

Environmentally Friendly Fuel by n-Heptane Isomerization: Kinetics of Catalyst Deactivation

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Abstract—Stringent environmental regulations demand reduced amounts of aromatics in a gasoline fuel. The aromatics have high octane rating and therefore by removing them from a gasoline fuel substantially decreases the quality of the gasoline. One way to improve the octane rating of heavy normal alkanes present in heavy naphtha, without converting them into aromatics, is to isomerize them over an acidic catalyst. Zeolites are acidic catalysts that are highly efficient for the isomerization reactions. In the present study, n-heptane is taken as a model component of heavy naphtha and kinetics of the deactivation of different Y zeolite catalysts during the hydroisomerization reaction is studied. Various deactivation rate laws are tested against the experimental data and the best-fit rate law is worked out. Relatively low activation energies for the deactivation process are obtained showing temperature has little effect on the rate of deactivation for the conditions studied in the present work.

Index Terms—Deactivation, zeolite Y, hydroisomerization, naphtha, isomerized gasoline.

I. INTRODUCTION

Aromatics constitute nearly 35% of the gasoline content. Aromatics are considered to have a high octane value (>100), therefore, they are an important part of a gasoline fuel. Removing aromatics from a gasoline pool will significantly affect the burning characteristics of the gasoline. In gasoline, aromatics come through reforming of naphtha where dehydrogenation and dehydrocyclization reactions convert cycloalkanes and n-alkanes to aromatics, respectively. As an example, reforming of cyclohexane and n-hexane present in naphtha will provide benzene in the final reformat. One way to improve the octane number of normal alkanes present in naphtha without converting them into aromatics is to isomerize them over an acidic catalyst. An isomerized product has substantially higher octane number than its corresponding n-alkane. E.g., n-octane has octane number <0, whereas isooctane has octane value of 100. As isoalkanes are more environmentally friendly [1]-[5] than their corresponding aromatics, a process that yields isomers of alkanes, but not the aromatics, is highly desirable. It is

important to mention here that, currently, at industrial scale no commercial plant is available for the isomerization of heavy naphtha.

The success of a catalytic process is mainly based on the availability of an appropriate catalyst. A good catalyst is the one which has high activity, selectivity, stability, and regeneration ability [6]. For the design of an industrial catalytic process, apart from the performance data of the catalyst, reaction kinetics of the reaction associated with the catalyst is also required. The kinetics of the reaction includes the kinetics of the reaction over a fresh catalyst or stable region of the catalyst and the deactivated region of the catalyst.

The kinetics of the isomerization reaction of n-heptane over a Pt loaded-zeolite catalyst is not studied widely. Only a handful of researchers [1], [7]-[9] carried out the kinetics of the hydroisomerization reaction. Usman and Alotaibi [1] studied initial rate kinetics of the n-heptane hydroisomerization for six Pt/zeolite catalysts. They developed kinetic expressions based on dual-site Langmuir-Hinshlewood-Hougen-Watson kinetic theory. In each case, the model equation developed based on the surface reaction rate controlling is found the best equation in representing the experimental data. The kinetics of the isomerization of n-heptane over eight Pt loaded zeolite Y catalysts is studied by Remy *et al.* [7]. The study was undertaken at a total pressure of 1.1 bar, n-heptane partial pressure of 0.0685 bar, and W/F_{A0} of 0.38 kg-s/mmol n-heptane. Holló *et al.* [8] employed the Pt loaded H-mordenite catalysts and the kinetics of the hydroisomerization reaction was carried out in the range of 453–493 K temperature, 5.0–40 bar pressure, and hydrogen to n-heptane ratio of 1–20. Saberi and Mao [9] studied Pt-HY and Pt-Zn-HY zeolite catalysts in the temperature range of 468 to 498 K. All of the above studies are carried out for the stable region of the catalyst where there is no deactivation. The deactivation kinetics of hydroisomerization of n-heptane over a Pt-loaded zeolite catalyst has not been found in the literature.

In the present study, n-heptane is taken as a model component of heavy naphtha and kinetics of the deactivation of the two different types of Y zeolite catalysts during the hydroisomerization reaction is studied. Various deactivation rate laws [10] are tested against the experimental data and the best-fit rate law is worked out. Discrimination among the rival models is carried out based on the sum of squares of the errors (SSE), F-value, t-values of the parameters, and kinetic significance of the parameters. To our knowledge, the deactivation kinetics has never been studied over a Pt loaded zeolite catalyst for the n-heptane hydroisomerization reaction.

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II. METHOD

The experimental data of n-heptane hydroisomerization was obtained over two Pt-loaded zeolite Y catalysts. The experiments were performed in a 1.02 cm I.D. stainless steel fixed bed reactor. The details of the catalyst preparation, characterization, and experimental system are given in Alotaibi *et al.* [11]. However, Table I gives some of the characterization properties such as bulk Si/Al ratio; surface area, pore volume, and pore size measured by N₂-BET technique; Pt content by ICP (Inductively Coupled Plasma Spectroscopy); and catalyst acidity by ammonia TPD (Temperature Programmed Desorption) of the two catalysts. The experimental data was obtained over various operating conditions. The temperature, pressure, and W/F_{A0} were maintained in the range of 210–250°C, 1–9 bar, and 0.352–1.41 s·g-cat/mol, respectively. The H₂ to n-heptane molar ratio was fixed at 9:1. The analyses of the reaction products were performed by GC-FID.

The experimental data of the conversion of n-heptane was used to carry out the kinetics of the reaction. For this, the regression of the experimental data in the stable region and in the deactivation region was carried out using a Fortran subroutine where in each case the sum of squares of the errors (SSE) was used as the objective function. Discrimination among the rival models was carried out based on SSE, F-value, t-values of the parameters, and kinetic significance of the parameters. By kinetic significance we mean the parameters are valid in the kinetic sense, i.e., rate constant or adsorption equilibrium constants are not negative and the values of the kinetic parameters are not significantly wavered giving unrealistically high or low values.

III. RESULTS AND DISCUSSION

For heterogeneous catalytic reactions, power law kinetics is generally not considered suitable as it does not take into account the presence of catalyst. A more realistic approach is to use Langmuir-Hinshelwood-Hougen-Watson (LHHW) theory which takes care of the adsorption-desorption phenomenon in the development of the kinetic rate equations [12]. The LHHW kinetic expressions can be developed assuming single-site surface reaction or dual-site surface reaction mechanisms. In a dual-site surface reaction mechanism, two active sites are involved in carrying out the surface reaction.

In a commonly accepted mechanism for the n-heptane hydroisomerization over a bifunctional catalyst, n-heptane initially undergoes dehydrogenation on a metal site to a respective heptene. The heptene so produced is then protonated and isomerized on an acid site. The isomerized heptene product is then deprotonated on an acid site and finally hydrogenated on a metal site to produce the corresponding isomerized heptane product.

Usman and Alotaibi [1] simplified the complex kinetic mechanism of isomerization by assuming that two sites are required for the surface reaction of hydroisomerization. They reasoned that hydrogenation-dehydrogenation occurs on one site and protonation-isomerization-deprotonation occurs on another site. Based on this dual-site mechanism and the

Langmuir-Hinshelwood-Hougen-Watson theory, Usman and Alotaibi [1] developed various kinetic model equations and tested them against the experimental data obtained over a range of fresh catalysts (in the stable region of the catalysts).

For the kinetic investigation in the present study, the kinetic models of Usman and Alotaibi [1] are fitted against the experimental data of two Pt-zeolite Y catalysts. For this purpose, the experimental tubular reactor was assumed to behave as one-dimensional plug flow reactor and the following differential equation was solved:

$$\frac{dX_A}{d\left(\frac{W}{F_{A0}}\right)} = (-r_A) \quad (1)$$

where, X_A is n-heptane conversion, W is weight of catalyst, F_{A0} is initial molar flowrate of n-heptane, and $(-r_A)$ is rate of consumption of n-heptane.

For each of the catalysts, the model equation based on the surface reaction (dehydrogenation-isomerization-hydrogenation) rate controlling with negligible inhibition caused by hydrogen was found as the best-fit kinetic expression. For both of the catalysts, various deactivation kinetic models (Table II) such as linear, power law, and exponential were also used with the best-fit kinetic rate equation obtained for the stable region of the catalysts. The following combined rate model was found suitable for each of the catalysts:

$$(-r_A) = \frac{kK_A p_A}{(1 + K_A p_A + K_B p_B)^2} A_0 t_d^{-k_d} \quad (2)$$

where, k is rate constant, K_A is adsorption equilibrium constant for n-heptane, K_B is adsorption equilibrium constant for the isomerized product, p_A is partial pressure of n-heptane in the reaction mixture, p_B is partial pressure of the isomerized product in the reaction mixture, A_0 is some deactivation parameter, t_d is deactivation time, and k_d is deactivation rate constant.

The temperature dependency of the rate constant was given by the following type of equation:

$$k = k_r \exp\left(B\left(1 - \frac{T_r}{T}\right)\right) \quad (3)$$

where, T is temperature of reaction, k_r is rate constant at reference temperature T_r defined below, and B is Arrhenius number or dimensionless activation energy defined as:

$$B = \frac{E}{RT_r} \quad (4)$$

T_r is taken as the average temperature (503.15 K) of all the temperatures studied in the experiments, E is activation energy, and R is universal gas constant. The form of the Arrhenius equation shown in Eq. 3 provides numerical convenience and facilitates in the convergence of the kinetic models subjected to the regression [13].

The temperature dependency of the adsorption equilibrium constants was given by:

$$K_i = K_{ir} \exp\left(B_i\left(1 - \frac{T_r}{T}\right)\right) \quad (5)$$

where, B_i is dimensionless heat of adsorption give by:

$$B_i = \frac{\Delta h_i}{RT_r} \quad (6)$$

Δh_i is enthalpy of adsorption of a component and R is gas constant.

The results of the regression of the experimental data for the two catalysts are shown in Table I and the parity chart between the model conversions and the experimental conversions for CAT-1 is shown in Fig. 1. For the stable catalyst region, the model equation (Eq. 2) slightly fitted better for CAT-2 giving lower SSE value and higher F-value. For CAT-1, the dimensional heat of adsorption is found positive, whereas it is negative for CAT-2. A positive value shows an endothermic adsorption process, while negative value determines an exothermic adsorption process.

Adsorption processes usually occur by the release of heat energy though the opposite is also possible. CAT-1 has given higher activation energy (130.5 kJ/mol) than CAT-2 (103.7 kJ/mol) suggesting increased effect of temperature on the rate of reaction for CAT-1. Activation energy for both the catalysts, in the range of 103.7–130.5 kJ/mol, is in line with the literature findings. Remy *et al.* [7] obtained apparent activation energies in the range of 125–140 kJ/mol, while doing experiments over eight Pt/zeolite Y samples. Holló *et al.* [8] reported an apparent activation energy of 118 kJ/mol with Pt-loaded H-mordenite and Saberi and Le Van Mao [9], on Pt-HY and Pt-Zn-HY zeolite catalysts, have found apparent activation energies of 94 and 143 kJ/mol, respectively.

TABLE I: RESULTS OF CATALYST CHARACTERIZATION AND KINETIC MODELING

Catalyst	Catalyst characterization	Parameters for fresh catalyst			Deactivation parameters	
CAT-1	<u>1.0wt%Pt/USY</u>	k_r (mol g-cat ⁻¹ s ⁻¹)	2.78×10^{-5}	A_0 (day ^{kd})	0.910	
		B	31.2	k_{dr}	7.75×10^{-2}	
	Si/Al (bulk molar)	2.90	E (kJ/mol)	130.5	B_d	3.74
	N ₂ -BET (m ² /g)	735.87	K_{Ar} (bar ⁻¹)	8.20	E_d (kJ/mol)	15.64
	Pore volume (cm ³ /g)	0.39	B_A	16.7	SSE	0.086
	Pore size (Å)	34.52	K_B (bar ⁻¹)	10.3	F	145.7
	Pt content (wt%)	0.83	SSE	0.049		
	NH ₃ -TPD (mmol/g)	0.30±0.01	F	146.1		
CAT-2	<u>1.0wt%Pt/USY</u>	k_r (mol g-cat ⁻¹ s ⁻¹)	2.84×10^{-5}	A_0 (day ^{kd})	1.12	
		B	24.8	k_{dr}	6.34×10^{-2}	
	Si/Al (bulk molar)	5.55	E (kJ/mol)	103.7	B_d	14.6
	N ₂ -BET (m ² /g)	872.97	K_{Ar} (bar ⁻¹)	9.67	E_d (kJ/mol)	61.08
	Pore volume (cm ³ /g)	0.47	B_A	-1.24	SSE	0.031
	Pore size (Å)	26.10	K_{Br} (bar ⁻¹)	9.73	F	384.9
	Pt content (wt%)	0.90	B_B	8.93		
	NH ₃ -TPD (mmol/g)	0.76±0.01	SSE	0.035		
		F	228.1			

TABLE II: DEACTIVATION MODELS TESTED IN THE PRESENT STUDY

Deactivation model	Mathematical form
Linear	$1 - k_d t_d$
First order power law	$k_d t_d$
Exponential	$e^{-k_d t_d}$
Reciprocal power law	$A_0 t_d^{-k_d}$

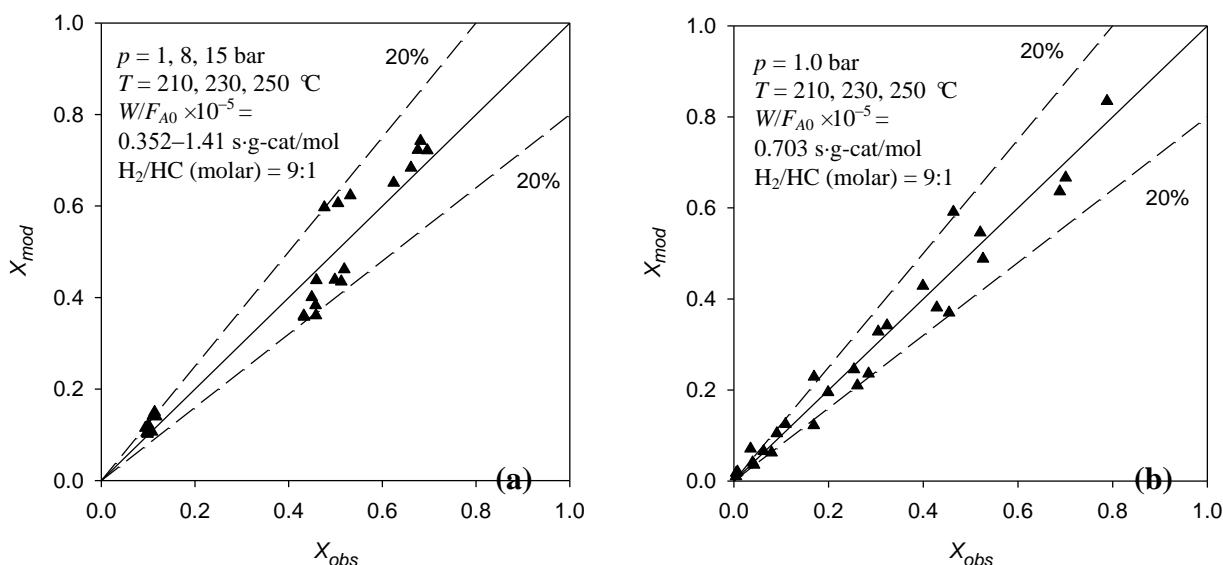


Fig. 1. Parity diagram for: a) the kinetic modeling over fresh CAT-1 and b) deactivation kinetics over CAT-1.

Comparing the kinetics of the two catalysts, it is observed that the catalyst (CAT-2) with higher surface area, Si/Al ratio, pore volume, and acidity has shown decreased activation energy for the stable region, whereas it provided relatively high activation energy of 61.08 kJ/mol, compared to 15.64 kJ/mol for CAT-1, for the deactivation kinetics. With both catalysts, low activation energy of the deactivation was obtained; representing the temperature has reduced effect on the deactivation of the catalysts at least in the range of temperatures studied in the present work. This may be due to the fact that the operating temperatures for the hydroisomerization reaction are lower (210 to 250 °C) and also the range between the maximum and minimum temperatures studied is only 40 °C.

IV. CONCLUSION

The experimental data for the n-heptane hydroisomerization over two different Pt-zeolite Y catalysts has been kinetically modeled both for the stable region (over the fresh catalyst) and the deactivation region.

The equation below, developed based on LHHW (Langmuir-Hinshelwood-Hougen-Watson) theory for the dual-site surface reaction, is found appropriate in fitting the experimental data for both the fresh and the deactivation regions of the catalysts.

$$(-r_A) = \frac{kK_A P_A}{(1 + K_A P_A + K_B P_B)^2} A_0 t_d^{-k_d}$$

For the stable region, activation energy for both the catalysts was found in the range of 103.7–130.5 kJ/mol which is in accordance to the literature findings.

Low activation energies (15.64–61.08 kJ/mol) for the deactivation process especially for the lower surface area and lower Si/Al ratio catalyst show temperature has little effect on the rate of deactivation for the conditions studied in the present work.

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