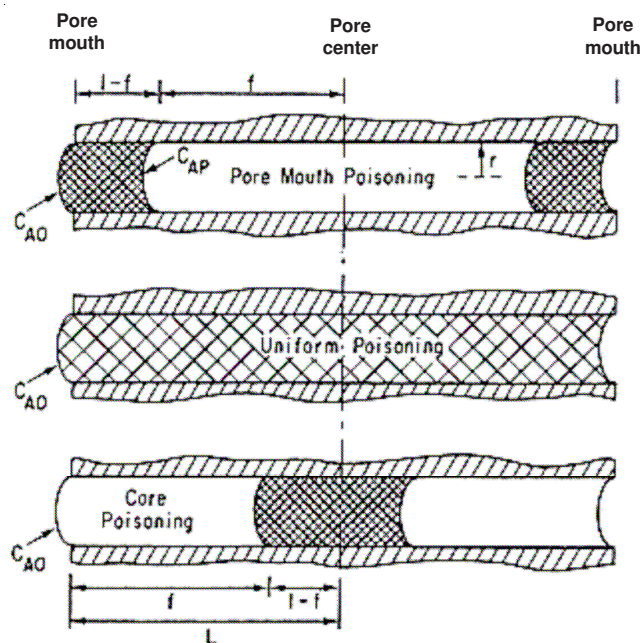


Fig. 1. Three limiting cases of poisoning and/or fouling

According to Romero *et al.*²⁸ the studies carried out until 1970 contemplate the catalyst activity as dependent only on the reaction time, linearly, exponentially, hyperbolically, potentially or according to the Elovich equation. But none of those equations gives information about the mechanism of the deactivation or on the influence of the operating conditions: temperature, concentration of reactants and products, catalyst conditions, *etc.*

Levenspiel^{29,30} proposed the use of two kinetic equations to describe the reaction system. Simple power-law deactivation rate expression (SPLE) of separable variables is based on the assumption that activity will ultimately decline or decays to zero with time.

$$-r_A = (-r_A)_0 \cdot a \quad \text{or} \quad a = \frac{-r_A}{(-r_A)_0}$$

$$r_d = -\frac{da}{dt} = k_d P_A^n a^m$$

TABLE-1
MECHANISMS OF CATALYST DEACTIVATION

Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase-support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapour-solid and solid-solid reactions	Chemical	Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion
		Loss of internal surface area due to mechanical-induced crushing of the catalyst particle

where a is the activity following the denomination of Szépe and Levenspiel²⁹ or the deactivation function designated as ϕ_A or Ψ_A by Beeckman and Froment³¹ or by Froment and Bischoff³².

Theoretically as well as experimentally, Jodra *et al.*³³, Butt *et al.*³⁴ and Corella *et al.*^{35,36}, have found cases of unseparable variables apply the following relation;

$$-\frac{da}{dt} = \psi(p_i, T)f(a) = \psi(p_i, T)a^m$$

may be empirical or may come from the development of a deactivation mechanism, which is a more fundamental approach to the analysis of catalyst deactivation.

It has been suggested by Butt *et al.*³⁴ that homogeneous catalyst surfaces of the Langmuir type lead to separable of power law forms and that heterogeneous surfaces lead to non-separable of Hougen-Watson forms.

More advanced models^{37,38} that so-called generalized power-law expression (GPLe) for modeling of catalyst deactivation phenomena, were proposed to account for the deactivation process, in which a residual or the steady-state activity, as approaches an non-zero asymptotic value at long times.

$$-\frac{da}{dt} = \psi(T, p)(a^m - a_s^m)$$

$$-\frac{da}{dt} = \psi(T, p)(a - a_s)^m$$

$$-\frac{da}{dt} = \psi(T, p)\left(\frac{a - a_s}{1 - a_s}\right)$$

where a is the activity and a_s is the activity at infinite reaction time, m is deactivation order.

Levenspiel³⁹ proposed 4 models of deactivation mechanic kinetics for parallel deactivation, series deactivation, side-by-side deactivation, (concentration) independent deactivation, respectively, as follow.

$$-\frac{da}{dt} = k_d C_A^n a^m$$

$$-\frac{da}{dt} = k_d C_R^n a^m$$

$$-\frac{da}{dt} = k_d C_P^n a^m$$

$$-\frac{da}{dt} = k_d a^m$$

Romero *et al.*²⁸ gave two procedures for the calculation of kinetic parameters for the deactivation of a Cu/SiO₂ catalyst. One is the analysis of the conversion data *versus* time, another is the temperature-time sequences. A summary of many laboratory investigations of deactivation kinetics has been presented by Butt⁴⁰.

Pt/C has excellent catalytic properties, but its major drawback is deactivation. In order to optimize the use of Pt/C in industrial hydrogenation processes, it is necessary to model the catalyst deactivation quantitatively. The aim should be to predict the behaviour of the hydrogenation batch a priori. The

present study concerns the deactivation of a Pt/C catalyst in the hydrogenation of nitrobenzene to *p*-aminophenol.

EXPERIMENTAL

Nitrobenzene, H₂SO₄ (98 %), dodecyl trimethyl ammonium bromide and dimethyl sulfoxide were obtained commercially with chemical purity 99 % or over. Standard *p*-aminophenol was purchased from Sinopharm Chemicals Reagent Co. Ltd., Hydrogen with 99.999 % purity (GB/T7445-95) was supplied by Nanjing Special Gas Factory. Nitrogen, with more than 99.5 % purity (GB/T7445-95) from a commercial source was directly used from the compressed gas cylinder. 2-5 % Pt/C catalyst was prepared by impregnation of charcoal (U-101, Tangshan United Carbon Technology Co. Ltd., China) with chloroplatinic acid solution followed by formaldehyde reduction in basic conditions.

A 500 L autoclave reactor with special gas-inducing turbine obtained from Hangzhou Yuanzheng Chemical Engineering Equipment Co. Ltd., China.

Procedure: A 500 L autoclave reactor with gas-inducing turbine was used for the hydrogenation experiment. The reactor was connected to a hydrogen reservoir held at a pressure higher than that of the reactor through a constant pressure regulator. Hydrogen was supplied from this reservoir to the reactor through a non-return valve. The gas consumed during the course of the reaction was monitored by the pressure drop in the reservoir vessel, measured using a transducer. Initial data were obtained at different temperatures, catalyst loading, agitation speed and partial pressure of hydrogen in a stirred high-pressure slurry reactor.

For a typical hydrogenation experiment the reactor was filled with nitrogen gas and charged with nitrobenzene, 2-5 % Pt/C catalyst, 14-18 % H₂SO₄ solution, quaternary ammonium salt and dimethyl sulfoxide. The contents were flushed with hydrogen while stirring. After the desired temperature was attained, the system was pressurized with hydrogen to a defined level. The course of the reaction was monitored by the observed pressure drop in the reservoir vessel as a function of time. Samples were analyzed at intervals during the reaction. Upon completion, the solid catalyst was separated by filtration. The filtrate was kept at temperature of 30 °C and adjusted to pH 5.0-5.5 and then extracted with toluene in order to remove aniline, unconverted nitrobenzene and traces of impurities. The pH of the aqueous layer after extraction was adjusted to 7 by the addition of aqueous ammonia leading to the complete precipitation of *p*-aminophenol.

RESULTS AND DISCUSSION

Deactivation model catalyst deactivation analysis for the hydrogenation of nitrobenzene to *p*-aminophenol: A quantitative description of deactivating systems is presented here in order to optimize the design and operation of catalytic processes, especially for fast deactivating systems.

The main problem in the simulation of the effect of catalyst deactivation by coke formation or poison deposition is modeling the rate of these phenomena. Whereas kinetic equations for the main reactions are now well recognized as an essential tool for process design and simulation, kinetic modeling of coke formation and catalyst deactivation is still considered

too complicated to be dealt with along the lines commonly accepted and used for the main reactions. As a result, over-simplified empirical equations with limited validity are derived from experimental work generally scheduled too late in the development of the process.

The catalyst deactivation kinetics was described with a reversible semi-empirical model, which lumped the physical and chemical reasons for deactivation to a simple two-parameter system.

In the reaction system, the amount of nitrobenzene decrease but the concentration of nitrobenzene remains content while the hydrogenation reaction proceed. Sintering, *e.g.*, thermal degradation of the catalyst might be neglected as hydrogenations were carried out at moderately low temperature (373 K). Loss of catalytic material due to attrition in moving or fluidized beds is a serious source of deactivation since the catalyst is continuously abraded away. Accordingly the availability of attrition-resistant catalysts for fluid-bed catalytic cracking is extremely important since the process operates with regeneration and catalyst recycle. A poison may act simply by blocking an active site (geometric effect) or may alter the adsorptivity of other species essentially by an electronic effect. Poisons can also modify the chemical nature of the active sites or result in the formation of new compounds (reconstruction) so that the catalyst performance is definitively altered.

Catalyst deactivation kinetics model and parameter estimation: It was shown that poisoning and fouling is the main source for deactivation and that kinetics of deactivation can be described by using a power-law equation. So the deactivation relating to nitrobenzene material can be thought to an independent deactivation. The formula of an independent deactivation, that is a simple power-law expression (SPLE) model, is most important that favourite to design, optimaion and data analysis.

As Levenspiel^{29,30} proposed, the use of two kinetic equations to describe the reaction system. Simple power-law deactivation expression (SPLE) of separable variables is based on the assumption that activity will ultimately decline or decays to zero with time.

$$-r_{\text{PAP}} = (-r_{\text{PAP}})_0 \cdot a$$

$$r_d = -\frac{da}{dt} = k_d a^m$$

We have deduced the formation kinetics of *p*-aminophenol, an exponential macro-kinetics form for hydrogenation of nitrobenzene to *p*-aminophenol in a four-phase system, the $(-r_{\text{PAP}})_0$ ⁴¹.

The deactivation specific content can be Arrhenius form

$$k_d = k_{d_0} \exp\left(-\frac{E_d}{RT}\right)$$

A logarithm for the SPLE model used to data analysis

$$\ln r_d = \ln k_d + m \cdot a$$

Linear regression analysis using the least squares method for the experimental data (Table-2 at 90 °C) gave the following (Fig. 1).

$$m = \frac{n\sum(a \ln r_d) - \sum a \sum \ln r_d}{n\sum a^2 - (\sum a)^2} = 0.0198$$

$$\ln k_d = \frac{\sum \ln r_d - m \sum a}{n} = 0.136, k_d = 1.145$$

Thus, a deactivation kinetics model of Pt/C catalyst for nitrobenzene hydrogenation to *p*-aminophenol at 0.1 MPa, 90 °C.

$$r_d = -\frac{da}{dt} = k_d a^m = 1.145 a^{0.0198}$$

Solution of the differential equation with the initial condition $t = 0, a = 1$ gives

$$\int_1^a -\frac{da}{a^{0.0198}} = \int_0^t 1.145 dt, a = (1 + 1.145t)^{1.0202}$$

The order for the deactivation kinetics, $m = 0.0198$, approach to 0, thus the deactivation kinetics approach to a constant, slightly fast than a constant deactivation kinetics.

Linear regression analysis using the least squares method for the experimental data (Table-2 at 80 °), gave the following (Fig. 1).

$$m = \frac{n\sum(a \ln r_d) - \sum a \sum \ln r_d}{n\sum a^2 - (\sum a)^2} = 0.0198$$

$$\ln k_d = \frac{\sum \ln r_d - m \sum a}{n} = 0.154, k_d = 1.166$$

A test plot of the deactivation model is shown in Fig. 2, which indicates a reasonable accordance with primary data.

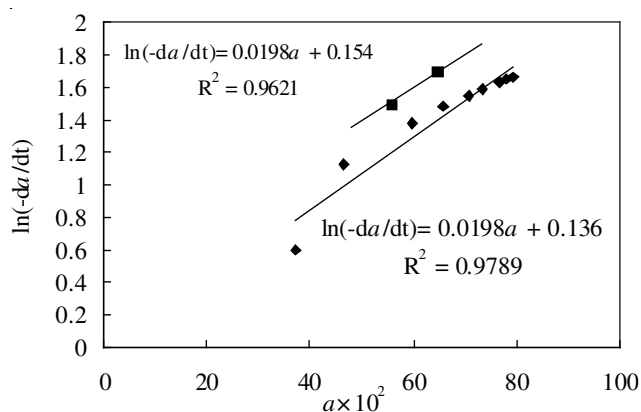


Fig. 2. $\ln\left(-\frac{da}{dt}\right)$ - a relationship

TABLE-2
EXPERIMENT RESULT OF THE CATALYST RECYCLE FOR Pt/C HYDROGENATION OF NITROBENZENE (AT 0.1 MPa 5Hr)

Recycle times of the catalyst	1	3	6	9	12	15	18	21	24	27
Accumulated reaction time	5	15	30	45	60	75	90	105	120	135
PAP yield (% , 90 °C)	80.2	79.3	78.1	76.6	73.4	70.8	65.9	59.8	46.4	37.3
PAP yield (% , 80 °C)	65.3	64.7	63.2	-	-	-	-	-	-	-

Estimation of the specific rate constant for the deactivation used to Arrhenius equation: Since the deactivation speed for the Pt/C catalyst increases with increasing temperature, according to the Arrhenius equation:

$$k_d = k_{d_0} \exp\left(-\frac{E_d}{RT}\right)$$

Or its logarithm form

$$\ln k_d = -\frac{E_d}{RT} + \ln k_{d_0}$$

The linear regression analysis results using the least squares method for the experimental data for the experimental data gave the following (Fig. 3).

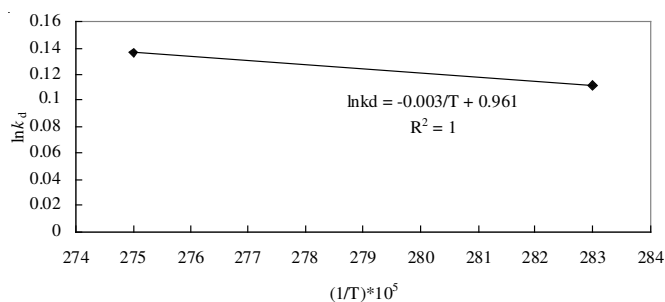


Fig. 3. $\ln k_d - \left(\frac{1}{T}\right)$ relationship

$$\frac{E_d}{R} = \frac{\sum \frac{1}{T} \sum \ln k_d - n \sum \left(\frac{1}{T} \ln k_d\right)}{n \sum \frac{1}{T^2} - \left(\sum \frac{1}{T}\right)^2} = 0.3075$$

The apparent activation energy of the deactivation was $E_d = 25.57$ kJ/mol and the rate constant ($\ln k_{d_0} = 0.961$) for the deactivation was 2.614

Giving the equation

$$k_d = k_{d_0} \exp\left(-\frac{E_d}{RT}\right) = 2.614 \exp\left(-\frac{25.57}{RT}\right)$$

So a deactivation kinetics model of Pt/C catalyst for nitrobenzene hydrogenation to *p*-aminophenol, as an independent deactivation, the simple power-law expression (SPLE) model is

$$\begin{aligned} r_d &= -\frac{da}{dt} = k_d a^m = k_{d_0} \exp\left(-\frac{E_d}{RT}\right) a^m \\ &= 2.614 \exp\left(-\frac{25.57}{RT}\right) a^{0.0198} \end{aligned}$$

Discussion and the selectivity for nitrobenzene hydrogenation to *p*-aminophenol: The separable kinetics have limitation, it can't explained the decrease of the catalyst selectivity with reaction time. Selectivity of *p*-aminophenol to aniline, will be decreased with the reaction time or reaction run, it can be explained by the consecutive reaction in the catalyst surface of nitrobenzene to *N*-phenylhydroxylamine then to aniline, influenced by inter-disperse and the catalyst deactivation step from the outer to the inner of the pore, influenced

by inter-disperse and the catalyst deactivation step from the outer to the inner of the pore, that accord with the so called pore mouth poisoning model²³.

The complexity of the deactivation phenomenon is widely recognized: Pore blockage is frequently coupled with site coverage, the catalyst surface is heterogeneous, the reacting network itself can be very complex, several causes of deactivation may act simultaneously, *etc.*

Commercial reactors undergoing catalyst decay are often controlled to produce constant conversion of reactants by gradually increasing the temperature with time on stream until the catalyst is no longer of use or higher temperatures result in unfavourable product selectivity.

Preventing poisoning

General principles of prevent inactivation: The reason of loss activity result by poisoning is the impurities in the raw materials adsorbed or combined in the catalyst surface. Some occasions are hard to recover the activity by regeneration, so it should be solve by adding the step of removing impurities from the raw materials or using other measures.

The following methods can be used to favouring the catalyst life (1) Ensure the purity of raw materials. Nitrobenzene should be free from thiophene and other sulfide impurities in the analytical reagent for the raw materials, even with high quality merchandise level of sulfuric acid can make catalyst inactivated completely. We can use 30 % H_2O_2 with sulfuric acid (AR) raw materials 2-4 h, the dosage is 0.11 % by weight of sulfuric acid, until it becomes clear and no longer emit bubbles and then heated at 80 °C water bath for 0.5 h to expulsion the remaining H_2O_2 . The experimental results show that the method can have a good effect. (2) The nitrogen protection. Before pass into the feed and hydrogen to response, we should first pass into a period of nitrogen to remove the residual oxygen and a small number of volatile catalytic poisons. After the end of the reaction, it should be purified under the protection of the nitrogen gas, this is mainly to ensure the purity of *p*-aminophenol and in order to prevent oxidation. (3) Isolated the air. Benner add the nitrobenzene one-time at the beginning of reaction, let the catalyst suspend in the rest of nitrobenzene at the end of reaction. That can avoid catalyst espousing in the air when filtering, it becomes more convenient to use catalytic repeatedly.

Conclusion

This first report on the deactivation kinetics of Pt/C catalyst for the hydrogenation of nitrobenzene to *p*-aminophenol in a four-phase reactor. We propose a independence deactivation simple power-law expression (SPLE) model depending on an exponential function of activity and temperature to quantitatively describe a selected result.

Notation

- a : Activity for catalyst.
- a_s : The activity at infinite reaction time, residual or the steady-state activity.
- r_d : Deactivation kinetics (h).
- da : Differential deactivation.
- dt : Differential time (h).
- k_d : Specific rate constant for deactivation kinetics.

- k_{d_0} : Specific rate constant for deactivation kinetics.
 E_d : Apparent activation energy for deactivation of Pt/C (kJ/mol).
 ϕ_A or ψ_A : The designated deactivation function.
 m : The deactivation order.
 R : Gas content, 8.314 kJ/kmol K.
 T : Reaction temperature (K).

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