Abstract: This review article provides an overview of the advances in the field of hydro-conversion of n-alkanes with particular stress on the promising ways to meet the requirements for improved quality of motor fuels and oils, which have been marked during the past decades. Particular attention is given to a catalyst formulation for conversion of n-alkanes to branched hydrocarbons. The particular challenge is to find an effective catalyst, which favors the isomerization of n-alkanes without too much cracking. The regulation of active sites and adsorption properties, as well as the topology of support surfaces, allows a potential predictive design of novel catalysts for conversion of n-alkanes into their branched isomers.

Subjects: Organic Chemistry; Physical Chemistry; Applied & Industrial Chemistry

Keywords: n-alkanes; isomerization; hydrocracking; solid acids; Zirconia-based catalysts

PUBLIC INTEREST STATEMENT

This paper provides a brief idea about the components, which are mainly responsible to enhance the efficiency of petroleum as fuel. This will certainly draw attention of common people. Cost-effective methods to prepare those components will also be interesting to the common mass.
1. Introduction

Isomerization is a chemical reaction that proceeds through the breaking and making of bonds, and is a special case of a molecular rearrangement. Simply, it is a process which changes just the orientation of the molecules within the molecule so that it becomes branched keeping the same molecular formula. (Hartmut & Ernst, 2003a; Murphree, 1951) It is now well in practice to isomerize the light paraffin by isomerizing straight chain alkanes to its corresponding branched chain isomers to enhance the octane numbers, and thus upgrading the gasoline composition to make it more eco-friendly, which subsequently increases the efficiency of the engine as new regulations affecting gasoline composition are enacted in many regions of the world. These regulations include lead phase down, benzene minimization and oxygen content requirements. (Hao, Qiang, & Ben-Xian, 2009) Light-naphtha isomerization plays a pivotal role in meeting octane demands in the gasoline pool, which result from both the lead phase down and the increasing market share for premium gasoline grades. (Hollo, Hancsok, & Kallo, 2002; Satoshi, 2003) By isomerization, we mean the skeletal isomerization of paraffins to more branched paraffins with the same carbon number. (Dhar, Vekariya, & Sharma, 2017; Marios, Denis, & Pierre, 2009) However, because of its nature, isomerization may also affect some of the naphthene components and could hydrogenate aromatics. (Maria, Juan, Fernando, Paula, & Jose, 2005) In fact, isomerization is the most economic pathway, which is accessible for reducing the benzene content in gasoline. (Galadima, Anderson, & Wells, 2009; Maria, Jose, & Araceli, 1997)

1.1. n-alkane isomerization and petroleum industry

Modern refiners are using isomerization process to produce high-octane gasoline components from low-octane light naphtha fractions. Petrol gasoline is an essential fuel for most of the passenger cars around the world. The components of petrol are various hydrocarbon compounds like benzene, toluene, xylene, methyl benzene, normal and isomers of hexane, heptane, octane, etc. Exhaust of petrol car is found to be polluting as it usually entails unburnt petrol, which is found to be a major health hazard. (Michael, 1985; Serra, Chica, & Corma, 2003) Especially, it becomes carcinogenic when the exhaust contains benzene, and as a result petrol containing more than 1.0% benzene has been banned in India. Since benzene is produced during reforming process of naphtha, it is necessary to make the feed free from C6 hydrocarbon, which could be precursor for generation of benzene. Since, C6 hydrocarbons (alkane and naphthene) are significant compositions of naphtha, removal of these will drastically reduce the yield of petrol. In this context, the role of alkane isomerization is inevitable as the octane number of light alkanes increases with the degree of branching. (Khalid, Hayam, Amel, & Jabir, 2007; Lovasic, Jambrec, Siftar, & Prostenik, 1990; Maria, Antoniod, Vicente, Paula, & Jose, 2008) For instance, the RON (Research Octane Number) of n-hexane is only 31 while the RON-s of 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane are 74, 76, 94, and 105, respectively. The effectiveness of the hydrocarbon as fuel ingredient increases with increase of its octane number. Isomerate product contains very low sulfur and benzene, making it ideal blending component in refinery gasoline pool. (Maloncy, Maschmeyer, & Jansen, 2005)

The octane rating of the components used in the manufacture of the various commercial gasoline grades gives an idea regarding the anti knocking quality of a given fuel or component. In the case of butanes, octane is not that important as the majority of isobutane is consumed in the production of motor fuel alkylate and oxygenates. While in the case of C5 and C6 alkanes, the most highly branched isomers have the highest-octane values. Octane values for C5 and C6 paraffin isomers are shown in Table 1. The two empirical octane measurement methods, research (ASTM Method 2699), and motor (ASTM Method 2700), measure antiknock characteristics at two severity levels. Often, the average of these two values, or (R + M)/2, is used to express the overall engine performance of a gasoline component or blend. (Ling, Wang, & Shen, 2009; Meyers, 2004)

Isopentane has nearly 30 numbers higher octane value than n-pentane. Similarly, the hexane isomer, 2, 2-dimethylbutane (2, 2-DMB) has an octane number about 67 which is certainly higher than n-hexane. Noticeably, highly branched isoparaffins are the desired isomers for motor fuel production. (Marios et al., 2009) Therefore, converting straight chain alkane into its corresponding
branched chain isomers is an inevitable method to produce high-performing fuel. (Maria et al., 2005) Hence, it is clear that production of branched alkane from straight chain via catalysis is a part and parcel of petroleum industry.

The used quantity of the fuel is in accordance with the type of the drive. (BP Statistical Review, 2013; Bridsal, 2013) Based on the fuel demand (Figure 1), liquid hydrocarbons (engine gasoline, diesel gas oil) are used in the widest range in inland transport. They must satisfy the most important general and special requirements, such as:

- long-time availability of quality and quantity all over the world
- good combustion properties such as high octane number (gasoline), high cetane number (Diesel fuels), relatively low combustion temperature (lower amount of NOx formation; lower load of construction materials), lower total harmful material emission, etc.

| Compound          | Research octane by ASTM 2699 | Motor octane by 2700 | R + M/2 |
|-------------------|------------------------------|----------------------|---------|
| n-Butane          | 93.8                         | 89.6                 | 91.7    |
| i-Butane          | 100.4                        | 97.6                 | 99.0    |
| n-Pentane         | 61.7                         | 62.6                 | 62.2    |
| i-Pentane         | 92.3                         | 90.3                 | 91.3    |
| n-Hexane          | 24.8                         | 26.0                 | 25.4    |
| 2-Methyl pentane  | 73.4                         | 73.5                 | 73.4    |
| 3-Methyl pentane  | 74.5                         | 74.3                 | 74.4    |
| 2,2-Dimethyl butane | 91.8                       | 93.4                 | 92.6    |

![Figure 1. Changing demand of fuel by type (toe: tonne of oil equivalent).](https://doi.org/10.1080/23312009.2018.1514686)
• very low sulfur content (≤ 10 mg/kg)
• reduced aromatic content; gasoline: benzene content ≤ 1.0 v/v%; total aromatic content ≤ 35 v/v% and diesel fuels: polyaromatic content ≤ 8%
• reduced olefin content
• gasoline ≤ 18 v/v%
• good blending ability with alternative components (not only with hydrocarbons but also with, for example, oxygen containing compounds)
• good additive sensibility and compatibility with additives (e.g. nozzle, valve and combustion chamber clearness)
• compatibility with motor oils
• fewer harmful matters in the exhaust gas
• user-friendly
• secure utilization
• easy biodegradation
• environmentally friendly (nontoxic)
• low book-cost, etc.

Based on these requirements, it can be unequivocally stated that it is only the quantity of paraffins (mainly iso- and cycloparaffins and, with less importantly n-paraffins) which is not limited directly or indirectly in fuels. The concentration of cycloparaffins containing suitable boiling points is low in crude oil, and their synthesis is still expensive. (Hancsok & Kasza, 2011)

1.2. Feasibility of alkane isomerization
The unreactive character of alkanes is explained by the unavailability of both lone pairs and empty orbitals. Carbon and hydrogen belong to the group of elements whose number of valence electrons equals to the number of valence orbitals available. The highest occupied molecular orbitals (HOMOs) are deep lying σ bonding orbitals, and the lowest unoccupied molecular orbitals (LUMOs) are high lying σ* levels. Thus, the bonding between C and H is very strong (dissociation energy: 377–461 kJ mol$^{-1}$). (Eisuke, Junko, & Kazunari, 2005; Khalid et al., 2007; Ross, 2012) The low polarity is another factor contributing to the unreactiveness of alkanes. Since branched alkanes are thermodynamically more stable than linear alkanes, catalytic conversions to branched isomers are feasible.

1.3. Thermodynamics of n-alkane isomerization
Reactions of alkane isomerization are slightly exothermic. Low reaction temperatures are favorable to obtain highly branched isomers from thermodynamic point of view. To summarize, high temperatures are necessary to activate and convert the unreactive alkanes, though low temperatures favor the desired highly branched isomers. An increase in temperature of metal site reactions shifts the equilibrium towards dehydrogenation, which may result in coke formation and poly-nuclear aromatics. (Maria et al., 2005; Murphree, 1951) Interestingly, increase of temperature does not affect acid site equilibrium, rather it raises rates of reactions. Hence, an optimum temperature must exist at which isomer formation is maximum, and that must be evaluated before fixing the operating temperature. Above this temperature, unwanted olefins, coke and poly nuclear aromatics may increase. Suppression of dehydrogenation is controlled by high hydrogen pressure. Excessive temperature and pressure will affect to result in more hydrocracking than isomerization. (Diaz & Mare, 1983) Figures 2–4, illustrate this trend. The most active catalyst, when all other variables are equal, is capable of producing the highest-octane products.

A dual-function catalyst containing a noble metal and an acid function most effectively catalyzes paraffin isomerization.
1.4. Generalized mechanism of isomerization of n-alkane

The isomerization of n-alkanes proceeds by a mechanism with carbenium ions as key intermediates. Carbenium ions are not only active species for the skeletal isomerization but also for undesired side reactions, which reduce the selectivity to the desired isomers. The alkane isomerization mechanisms of acid and bifunctional catalysts are described in this section, at first of the monofunctional homogeneous and then of the heterogeneous acid catalysts. Bifunctional heterogeneous catalysts contain acid sites and metallic sites for skeletal isomerization and hydrogenation/dehydrogenation reactions respectively. (Guisnet, Thomazeau, Lemberton, & Mignard, 1995; Weitkamp, Gerhardt, & Jacobs, 1985) The isomerization mechanism on the acidic sites of these bifunctional catalysts corresponds to the mechanism of monofunctional acidic catalysts.

Figure 2. Butane fraction equilibrium.

Figure 3. Pentane fraction equilibrium.

Figure 4. Hexane fraction equilibrium.
1.4.1. Mechanism of the acid catalyzed alkane isomerization

The catalytic cycle of the acid catalyzed isomerization involves chain initiation to form the first active carbenium ion species, carbenium ion rearrangement and the chain propagation. This segment includes possible side reactions and mechanistic considerations of the cracking inhibitor hydrogen in the presence of carbenium ions.

1.4.1.1. Initial step of the alkane isomerization reaction. Olah et al., studied intensively superacids and hydrocarbon chemistry with these superacidic catalysts, amongst other reactions also investigated the alkane isomerization. (Olah, Prakash, Molnar, & Sommer, 2009a; Olah GA, Molnar A, Hydrocarbon Chemistry, 2003) The initial step, namely the formation of the carbenium ion, occurs in superacids by abstracting a hydride ion. (Scheme 1)

The isomerization reaction may occur at much lower rate or even does not take place at all without an appropriate level of acidity. Sulfuric acid (H₂O = −11.9), the threshold to superacidity, is not acidic enough for the skeletal isomerization of n-alkanes. (Olah GA, Molnar A, Hydrocarbon Chemistry, 2003) Another possibility of carbenium ion generation involves the use of organic halides in the presence of strong Lewis acids (Scheme 2). (Olah, 1964a) Lewis acids are capable of eliminating the halide. This catalyst system is well known from the Friedel-Crafts chemistry. (Olah, 1964b)

In addition, acidic catalysts are capable of alkene protonation, which is shown in Scheme 3.

The generation of alkenes in turn depends on reaction intermediates and catalyst types. In acidic, metal free catalysts, alkenes can originate from cracking side reactions (Weitkamp, Jacobs, & Martens, 1983) or can be formed by deprotonation of carbenium ions. The carbenium ion is in equilibrium with the corresponding alkene in every acidic media (Scheme 3). (Olah, 1964a) Hydride abstraction by alkyl carbenium ions acting as strong Lewis acids is well known as chain
propagation step in hydrocarbon chemistry (Scheme 6). (Olah et al., 2009a; Sommer, Jost, & Hachoumy, 1997) Simultaneously, a new carbenium ion is generated.

1.4.1.2. Skeletal isomerization of carbenium ions. It is convenient to distinguish between type A (non-branching) and type B (branching) rearrangements of alkyl carbenium ions. (Brouwer & Oelderik, 1968) Type A rearrangements are generally much faster than type B rearrangements. (Weitkamp & Farag, 1978) It is widely accepted that type A rearrangements proceed via classical alkyl and hydride shift (Scheme 4) while type B via non-classical protonated cyclopropane (PCP) rearrangement (Scheme 5). Application of the classical mechanism for type B rearrangement is implausible since it would result in primary carbonium ions as intermediates, which are known to have high energy contents. Only n-alkanes, larger than n-butane, can be isomerized via the PCP intermediate. Evidence for this PCP mechanism was provided by Brouwer (Brouwer & Oelderik, 1968) and Weitkamp. (Weitkamp, 1982, 2012)

The stability of carbenium ions depends on the groups, which are attached to the positively charged carbon. It increases in the following order because of the electron donating field effect (+ I) of the alkyl groups: primary R+ < secondary R+ < tertiary R+. Therefore, carbenium ions rearrange to the thermodynamically more stable carbenium ion species.

1.4.1.3. Chain propagation. The rearranged carbenium ions can abstract a hydride from an alkane to give the corresponding iso-alkane and a new carbenium ion (Scheme 6). (Olah et al., 2009a) Therewith, the catalytic cycle is closed.

This catalytic cycle is controlled by two kinetic and two thermodynamic parameters. (Olah et al., 2009a) Skeletal isomerization of carbenium ions is kinetically controlled by the relative rates of hydrogen shift, alkyl shift as well as PCP formation, while thermodynamically it is controlled by the relative stabilities of the carbenium ions. The chain propagation, however, is kinetically controlled by the hydride transfer from excess of starting hydrocarbons, and by the relative thermodynamic stabilities of the various hydrocarbon isomers. The stability of intermediate carbenium ions is different from that of hydrocarbons.
1.4.1.4. Possible side reactions in acidic isomerization catalysis. Carbenium ions are not only key intermediates for the isomerization but also for some side reactions like cracking or alkylation. Thus, selectivity to the desired isomerized alkanes decreases and the thermodynamical equilibrium within the isomers is never reached. (Chica & Corma, 2007) Many parallel and consecutive reactions take place during acid catalyzed alkane isomerization. Even with a pure model compound, like n-hexane or n-octane, a large number of products are formed.

Catalytic cracking on monofunctional acidic catalysts: Two different mechanisms can be distinguished for the alkane cracking such as the bimolecular cracking via carbenium ions and the monomolecular cracking via carbonium ions. The general concept of carbcocations includes all cations of carbon-containing compounds, which can be differentiated into two limiting cases: (i) trivalent (“classical”) carbenium ions and (ii) five or higher coordinated (“nonclassical”) carbonium ions. (Olah et al., 2009a) For bimolecular cracking, the carbenium ion formation is followed by a bond scission. (Corma & Orchilles, 2000; Corma, Planelles, & Tomas, 1985; Weitkamp, 2012; Weitkamp et al., 1983) The C-C bond cleavage occurs in β-position to the positive charge of the carbenium ion, whereby a new carbenium ion and an alkene is formed. Depending on the type of cracked carbenium ion and the new formed carbenium ion (primary, secondary or tertiary), different modes of β-scission can be distinguished (type A, type B1, type B2, type C, and type D) (Scheme 7). (Weitkamp et al., 1983) Chain length and degree of branching of the carbenium ion determine the mode of β-scission. Rate constants strongly decrease from type A to type D β-scissions. (Corma et al., 1997; Weitkamp, 2012) Theoretically, hexane isomers can only crack according to type D and C, whereas type D is unlikely at mild temperatures (below 523 K) because of the high-energy content of the primary carbenium ion intermediate. On the contrary, all modes of β-scission are open for octane isomers. Lower selectivities for long-chain alkanes (C > 6) and especially for multibranched long-chain alkanes are the consequences here.

In the monomolecular cracking, called Haag and Dessau’s mechanism, a solid acidic catalyst protonates an alkane to generate carbenium ion transition states that collapse to produce alkanes (or hydrogen) and carbenium ions. (Haag, Dessau, & Lago, 1991; Kotrel, Knozinger, & Gates, 2000) The cracking products include hydrogen, methane and ethane, in contrast to those of classical catalytic cracking. Reaction temperatures about 800 K are necessary for the Haag-Dessau-cracking mechanism. Protolytic cracking on solid acids is only kinetically significant when alkene concentration is low because alkenes are much better proton acceptors than alkanes. Alkene protonation leads to classical catalytic cracking.
Another different type of side reaction involving carbenium ions as active species is the alkylation reaction. (Corma & Martinez, 1993) An alkene is alkylated by a carbenium ion, producing a new and higher molecular carbenium ion. Again, the alkene can be formed byScheme 7. Modes of β-scission of alkylcarbenium ions; (Weitkamp et al., 1983) parameter \( m \) is the minimum number of C-atoms of the carbenium ion to crack according to the corresponding mode of β-scission.

Scheme 8. Haag–Dessau cracking mechanism for an alkane molecule (RH) proceeding via a carbonium ion transition state. (Haag et al., 1991).

Scheme 9. Alkylation of isobutane with 2-butene.

Alkylation reaction. Another different type of side reaction involving carbenium ions as active species is the alkylation reaction. (Corma & Martinez, 1993) An alkene is alkylated by a carbenium ion, producing a new and higher molecular carbenium ion. Again, the alkene can be formed by
cracking via β-scission or deprotonation of carbenium ions. The catalytic cycle is also maintained by hydride transfer from an alkane to the carbenium ion.

Coke formation on solid acidic catalysts. Formation and retention of heavy side products takes place on solid catalysts in the pores, on the outer surface or on both. The formation of these non-desorbed products is called coke and represents the most frequent cause of catalyst deactivation in industrial processes. It is differentiated between coke formation at low temperatures (< 473 K) and high temperatures (> 623 K). (Guisnet & Magnoux, 2001) Low-temperature coke is non-aromatic. Carbonaceous deposits are directly formed from unsaturated compounds like alkenes or cyclic alkenes in oligomerization/polymerization reaction but not from alkanes and cycloalkanes.

1.4.1.5. Cracking inhibitor hydrogen. Hydrogen can react with carbenium ions. This fact was shown for liquid superacidic catalysts (Bickel, Goasbeek, Hogeveen, Oelderik, & Platteeuw, 0000) and solid metal free acidic catalysts. (Corma, Sanchez, & Tomas, 1983; Ebitani, Tsuji, Hattori, & Kita, 1992; Meusinger & Corma, 1995, 1996) Thus, hydrogen pressure can be responsible for higher isomer selectivity circumventing consecutive cracking reactions of branched alkanes. However, hydrogen can also have a negative influence on the rate of isomerization and cracking because it is the reverse reaction of carbenium ion generation (Scheme 1). A possible mechanism for the hydrogen-carbenium ion reaction was proposed based on theoretical calculations: hydrogen and carbenium ions can interact via the formation of the H₂-carbenium ion-complex with subsequent evolution to the corresponding alkane and proton. (Corma et al., 1983)

The alkane isomerization on metallic catalysts is believed to proceed through an olefin intermediate (Eisuke et al., 2005; Ross, 2012) which is formed by paraffin dehydrogenation on the metal site.

![Scheme 1](image)

(1)

Although the equilibrium conversion of the paraffin in reaction (1) is low at paraffin isomerization conditions, sufficient olefins are present to be converted to a carbenium ion by the strong acid site.

![Scheme 2](image)

(2)

The formation of the carbenium ion removes olefin products from reaction (1) and allows the equilibrium in reaction (1) to proceed. The carbenium ion in reaction (2) undergoes a skeletal isomerization, probably through a cycloalkyl intermediate as
reaction (3) proceeds with difficulty because it requires the formation of a primary carbonium ion at some point in the reaction. Nevertheless, the strong acidity of isomerization catalysts provides enough driving force for the reaction to proceed at high rates. (Diaz & Mare, 1983) The i-paraffinic carbonium ion is then converted to an olefin through loss of a proton to the catalyst site.

In the last step, the isoolefin intermediate is hydrogenated rapidly back to the analogous isoparaffin.

In addition to these primary reaction pathways, some evidences indicate the existence of a bimolecular reaction mechanism, in which olefinic intermediates dimerize, internal carbon atoms are protonated, skeletal isomerization occurs and the dimer undergoes beta scission which results in the product isoparaffin. In addition to the C13 labeling experiments that support this mechanism, a relatively small amount of hydrocarbons containing higher carbon numbers than the feed are always found in the reaction as byproducts. (Gary, 2001; Urquieta, 2002) The bimolecular mechanism has a minor impact on commercial isomerization processing.

Developments in the isomerization are usually based on the introduction of new, more active or more stable catalysts. Isomerization reactions are usually reversible reactions and attain equilibrium at lower temperature with highest concentration of isomeric products. The role of catalyst in isomerization is, therefore, extremely important. The intensity of unwanted side reactions diminishes at lower temperatures as higher temperature favors unwanted cracking, hydrogenation, polymerization reactions. (Goodarz, Morteza, Sayed, Huuhtanen, & Hamid, 2008; Lovasic et al.,
1990; Maria et al., 2008; Ross, 2012) For that reason, isomerizing catalysts must ensure the optimal rate of reactions at as low temperature as possible. (Hadi, 2007; Maria et al., 2005)

Alkane-isomerization is basically of two types in broader sense-(i) isomerization in presence of hydrogen gas, that is, hydroisomerization and (ii) isomerization in absence of hydrogen gas. The alkane-isomerization catalysts are basically of four types: (Meyers, 2004) (a) hydroisomerization catalyst (aluminum chloride, zeolite, metal doped zeolite etc.), (b) solid super acidic catalyst (halogenated alumina, La$_2$O$_3$-TiO$_2$ etc.), (c) hetero poly acid catalysts, and (d) ionic liquid catalysts (PF$_6^-$, BF$_4^-$, alkyl substituted pyridinium ion, etc.). (Hartmut & Ernst, 2003b)

1.5. Classification of n-alkane isomerization catalysts

1.5.1. Hydroisomerization catalysts

Hydroisomerization process converts the normal hydrocarbon to its isomer, which has high octane number like benzene. However, they are not carcinogenic like benzene, and hence non hazardous. It is a simple and cost-effective process for octane number enhancement compared with other octane number-improving processes. In this process, the light normal alkanes (n-butane, n-pentane, n-hexane, etc.) are isomerized to their more branched counterparts in the presence of hydrogen over a bifunctional catalyst normally. To prevent coke deposition, isomerization is carried out at an elevated pressure in a hydrogen atmosphere. (Ling et al., 2009; Novaro et al., 2000; Ping, Xz, Ruiping, & Xiaqian, 2009) Industrial processes are carried out at 400–480°C temperature and 1.4–10.5 MPa pressure. Catalysts commonly used for isomerization are Friedel-Craft catalyst, tungsten sulfide, bifunctional catalysts, zeolite-containing catalysts with noble metals like Pt or Pd, and complex (bifunctional and zeolite containing Friedel-Craft catalysts). With Friedel-Craft catalysts, isomerization can be effected at 2 MPa and 40–120°C or even at 24–50°C (with bromine base catalysts). (Rachid, Franco, & Chem, 2006) The advantage offered by these catalysts is that the presence of small quantities of water in the n-alkane feedstock can lead to the formation of strongly polarized hydroxyl group (O—H), which has consequent effect of increasing the isomerization rate. In the presence of certain catalysts such as aluminum chloride with promoters, isomerization of paraffins can be carried out at the room temperature. Recent studies (Khalid et al., 2007; Michael, 1985; Rafael et al., 2008) have shown that the isomerization of paraffinic hydrocarbons in the presence of aluminum chloride is accelerated substantially if the reaction mixture contains traces of olefins. Catalysts of this type are however strong acids and can cause the corrosion of the equipment, because of which they are not used widely in the industry. Other catalysts of isomerization (except for those of the Friedel-Craft type) require higher temperature and pressure of hydrogen, which results in the formation of a large amount of side products. (Michael, 1985) The isomerization of olefins can proceed by the formation of isoolefins or by double bond transfer. Isomerization of naphthenes occurs with the transformation into olefins or with a change in the number of carbon atoms in the cycle. There are many other types of isomerization reaction, for instance, isomerization of alkyl benzene hydrocarbons, including xylenes, etc. All these reactions occur through the common carbocation mechanism. As discussed earlier, the hydroisomerization reaction takes place in the hydrogen atmosphere whose role is to suppress polymerization and cracking reactions, which might deactivate the catalyst. The isomerization reaction is nearly a thermo-neutral reaction and does not require heat supply to the reactors from outside and hence can be carried out in a single reactor. (Maria et al., 2005) This concept is applicable for both the hydroisomerization as well as normal isomerization of alkanes.

The elimination of tetraethyl lead over the last 30 years as a means of improving the antiknock properties of gasoline, and more recent regulations restricting motor fuel composition have led refiners to select alternative means of producing high-quality gasoline. Because of many limitations such as benzene concentration restrictions, potential limitations on total aromatics concentration, and end-point and olefin content limitations, also the choices of high-quality gasoline blending components available in the typical refinery are limited. As a result, isomerate, the gasoline-blending component from light paraffin isomerization, is an ideal choice. (Maloncy
et al., 2005; Meyers, 2004) Another equally valuable blending component is alkylating resulting primarily from the acid-catalyzed reaction of isobutene with an aliphatic olefin. Both isomerization and alkylation yield highly branched, high-octane paraffinic blending components, which by themselves can satisfy the strictest environmental requirements. Because of the heightened demand for isomerate, refiners continue to strive for effective and economic means of producing valuable blending component. (Hollo et al., 2002)

An aluminum chloride catalyst for alkane isomerization was first developed in the 1930s. (Hao et al., 2009) The original application was for the conversion of n-butane to isobutane, which was, and still is, reacted with C\textsubscript{3}, C\textsubscript{4}, and C\textsubscript{5} olefins to produce motor fuel alkylate. The first application of this high-octane product was in the production of high-octane aviation gasoline. Subsequent developments of this predominantly Lewis acid catalyst resulted in the current alumina-supported bifunctional catalyst. UOP\textsuperscript{\textregistered}’s I-8 catalyst is one commercial example of this catalyst system, which has shown wide commercial application since 1981. Chloride alumina, the highest-activity paraffin isomerization catalyst available, increases the octane of a typical light-naphtha stream from about 70 to as high as 85 RONC in a once-through paraffin isomerization unit. Higher product octanes, up to 93 RONC, can be obtained by recycling low-octane hydrocarbons. The C + 5 yield from chloride alumina catalysts is the highest from any commercial catalyst because of high catalyst selectivity and low operating temperature. (Satoshi, 2003) Since chloride alumina systems are not economically regenerable, eventual reloading of the isomerization catalyst must be considered. Nevertheless, the chloride alumina system is often the most-economic choice because of its inherent high activity. In addition, only chloride alumina catalysts have enough activity to economically isomerize butanes. As a result of ongoing intensive research and development in paraffin isomerization technology, UOP’s I-80 catalyst is one of the highest-activity chloride alumina catalysts currently available. (Hollo et al., 2002) The I-80 catalyst, is significantly more active than the I-8 catalyst, which is based on a unique formulation and manufacturing technique. By simply reloading the I-80 catalyst in existing reactors, a gain of 0.5–1.0 RON can be realized compared to the product RON with the use of I-8 catalyst.

Zeolitic isomerization catalysts, such as UOP’s HS-10\textsuperscript{TM} or I-7\textsuperscript{TM} catalysts, operate at higher temperatures than chloride alumina catalysts. The maximum octane number of product can be achieved, which is limited by the unfavorable equilibrium at these conditions. Yields are also lower as a result of the higher operating temperature and the less selective characteristics of zeolitic catalysts. A typical octane upgrade for a once through zeolitic isomerization unit is from 70 to about 79 RONC. Higher product octanes (Navaro et al., 2000; Ping et al., 2009) can be obtained in a recycle operation, such as a Tip\textsuperscript{TM} unit. The advantages of zeolitic isomerization catalysts are that they are not permanently deactivated by water or other oxygenates, though temporary deactivation of these catalysts happen. (Marios et al., 2009)

A typical metal oxide catalyst, UOP’s LPI-100 catalyst (Hollo et al., 2002; Satoshi, 2003) has a considerable higher activity than that of traditional zeolitic catalysts, and this activity advantage is equivalent to about 80°C lower reaction temperature. The lower reaction temperature allows the product with a significantly higher product octane, about 82 RONC for a typical feed or three numbers higher than that of a zeolitic catalyst. (Marios et al., 2009) Similar to zeolitic catalysts, the LPI-100 catalyst is not permanently deactivated by water or oxygenates in the feedstock. These catalysts are also fully regenerable using a simple oxidation procedure that is comparable to the one that is used for zeolitic catalysts. (Maria et al., 2005) The high activity of the LPI-100 catalyst makes it an ideal choice for revamping existing zeolitic isomerization units for higher capacity and higher-octane isomerate, and also for new units where the full performance advantage of chloride alumina catalysts is not required or where the refiner is concerned about contaminants in the feedstock. (Galadima et al., 2009; Maria et al., 1997; Serra et al., 2003)

Molybdenum oxide based catalysts such as partially reduced MoO\textsubscript{3} and Molybdenum oxycarbides were also reported to play a considerable role in n-alkanes isomerization. A group of researchers carried out a study on the isomerization of n-pentane, in which molybdenum oxide
treated with hydrogen as a reducing agent. Unreduced MoO$_3$ was found to be inactive at the employed reaction conditions (573 K and atmospheric pressure). However, H$_2$ reduction of MoO$_3$ at higher temperature (623 K) promotes both the activity of isomerization and selectivity. In comparative term, the reduced catalyst shows appreciable activity higher than a tested bifunctional zeolite (0.5 wt. %/Pt/USY Zeolite). (Maria et al., 1997, 2005) The main drawback of this type of catalyst is that the reaction is carried out at high pressure of hydrogen (20–70 kg cm$^{-2}$), which is too much to be consumed in the process.

The mechanism of the process consists of the following three elementary steps. (Galadima et al., 2009; Lovasic et al., 1990; Serra et al., 2003) At first, the n-alkane is dehydrogenated on the metal surface to a corresponding alkene. Secondly, the produced alkene is then adsorbed on the Brønsted acid sites, resulting carbenium ion in the transition state, which isomerizes and consequently desorbs. In addition, the third, the i-alkene produced is hydrogenated on the metal surface to an i-alkane.

1.5.2. Solid super acidic catalysts
Catalyst activity and the lowest operating temperature are important to achieve an economic operation. Hence, in our present summary, we have stressed on super acidic catalysts, which need very low temperature and pressure to isomerize n-alkanes. In primary reaction pathway of alkane isomerization, it is shown that the primary functionality of a paraffin isomerization catalyst is to protonate a secondary carbon atom. All known paraffin isomerization catalysts have a combination of strong Lewis and Brønsted acid sites, which result in varying levels of protonation activity. (Rachid et al., 2006)

In addition to a strong acid function, isomerization catalysts must also be capable of hydrogenolysis, which not only assists in the protonation step, but also helps to saturate olefin intermediates and aromatic hydrocarbons, and also assists in the ring opening of cycloparaffins. This function also gives stability to isomerization catalysts, thereby improving the process economics.

Sulfated metal oxide catalysts, which have been described as solid super acids, exhibit high activity for paraffin isomerization reactions. (Arata, Matsuhashi, Hinob, & Nakamura, 1990; Boronat, Viruela, & Corma, 1996) These metal oxides form the basis of the new generation of isomerization catalysts, which have been actively discussed in the scientific literature in recent years. (Boronat et al., 1996) These catalysts are most commonly tin oxide (SnO$_2$), zirconium oxide (ZrO$_2$), titanium oxide (TiO$_2$), or ferric oxide (Fe$_2$O$_3$) those have been sulfated by reaction with sulfuric acid or ammonium sulfate. Sulfated alumina is not an active catalyst for hydrocarbon reactions. Zirconia (zirconium oxide) when merged with anions such as sulfate gives a catalyst with very high acid strength, which is highly effective catalyst for hydrocarbon isomerization. (Arata et al., 1990) In 1962, Holm and Bailey first mentioned sulfated zirconia as an isomerization catalyst in a patent. (Boronat et al., 1996; Satoshi, 2003) In 1979, Hino and Arata (Hino & Arata, 1994) published that sulfated zirconia was active for n-butane isomerization at 100°C. Thereby, they confirmed the super acidic nature, which is responsible for its catalytic activity with the help of Hammett indicators. (Arata et al., 1990) In 1992, a group of researchers (Keogh, Srinivasan, & Davis, 1995) found that n-butane could be isomerized at as low temperature as 35°C, over SZ promoted by iron and manganese (FMSZ). The promoters increased the isomerization activity by almost three orders of magnitude; this was ascribed to an increase in the acid strength of the catalysts. (Boronat et al., 1996) The assignment of super acidity has now been abandoned by most groups. Since the discovery of iron and manganese, the promoting effect of a wide range of other metals has been studied. (Ling et al., 2009; Maria et al., 1997) Not only the strength of the acid matters for enhanced activity and selectivity, but also the type of acidity, that is, Brønsted or Lewis, is important. There are different opinions on whether it is Lewis or Brønsted acidity that gives sulfated zirconia its catalytic activity, or if it is a combination of the two types. A group of researchers found that Lewis acidity is essential for the isomerization activity, but activity from Brønsted sites are not excluded. Both the Brønsted sites and Lewis acid sites coexist on the SZ
surface. (Arata et al., 1990; Chao, Wu, & Leu, 1995; Hino & Arata, 1994) Several research scientists have worked on the optimized ratio between Lewis and Brønsted acids for maximization of the catalytic activity, (Matsuhashi, Shibata, Nakamura, & Arata, 1999) but the confirmed optimized ratio is still under investigation.

1.5.3. Hetero poly acid catalysts

Another class of highly acidic materials is the hetero poly acids (HPA). HPAs are considered as complex proton acids consisting of polyxo xometalate anions (hetero polyanions) in which metal −oxygen octahedra forms the basic structural units. Solid HPAs are known to form ionic crystals comprising of hetero poly anions, cations like H⁺, H₃O⁺, H₂O роль+, etc. and hydration water. In line with their strong Brønsted acidity, HPAs possess three types of outer oxygen atoms serving as potential protonation units. This structure allows high proton mobility and the corresponding hetero poly anions can stabilize cationic paraffin intermediates. Similarly, changing chemical composition can easily vary their acid-base and redox characteristics. One of the most interesting compounds for acidic reactions is H₃PW₁₂O₄₀ and its cesium salts. (Olah, Prakash, Molnar, & Sommer, 2009b) These materials are able to catalyze the isomerization of alkanes at moderate temperatures. (Gregory, 2008; Rotello, 2003) A group of researchers (Gregory, 2008) found that the stationary activity and selectivity of Cs₂₅,₅H₃₇₅PW₁₂O₄₀ were much higher than those of sulfated Zirconia at 573 K, and they concluded that the high catalytic performance of this catalyst was due to its low deactivation and strong acidity. Commercially available hetero poly acids such as H₅SiW₁₂O₄₀, H₇PMO₁₂O₄₀, and H₆SiMo₁₂O₄₀ and their metal (s) promoted species are another category of solid acids catalysts with good potentials in isomerization and other industrial processes. However, the preparation methods of these catalysts are costly, complex, and time consuming. The stability of these catalysts is also low. Reactions involving solid HPAs are usually carried out with utmost care because they show properties close to those of solutions. These catalysts have discrete and mobile ionic structures, and they absorb a large amount of polar molecules, such as alcohols, ethers, amines, etc. in the catalyst bulk, yielding HPA solvates. (Boronat et al., 1996) Simultaneous presence of platinum and hydrogen inhibits and suppresses the isomerization of n-pentane at 423 K over HPA-based catalysts.

1.5.4. Ionic liquid catalyst

Ionic liquids (ILs) consist completely of ions and have, by definition, a melting point (Tm) < 373K as well as very low vapor pressure when used below their decomposition temperatures. (Hammett & Deyrup, 1932; Paul & Long, 1957) Of late, ionic liquids offer an alternative hydrocarbon-isomerization method through catalysis. ILs are nontoxic in nature and they have low saturation vapor pressure. Chloroaluminate ILs are the most common catalysts in this category. (Meyers, 2004; Murphree, 1951; Olah et al., 2009b) Though these catalysts are effective, they undergo rapid partial deactivation and also their preparation is costly and time consuming as well.

1.5.5. Characteristic properties of acidic halometallate ILs

Chloroaluminate ILs, low-temperature molten salts, were discovered in the 1940s. (Hurley, 1948; Hurley & Wier, 1951a, 1951b; Wier & Hurley, 1948) The application of mixtures of 1-ethylpyridinium bromide/aluminum chloride ([Epyr]Br/AlCl₃) to the electro deposition of aluminum was described. The system [Epyr]Br/AlCl₃ is only liquid at or below room temperature with compositions between 63 and 68 mol. % of AlCl₃. Not until 1975, Osteryoung and Gilbert studied the chemical and physical properties of ILs made from 1-butylpyridinium chloride/aluminum chloride ([BPy]Cl/AlCl₃). (Gole, Gilbert, & Osteryoung, 1978c) This molten salt is liquid at room temperature in case of AlCl₃ content between x(AlCl₃) = 0.43–0.66. (Robinson & Osteryoung, 1979; Takahashi, Koura, Kohara, Saboungi, & Curtiss, 1999) First applications of chloroaluminate ILs included mostly battery electrolytes. (Carlin, Truelove, & Osteryoung, 1992; Karpinski & Osteryoung, 1984; Nardi, Hussey, & King, 1978; Wilkes, Levisky, Wilson, & Hussey, 1982) The synthesis of the IL [EMIM]Cl/AlCl₃ established a system with a liquid range much wider than that of Hurley and Wier (Hurley & Wier, 1951a, 1951b) or Osteryoung: (Gole, Gilbert, & Osteryoung, 1978b) It is a liquid at room temperature from x(AlCl₃) = 0.33–0.67. (Aa, Jr, Ja, & Js, 1984; Aa et al., 1984; Elias & Wilkes, 1994;
Scheme 10. Thermodynamic equilibrium parameter of reactions occurring in AlCl3 based ILs. (Oye et al., 1991).

| Reaction | log K (200°C) |
|----------|--------------|
| 1. [AlCl4]− ⇌ Cl− + AlCl3 | -16.67 |
| 2. [Al2Cl7]− ⇌ [AlCl4]− + AlCl3 | -2.54 |
| 3. [Al3Cl10]− ⇌ [Al2Cl7]− + AlCl3 | -0.90 |
| 4. [Al4Cl13]− ⇌ [Al3Cl10]− + AlCl3 | -0.34 |

Oye, Jagtoyen, Oksefjell, & Wilkes, 1991; Wilkes, Frye, & Reynolds, 1983; Wilkes, Levisky, Pflug, Hussey, & Scheffler, 1982; Wilkes et al., 1982) Depending on the mole fraction of AlCl3, chloroaluminate systems are Lewis basic at x(AlCl3) < 0.5, neutral at x(AlCl3) = 0.5 or Lewis acidic at x(AlCl3) > 0.5. (Welton, 1999) Hence, predominant species in basic melts are Cl− and [AlCl4]− and in acidic melts, these are [Al2Cl7]− and [Al3Cl10]−. The maximum amount of AlCl3 is limited by the liquid range of the chloroaluminate IL to two mol. AlCl3 per mol [cation]Cl. (Welton, 1999)

2. Conclusion
The present review aims to describe n-alkane isomerization process to date available and its mechanism. The isomerization process was summarized, reviewed with emphasis on reaction chemistry of reaction, catalyst developments, recent advances in process technology and commercial processes. Various alkane isomerization processes based on different catalysts were compared thoroughly in detail with their advantages and disadvantages. This article would be highly helpful to the researchers in the field of petroleum products as well as refiners for the selection assortment of suitable technology for their isomerization units to upgrade their naphtha streams with respect to octave number and benzene.

Funding
The authors received no direct funding for this research.

Author contributions
AD and RLV designed the review structure wrote the first draft, PB helps to brought it to its final state.

Competing Interest
The authors declares no competing interests.

Author details
Abhishek Dhar
E-mail: abhishek2000@gmail.com
Rohit L. Vekariya
E-mail: rohit.vekariya@tdt.edu.vn
Poonam Bhdaja
E-mail: poonam.bhdaja@tdtu.edu.vn
1 Department of Chemical Engineering, University of Calcutta 700 009, 92, Acharya Prafulla Chandra Road, Kolkata, India.
2 School of Chemical Engineering, Fuzhou University, Fuzhou 350116, Fujian Province, PR, China.
3 Department for Management of Science and Technology Development, Ton Duc Thang University, Ho Chi Minh City, Vietnam.
4 Faculty of Environment and Labour Safety, Ton Duc Thang University, Ho Chi Minh City, Vietnam.

References
Arata, K., Matsuhashi, H., Hinob, M., & Nakamuraa, H. (1990). Advancement Catal, 81, 17–30.
Bickel, A. F., Gaasbeek, C. J., Hogeveen, H., Oelderik, J. M., Platteeuw. J. C. (1967). Chemical Communications, 634-635. doi: 10.1039/C19670000634
Boromat, M., Viruela, P., & Corma, A. (1996). Journal Physical Chemical, 100, 633-637. doi:10.1021/jp9514077
BP Statistical Review 2013, June.
Brouwer, D. M., & Oelderik, J. M. (1968). Recueil des Travaux Chimiques des Pays-Bas, 87, 721-736. doi:10.1006/jcat.1995.1293
Calemma, V., Peratello, S., Perego, C. (2000). Applied Catalysis A., 190, 207-218.
Carlin, R. T., Truelove, P. C., & Osteryoung, R. A. (1992). Electrochemical and spectroscopic study of anthracene in a mixed Lewis—Brønsted acid ambient temperature molten salt system. Electrochimica Acta, 37, 2615–2625. doi:10.1016/0013-4686(92)87076-1
Chao, K. J., Wu, H. C., & Lee, L. J. (1995). Skeletal Isomerization of n-Butane on Zeolites and Sulfated Zirconium Oxide Promoted by Platinum: Effect of Reaction Pressure. Journal Catal, 157, 289–293. doi:10.1006/jcat.1995.1293
Chica, A., & Corma, A. (2007). Chemie Ingenieur Technik-CIT, 79, 857–870. doi:10.1002/cite.200700030
Corma, A., & Martinez, A. (1993). Rcatal Sciences Engineering, 35, 483–570.
Corma, A., Martinez, A., Pergher, S., Peratello, S., Perego, C., & Bellusi, G. (1997). Applications Catal A: General, 152, 107–125. doi:10.1016/S0926-860X(96)00338-9

Citation information
Cite this article as: n-Alkane isomerization by catalysis—a method of industrial importance: An overview, Abhishek Dhar, Rohit L. Vekariya & Poonam Bhdaja, Cogent Chemistry (2018), 4: 1514686.
Corma, A., & Orchilles, A. V. (2000). Micropor Mesopor Materials, 35-36, 21–30. doi:10.1016/S1387-1811(99)00205-X
Corma, A., Planelles, J., & Tomas, F. (1985). Journal Catal, 94, 445–454. doi:10.1016/0021-9517(85)90209-X
Corma, A., Sanchez, J., & Tomas, F. (1983). Journal Molecular Catal, 19, 9–15. doi:10.1016/0304-5102(83)80015-7
Dhar, A., Vekariya, R. L., & Sharma, P. (2017). Petroleum, 3, 489-495.
Diaz, G., & Mare, G. (1983). Journal Catal, 82, 13-25. doi:10.1016/0021-9517(83)90113-6
Ebitani, K., Tsujii, J., Hattori, H., & Kita, H. (1992). Activation of molecular hydrogen into protonic acid sites over metal-free H-ZSM-5 catalyst. Journal Catal, 138, 750–753. doi:10.1016/0021-9517(92)90322-9
Eisuke, Y., Junko, N. K., & Kazunari, D. (2005). Journal Physical Chemical, 109, 1464–1472.
Eliaa, A. M., & Wilkes, J. S. (1994). Densities, molar volumes, and thermal expansivities of 1-methyl-3-ethylimidazolium chloride + aluminum chloride + alkali-metal halide molten salts. Journal Chemical Engineering Data, 39, 79–82. doi:10.1021/je010360b
Fannin, A. A., Floreani, D. A., Jr., L., A., Landers, J. S., Piersma, B. J., Stich, D. J., Vaughn, R. L., Wilkes, J. S., Williams, J. L. (1984). Properties of 1,3-dialkylimidazolium chloride aluminum-chloride ionic liquids. 2. Phase transitions, density, electrical conductivities, and viscosities. The Journal of Physical Chemistry, 88, 2614–2621. doi:10.1021/j1506560a037
Galadima, A., Anderson, J. A., & Wells, R. P. K. (2009). Sciences World Journal, 4, 15–18.
Gale, R. J., Gilbert, B., & Osteroyung, R. A. (1978c). Inorganic Chemistry, 17, 2728–2739. doi:10.1021/ic5018800
Gale, R. J., Gilbert, B., & Osteroyung, R. A. (1978b). Raman spectra of molten aluminum chloride: 1-butylpyridinium chloride systems at ambient temperatures. Inorganic Chemistry, 17, 2728–2729. doi:10.1021/ic5018800
Gary, J. H. (2001). Petroleum Refining (4th ed.). New York: Marcel Dekker.
Goodarz, T., Morteza, S., Sayed, J. R., Huuhtanen, K., & Hamid, I. (2008). Synthesis and activity measurement of some bifunctional platinum loaded beta zeolite catalysts for n-heptane hydroisomerization. Journal Industrial Engineering Chemical, 14, 614–621. doi:10.1016/j.jiec.2008.04.001
Greven, T. (2008). Nanotechnology. New York: Springer.
Guisnet, M., & Magnoux, P. (2001). Applications Catal: General, 212, 83–96. doi:10.1016/S0926-860X(00)00865-0
Guisnet, M., Thomazeau, C., Lemberton, J. L., & Mignard, S. (1995). Journal Catal, 151, 102–110. doi:10.1016/0021-9515(95)10113-9
Hoag, W. O., Dessau, R. M., & Lago, R. M. (1991). Studies SurfSciences Catal, 60, 255–265.
Hadi, M. (2007) Kinetic Study of Catalytic Hexane Isomerization, [M. Sc. thesis], Baghdad.
Hammett, L. P., & Deyrup, L. P. (1932). Journal of the American Chemical Society, 54, 2721–2739. doi:10.1021/ja1346605
Hancok, J., & Kaszo, T. (2011). The importance of isoparaffins at the modern engine fuel production. In W. Bartz (Ed.), Proceedings of 8th international colloquium fuels, 2011 international colloquium fuels, 19–20 January 2011 (pp. 361–373). Stuttgart/ Ostfildern, Germany, Esslingen: TAE.
Meyers, R. A. (2004). *Handbook of petroleum refining processes*. McGraw Hill Education.

Michael, J. B. (1985). *Industrial Engineering Chemical Products Researcher Developments*, 24, 540–544. doi:10.1016/S0003-2029(01)80010-0

Murphree, E. V. (1953). *Progress Petroleum Technological*. ACS, Volume 5, Chapter 658–59.

Nardi, J. C., Hussey, C. L., & King, L. A. (1978) US412245A.

Novaro, O., Munoz, E., Boldu, J. L., Bokhimi, X., Wang, J. A., Lopez, T., & Gomez, R. (2008). *Applications Catal A: General*, 199, 211–220. doi:10.1016/S0926-860X(09)00591-1

Olah, G. A. (1964a). Friedel-crafts and related reactions, isomerization of saturated hydrocarbons. H. Pines & N. E. Hoffman (ed), (Vol. 2, pp. 1211–1217). New York: Interscience Publishers.

Olah, G. A. (1964b). Friedel-crafts and related reactions, alkylation of aromatics with haloalkanes. F. A. Drahowzal (ed), (Vol. 1, pp. 417–475). New York: Inter. Sci. Publishers.

Olah GA, Molnar A, Hydrocarbon Chemistry. Paul, M. A., & Long, F. A. (1957). Inorganic Chemistry, 2nd ed, Industrial Engineering Chemical Products Researcher Developments, 21, 550–558. doi:10.1016/S0926-860X(99)00105-7

Olah, G. A., Prakash, G. K. S., Molnar, A., & Sommer, J. (2009a). *Superacid Chemistry*. 2nd ed., Hoboken, New Jersey, Wiley, 1:501–539.

Olah, G. A., Prakash, G. K. S., Molnar, A., & Sommer, J. (2009b). 2nd ed., Hoboken, New Jersey, Wiley 1:341:501–539.

Oye, H. A., Jagtzyen, M., Oksefjell, T., & Wilkes, J. S. (1991). Vapour pressure and thermodynamics of the system 1-methyl-3-ethyl-imidazolium chloride - aluminium chloride. *Materials Sciences Forum*, 73–75, 181–189. doi:10.4028/www.scientific.net/MSF.73-75

Paul, M. A., & Long, F. A. (1957). *Chemical Reviews*, 57, 1–45. doi:10.1021/cr50013a001

Ping, L., Xz, J., Ruiping, W., & Xiaoqian, R. (2009). Catalytic performances of dealuminated H3 zeolite supported Pt catalysts doped with Cr in hydroisomerization of n-heptane. *Chemical Engineering Journal*, 148, 184–190. doi:10.1016/j.cej.2008.12.016

Rachid, I., Franco, G., & Chems, E. C. (2006). Palladium-Sulfated zirconium pillared montmorillonite: Catalytic evaluation in light naphtha hydroisomerization reaction. *Catal Today*, 113, 174–177. doi:10.1016/j.cattod.2005.11.063

Rafael, R., Andrew, M. B., Manuel, S., Francisco, J. R., Cesar, J., Juan, P. G., & Goginathan, S. (2008). Effect of the impregnation order on the nature of metal particles of bi-functional Pt/Pd-supported zeolite Beta materials and on their catalytic activity for the hydroisomerization of alkanes. *Journal Catal*, 254, 12–26. doi:10.1016/j.jcat.2007.10.022

Robinson, J., & Osteryoung, R. A. (1979). *Journal of the American Chemical Society*, 101, 323–327. doi:10.1021/ja00496a008

Ross, J. R. H. (2012). Heterogeneous catalysis: Fundamentals and applications. Netherlands: Elsevier.

Rotello, V. M. (2003). *Nanoparticles: Building blocks for nanotechnology* (1st ed.). New York: Springer.

Satoshi, F. (2001). *Applications Catal A: General*, 251, 285–293. doi:10.1016/S0926-860X(02)00360-0

Serra, J. M., Chica, A., & Corma, A. (2003). *Applications Catal A: General*, 239, 35–42. doi:10.1016/S0926-860X(02)00371-X

Sommer, J., Jost, R., & Hachoumy, M. (1997). *Catal Today*, 38, 309–319. doi:10.1016/S0921-5861(97)81501-3

Takahashi, S., Koura, N., Kohara, S., Saboungi, M. L., & Curtiss, L. A. (1999). *Plasmas Jons*, 2, 91–105. doi:10.1016/S1288-3255(99)00105-7

Urquieta, G. (2002). *Brazilian Journal Chemical Engineering*, 19, 335–342. doi:10.1590/S0104-66322002000300008

Weitkamp, J. (1982). *Industrial Engineering Chemical Products Researcher Developments*, 21, 550–558. doi:10.1016/S0926-860X(99)00105-7

Weitkamp, J. (2012). *Chemical Cat Chemical*, 4, 292–306. doi:10.1016/S1288-3255(99)00105-7

Weitkamp, J., & Farag, H. (1978). *Acta Physica et Chemica*, 24, 327–333.

Welton, T. (1999). *Room-Temperature Ionic liquids. solvents for synthesis and catalysis* Chemical Reviews, 99, 2071–2083.

Wier, T. P., & Hurley, F. H., Jr (1948) US2446349.

Wilkes, J. S., Frye, J. S., & Reynolds, G. F. (1983). Aluminum-27 and carbon-13 NMR studies of aluminum chloride-dialkytrimidazolium chloride molten salts. *Inorganic Chemical*, 22, 3870–3872. doi:10.1016/S0920-5861(97)81501-3

Wilkes, J. S., Levisky, J. A., Pflug, J. L., Hussey, C. L., & Scheffler, T. B. (1982). Composition determinations of liquid chloroaluminate molten salts by nuclear magnetic resonance spectrometry. *Analysis Chemical*, 54, 2378–2379. doi:10.1021/ac00250a055

Wilkes, J. S., Levisky, J. A., Wilson, R. A., & Hussey, C. L. (1982). Dialkytrimidazolium chloroaluminate melts: A new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis. *Inorganic Chemical*, 21, 1263–1264. doi:10.1021/ic00133o078
