Kinetic Modeling of Light Naphtha Isomerization on Pt/Cl-Al_2O_3 Catalyst

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Abstract
To kinetic modeling of light naphtha isomerization depending on acid site concentration of Pt/Cl-Al_2O_3 catalyst, the mechanism of the reaction has been discussed. This reaction includes three steps: paraffin dehydrogenation, olefin isomerization, and branched olefin hydrogenation. It is supposed that paraffin dehydrogenation and hydrogenation of branched olefin are in chemical equilibrium. Equilibrium constants of these reactions have been calculated. These have been used instead of reactants and product concentrations in the total rate model. The isomerization of normal olefin includes three steps. Such as normal olefin adsorption on acid sites, normal olefin branching, and desorption of branched olefin. It is assumed that the differential concentrations of reactants on acid sites are small, therefore the rates of these reactions are equal. The model in general form would be obtained when rate equations are solved by MATLAB. It is assumed that each step could be a rate controller. So, the general model can be simplified into three forms. At last, each model is tested with authorized investigation data. Rate dependency on catalyst acidity is measured in two states for each of the models: a whole total Lewis and Bronsted acid sites, and just Bronsted acid sites. The results show, that the models, which are obtained by isomerization and adsorption rate controlling steps, show acceptable results. If the catalyst production temperature increases to 300 ℃ and the concentration of Bronsted acid sites is less than 0.130 mmol. gr^{-1} CAT, placing the concentration of Bronsted sites in the model without considering the concentration of Lewis sites shows more accurate results in calculating the overall reaction rate.

Keywords: Light Naphtha Isomerization Kinetic, Chlorinated Alumina Acidity, Pt/Cl-Al_2O_3 Catalyst
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Introduction

Industrial processes are complex set of reactions affecting each other, so it is necessary to design a model that takes into account all the details of the reactions. As, it is possible to mention the modeling of light naphtha isomerization processes (Surla et al., 2011), catalytic cracking (Feng, 1993), hydrocracking (Guillaume, 2011). Naphtha isomerization is one of the present reactions in catalytic conversion process of heavy naphtha. Since the 1950s, Metal-acid bifunctional catalysts have been of the upmost importance in industrial processes. Then their application has expanded

to a myriad of industrial processes, the most acknowledged being hydrocracking (Pascal and Hervé, 2013). The tuning of the ratio of metal to acid sites in this type of catalyst is one key parameter for optimal performance. Indeed, a strong predominance of one function or the other will not only impair the bifunctional mechanism; it can also benefit monofunctional pathways. This concept was first described by Weisz (1962) in the form of an intimacy criterion which indicates the maximum distance between the metal and acid functions for which there is no mass transport inhibition. This is particularly critical for the mechanical mixtures of two monofunctional components. When working with model molecule reactions and with catalysts in which the metal function has been impregnated directly of an acid support, diffusional limitations are not critical. This is apparent in the criteria needed to achieve the "ideal bifunctional catalyst" as described by Guisnet (2013). The number of acid catalyzed steps is characteristic of the intimacy between metallic and acid sites in Pt/(Al_2O_3)-HBEA catalysts (Batalha et al. 2013). The concept of ideal bifunctionality has been widely used in the study of hydroisomerization and hydrocracking reactions, so that "ideal bifunctionality" and "ideal hydrocracking" are sometimes used interchangeably (Samad, et al. 2016). The model catalyst of Pt/zeolite is overwhelmingly used in bifunctionality studies and it has allowed for the two key parameters, metal/acid balance and inter-site distance, to be varied with relative ease. Progressively increasing the Pt loading increases the metal/acid balance (Gutierrez-Acebo et al., 2018; Mendes, 2017). Samimi (2021) showed the catalyst is highly active at 80-100 °C; however, due to corrosion, environmental issues, and the lack of appropriate selectivity, it has not been commonly used. Results revealed that, the best range of temperature of light Naphtha in feed was less 30 ℃, pressure of recycle gas was more than 35 bar, the H_2/HC was less than 0.05, conditions of feed (temperature was less than 35 ℃, pressure was more than 19 bar), optimum pH was less than 5.5 and the ratio of metal and acidic site in catalyst was under 6. Abdolkarimi et al. (2022) presented a data-driven adaptive model is developed to predict the variables indicating gasoline quality in the light naphtha isomerization process and determine the optimal conditions leading to improved gasoline quality. The variables that indicate gasoline quality are research octane number (RON), benzene volume percentage (BVP), and Reid vapor pressure (RVP). In addition to the influential operating variables of pressure, temperature, feed weight hourly space velocity (WHSV), and hydrogen to naphtha feed molar ratio, the model considers benzene's feed concentration and cycloparaffin content. Experiments was conducted using commercial Pt/Al_2O_3-CCl_4 catalyst in a pilot-scale packed-bed reactor. The optimal conditions were computed using the DLS-SVR model and co-evolutionary particle swarm optimization algorithm (CPSO). The optimal operation of the reactor yielded a 6.78-unit increase in gasoline RON and a minimum BVP of 0.394 %. The results demonstrate that the proposed DLS-SVR model can accurately predict the variables indicating the quality of isomerate gasoline. Due to the concerns that exist in the world about aromatic compounds and benzene in the structure of gasoline, its removal has been the focus of environmental organizations in the world. Although the research of researchers to find a suitable additive continues, the isomerization process of pentane and hexane can act as a suitable substitute to increase the octane number of gasoline (Meyers, 2016). Many studies have been conducted on the kinetics of the isomerization process of normal pentane and normal hexane on different catalysts (Holló et al.; 2002; Hosten, et al., 1971).

The purpose of this research is to present a kinetic model of light naphtha isomerization according to the concentration of acid sites of Pt/Cl-Al_2O_3 catalyst, the concentration of raw materials and products.

Method

In this research, a model including dehydrogenation of paraffin and hydrogenation of branched olefins is proposed for the isomerization reaction of light naphtha. Dehydrogenation of paraffin and hydrogenation of olefins are considered steps in equilibrium. The equilibrium constants of these reactions are calculated and they are used instead of the respective concentrations in the final rate equation. It is assumed that the isomerization stage of olefins includes the absorption of normal olefins on the active sites, the branching of normal olefins, and the removal of branched olefins. Assuming that the conditions are stable, the reaction speed is assumed to be the same in all 3 stages, and by solving the resulting device in MATLAB software, a solution for the overall speed equation is obtained. Assuming that each step is the slowest step and controls the overall speed of the reaction, the overall speed model is summarized for each of the 3 mentioned steps. Finally, each model has been tested with the data of a valid article. The concentration of effective acidic sites in the two states are placed and tested in the speed models: 1- the sum of Lewis and Bronsted acidic sites and 2- the concentration of Bronsted acidic sites.

Results

The mechanism of the isomerization reaction depends on whether the catalyst is monofunctional or bifunctional (Ono, 2003). In both types of catalysts, the formation and branching stage of carbenium ion is the most important stage of isomerization. For the concentration of all acidic sites, the following relationship is established:

$$C_t = C_I + \hat{C}_M + \hat{C}_N \rightarrow C_I = C_t - \hat{C}_M - \hat{C}_N,$$

M= Normal olefin, N= Branched olefin, C_M= The concentration of M in the boundary layer, $\hat{C}_M$ = The concentration of M adsorbed on the active surface of the catalyst, $\hat{C}_N$ = The concentration of N adsorbed on the active surface of the catalyst, C_N = N concentration in the boundary layer, C_t = The concentration of all acid sites, C_I = Concentration of empty acid sites.

The absorption rate of M on the active site (similar to the reaction rate of step 3) is equal to:

r_3 =The absorption rate of M- the excretion rate of M.

$$r_3 = k_M C_M C_l - k_M^{-1}\hat{C}_M = k_M C_M\left(C_t - \hat{C}_M - \hat{C}_N\right) - k_M^{-1}\hat{C}_M \quad (1)$$

k_M= Rate constant of the absorption reaction (M), k_M^{-1}= The rate constant of the elimination reaction (M).

The reaction rate of converting M to N on the active surface of the catalyst is equal to:

$$r_4 = k_{isom}\hat{C}_M - k_{isom}^{-1}\hat{C}_N = k_{isom}^{-1}\left(K_{sr}\hat{C}_M - \hat{C}_N\right) \quad (2)$$

The rate of removal of N from the active site, which is the same rate as the reaction of step 5, is as follows:

$r_5 =$ The excretion rate of M - the absorption rate of M.

$$r_5 = k_N^{-1}\hat{C}_N - k_N^{-1}\hat{C}_N\left(C_t - \hat{C}_M - \hat{C}_N\right), \quad (3)$$

k_N= The rate constant of N absorption reaction, $k_N^{-1} =$ The rate constant of the N disposal reaction. The velocity equations can be written as follows:

$$K_M = \frac{k_M}{k_M^{-1}}, K_N = \frac{k_N}{k_N^{-1}}, K_{sr} = \frac{k_{isom}}{k_{isom}^{-1}},$$

$K_M =$ Equilibrium constant of normal olefin adsorption reaction (M), $K_N =$ Equilibrium constant of branched olefin elimination reaction (N), $K_{sr} =$ Equilibrium constant of normal isomerization reaction of olefin on acidic site.

Assuming that there is no rate-controlling step and that the changes in M and N concentrations are insignificant at different times (the reaction is stable on the acid site), the reaction speed is equal in all three steps:

$$r_M = r_3 = r_4 = r_5.$$

In the obtained model, the overall rate equation is normal olefin isomerization without considering the rate controlling step. In order to obtain the reaction speed in terms of measurable variables, $\hat{C}_M$ and $\hat{C}_N$ should be calculated in terms of other variables, therefore, assuming the normal reaction stage of olefins on the acid site is the speed controller, the solution of the device is three equations and three Unknowns (1), (2) and (3) using MATLAB (R 2022) software, the speed equation is summarized as follows:

$$k_M, k_N \gg k_{isom} \rightarrow r_M = \frac{k_{isom}K_M C_t\left(C_M - \frac{C_N}{K}\right)}{1 + K_M C_M + K_N C_N},$$

$$K = \frac{K_{sr}K_M}{K_N}.$$

The isomerization rate equations of olefins can be generalized to the isomerization rate equations of paraffin by multiplying the equilibrium coefficient of hydrogenation reaction in K_M and dehydrogenation in K_N. The rate equation of paraffin isomerization, taking into account that the olefin isomerization step on the acid site is the rate controlling step as follows:

$$k_M, k_N \gg k_{isom} \rightarrow r_A = \frac{k_{isom}K_M K_D C_t\left(C_A - \frac{C_B}{K}\right)}{p_{H_2} + K_M K_D C_A + \frac{C_B}{K_N K_H}}.$$

Assuming that the linear olefin absorption step is the rate controller of the reaction:

$$k_{isom}, k_N \gg k_M \rightarrow r_A = \frac{k_{isom} K_D C_t (C_A - \frac{C_B}{K})}{p_{H2} + \frac{C_B}{K_N K_H K_{sr}} + \frac{C_B}{K_N K_H}}.$$

Assuming that the branched olefin elimination step is the rate controller of the reaction:

$$k_{isom}, k_M \gg k_N \rightarrow r_A = \frac{k_{isom} K_M K_D K_{sr} C_t (C_A - \frac{C_B}{K})}{p_{H2} + K_M K_D C_A + K_M K_D K_{sr} C_A}.$$

Determination of equilibrium constants from thermodynamic relationships:

$\Delta G_f^0(I) =$ Gibbs free energy of a mixture of isomers of a group under standard conditions, $\Delta G_f^0(i) =$ Gibbs free energy of the i-th isomer in standard conditions,

N= The number of hydrocarbon isomers,

x_i =The molar component of the i-th compound.

The total Gibbs energy changes in the normal mixture of paraffin and their isomers are calculated from the following relations:

$$\Delta G_f^0(I) = \sum_{i=1}^{N_I} x_i \, \Delta G_f^0(I) + RT \sum_{i=1}^{N_I} x_i \, ln x_i,$$

$$ln \frac{K_2}{K_1} = \frac{-\Delta H_r}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right],$$

$$\Delta H_r = \Delta H_f^{Product} - \Delta H_f^{Reactant},$$

$$\Delta H_f^0(I) = \sum_{i=1}^{N_I} x_i \, \Delta H_f^0(I).$$

ΔH is enthalpy of reaction. To calculate ΔH of each reaction, data related to the enthalpy of formation of normal paraffin and their isomers and normal olefins and their isomers are required. This information is available in Alberti's article (Alberty and Gehrig 1984). Using the data of Alberty and Gehrig's article, the equilibrium constant is calculated. These values can be obtained with a reference temperature (for example, 298 degrees Kelvin (K)) and then extended to other temperatures. Also, the Gibbs free energy of elements, such as hydrogen, is zero.

$$n - Pentane \rightleftarrows 1 - Pentene + H_2,$$

$$\Delta G_r^{298} = \Delta G_f^{1-Penten} - \Delta G_f^{n-Pentane} = 79.25 - (-8.33) = 87.58\ KJ\ mol^{-1},$$

$$K_D^{298} = exp\left(\frac{-\Delta G_r^{298}}{RT}\right) = exp\left(\frac{-87580}{8.314 \times 298.15}\right) = 4.52 \times 10^{-1}\ ,$$

$$\Delta H_r^{298} = \Delta H_f^{1-Pentene} - \Delta H_f^{n-Pentane} = -20.9 - (-146.4) = 125.4\ KJ\ mol^{-1}.$$

Having the reaction temperature T_2, the dehydrogenation coefficient at that temperature (K_{D_2}) is calculated as follows:

$$ln\frac{K_{D_2}}{4.52\times10^{-16}} = \frac{-\Delta H_r}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{-125480}{8.314}\left[\frac{1}{T_2} - 3.35 \times 10^{-3}\right].$$

Normal dehydrogenation of hexane is similar to normal dehydrogenation of pentane. At the temperature of 298.15 degrees Kelvin (K) and using the data of Alberty and Gehrig's article:

$$n - Hexane \rightleftarrows 1 - Hexene + H_2,$$

$$\Delta G_r^{298} = \Delta G_f^{1-Hexene} - \Delta G_f^{n-Hexane} = 87.61 - (-0.01) = 87.62\ KJ\ mol^{-1},$$

$$K_D^{298} = exp\left(\frac{-\Delta G_r^{298}}{RT}\right) = \exp\left(\frac{-87620}{8.314\times298.15}\right) = 4.45 \times 10^{-16}.$$

In the same way the other equilibrium constants for hexane are calculated and presented in Table 1.

Table 1. Equilibrium constants calculated for the normal isomerization rate equation of hexane Researcher's findings.

Temperature (°C)	K	K_D	K_H	K_M	K_N
150	3.27	1.29×10^{-9}	4041739.7	$3.77\times10^{+19}$	2.65×10^{-20}
200	1.85	5.54×10^{-8}	139799.2	$9.95\times10^{+14}$	1×10^{-15}
250	1.16	1.16×10^{-6}	9198.6	$1.97\times10^{+11}$	5.08×10^{-12}
300	0.79	1.44×10^{-5}	973	$1.73\times10^{+8}$	5.80×10^{-9}
350	0.57	1.19×10^{-4}	147.6	$4.68\times10^{+5}$	2.14×10^{-6}

Table (1) shows the calculated equilibrium constants for the normal isomerization rate equation of hexane. In the kinetic equation, in order to calculate the reaction rate constant, it is necessary to calculate the activation energy and projection factor. Due to the unavailability of these values in Chu's article (1998), was used Bursian's (1974) article information to calculate them. The

activation energy is considered as the average of these values and its value is 46 kJ/mol. Therefore, using the given rate equation, the reaction rate is calculated. The partial pressure of hydrogen in terms of atmosphere is calculated as follows:

$$p_{H_2} = 20Kg(cm^2)^{-1} \times 9.80665 \frac{Pa}{Kg(cm^2)^{-1}} \times \frac{1}{1.013 \times (10)^5 \frac{Pa}{atm}} = 19.3616atm$$

Having H_2/HC ratio and using the ideal gas law, the number of normal moles of pentane in the feed is calculated and then its partial pressure is obtained. Because the molecular mass of normal pentane and isopentane is the same, their weight and molar percentages are also the same:

$$p_{nC_5} = p_{H_2} \times \frac{n_{HC}}{n_{H_2}} \times \frac{n_{nC_5}}{n_{HC}} \times R \times T,$$

$$= \left(\frac{19.3616 \times 1}{8.314 \times (130 + 273.15)}\right) \times \frac{1}{2} \times 0.993 \times 8.314 \times (130 + 273.15) = 9.61303atm.$$

The same method is used to calculate the initial partial pressure of isopentane. The produced amount of isopentane is subtracted from the initial amount:

$$p_{iC_5} = \left(\frac{19.3616 \times 1}{8.314 \times (130 + 273.15)}\right) \times \frac{1}{2} \times (0.7 - 0.07) \times 8.314 \times (130 + 273.15)$$
$$= 6.1atm.$$

Considering that the reaction rate constant at 130 ℃ is equal to K=79.2×10^{-3} and the equilibrium constant is 5.32 K, the reaction rate is calculated as bellow:

$$r = \left[k_{rev}\left(\frac{P_{nC_5}}{P_{H_2}}\right)^{0.125} - 0.0000197t\right] \times \left[KP_{nC_5} - (K+1)P_{iC_5}\right]$$

$$= \left[2.79 \times 10^{-3} \times \left(\frac{9.61}{19.36}\right)^{0.125}\right] \times [5.32 \times 9.61 - (5.32 + 1) \times 6.1]$$
$$= 9.73 \times 10^{-1} atmhr^{-1}.$$

$$r = \frac{C_t K_{isom} K_A K_D (P_{nC_5} - \frac{P_{iC_5}}{K})}{P_{H2} + K_A K_D P_{nC_5} + \frac{P_{iC_5}}{K_H K_R}},$$

$$9.73 \times 10^{-1} atmhr^{-1} = \frac{0.736 \times K_{isom} \times 3.63 \times 10^{12} \times 2.26 \times 10^{-1} \times (9.61 - \frac{6.1}{6.08})}{19.36 + .63 \times 10^{12} \times 2.26 \times 10^{-10} \times 9.61 \frac{6.1}{8.29 \times 10^7 \times 2.75 \times 10^{-13}}},$$

$$K_{isom} = 4.96 \times 10^4 mol(mol\ Acid\ Sites.h.atm)^{-1},$$

$$K_{isom} = A_{isom} \times exp\left(\frac{-E_\alpha}{RT}\right) \Longrightarrow 4.96 \times 10^4 = A_{isom} \times exp\left(\frac{-46000}{8.314 \times (130 + 273.15)}\right),$$

$$A_{isom} = 4.53 \times 10^{10} mol(mol\ Acid\ Sites.h.atm)^{-1}.$$

Table 2: The calculated speed comparison of the model with the actual speed (Researcher's findings).

Catalyst production temperature (℃)	150			200			300		
Bronsted sites concentration [mmol. gr^{-1} CAT]	0.214			0.221			0.131		
Model	Calculated rate	Effective acidic sites	% Error	Calculated rate	Effective acidic sites	% Error	Calculated rate	Effective acidic sites	% Error
$r_A = \frac{K_{isom}K_MK_DC_t(C_A - \frac{C_B}{K})}{P_{H2} + \frac{K_MK_DC_B}{K} + \frac{C_B}{K_NK_H}}$	0.058	Bronsted +Lewis2	-14	0.056	Bronsted +Lewis2	-7	0.03	Bronsted	10
$r_A = \frac{K_{isom}K_MK_DC_t(C_A - \frac{C_B}{K})}{P_{H2} + \sqrt{\frac{K_MK_DC_B}{K}} + \frac{C_B}{K_NK_H}}$	0.058	Bronsted +Lewis2	-14	0.056	Bronsted +Lewis2	-7	0.029	Bronsted	-10
$r_A = \frac{K_{isom}K_MK_DC_t(C_A - \frac{C_B}{K})}{P_{H2} + \frac{K_MK_DC_B}{K} + \frac{C_B}{K_NK_H}}$	0.054	Bronsted +Lewis2	-19	0.053	Bronsted +Lewis2	-12	0.028	Bronsted	3
$r_A = \frac{K_{isom}K_MK_DC_t(C_A - \frac{C_B}{K})}{P_{H2} + \frac{K_MK_DC_B}{K} + \frac{C_B}{K_NK_H}}$	0.058	Bronsted +Lewis2	-14	0.056	Bronsted +Lewis2	-7	0.03	Bronsted	10

In Table (2), the values of the actual speed of the reaction in the above conditions in different concentrations of acidic sites have been calculated and compared. The results show that by increasing the catalyst production temperature to 300 ℃, the concentration of Bronsted sites in the model, regardless of the concentration of Lewis sites, shows more accurate results in calculating the overall reaction rate. If Bronsted acid sites concentrations are less than 0.130 mmol. gr^{-1} CAT, it is favorite to consider just Bronsted acid sites concentration in model. On the other hand, if Bronsted acid sites concentrations are more than 0.130 mmol. gr^{-1} CAT, it is better to consider both of Bronsted and Lewis acid sites.

Discussion and conclusion

In this research, a mechanism was considered for the isomerization reaction of light naphtha. A solution was obtained for the general rate equation. Finally, each model has been tested with the data of a valid article. The results showed that the catalyst manufacturing temperature should increase up to 300 ℃, putting the concentration of Bronsted sites shows more accurate results in calculating the overall reaction speed without considering the concentration of Lewis sites. Because the activation energy is always positive and the temperature has a direct relationship with the reaction rate constant. Although increasing the pressure does not change the equilibrium concentrations, it reduces the speed of reaching these concentrations (Raseev, 2003). In addition to decreasing the rate of isomerization, increasing the pressure also decreases the rate of the coking and cracking reaction. The optimal pressure depends on the type of catalyst. Increasing the pressure improves the selectivity of the reaction towards isomerization. While the selectivity of the cracking reaction and the conversion rate decrease. A higher molar ratio of hydrogen to feed ratio (H_2/HC) has a positive effect on the performance of the catalyst, considering the prevention of coke formation, and increases the stability of the catalyst over time (Tomishige et al., 2000). In the same operating conditions, with the increase in hydrogen to feed ratio, the feed conversion rate increases, but the selectivity is optimal only in a certain ratio. The existence of aromatics is one of the serious problems of industrial isomerization units. Usually, aromatics should not make up more than 5% of the weight of food. These substances release heat of about 208 kcal/mol in the hydrogenation reaction of olefins (Sherman, J. (1939). Therefore, the temperature in the reactor increases up to 60 degrees Celsius. Increasing temperature is harmful to isomerization reactions. The concentration of acid sites is directly related to the reaction speed. Based on Table (2), it is suggested that the catalyst of the sum of Bronsted and Lewis type II concentration should be considered in Bronsted site concentrations less than 0.131 mmol. gr^{-1} CAT. Also, in concentrations higher than 0.131 mmol. gr^{-1} CAT, only the concentration of Bronsted locations should be considered. Isomerization and cracking of hydrocarbons are both performed on acidic sites. Increasing the concentration and strength of acid sites accelerates the reaction. In the isomerization process, the cracking reaction is an undesirable reaction.

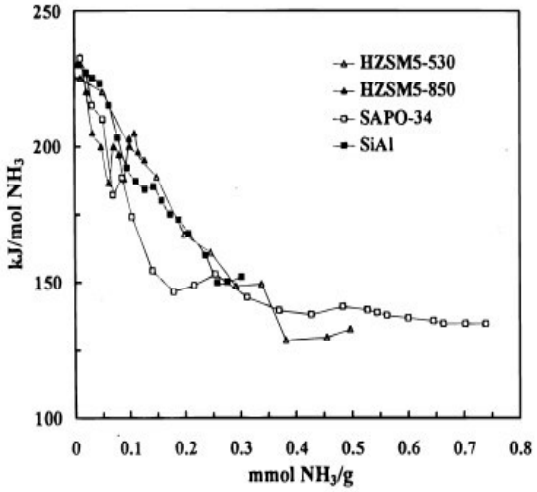


Figure 1: The strength and number of acid sites in some types of the zeolite base catalysts.

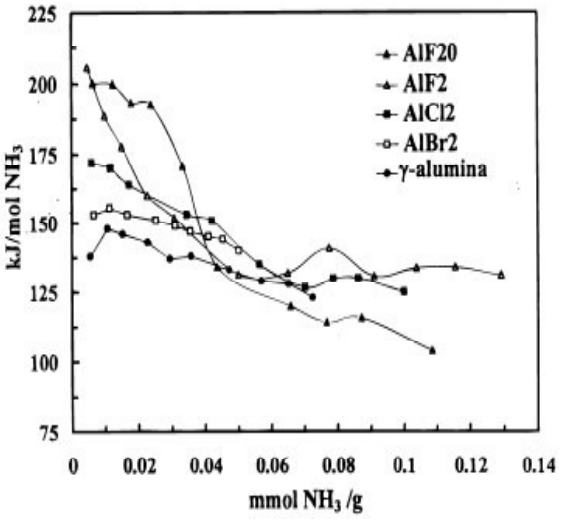


Figure 2: Strength and number of acid sites in some types of the alumina base catalysts.

Table 3: The effect of calcination temperature on selectivity and activity of the halogenated alumina catalysts for 1-butene isomerization (Llorens et al. 1998).

	Calcination conditions of the catalyst	Reaction conditions			Distribution of products		
Catalyst	Temperature (°C)	Time (hours)	Temperature (°C)	Time (hours)	Molar percentage of 1 and 2 carbon products	The molar percentage of products with more than 5 carbons	Molar butene percentage
AlF1	500	1	400	0.195	30.4	22.1	47.5
AlF1	550	1	400	0.195	13.6	26.9	59.5
AlF1	550	4	400	0.195	3.4	31.0	65.6
AlF2	500	1	400	0.195	7.3	61.0	31.7
AlF2	550	1	400	0.195	6.3	48.0	45.7
AlF2	550	4	400	0.195	4.0	30.6	65.4
AlF20	550	4	400	0.195	5.5	37.6	56.8
AlCl2	500	1	400	0.195	1.2	3.0	95.7
AlCl2	500	1	400	0.250	1	1.5	97.5
AlCl2	500	1	450	0.148	2.2	3.8	94.0
AlCl2	500	1	500	0.148	5.8	9.2	85.0
AlBr2	500	1	400	0.148	0.25	0.40	99.35
AlBr2	500	1	500	0.148	1	1.40	97.6

HZSM-5	530	2	250	0.020	0.3	3.2	93.8
HZSM-5	530	2	300	0.040	11.6	59.7	28.7
HZSM-5	650	2	300	0.020	9.8	2.1	88.1
HZSM-5	650	2	400	0.020	53.3	16.2	30.5
HZSM-5	650	4	300	0.050	9.5	2.21	69.3
HZSM-5	750	2	300	0.072	15.6	62.8	21.5
HZSM-5	850	2	350	0.030	1.3	2.20	78.5
SAPO-34	550	2	450	0.148	2.8	0.5	7.96
SAPO-34	550	2	400	0.148	7.6	0.4	0.92
Si-Al	550	2	400	0.148	5.5	12.9	81.6
Si-Al	650	4	400	0.148	2.8	6.9	90.3
γ-Al_2O_3	500	1	400	0.195	0.5	0.8	7.98
γ-Al_2O_3	550	4	425	0.148	0.2	0.7	1.99

The results of Llorens et al. (1998) showed that cracking mainly occurs for hydrocarbons with more than 6 carbon atoms (Figures 1 and 2). Cracking for hydrocarbons with 3 and 4 carbon atoms is done on acid sites. Cracking has a direct relationship with the number and strength of acid sites. By survey Figures 1 and 2 and Table 3, although the strength and number of total acid sites in zeolite catalysts are more than that of halogenated alumina-based catalysts, their activity and selectivity in the isomerization reaction are much higher. Because the number of Bronsted acid sites is more in halogenated alumina base catalysts. The results of Table 3 show that the higher the calcination temperature of the catalyst, the lower the total number of acid sites. It is suggested for future research:

1- Calculation of the reaction rate model from the single-phenomenon method, taking into account all side reactions,
2- Obtaining a model to calculate the optimal ratio of acid to metal sites.

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