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Review Article

Considering different kinds of gasoline unit catalysts

Amir Samimi[a], Soroush Zarinabadi[b,*], Amir Hossein Shahbazi Kootenaei[a], Alireza Azimi[a], Masoumeh Mirzaei[a]

[a] Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran
[b] Department of Engineering, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran

ARTICLE INFORMATION

ABSTRACT

The aim of this study is to investigate naphtha Gasoline unit catalysts. In two-factor catalysts, platinum or palladium was used as the active metal on the base alumina chloride, zirconia, and zeolite. Considering the fact that refining and gasoline processes are expanding and refineries in Iran are required to produce cleaner fuels that meet environmental standards, investigating different kinds of light naphtha gasoline unit catalysts can greatly help to promote production of clean fuel and make production process more efficient. Light naphtha gasoline is normally conversion of normal pentane and normal hexane compounds to its branched compounds. Also Light naphtha its derivatives and it is done by chlorinated ammonia or zeolite catalysts in one or some fixed bed reactors. Activity of two-factor catalysts strongly depends on acidic and metal sites. For example, in catalyst Pt./HY, which is a kind of zeolite catalyst for Gasoline Units, the optimal ratio of strong acidic sites to metal sites in n-heptane Gasoline is determined to be less than 6. In this work, various kinds of catalysts used in isomerization unit were identified and considered.

Graphical Abstract

Corresponding author, email: soroushzarinabadi@iauahvaz.ac.ir (S. Zarinabadi).
Tel.: +98 916 652 3309

Introduction

The history of catalyst use dates back to 2000 years. The first cases of using catalysts were baking bread and making cheese and wine. Ancient people found that adding a little bit of cooked bread to a new bakery is mandatory. In 1835, Brazil collected and summarized the observations of former chemists, and stated that small quantities of a foreign agent could seriously affect chemical reactions [1]. This mysterious force applied to materials was called the catalytic force. In 1894, Stallard developed the theory of Brazilius. He stated that the catalysts are substances that increase the speed of chemical reactions without consuming them. Today, catalysts play a major role in the global economy [1]. Catalyst is a substance affecting the reaction however; it will remain unchanged at the end of reaction. In chemistry, catalysis changes the reaction speed by creating a different molecular pathway (mechanism) for the reaction. "Catalytic" is the study and use of catalysts and the creation of catalytic processes. The industrial catalysts are of immense importance. About one-third of GNP in the United States has used catalysts at least in one part of the production process. Usually, when talking about a catalyst, the reaction speed increases in our minds, while the catalyst it can quickly accelerate or slow down the formation of a specific product type [2]. A catalyst only changes the reaction speed and does not affect the balance. In other words, the speed of reaching the equilibrium point is changed.

Gasoline Units

Naphtha gasoline is one of the reactions exists in heavy naphtha catalytic conversion process and it has been investigated with other reactions and independently. The first gasoline catalyst was aluminium chloride, which used in 1933 by Nenitescu and Dragan [1]. The catalyst

is highly active at ranging from 80 °C to 100 °C. However, due to corrosion, environmental issues, and the lack of selectivity, it was not used a lot [2]. Also, due to the fact that conversion catalysts react at 320-450 °C and gasoline is not properly at this temperature, this catalyst could not show good activity in gasoline of light alkanes. Many studies have been conducted on the kinetics of gasoline process of normal pentane and normal hexane on different catalysts. Initial studies have been conducted on catalytic conversion and kinetic data are presented mainly for the temperatures above 370 °C [3].

Heterogeneous Industrial Catalysts

The first industrial-scale heterogeneous catalytic process was carried out in 1875. In this process, platinum was used oxidize SO_2 to SO_3, which was produced by sulphuric acid after being absorbed into the aqueous solution. Platinum is not suitable to be used with vanadium oxide and potassium sulphate on silica, and is replaced with the first industrial-scale heterogeneous catalytic process. These catalysts are more resistant to poisoning and today they are used in SO_2 reactors.

In addition, catalytic reactions of another purpose were introduced by various scientists. Among these are the extensive studies by Stawald in 1903 on ammonia oxidation on platinum gratings to produce nitrous oxide for conversion to nitric acid, the synthesis of ammonia from its constituent elements during the years 1908 to 1914 in the process presented. Also Bush was using the catalyst that Mitsch introduced, methanol production of carbon monoxide and hydrogen occurred in the Fisher-Tropsch process in the 1930 s. Partial oxidation of methanol to convert to formaldehyde at an industrial scale that began in Germany in 1890, the conversion of naphthalene to malic anhydride in the industrial scale of the 1920 s

and the conversion of gasoline to malic anhydride in the industrial scale in 1928, was the commercial production of ethylene oxide from oxidation the partial ethylene was made by carbide. In the process of producing crude oil for fuel, the first catalytic process was catalytic cracking, which was carried out in 1937. The refining process, which was done using a molybdenum/alumina catalyst to increase the number of gasoline octane (by ringing the paraffin and dehydrogenating them and producing aromatics), began in the United States and Germany before the 1945-1950. Then, in the 1950 s, this process was performed using platinum/alumina catalyst. The first catastrophic hydrocracking was used in England and Germany before World War II. At the time, this process was relatively uneconomic, but later became more commonplace with the replacement of newer catalysts. Hydride sulfurization and hydrogenation processes have expanded rapidly over the past two decades and are now a major process in the oil industry. Information about some catalysis is mention in Table 1.

The suitability of a catalyst for the industrial process largely depends on three properties including, activity, selectivity, and sustainability. The answer to the question of which of the most important factors is very difficult, since the expectations of each catalyst are different for different processes.

Activity

Activity is a measure of the velocity of one or more reactions in the presence of a catalyst. The reaction rate (r) is calculated with respect to the rate of change of the reactant a material by time relative to the catalyst volume.

r = (Reactant Converts the amount of matter) / (time x catalyst mass or volume) (mol L $^{-1}$ or mol Kg $^{-1}$ h $^{-1}$))

For example, $r\_A = 〚dn〛\_A / (V\,dt)$ or $〚dn〛\_A / (W\,dt)$

If the reaction is primitive, we can consider the velocity to be the product of two independent terms:

$r\_A = f(T)\,f(C\_A)$

The term temperature is usually indicated by Arrhenius's relationship:

$f(T) = k = k\_o\,e^{(-E/RT)}$

E: activation energy

k_o: frequency of collision

R: Fixed gases

T: Absolute temperature

The expression concentration is expressed by the power of CA.

Note: The primary response is the mechanism that can be easily represented by an equation and consists of one step.

The other criterion of catalyst activity is called the turnover frequency. Before describing this parameter for a catalyst site, we will give a brief explanation. In a paper that marks the turning point in the theory of catalysts, Taylor states that the catalyst does not have a reaction at all levels of the catalyst, but only in certain centres or active locations. He called these sites an active site. An active site is a point on the surface of the catalyst, which can create strong chemical bonds with an atom or molecule. Frequency Conversion (TOF) is the number of molecules that respond every second on an active site:

TOF = (volume reaction rate) / (unit volume in site number) = mole / (volume × time) × volume / mol = 1 / time

Sustainability

Chemical, thermal, and mechanical stability of catalyst determines the life of the catalyst in the industrial reactors. Catalyst stability can be expressed in terms of activity or selectivity variation in time. Catalysts that lose their activity during the process can often be

retrieved before they have to be replaced. The overall lifecycle of a catalyst is critical to the economic justification of a process.

Selectivity

The selectivity of a substance is a fraction of the products that matter.

Time Scales in Catalyst

Indicator times in which catalytic events occur at that interval are slightly proportional to the longitudinal scales discussed above. The activation and breakdown of a chemical bond within a molecule occurs within the Pico-

secretion range. Completing the entire reaction cycle from formation of complex between the catalyst and the reactor until the separation of the product can vary from microseconds to the fastest enzyme reaction to a minute for complex reactions on the surface. At the mesoscopic scale, penetration into and out of the cavities through the formation of catalytic particles may take a few seconds to several minutes. The residence time of the molecules inside the reactor varies between seconds and infinitely, which is infinitely time-consuming when it is converted to unwanted products like coke and remains on the catalyst.

Table 1. Profile of Catalyst, Operating Parameters, and the Speed of Reaction in the Process of Gasoline Units

Gasoline Speed Equation	Feed	Catalyst
$r = k_1(\frac{p_A}{p_{H_2}}) - k_2(\frac{p_B}{p_{H_2}})$	n-Butane	Pt./Cl-Al$_2$O$_3$
$r = [k_{rev}(\frac{p_A}{p_{H_2}})^{0.125} - 0.0000197t]$	n-Pentane	Pt./Cl-Al$_2$O$_3$
$r = \dfrac{C_t k_{isom} K_M K_D (p_A - \frac{p_B}{K})}{[p_{H_2} + K_M K_D p_A + \frac{p_B}{K_H K_N}]}$	n-Pentance	Pt./ Al$_2$O$_3$

Conversion Number (Turnover Number)

The conversion number is the maximum use that can be made of a catalyst for a specific reaction under specific conditions. This parameter is measured by the number of molecular reactions that occur with reactive cycles occurring on catalyst sites until activity is lost.

TON = TOF (1 / S) × Catalyst Length (S)

For industrial applications, TON is in the range of 6 10 to 7 10.

In practice, simple performance criteria are often sufficient. For scale measurements such as catalyst selection, optimization and passive studies are sufficient. For comparative measurements such as catalyst selection, optimization and deactivation studies, the following activity criteria can also be used.

➢ Converting under constant reaction conditions
➢ Scope velocity for a constant and specific conversion
➢ The temperature required for a specific conversion

Catalysts are often examined and compared in operational test reactors that are used continuously and where constants are obtained at constant spatial speeds. Spatial velocity is the volume flux (Q) divided by the catalyst mass (W).

Spatial velocity = Q / W (m ^ 3 Kg ^ (- 1) S ^ (-1))

The conversion (XA) is equal to the ratio of the reactive amount A converted to its initial value in the reactor. In the discontinuous reactor, $X\_A = (n\_ (A\_o) -n\_A) / n\_ (A\_o)$ and in the continuous reactor $X\_A = (F\_ (A\_o) -F\_A) / F\_ (A\_o)$.

By comparing the conversion of A at the same spatial velocity, two catalysts can be evaluated. On the other hand, the catalyst can be compared in terms of spatial velocity. Any catalyst with lower spatial speeds requires more catalytic masses. Of course, such measurements should be made at a constant temperature, pressure and ratio of raw material. The other scale is the space-time yield. With this parameter, it is possible to compare reactors of different size and structure.

STY = (optimal amount of product) / (volume catalyst × time) (mol L ^ (-1) h ^ (- 1))

Determining the temperature required for a particular conversion is a dictitious method for comparing catalysts. The catalyst is best to make optimal conversion at a lower temperature. However, this method is not recommended because most kinetics are different at higher temperatures, which increases the likelihood of confusion in interpretation. It is better to measure catalyst deactivation in experimental laboratories.

One-Factor Catalysts

Friedel-Kraft's Catalysts

The most well- known catalyst is aluminium dichloride. This catalyst was the first catalyst used in Gasoline to catalyse the homogeneous reaction [4]. Because of the low temperature (80-100 °C), alkanes gasoline reaction would be conducted well. Now, due to the environmental problems caused by acidic wastewater, the difficulty of separating the catalyst from the product, and corrosion problems, this is not used anymore. A few other examples of these catalysts include: $FeCl_3$-$SbCl_3$. in the presence of a small amount of water, these catalysts form hydroxyl group (OH-), which is highly polar and reinforces gasoline units [5].

Two- Factor Catalysts

In two-factor catalysts, platinum or palladium is used as the active metal on the base alumina chloride, zirconia, and zeolite. Two-factor Gasoline catalysts may be divided into the following types:

➢ Alumina chloride-based catalysts.
➢ Zeolite-based catalysts such as: H-Mordents, ZSM-5, H-, Fujasite (USY) [6].
➢ Zirconium oxide- based catalysts (Zirconia), which are divided into two types of zirconia sulphides and zirconia tungsten.
➢ Catalyst based Alumina.
➢ Catalysts with hetero-poly acid structure, the most famous of which is Tungsten Phosphoric Acid [7].
➢ Molybdenum –based catalysts

Alumina Chloride-Based Catalysts

Alumina oxide and aluminium is a chemical compound with a melting point of about 200 °C and viscosity of 4. This oxide is insoluble in water and organic liquids and it is poorly soluble in acids and strong alkaline [8]. Alumina appears in the two crystal forms, the alpha alumina formed from colourless octahedral crystals and gamma alumina formed by cubic crystals with a viscosity of about 3.6 which are convertible into alpha form at high temperatures. The most common form of crystalline alumina is aluminium alpha oxide, known as a grinder, which can make an element turn reddish. The initial cell of it includes two formula from aluminium oxide. Oxygen ions almost result in the formation of compressed octahedral structure and aluminium ions fill 2/3 of porous Octagon holes [9].

Common Characteristics of Alumina Catalyst

➢ Appropriate strength and stiffness.
➢ Appropriate corrosion and strength.
➢ Appropriate temperature stability.
➢ Wonderful dielectric conductor feature.
➢ Low tangent loss.

Thanks to their selectivity, high activity, and reaction at low temperature (120 to 150 °C), these catalysts are greatly paid attention to by refineries. Since they react at low temperatures, octane number of the product of the catalysts is 3 to 4 points higher than zeolite catalysts [9]. Therefore, in spite of the cost of installation of peripherals such as naphtha treatment unit, food driers, caustic detergents, administration costs of chlorinated substances, and costs of corrosion, they are still preferred to zeolite catalysts. The catalyst food must be free of water, sulphur, H_2S, CO, CO_2, and compounds with nitrogen and oxygen [9].

Zeolite - Based Catalysts

These catalyst are one of the best in the process of Gasoline Units. Unlike zirconia and alumina-chloride -based catalysts, they have good resistance to water. In addition, unlike zirconia, they are not vulnerable to hydrogen at hydro Gasoline reaction and have good resistance against sulphur and other catalyst poisons such as nitrogen and oxygen. Another advantage of zeolite-based catalysts is their good capability of restoring [10]. However, since the reaction temperature is between 230 and 270 °C, maximum concentration of the produced isomers (equilibrium concentration) is lower than alumina chloride catalysts. High temperatures is in favour dehydrogenation reaction and produces more aromatic. One of the most important parameters of light naphtha hydro Gasoline on zeolites is the effect of their size [11]. The comparison of the two types of zeolite-based catalyst Pt./ Hβ and Pt./HM at 190 to 310°C showed, Pt./Hβ has higher activity and selectivity than paraffin Gasoline Units, which is due to its larger holes. In identical operating conditions, as the ratio of silica to alumina increases in zeolite network, its acid strength increases and its conversion and selectivity of catalyst for Gasoline is reduced [12].
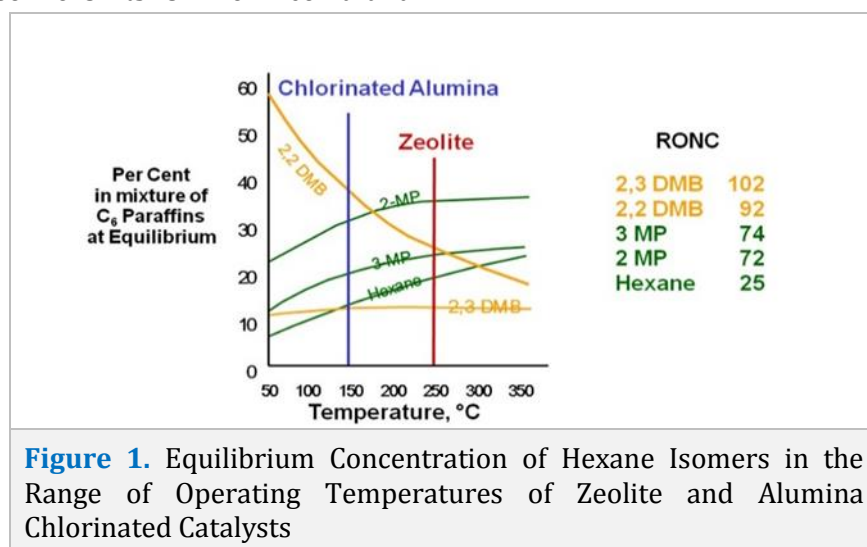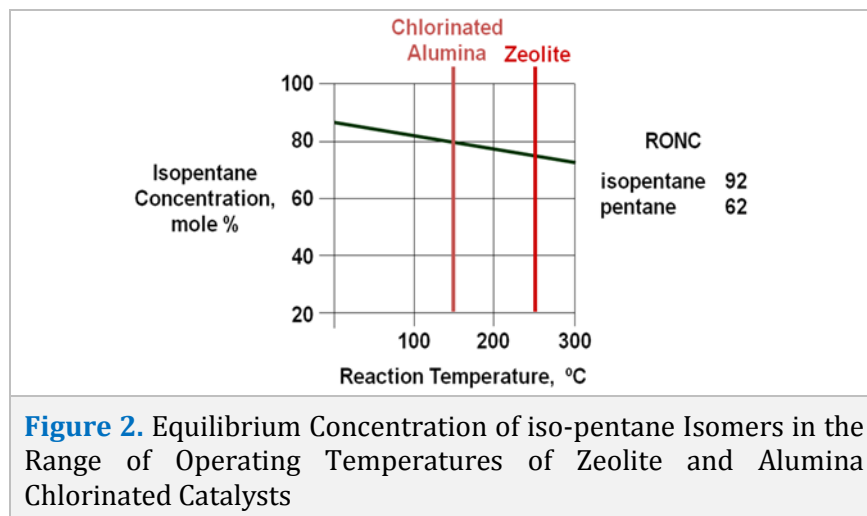

Figure 1. Equilibrium Concentration of Hexane Isomers in the Range of Operating Temperatures of Zeolite and Alumina Chlorinated Catalysts

Figure 2. Equilibrium Concentration of iso-pentane Isomers in the Range of Operating Temperatures of Zeolite and Alumina Chlorinated Catalysts

Zeolites

Zeolites are micro porous crystalline solids with very specific structures. Generally, they contain silicon, aluminium, and oxygen in the main structure and cations, water, or other molecules into the pore spaces. Zeolite is naturally created as a mineral or synthetic substance [13]. In the West, the main applications for petrochemical cracking are ion exchange, water and gas separation, and removing gases and solvents. They are also used in Agriculture, livestock, and the building. They are often referred to as molecular sieves [14]. Zeolites have the potential to act as a catalyst in chemical reactions occurring in their internal cavities. An important class of reactions are those that are catalysed by converted zeolite catalysts or hydrogen. In such reactions, the existing cavities cause a sharp increase in acidic power. It is used in many organic reactions such as crude oil cracking, Gasoline Units, and synthesis of zeolites. The shape and size of a particular porosity system has a spatial effect on the reaction and controls the availability of reactors and products [15, 16, and 17].

Therefore, zeolites are often referred to as catalysts capable of shape selection. Now, the unique features of zeolite catalysts are being paid attention to in order to perform a special synthesis of valuable chemicals such as pharmaceuticals and cosmetics [18]. The following features are the main reasons for the attractiveness of zeolites as catalysts, ion exchangers, and absorbents: [19]

➢ Specific crystal structure.
➢ High internal surface area.
➢ Homogeneous holes with the same size or several different sizes.
➢ High temperature stability.
➢ Lots of acidic places so that ions are exchanged with protons
➢ The ability to concentrate hydrocarbons

Prepairing Barium- Zeolite

Ba Y is prepared by ion exchange of initial zeolite NaY with a barium chloride solution (3 N). So, 360642 gm. of barium chloride in 100 mL distilled water is stirred in the vicinity of 20 gm of zeolite for an hour at a temperature of 50 °C. Zeolite in solution remains for 72 h at 25 °C. Barium zeolite are then filtered and washed in distilled water to be free of chloride ions and then dried at a temperature of 110 °C for 24 hours. The dried sample is then calculated in the presence of O_2 for five hours at 550 °C. Then, the temperature is raised to 550 °C with the speed of 10 °C/min. Chemical analysis has shown that

82% of Na or Ba is exchanged in zeolite Y. This is done in Institutes of Geological and mineralogical studies [19, 20, and 21].

HY Zeolite Preparation

H Y was prepared using ion exchange of initial zeolite NaY with a ammonium chloride solution. So, 160047 gm of ammonium chloride in 100 mL distilled water is stirred in the vicinity of 20 gm of zeolite for 1 h at 50 °C. Zeolite in solution remains for 72 h at 25 °C. Ammonium zeolite was then filtered and washed in distilled water to be free of chloride ions and then dried at 110 °C for 24 h. The dried sample was calculated in the presence of O_2 for 7 h at 500 °C. Then, the temperature raised to 550 °C [22, 23]. Chemical analysis revealed that 78% of Na was exchanged by ammonium chloride for the formation of HY. This was done in Institutes of Geological and mineralogical studies [3].

Preparation of Pt. /Al$_2$O$_3$

Al_2O_3 (with a spherical shape and an average size of 3 mm) was loaded by impermeability of aqueous Hexa-Chloro-platinum solution. Therefore, Hexa-Chloro-platinum acid was dissolved in 25 mL of distilled water. Then, 20 gm. of sample Al_2O_3 was added to the solution and then stirred for 4 h at 25 °C. It remained at room temperature for 24 h. This mixture was then stirred some hours [24, 25]. The resulting catalyst was dired at 110 °C for 25 h in air. Then the catalyst was calcinated at 400 °C for 3 h and restored in hydrogen environment at 350 °C for 3 h [25].

Zirconia-Based Catalysts

These catalysts are highly acidic and active. They properly do Gasoline reaction at 170-200 °C. Among the advantages of these catalyst is their high selectivity. However, disadvantage of these catalyst is their low resistance to water and hydrogen gas. In the presence of hydrogen, sulphate ion (SO_4) existing in the structure of the catalyst reacts with this gas and produces H_2S. Another disadvantage of this catalyst is the formation of coke on the catalyst and poisoning with water. The catalyst is available in the forms:

➢ Sulphate-based (metal sulphates), and combined with other oxides such as tungsten oxide.
➢ Gasoline reaction of these catalysts occurs at a pressure of (20 to 70 Barg) hydrogen.

Molybdenum –Based Catalysts

These catalysts have good resistance to sulphur compounds but it is difficult to restore them and they do not have a good thermal stability, especially in the temperature range of 80 to 190 °C [26, 27]. MoO_3 restoration with hydrogen gas at 350 °C improves the activity and selectivity of the catalyst for Gasoline process. The catalyst can be used as an alternative to two-factor zeolite catalysts. Not-restored MoO_3 in catalyst can gain its activity and selectivity after a long time (5- 10 h). The presence of 10 wt% Ni is effective in consolidation of activity in the Gasoline reaction (without a change in the selection of the catalyst). In the Gasoline of n-hexane, it was found that this catalyst has very high selectivity (above 90%) in the production of isomers with one and two methyl groups (CH_3). The catalyst has great resistance to sulphur and nitrogen compounds in the feed. Catalysts based on molybdenum oxide have good selectivity and good activity in the Gasoline of normal butane, normal pentane, and normal hexane. In addition, compared to the catalyst of Friedel –Kraft, they have less wastage and are environmentally more appropriate [17].

Hetero-Poly Acids

Heterogeneous multiple acid is a kind of acid which is created by combining hydrogen and oxygen with metals and non-metals and is composed of the following parts:

➢ Tungsten, vanadium or molybdenum metal atom.

➢ Oxygen atom.

➢ Heterogeneous atom: it consists of a member of row P (elements of group 5 to 10 of the periodic table) the atoms of which are being filled in the substrate of p orbitals; Such as silica, phosphorus, and arsenic.

➢ Acidic hydrogen atoms.

➢ Anion mixed with acid such as Phosphor Tungstate: Anion [12].

➢ Added atoms (such as tungsten) that is linked by oxygen atoms to form a heterogeneous cluster of atoms. A few different types of hetero-poly acids have been shown in Figure 3.
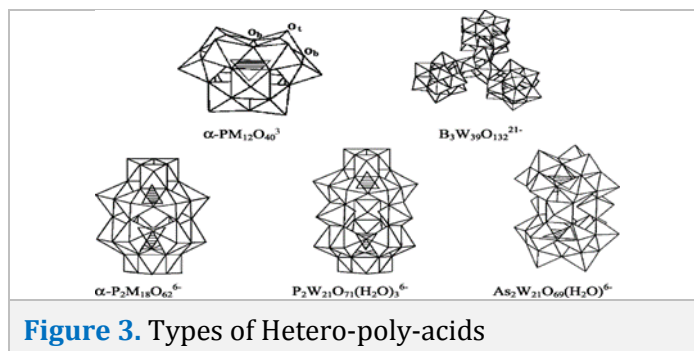

Figure 3. Types of Hetero-poly-acids

Hetero-poly acids have stronger acid sites than some other acid catalysts such as silica-alumina. Their good thermal stability is the cause of the loss of acidity, especially at a temperature between 350 to 450 °C. Commercial HPA catalyst regeneration is done at high temperatures, due to their thermal stability. Adding platinum and palladium has a positive effect on the thermal stability and restoration of them [27].

Nature of Acid Sites of Catalyst

Lewis acid sites are parts of catalyst that are willing and according to acid Lewis's definition. It is while Brunched acidic sites are parts of catalyst which eliminate most hydroxyl groups (OH$^-$) in high temperature. This leads to the formation of aluminium ions with partial graft that behave like a Lewis acid sites. The remaining hydroxyl groups on the surface of alumina either do not have acidic nature or they hav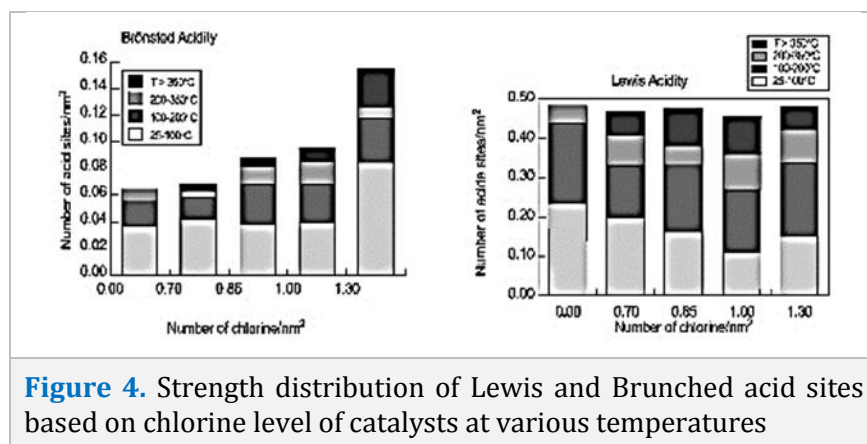e very weak acidity. In determining the acidity of alumina through absorption of ammonia, it has been shown that alumina alone does not have Brunched acidity site, but Lewis site has always been observed.

Halogenating alumina reinforces some Lewis acid sites and since halogens have high electronegativity power, they increase acid strength by bonding aluminium atoms. After transplantation with aluminium atoms to increase the acid strength. Therefore, new Lewis acid sites with higher acid strength are produced. The experimental results show that the Gasoline activity is closely related to the activity of acidic sites and at least Lewis acid sites are required for the Gasoline reaction. Lewis and Brunched acid sites are required for branched hydrocarbon reaction. During the process, chlorine compounds C_2Cl_4, CCl_4, $CHCl_3$, CH_3Cl, $AlCl_3$, and hydrogen gas are injected into the system. Chlorinated compounds react with hydrogen and produce HCl gas. Hydrogen ions form Brunched sites after surface chlorination

[28]. Brunched sites have strong acidity since Carboniom ions are absorbed and branched on them. The rate of Carboniom ions branching depends on the number of Brunched acidic sites [29]. Therefore, the amount of injection of chlorine additives should be such that the necessary balance between Lewis and Brunched sites is established. Brunched acidic sites are unstable and they are released after reaction with HCl alkanes. Therefore, it is necessary to continuously inject chlorinated additives to maintain Brunched sites and stability of the catalyst [28].

Effect on Catalyst

Chlorination of catalyst with different materials alter its performance in Gasoline Units. Table 2 demonstrates the change in the number of acid sites caused by chlorinated materials significantly changes n-butane Gasoline reaction activity and selectivity. Adding chlorine not only increases the number of strong Brunched acidic sites but also increases the number of weak Brunched acidic sites. The total number of Brunched acidic sites increase as chlorine levels increases. In general, it can be concluded chlorination increases strong Lewis and Brunched sites but decrease weak Lewis sites [30]. The reducing in the number of Lewis sites and the increase in strong sites reflect the fact that chlorination strengthens the weak Lewis sites.

Figure 4. Strength distribution of Lewis and Brunched acid sites based on chlorine level of catalysts at various temperatures

Measuring the Strength of Acidic Sites

To measure the strength and concentration of acid sites, different materials can be used as a probe such as TMP or ammonia [31]. To measure the number of acidic sites and acidity power, the disposal of these materials from acidic sites is measured at different temperatures. These measurements can be done by NMR or temperature programmed method. Having chlorinating gamma alumina with chloroform, Hong Sang et al investigated catalyst acid sites and concluded that acid sites can be classified into three categories: Lewis

sites type one with peak Chemical Shift graph of 44 ppm, and Lewis sites type two with peak Chemical Shift graph of 54 ppm. Lewis sites type 2 are the sites produced by converting Brunched to Lewis sites as a result of temperature rise [32]. Brunched sites at 500 °C, to a large extent, convert to Lewis type 2 sites whereas Lewis first sites are fixed. To determine the effect of chlorination temperature on the acidity of catalyst, Sang et al reacted TMP with acidic place at 25 °C. TMP excretion measured with NMR showed that the concentration of Brunched acidic site remains

almost constant at 200 °C. However, refining operations with catalyst nitrogen at over 300 °C showed that the concentrations of Brunched sites significantly decreases.

Optimum PH for the Reaction of Gasoline Units

Gasoline and cracking of hydrocarbons are both done on acid sites. In the process of Gasoline Units, cracking reaction is an unpleasant reaction and must be reduced. Loners et al. studied the effect of number and strength of acid sites in Gasoline reactions and investigated normal butane cracking on zeolite, alumina, and halogenated alumina catalysts. They compared acid strength and distribution power of different catalysts through absorbing ammonia [30]. Cracking mainly occurs for hydrocarbons with more than 6 carbon atoms, part of the cracking that produces hydrocarbons with 3 and 4 carbon atoms is done on acidic sites and is in direct proportion to the number and strength of acid sites. In general, although the strength and number of the acid sites (total of Brunched and Lewis acid sites) in zeolite catalysts are more than halogenated alumina-based catalysts, because of the high number of Brunched acidic sites in halogenated alumina-based catalysts, they have higher activity and selectivity in the Gasoline reaction.
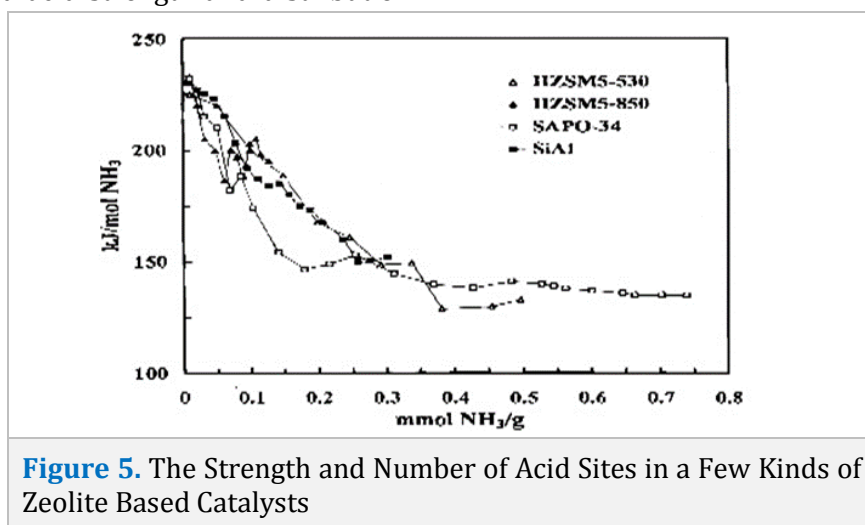

Figure 5. The Strength and Number of Acid Sites in a Few Kinds of Zeolite Based Catalysts
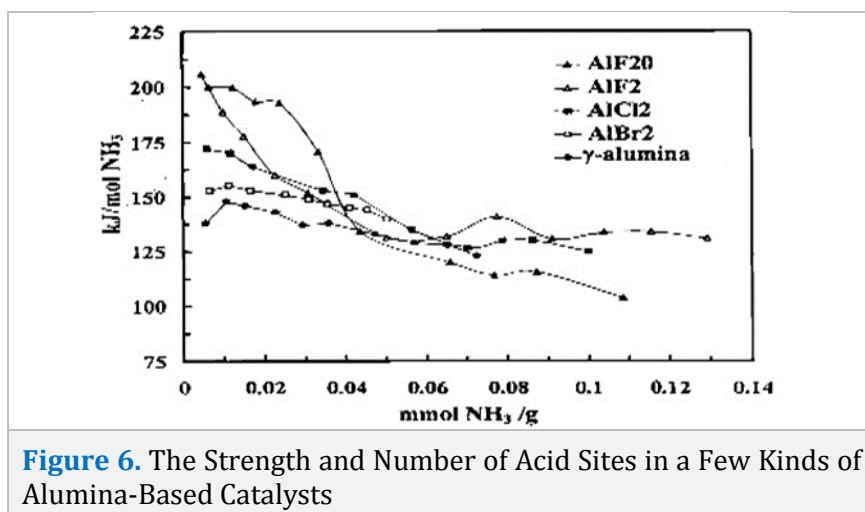

Figure 6. The Strength and Number of Acid Sites in a Few Kinds of Alumina-Based Catalysts

For catalyst HZSM-5, the activity of catalyst increases as the reaction temperature goes up, but selectivity of Gasoline is highly undesirable. The majority of strong acid sites of this catalyst are on the surface. Therefore, it can be concluded that surface acidic sites are not suitable for Gasoline reaction. Compared to other zeolite catalysts, SAPO-34, which has the highest number of acid sites and the smallest holes, does the Gasoline of double bond Gasoline better, which of course is not the desired reaction. Due to the number of acid sites and low acid strength, gamma-alumina catalyst does not have the required activity and selectivity. Among halogenated catalyst, chlorinated alumina has the best activity and selectivity [19]. In light naphtha Gasoline catalysts, acidity strength must not be so high that adverse reactions such as polymerization of coke and cracking formation increase. The acid strength of about 140 to 150 kJ mole ammonia is enough for normal butane Gasoline and further increase of it decreases normal butane Gasoline selectivity [18].

The Ratio between Metal and Acid Sites in Catalyst

The activity of two-factor catalysts strongly depends on acidic and metal sites. For example, in catalyst Pt./ HY, which is a kind of zeolite catalyst for Gasoline Units, the optimal ratio of strong acidic sites to metal sites in n-heptane Gasoline is determined to be less than 6. This ratio affects selectivity of catalyst and reactions such as cracking. To determine the optimal ratio of metal, metal poisons are used to decrease the effect of metal on selectivity of reaction. High levels of platinum increases cracking reactions. On the other hand, reducing the amount of platinum decreases dehydrogenation and activity of catalyst. To compensate for the reduction in catalyst activity due to poisoning of platinum metal, reaction temperature is increased, leading to an increase in the cracking reactions [2]. The greater the distance between metal and acid sites and the less the distribution of the metal, the slower the practice of hydrogenation and the more the opportunity for adverse reactions such as oligomerization. Metal accumulation around acidic site could clog it and reduce the adsorption of acidic molecules on acidic site. Such conditions reduce the acidity of catalyst.

Table 2. Effect of Chlorinating alumina with Different Materials on the Number of Acidic Sites and Gasoline rate

Temperature(°C)	The percentage of selectivity for iso-butane	Gasoline activity /mol h^{-1} g^{-1}	Strong acidic sites	catalyst
386	40	$0.23*10^{-4}$	0.27	Al_2O_3
386	30	$0.3*10^{-4}$	0.48	Al_2O_3+HCl
290	80-90	$0.38*10^{-4}$	0.6	$Al_2O_3+CCl_4$
290	90-97	$0.91*10^{-4}$	1.04	$Al_2O_3+AlCl_3$
290	80	$0.3*10^{-4}$	0.38	SiO_2+AlCl_3
386	1	$0.08*10^{-5}$	0.04	Al_2O_3+Na

Lee et.al showed although the acidity of the catalyst Pt./H is lower than Pt./HMOR, because of the larger pore size and appropriate distribution of platinum metal, its activity in n-hexane Gasoline is higher. Melchior et.al determined the optimum ratio of platinum sites to acidic sites in chlorinated alumina-based catalysts as follows: Their results showed that as the time and temperature of chlorinating catalyst increases, platinum distribution is reduced. In addition to factors such as low

proportion of metal, and its Centration during catalyst formation process, partial pressure of hydrogen disrupts the balance between metal and acid sites. During the Gasoline process, operating conditions can affect the performance of catalyst and change it [30].

Table 3. Effect of the Calcination Temperature on Selectivity and Activity of Halogenated Alumina Catalysts for Butane 1 Gasoline Units

Distribution of Products			Reaction Conditions			Catalyst Calcination		Catalyst
Time (hour)	Temperature (°C)	Temperature (°C)	Time (hour)	Temperature (°C)	Temperature (°C)	Time (hour)	Temperature (°C)	
44.3	22.9	31.1	0.85	0.197	380	2	600	AlF_1
58.5	27.1	12.5	0.85	0.197	380	2	600	AlF_1
31.85	62	7.5	0.85	0.197	380	2	600	AlF_2
63.85	31.1	4.1	0.85	0.197	380	2	600	AlF_2
55.9	37.5	5.6	0.85	0.197	380	2	600	AlF_{20}
96.1	2.9	1.35	0.85	0.197	390	2	550	$AlCl_2$
84.85	9.31	5.99	0.9	0.151	390	2	550	$AlCl_2$
99.55	0.38	0.249	0.9	0.151	390	2	550	$AlBr_2$

Catalytic Test

Determining the activity of a catalyst does not seem straightforward. We would prefer to measure activity in a zero conversion to obtain results that are affected by thermodynamic constraints, such as the constraints caused by the moderation between products and reactants. We also need data that is measured under conditions of specific gas concentration and temperature. This item may be problematic in fast and heavily heat-soaked processes because it causes gas to overheat or heat up during the reaction.

Usually a low sample of a catalyst (or even a diluted sample) is placed inside the PFR or CSTR and the speed is determined. The second mode is preferred because gradients are avoided and it makes it easier to describe reactions and kinetic **modelling**. If everything goes right, speed is expressed by the activity of each site multiplied by the number of sites in the catalyst. In a metal catalyst, it is always assumed that the number of sites is proportional to the level of metals determined by chemical absorption. The division of speed results in the number of sites, TOF. As we said earlier, this number is important if we are to compare the intrinsic activity of the catalysts. However, TOF is not necessarily important in industrial applications, because catalyst activity is more important than its unit volume.

Ten Commandments for Catalytic Testing

A review of all the features of the catalytic test and discussion of problems that may occur can be found in the "Ten Commandments for Catalyst Test", which include:

1) Setting Goals: What is the purpose of the test? This goal is, for example, the specific activity and reaction mechanism, or the long-term industrial use desired.
2) Use an effective strategy to test: What are the important parameters and how best to determine.
3) Choose the correct type of reactor for testing: There are a large number of different reactors. The above-mentioned CSTR and plug-in reactors are usually preferred in

laboratory research applications. But other forms may also be considered to simulate real industrial conditions.

4) Establishing an ideal flow pattern: It is often assumed that this is done in Plug reactors, but are all the conditions for ideal mix to be satisfied? For example, a rule of thumb is that the diameter (d) of a PFR must be at least ten times the diamet*er of the catalyst particle* to remove the effect of the reactor wall. Also, the amount of catalyst should be sufficient to achieve the axial gradient. The other law is that the length of the bed (L) should be fifty times the diameter of the particle. Bigger values are preferred, but higher lengths may cause temperature gradients and pressure drop.

5) Ensure that the temperature is the same: even a slight deviation from the measured temperature can have a great effect on the activity. Because the speed with the temperature is in accordance with the arrinosis equation. The temperature gradient can be reacted in the catalyst bed or inside the catalyst particles due to the thermosetting behaviour.

6) Minimizing the effects of transfer phenomena: If the kinetic efficiency of the catalyst is of interest, it is important to delete the transfer restrictions as it results in false data. Determining TOF for different gas velocities and different catalyst particle sizes is a way to understand the constraints of the transfer. So the good starting point for catalytic tests is as follows:

➢ Small catalyst particles: eliminates the penetration limitation inside the particle.

➢ Low conversion: eliminates the temperature gradient and always has to be chosen when the kinetics are desired. Here, dilution with an inert substance may be necessary.

➢ Medium temperatures: to get the gradients

7. Getting meaningful catalyst data: Usually for TOF kinetics purposes. But parameters such as selectivity and efficiency are important for judging the potential of the catalyst. Instead of expressing activity as TOF, it can be reported as follows:

➢ The reaction rate per unit mass or catalyst volume

➢ Spatial speed
It should also be noted that the expression of catalyst activity in the form of a temperature at which a definite conversion is not recommended is not recommended, since the overall speed of a catalytic reaction depends complexly on temperature.

8) Determination of catalyst stability: How fast does it lose its activity and why is it disabled? How catalytic is sensitive to various contaminations that may be present in real conditions within the feed?

9) Get Good Laboratory Techniques: Always make comparisons with experiments that are under the same conditions. Check for repeatability and check that trials are not limited by trivial factors such as thermodynamics. Check the cleanliness and perform the blank run for the reactor, as well as any inactive fillers if used.

10) Report clearly the findings: state in detail the conditions in which the catalyst is tested, and provide relevant data such as activity, selectivity, and conversion as defined.

Conclusion

In this work, we studied various catalysts of the isomerization unit. The results indicated that the high acidity and ratio of metal to acidic location in the catalyst greatly affects its activity. The performance temperature in the single reactor and the simultaneous profile of temperature, pressure, and the amount of hydrogen, influencing the catalyst deactivation, which needs further evaluation. The results also

revealed that the distribution of acidic locations in terms of chlorine catalyst at different temperatures, indicating that the uniform distribution of temperature in the reactor bed can greatly improve the catalyst activity.

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References

[1]. Changhua S., Hui Liu., Yuan L., Shuai G., Hongwei W., Wenshuai Z., Yonghui C., Changri H., Huaming L. *Chinese J. Chem.*, 2014, **32**:434

[2]. Weifeng H., Hongye SU., Yongyou HU., Jian C., *Chinese J. Chem. Eng.*, 2006, 14:584

[3]. Jinhwa C., Suchol L., Jongju Ha., Soonho S., Kwangmin C. *Chinese J. Chem.*, 2010, **28**:1085

[4]. Weifeng H., Hongye S., Shengjing M., Jian C., *Chinese J. Chem. Eng*, 2007, **15**:75

[5]. Qiang G., Linyi B., Xiaojing Z., Peng W., Peizhou Li., Yongfei Z., Ruqiang Z., Yanli Zh. *Chinese J. Chem.*, 2014, **33**:90

[6]. Samimi A., Zarinabadi S., Shahbazi A., Azimi A., Mirzaei M., *Iran. Chem. Commun.,* 2019**, 7**: 681

[7]. Majid S., Navid M., Rahmat S. *International J. Appl. Eng. Res.*, 2011, **2**:110

[8]. Taoufiq G., Dua V., *Comput. Chem. Eng.*, 2011, **35**:1838

[9]. Gyngazova M., Kravtsor A., Ivanchina E., Korolenko M., Uvarkina D. *Catalysis in Industry*, 2010, **2**:620

[10]. Arani H.M., Shirvani M., Safdarian K., Dorostkar E. *J. Chem. Eng.*, 2009, **26**:723

[11]. Varga T., Szeifert F., Abonyi J. *Eng. Appl. Artif. Intell*, 2009, **22**: 569

[12]. Quinn G.P., Keough M.J. *Experimental Design and Data Analysis for Biologists,* Cambridge University Press, Cambridge, UK, 2002, pp. 111-117

[13]. Floudas CA., X Lin. *Comput. Chem. Eng.*, 2004, **28**: 2109

[14]. Wu D., Ierapetritou M. *Chem. Eng. Process.*, 2007, **46**:1129

[15]. Davood I., Mohsen K., Shahram A., Mitra J., Razieh R., Mohamad Reza R. *Chem. Eng. Res. Des.,* 2014, **92**:1704

[16]. Sa'idi M., Mostoufi N., Sotudeh-Gharebagh R. *Int. J. Appl. Eng. Res.*, 2011, **2**:115.

[17]. Smania P., Pinto J.M. *Comput. Aided Chem. Eng.*, 2003, **15**:1038

[18]. Palmer R., Kao S., Tong C., Shipman D. Hydrocarbon processing, 2008, **87**:55

[19]. Engell S., Harjunkoski I. *Comput. Chem. Eng.*, 2012, **47**:121

[20]. Raseev S. *Catalytic Reforming in Thermal and Catalytic Process in Petroleum Reforming, Science and Technology*, Marcel Dekker Inc., New York, U.S.A, 2003, pp. 193-196

[21]. Sohn S., Kim J. *Expert Syst. Appl.,* 2012, **39**:4007

[22]. Tabatabaee M., Hedayati A., Samimi A., *Science Road Journal*, 2015, **03**, 6

[23]. Gueddar T., Dua V., *Comput. Chem. Eng.*, 2011, **35**, 1838

[24]. Gao X., Shang C., Jiang Y., Chen T., Huang D., *AIChE J.*, 2018, **60**:2525

[25]. Jia Z., Ierapetritou M., Kelly J. D., *Indust. Eng. Chem. Res.*, 2003, **42**:3085

[26]. Jia Z., Ierapetritou M. *Comput. Chem. Eng.*, 2004, **28**:1001

[27]. Gyngazova M., Chekantsev N., Korolenko M., Ivanchina E., Kravtsov A. *Catalysis in Industry*, 2012, **4** :284

[28]. Iranshah D., Karimi M., Amiri SH., Jafari M., Rafiei R., Rahimpour M.R. *Chem. Eng. Res. Des.*, 2014, **92**:1704

[29]. Stijepovic M., Ostojic A., Milenkovic I., Linke P., *Energ. Fuel*, 2009, **23**:979

[30]. Arani H., Shirvani M., Safdarian K., Dorostkar E. *J., Chem. Eng.*, 2009, **26**: 723

[31]. Palmer, R., Kao, S., Tong, C., Shipman, D., *Consider options to lower benzene levels in Gasoline*, Hydrocarbon processing, Houston, Texas, U.S.A, 2008, p. 55-66

[32]. Gembiki S. A Biographical Memoir of Veladimir Haensel, 3rd ed., *the National Academy of Sciences*, Washington DC, 2006

[33]. Moghadasi, Z., *J. Med. Chem. Sci.*, 2019, **2**:35

[34]. Mohammadi R., Sajjadi A., *J. Med. Chem. Sci.*, 2019, **2**:41

[35]. Sajjadi A., Moosavi S.M. *J. Med. Chem. Sci.*, 2018, **1**:1