

A Deactivation Correlation for Platinum Y-Zeolite in n-Hexane Isomerization

Haiyam Mohammed A. Al-Raheem*

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Abstract

The objective of the present work is to realize the kinetic modeling regarding deactivation of Pt-HY zeolite and monitor the isomerization reaction of n-hexane. The catalyst has been prepared with 0.4% Pt and evaluated during the isomerization reaction of n-hexane. Based on the results of catalytic investigation, a kinetic model was proposed to deactivate the catalyst by coke formation. The present method provides information on apparent overall kinetics as well as deactivation parameters and would seem to provide a rapid method for screening of reaction/deactivation behavior. Accordingly the deactivation order was found to be 3.72. The obtained correlation of deactivation predicts the activity pattern under the applied reaction conditions, closely mimics those observed experimentally, and spans those obtained from empirical correlations.

Keywords: isomerization; zeolite Y; kinetics; deactivation; coke formation

فقدان فعالية العامل المساعد زيولايت نوع Y لتفاعل ازمرة الهكسان

الخلاصة

في هذه الدراسة تم دراسة فقدان فعالية العامل المساعد من نوع زيولايت Y والمحمل عليه نسبة من البلاتين تعادل (4%) اثناء تفاعل الازمرة للهكسان. من خلال البحث وجد ان فعالية العامل المساعد تجاه تفاعل الازمرة عالية في بداية التفاعل وبعد مرور فترة من الزمن نلاحظ فقدان سريع وواضح للفعالية. فقدان الفعالية يعزو بشكل رئيسي الى ترسب المركبات الكربونية على سطح ومسامات العامل المساعد المستخدم في تفاعلات الازمرة. في هذا البحث تم ايجاد علاقة يمكن التنبؤ من خلالها وبشكل سريع بسلوك وديناميكية تفاعل الازمرة فضلا عن ايجاد المعاملات الخاصة بفقدان الفعالية والذي يعطي وصفا جيدا للملاحظات العملية.

1. Introduction

Zeolites are of industrial and theoretical importance, because they allow studying the nature of their active sites and their elementary reactions. On the other hand, they contribute to produce more economic novel petrochemicals and develop fine chemical processes

because of their selective behavior as catalyst. The Faujasite zeolite is a natural compound which has demonstrated great performance as a catalyst because of its intrinsic properties and selectivity according to its porous system.

Hydroconversion of paraffins on Pt-supported solid acid is widely believed to proceed through the following steps [1,2]: Dehydrogenation of paraffin to olefin on Pt surface; transfer of the olefin to an acidic site for protonation to carbonium ion; isomerization and/or cracking of carbonium ion and deprotonation an acidic site to olefin; and transfer of the product olefin to Pt site for hydrogenation to the final paraffin. Zeolite Y catalyst came into wide application, for these reactions, because of their levels of sophisticated structures able to "guide" to desired products via shape selectivity. The complete process of converting a given feedstock into a required product stream in a catalytic reactor is complicated and involves chemical and physical steps occurring both simultaneously and in sequence. Of prime importance is the chemical activity of the catalyst. This must be adequate to fulfill the requirements of the process and the catalyst activity should have a reasonable life. Unfortunately most catalyst used in heterogeneous catalytic processes is subject to a decrease in the initial activity over a period of time [3,4]. The time required for the activity of a catalyst to fall to an undesirable level varies with the severity of the process conditions and with the type of reaction being catalyzed. Because of the intrinsic association of catalyst deactivation with the main chemical reactions, fouling by coke cannot be eliminated by purification of the feed or use of guard catalyst; if reaction occurs, coke deposition must also necessarily occur according to the overall chemistry of the process. In this case, the kinetics of the basic

reaction and the deactivation regularities, especially those concerning the deactivating agents (coke) are mutually dependent. However, coke can be minimized by appropriate choice of reactor and operating conditions, and in some cases by modification of the catalyst. The presence of coke on the catalyst with different natures, compositions, and structures influences significantly the catalytic activity and alter the selectivity for the required isomerization products and a consequent reduction in the product octane number and lifetime of the catalyst. In fact the active sites of the zeolites are located in typical well defined pores (cavities, channels and intersections of channels) and with almost similar dimensions to organic molecules. Therefore, pores are real nanoreactors where, in one hand, the desired reaction occurs and, in the other hand, side coke is produced, limiting its growth to the size of the pores [5,6]. Coke deposition is a complex reaction that results from both the production of coke precursors and their destruction. The metal plays a prominent part in the reaction, (i) by yielding olefins, which can be polymerized on the acidic sites of the support, (ii) by stabilizing carbonaceous deposits through dehydrogenation by an inverse spill-over effect and (iii) by destroying coke precursors [7].

A number of different approaches of varying levels of sophistication have been developed to model the deactivation behavior associated with coke formation starting with the pioneering work of Voorhies, who related the amount of coke formed on

the catalyst to the time of reaction. Other empirical approaches directly relate the reduction in catalytic activity to the amount of coke accumulated on the catalyst surface. Generally, the kinetics of a catalyst deactivation is a function of temperature, time, pressure and the concentrations of different substances [8,9]. To summarize, there are a number of theoretical treatments of deactivation by coking. All, however, require parameter estimation in order to obtain predictive results. Although coke deposition may be the "true" variable in the deactivation process, this has to be linked with time by some form of deactivation to obtain some indication of how long a catalyst may remain on stream before replacement or regeneration is necessary.

In this study, deactivation by coke formation through the hydroisomerization of n-hexane over platinum containing Faujasite zeolite is investigated. The kinetic model proposed will give information about the catalyst behavior in relation to time on stream and on the evolution of catalyst activity.

2. EXPERIMENTAL WORK

2.1. Introduction

The experiments were carried out on platinum supported zeolite, faujasite type Y, which was in the sodium form. The sodium ions were exchanged with ammonium. A zeolite –supported platinum catalyst was prepared using hexachloroplatinic acid as an impregnating solution. The resultant catalyst performance was studied for n-hexane isomerization. Catalytic activity studies were carried out by

using a micro-catalytic reactor unit for hydroconversion of n-hexane.

2.2 Materials

The sodium form of zeolite Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 14.0$), was purchased from United Catalyst India Ltd., as a powder with total surface area of $477 \text{ m}^2/\text{g}$.

Hexachloroplatinic acid (40% Pt) was obtained from Fluka AG.

Other chemicals namely ammonium chloride and n-hexane were obtained from AKZO chmi. Hydrogen gas (99.9975%) was delivered by Al-Mansour Plant.

2.3 Modification of Na-Y Zeolite Catalyst

The conversion to protonated form was carried out by ion-exchanging of the original zeolite (NaY) with ammonium chloride solution followed by subsequent exchanging for 4 days. The exchanged results show 87% of exchanging rate of Na^+ by NH_4 .

The exchanged zeolite was filtered off, washed and dried at 110°C for 10 hours. The prepared sample was washed with deionized water to be free of chloride ions, and drying procedures were repeated twice. The obtained zeolite calcined in air at 500°C for 8 hours to obtain the HY form.

2.4 Preparation of Pt/HY catalyst

The exchanged zeolite HY was loaded with Pt at concentration of 0.4 wt % by impregnation with aqueous solution of hexachloroplatinic acid H_2PtCl_6 . The prepared solution was added drop wise to the zeolite with mixing for 4 hours at 25°C . The mixture was then left at room temperature for 24 hours; it was stirred intermediately during this time.

The mixture was then slowly evaporated to dryness over a period of 8 hours at temperature of 75°C. The resulting catalysts were dried in air at 110°C for an additional 12 hours. Then, the samples were calcined in air at 550°C for 10 hours. The calcined catalyst was finally reduced at 350°C in flowing hydrogen for 3 hours prior to utilization. Then, the sample is referred to as Pt/HY catalyst [5,10].

2.5 Catalytic Unit

The experimental apparatus employed throughout this investigation is shown in figure (1). The reaction was carried out in a conventional fixed bed flow-type catalytic reactor of stainless steel with 24 mm internal diameter, 28 mm external diameter, and 30 cm height. There were three sections in the reactor, the first one was the preheating zone filled with glass beads, the middle section was the reaction zone where 8 g of the catalyst bed was located and the third zone was filled with glass beads to maintain and stabilize the temperature and flow inside the reactor. The reactor was electrically heated and automatically controlled. The temperature at the reactor center of the catalyst bed and at different points in reactor and system, were determined by manufacturing interface system, (Computerized Temperature Measurement System).

2.6 Procedure

Before each run the catalyst was dried at 110°C in nitrogen flow for one hour and then reduced at 350°C in hydrogen flow for three hours. The Pt-decationized (HY) zeolite has been studied under the following operating conditions: Temperature (375°C),

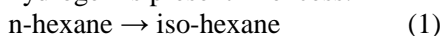
pressure (1 atm), hydrogen/hydrocarbon molar ratio was 4, and liquid hourly space velocity was 1.8h⁻¹.

The effluent reactor was analyzed in a gas chromatograph (Shimadzu Gc-2014) flame ionization detector coupled to stainless steel capillary column with an inside diameter of 3.175 mm and length of 2 m and using N₂ as a carrier gas.

To determine the amount of coke formed during reaction time-on-stream, the catalyst was weighed before and after the experiment. The difference in weights gave the weight gain due to coke deposition. The spent catalyst was also calcined at 500°C for a period of 6 hours and then cooled at room temperature, and the difference between the weight of catalyst before and after calcination was taken as the weight of coke.

3. KINETIC MODEL: It is known that the production velocity of coke, its composition and deactivating effect is dependent on the pores of the zeolites, the acidity and the operational conditions, such as temperature, pressure and composition. A better understanding of the interaction between the hydrocarbons and the catalytic sites leading to coke formation and a more detailed of its rate might contribute to the development of catalysts generating less coke and/or less subject to deactivation. To reach this goal it has to be kept in mind that the study of coke formation and the associated catalyst deactivation is not different from the study of any catalytic process; coke is formed through one reactions, involving intermediates also

acting in the "main" reactions [11,12]. The influence of the coke on the reaction(s) causing catalyst deactivation is then naturally dealt with in terms of real variables and the elementary steps. Presently this is still done in an empirical way by multiplying the main reaction(s) by a deactivation function which is often related to time. The catalytic deactivation makes it difficult to determine the kinetic parameters and the reaction trajectory. This adjustment is normally done by the quantitative specification of the catalyst activity, $a(t)$. This model deals with the conversion of n-hexane on HY zeolite catalyst in a typical condition in which hydrogen is present in excess.



In describing the deactivation process due to coking, the following assumptions were applied:

- The main reaction is first order in the feed component, and at a fixed total pressure.
- Zero order in hydrogen, In effect, the hydrogen dependence is combined in to the rate coefficient since hydrogen partial pressure essentially is constant
- The conversion has been used as a measure of activity.
- Two lump scheme: simultaneous-consecutive deactivation process with both reactant and product coke precursors.
- The separable deactivation kinetic approach is applied.

The decomposition velocity of reagent A (hexane) on a catalyst that was already used during a period of time t , is [12]:

$$-r_A = a(t) k(T) f_n(C_A, C_b, \dots, C_i) \quad (2)$$

Where:

$-r_A$ = Velocity of the catalyst deactivation reaction, as a function of time.

$a(t)$ = Catalyst activity, as a function of time.

$k(T)$ = Specific velocity of the reaction, as a function of temperature.

C_i = Concentration of reagents, products, or impurities, in the gaseous phase.

Thus for separable deactivation kinetics [1]:

$$-r_A = k P_A \quad (3)$$

and in this work it will be used in terms of concentration, according to equation:

$$-r_A' = k' C_A a \quad (4)$$

The rate of catalyst decay, r_d , can be expressed in rate law analogous to equation (2):

$$-r_d = a(t) k_d(T) q(C_A, C_b, \dots, C_i) \quad (5)$$

Where:

k_d = Rate of catalyst decay, as a function of temperature.

Equation (5) can be simplified as follows:

$$-da/dt = k_d' a \quad (6)$$

For a fixed bed reactor with plug flow of fluid and constant volumetric flow rate, v_o , through a certain mass of catalyst, W , the combined mole balance and rate law,

$$v_o dC_A/dW = -k a(t) C_A \quad (7)$$

$$a(t) = (v_o/Wk) \ln 1/1-x \quad (8)$$

Assumption of zero order for the catalyst deactivation step gives:

$$a(t) = 1 - \beta_o t = (v_o/Wk) \ln 1/1-x \quad (9)$$

Replacing the expression $K_R = Wk/v_o$ and reorganizing equation 9, one gets:

$$\ln 1/1-x = K_R - \beta_o K_R t \quad (10)$$

A plot of $\ln 1/1-x$ versus t should therefore result in a straight line. If the zero order deactivation reaction is not fitted to the data, the first order deactivation should be tested:

$$a(t) = e^{-\beta_1 t} = (v_o/Wk) \ln 1/1-x \quad (11)$$

Replacing $K_R = Wk/v_o$ and applying \ln at both sides:

$$\ln \ln 1/1-x = -\ln K_R - \beta_1 t \quad (12)$$

This time, a plot of $\ln \ln 1/1-x$ versus t should result in a straight line, whose slope is the time constant of the deactivation. The value of constant K can be calculated from the linear coefficient of the fitted line.

If the deactivation of the first order does not still represent the data, the second order could be tested:

$$a(t) = 1/1 + \beta_2 t = (1/K_R) \ln 1/1-x \quad (13)$$

$$1/\ln(1/1-x) = 1/K_R + (\beta_2/K_R) \cdot t \quad (14)$$

Consequently, both K_R and β_2 can be estimated from the graph of $1/\ln(1/1-x)$ as a function of time t . In fact, further assumptions are required until the law of deactivation is determined. The β_i s are parameters of deactivation order..

4. RESULTS AND DISCUSSION

4.1 The formation of coke on the catalyst due to the effect of time-on-stream was studied by mass balance technique. In this study the amount of coke formed during reaction was found to be 25 mg coke/gm catalyst.

4.2 The evaluation of the catalytic activity as of the isomerization reaction of n-hexane is presented in Figure 2 and Figure 3. From the activity decay profile, a fast catalyst deactivation caused by the deposition of carbonaceous material on the catalyst surface and pores at the first 50 minute reaction time can be observed. This indicates that deactivation of the metal function is the main reason for the initial deactivation, which is attributed to high hydrogenation-dehydrogenation capacity of platinum, according to the

conclusions submitted by the work of Jorge et al. [3]. In this case, the residual activity is reached after one hour. An important aspect that has to analyze from the catalytic activity data that deactivation is seen to take place in two distinct regimes; a rapid initial step followed by more gradual decline. These regimes sometimes referred to as "fast" and "slow" coke, respectively, and probably correspond to the initial deposition of carbonaceous layer with considerable C⁺ character, followed by the transformation to more graphitic structures, which is confirmed by the difference in the observed coke colour between brown and black. After 300 min time on stream the conversion reaches a plateau where it is stable. At this plateau the activity is 20% of the initial activity, and almost remained stable without further decrease trend. The observed steady state of the catalyst can be associated to the relative strength and to the amount of active sites as well as to the hydrogenation power of platinum which avoids the hydrocarbon residues to block the active sites. The increase in the stability is also due to the higher tendency of coke formation, which is a useful consequence in a suppression of the hydrogenolytic activity of the virgin catalyst. The presence of hydrogen in the reaction zone is essential to minimize coke formation. However, it should be noted that since the dehydrogenation involves the production of hydrogen, the addition of hydrogen in the feed will inevitably lower the equilibrium conversion. This conclusion is in agreement with the work of Froment [14].

Aiming to estimate the reaction and deactivation parameters, several models were tested, among which the empirical model proposed by Voorhies [13] presented the most satisfactory results for the deactivation of the catalyst. This model is proposed as follows:

$$a(t) = A_0 t^{-\beta} \quad (15)$$

Where A_0 and β are deactivation parameters, and the order of deactivation (γ) is calculated by:

$$\gamma = (\beta+1)/\beta \quad (16)$$

In figure (4) different tested models for the catalyst are plotted as an example that Voorhies model satisfactorily represents the experimental data. It is possible to verify that the deactivation order of 0, 1, and 2 do not agree with the kinetic model of the first order reaction. According to the Voorhies model, the deactivation order is 3.72, calculated with equation 16. Therefore, the following equation:

$$\ln 1/1-x = A_0 K_R t^{-\beta} \quad (17)$$

Can be expressed with:

$$\ln 1/1-x = 0.436 t^{-0.367} \quad (18)$$

5. CONCLUSIONS

The deactivation of bifunctional catalysts and the changes in selectivity of products formed occur due to the deposition of coke on both the metal and acid functions. The metallic function deactivates rapidly at first due to coking but then [7] reaches a steady state due to equilibrium between coke formation and its removal.

The proposed kinetic correlation appears to work well with the reaction experimental data. Kinetics parameters for the deactivation reaction were estimated. The approach is attractive because it works directly with

conversion data rather than indirectly with coke on catalyst and provides at least a first estimate of reaction and deactivation rate parameters. A larger data base is required for more thorough exploration, particularly of time-on-stream correlation.

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Table (1) Total conversion of n-hexane

Time(hr)	Conversion %	Time(hr)	Conversion %
0.0833	0.662	2.667	0.262
0.1667	0.569	3.000	0.253
0.250	0.516	3.333	0.244
0.333	0.478	3.667	0.238
0.500	0.430	4.000	0.235
0.8333	0.372	4.333	0.230
1.000	0.353	4.667	0.226
1.333	0.325	5.000	0.218
1.667	0.303	5.333	0.214
2.000	0.287	5.667	0.210
2.333	0.273	6.000	0.208

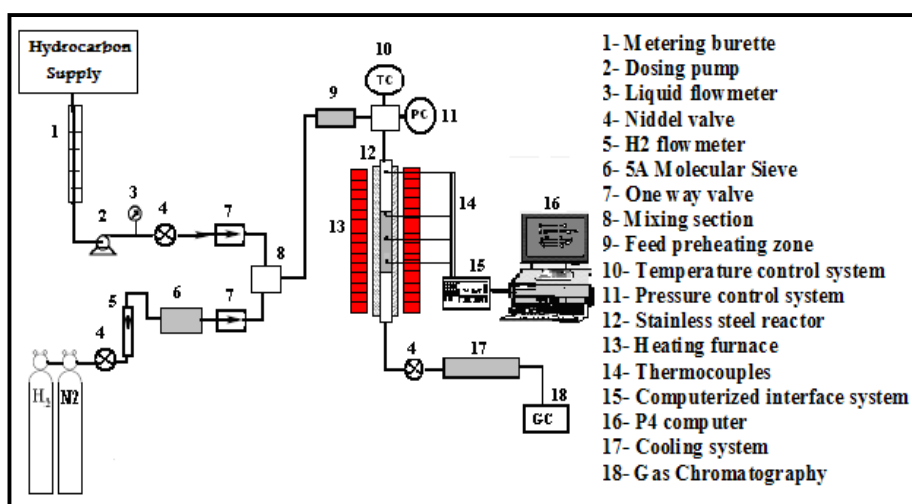


Figure.1 Schematic diagram of the experimental apparatus

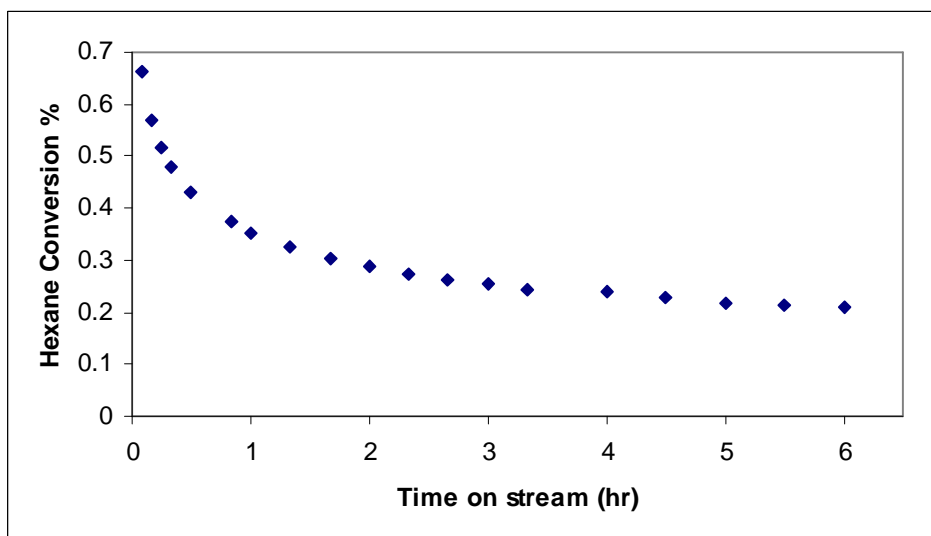


Figure.2 Total conversion of n-hexane as a function of time on stream

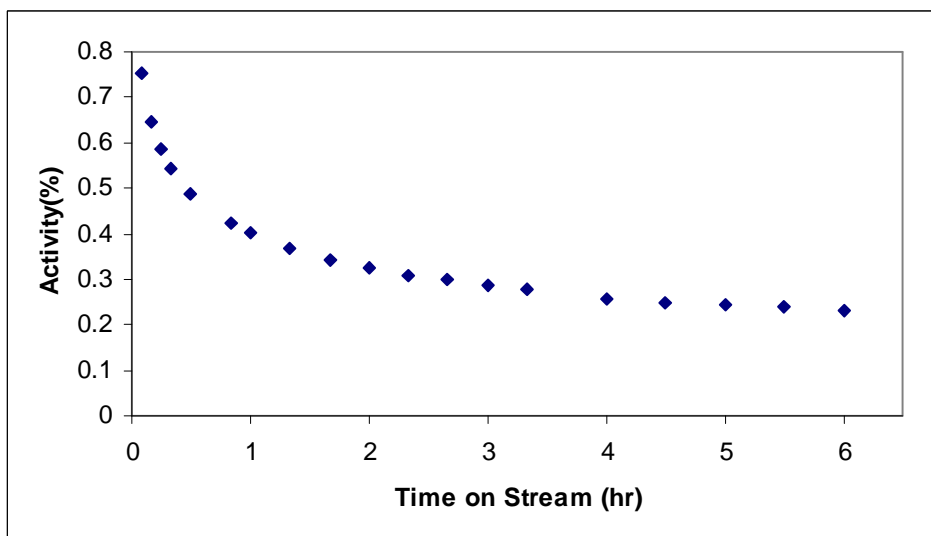


Figure.3 Activity of n-hexane for H-Y zeolite catalyst

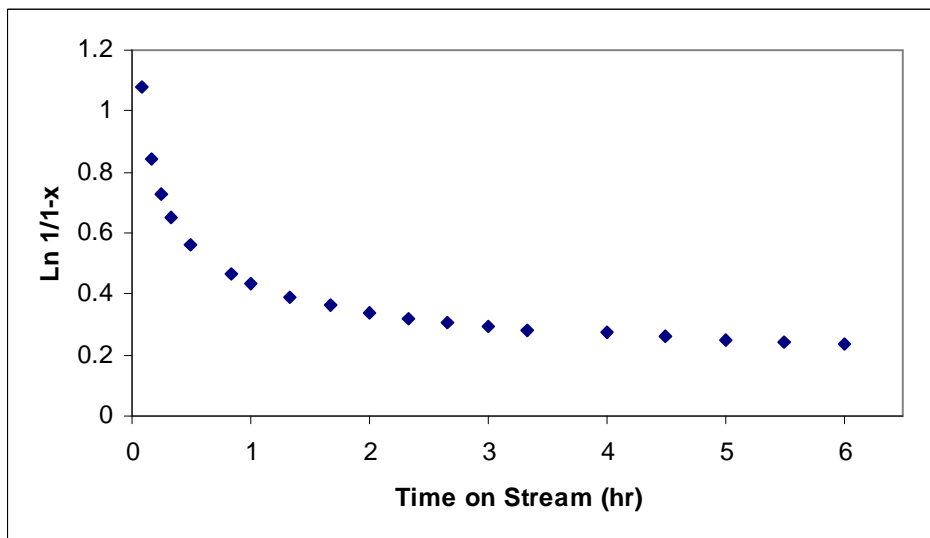


Figure.4.a

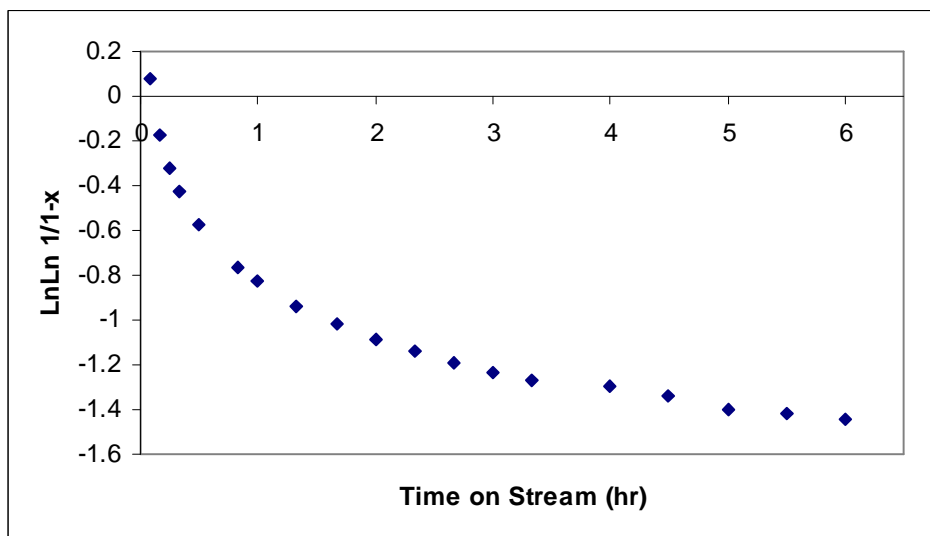


Figure.4.b

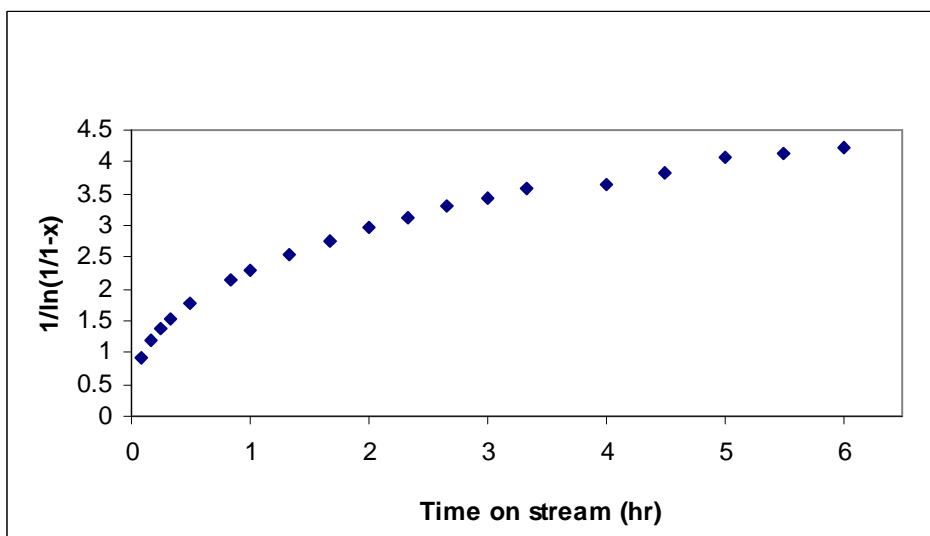


Figure.4.c

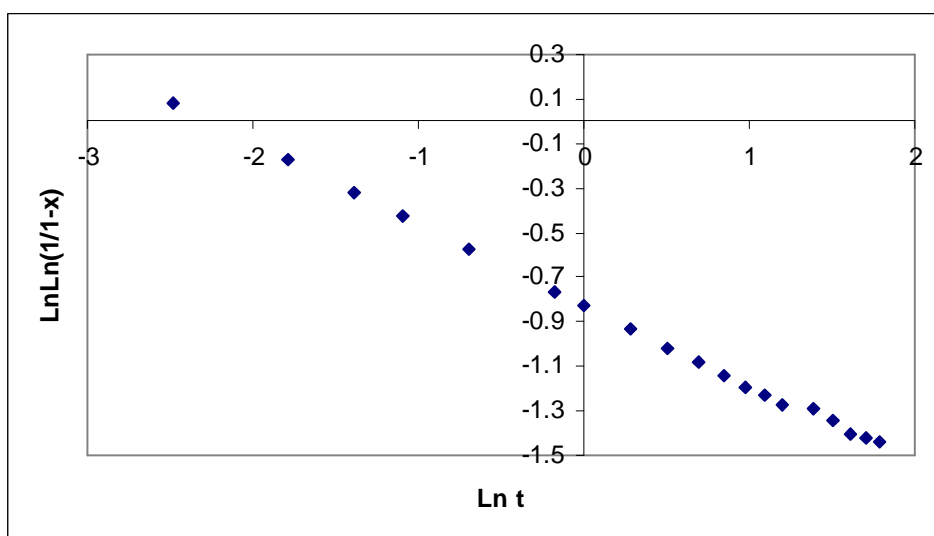


Figure.4.d

Figure.4 Different tested kinetic models for H-Y zeolite catalyst according to the following deactivation orders: (a) 0, (b) 1, (c) 2, (d)3.72