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Developments and Uses of Lewis Acids: From Conventional Catalysts to Modern Green Catalysts

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Abstract

Lewis acids have played a pivotal role in organic synthesis. The inherent Lewis acidity of semimetal or metal ions, which stems from possession of empty orbitals or electron-accepting ability/electron pair affinity, has granted them the ability to catalyze various and numerous organic functional group transformations and methods for carbon-carbon (C-C) bond formation reactions. Lewis acids have developed from conventional catalysts to modern green ones that have enabled a wide range of chemical transformations and chemical processes of applications in various fields, such as pharmaceutical and petroleum/petrochemical industries. The chapter begins with a definition and description of Lewis acids and their significance in chemistry as an electronic science. The chapter then covers the uses and applications of Lewis acids as homogeneous catalysts in conventional organic reactions that employ and/or are Lewis-acids catalysts. Coverage continues on the importance of developments and inception of green and environmentally benign Lewis acids that can help preserve the environment, in a manifestation of green chemistry principles. Illustrations of the importance and applications of green Lewis acids in Lewis acid-catalyzed organic reactions and C-C bond formation reactions are covered. The chapter aims at introducing and stimulating the reader to Lewis acids, their description, and significance in synthetic organic chemistry in particular and in chemistry as a whole.

Keywords: Lewis acids, empty orbitals, Lewis-acid catalysis, homogenous catalysts, green Lewis acids

1. Introduction

According to Gilbert Lewis, a Lewis acid is a substance (atom, ion, or molecule) that contains or possesses an empty/vacant or unfilled atomic or molecular orbital that is capable of accepting or accommodating an electron pair [1–8]. This implies that substances with an incomplete or unsatisfied octet act as Lewis acids. An electron pair donor, a Lewis base, performs the donation of the electron pair from its highest
occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO) of the Lewis acid (Figure 1). Thus, in simple terms, a Lewis acid is an electron pair acceptor. The process of accepting an electron pair by a Lewis acid from a Lewis base results in the formation of a Lewis complex or adduct with a new coordinate covalent bond/dative bond or σ bond. Lewis acidity is closely linked and intertwined with electrophilicity. Thus, due to their electron deficiency, electrophiles with positive or partially positive characters as a result of electronic effects (inductive and electronic) manifest themselves as electron pair acceptors. Hence, Lewis acidity parallels electrophilicity in a similar manner that Lewis basicity parallels nucleophilicity.

Typical general examples of Lewis acids are based on B or boranes (BR\textsubscript{3}) [6], such as BH\textsubscript{3} and BF\textsubscript{3} and aluminum compounds, AlR\textsubscript{3}, such as AlCl\textsubscript{3}. Other examples include alkali (M\textsuperscript{+}) metal ions, such as K\textsuperscript{+} and alkaline earth metal ions (M\textsuperscript{2+}), such as Ca\textsuperscript{2+} and transition metal ions, such as Mn\textsuperscript{2+}. Other examples of Lewis acids include the proton, H\textsuperscript{+}, carbocations, R\textsubscript{3}C\textsuperscript{+} [8], and electron-deficient π-systems. The vast majority of Lewis acids are metal-based, such as those based on Al, Ti, Mg, and Mn. Some are metalloid/semimetal-based, such as those based on B [6] and Si [7]. A typical example of a Lewis acid-Lewis base reaction is the reaction between BF\textsubscript{3} (Lewis acid) and NH\textsubscript{3} (Lewis base) (Figure 2).

Conventional Lewis acids have long been used as catalysts and played significant roles in various chemical transformations, particularly organic synthetic reactions. Notably, in oxidation and reduction reactions, electrophilic aromatic substitution reactions exemplified by Friedel-Crafts alkylation and acylation, and halogenation reactions of benzene. Conventional Lewis acids have catalyzed other numerous organic reactions typified by the Diels-Alder reaction, Alder-ene reaction, aldol reaction, reactions of silyl enol ethers (direct (1,2-) addition, and conjugate (1,4-) addition) and acylation of ketones.
2. Conventional uses of Lewis acids in organic synthesis

Lewis acids have been used and applied in numerous organic transformations. They have been in various functional group transformations and C-C/C-X bond formation reactions [9–11]. Below are selected representative reactions that are only intended to highlight the importance of Lewis acids in organic synthesis but by no means a comprehensive review of all organic transformations catalyzed by Lewis acids. For additional details, the reader is advised to consult the original literature.

2.1 Oxidation reactions

Primary alcohols and secondary alcohols can be oxidized to the corresponding aldehydes and ketones, respectively, using TPAP/NMO oxidation method (TPAP: tetrapropylammonium perruthenate, NMO: N-methyl morpholine N-oxide) (Figure 3) [12].

The perruthenate ion acts as a Lewis acid on its Ru center (Figure 4). The reaction is initiated by the reaction of the Lewis basic alcohol and the Lewis acidic Ru on the perruthenate ion to give an intermediate that leads to the product aldehyde. The resultant Lewis acidic Ru (RuO$_3$H) species then reacts with the O-Lewis basic NMO to regenerate the Lewis acidic perruthenate catalyst.

Allylic and benzylic alcohols can be selectively oxidized to the corresponding aldehydes using activated MnO$_2$ (Figure 5) [13, 14].

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**Figure 3.**
Oxidation of alcohols using Lewis acidic TPAP/NMO.

**Figure 4.**
Mechanism of the TPAP/NMO oxidation of alcohols.
In the reaction, MnO$_2$ functions as a Lewis acid that accepts an electron pair from the Lewis basic O of the alcohol (Figure 6).

It has been reported that oxidation of alcohols to the corresponding ketones with potassium permanganate, KMnO$_4$, can be accelerated using Lewis acids, such as BF$_3$, Sc(OTf)$_3$, Zn(OTf)$_2$, Ca(OTf)$_2$, and Ba(OTf)$_2$ (Figure 7) [15]. The reaction is understood to be initiated by an initial reaction between the Lewis acid and the Lewis basic permanganate ion, MnO$_4^-$, leading to a Lewis adduct that affects the oxidation reaction (Figure 7).

Oxidation of sulfides to the corresponding ketones by KMnO$_4$ could be enhanced using the Lewis acidic FeCl$_3$ (Figure 8) [16]. The reaction is initiated by a Lewis complex that is formed upon the reaction of the Lewis basic permanganate, MnO$_4^-$, and the Lewis acidic FeCl$_3$ (Figure 8).

Figure 5. Oxidation of allylic and benzylic alcohols with MnO$_2$.

Figure 6. The reaction between the Lewis acidic MnO$_2$ with allylic alcohol.

Figure 7. Acceleration of alcohol KMnO$_4$ oxidation by Lewis acids.
2.2 Reduction reactions

Esters can be reduced to the corresponding aldehydes using DIBAL-H (diisobutylaluminum hydride) at very low temperatures (~78°C) [17]. DIBAL-H acts as a Lewis acid, thus accepting an electron pair from the Lewis basic ester (Figure 9). The conversion of the ester into the corresponding aldehyde lies in the formation of the Lewis complex that leads to a tetrahedral intermediate that leads to the aldehyde upon aqueous workup.

Lewis acids have been used as reducing agents in various functional group transformations. Based on the electron deficiency of Lewis acids, which stems from the presence of empty orbitals, they react with electron-rich carboxylic acids and carboxylic acid derivatives, such as amides. In this regard, borane, BH$_3$, is found to be an excellent reducing agent for amides [18] and carboxylic acids [19] to primary amines (Figure 10) and primary alcohols, respectively. Borane, BH$_3$, is a mild reducing agent

Figure 8. Acceleration of sulfide KMnO$_4$ oxidation by Lewis acidic FeCl$_3$.

Figure 9. Reduction of esters with Lewis acidic DIBAL-H at very low temperature.

Figure 10. Reduction of amides using borane, BH$_3$. 

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that is used instead of the more reactive LiAlH₄ that requires special handling procedures. The gaseous BH₃ is conveniently used as a liquid complex with diethyl ether (BH₃·Et₂O), tetrahydrofuran (BH₃·THF), or dimethyl sulfide (BH₃·DMS). The utility of BH₃ as an amide-reducing agent is extended to its chemoselective reduction ability of amides in the presence of less electron-rich carboxylic acid derivatives such as esters.

Mechanistically, amides utilize the N lone pair for donation to an empty p orbital in the Lewis acidic B in BH₃. In this manner, a Lewis adduct is formed from which a hydride transfer is initiated from the nucleophilic B to the electrophilic C affecting eventually leading to the reduction of the amide to the primary amine (Figure 11).

Similarly, carboxylic acids can conveniently be reduced with borane to give the corresponding primary alcohols (Figure 12). Borane has proven to be a highly efficient chemoselective reducing agent for carboxylic acids in the presence of less electron-rich carbonyl groups such as esters (Figure 12).

Sodium borohydride, NaBH₄, is known as a mild reducing agent for aldehydes and ketones. If an α,β-unsaturated carbonyl compound, such as the α,β-unsaturated ketone shown (Figure 13), is treated with NaBH₄, reduction of the both carbonyl group and the double bond takes place. Thus, the reaction is not regioselective/chemoselective. Chemoselective reduction of the carbonyl group in α,β-unsaturated ketone, while keeping the double bond intact, can be nicely achieved by adding the

![Figure 11.](image1.png)
The mechanism for the reduction of amides using borane, BH₃.

![Figure 12.](image2.png)
Reduction of carboxylic acids using borane, BH₃.

![Figure 13.](image3.png)
Chemoselective reduction of α,β-unsaturated carbonyl compounds using NaBH₄-CeCl₃ reduction (Luche reduction).
Lewis acidic cerium chloride, CeCl\(_3\) (Figure 13). The NaBH\(_4\)-CeCl\(_3\) reduction method is known as Luche reduction [20].

The role of the Lewis acidic CeCl\(_3\) lies in its reaction with Lewis basic O of the carbonyl group. That is by donation of an electron pair from O to an empty orbital in Ce (Figure 14). The Lewis complex produced facilitates subsequent and chemoselective reduction of the ketone by NaBH\(_4\)/CeCl\(_3\) in the presence of the C=O bond.

### 2.3 Electrophilic aromatic substitution: Friedel-crafts alkylation and acylation

Traditionally, Lewis acids have been used as catalysts in electrophilic aromatic substitution reactions of benzenes as typified by Friedel-Crafts alkylation and acylation reactions. The Friedel-Crafts alkylation employs benzene as a starting reactant that is reacted with an alkyl halide in the presence of AlX\(_3\) as a catalyst (Figure 15) [21].

Due to the inherent stability of benzene, the Lewis acid catalyst is essential for the reaction. That is, no reaction would take place in the absence of a Lewis acid catalyst. Benzene needs a highly electrophilic species to react with in order for the electrophilic aromatic substitution to take place. Although alkyl halides are electrophilic by inductive effect, they are not sufficiently electrophilic for benzene to lose aromaticity and react with them. This will require a high-energy barrier to overcome. The role of the AlX\(_3\) Lewis acid catalyst lies in its reaction with the Lewis basic alkyl halide. The alkyl halide donates one of the electron pairs on the halogen to the empty p orbital on Al in AlX\(_3\). That is employing a HOMO from X in RX to the LUMO on Al in AlX\(_3\). This results in the formation of the Lewis adduct, where a new \(\sigma\) bond between X and Al has formed. This Lewis adduct is a highly electrophilic species that is sufficiently electrophilic for the stable nucleophilic benzene (Figure 16).

The resultant Lewis adduct imparts a positive/electrophilic character on C bonded to X in the adduct. From a mechanistic point of view, this intermediate is susceptible to benzene nucleophilic attack. Alternatively, the electrophilic Lewis adduct can also

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**Figure 14.**
The role of CeCl\(_3\) in NaBH\(_4\)-CeCl\(_3\) reduction (Luche reduction).

**Figure 15.**
Friedel-crafts alkylation of benzene.
Electrophile and Lewis Acid

be envisioned to undergo dissociation to an electrophilic carbocation intermediate setting stage for nucleophilic attack by benzene (Figure 16). The figure below shows examples of Friedel-Crafts alkylation of benzene (Figure 17).

Friedel-Crafts acylation of benzene is the reaction of benzene with an acid halide (or anhydride) in the presence of a Lewis acidic AlX₃ (Figure 18) [21].

As in the Friedel-Crafts alkylation reaction, the Lewis acid catalyst is essential for the Friedel-Crafts acylation reaction. The role of the AlX₃ Lewis acid catalyst lies in its reaction with the Lewis basic acid halide. The acid halide acts as a Lewis base employing one of the electron pairs on the halogen. Thus, an electron pair is donated from the Lewis basic X to the empty p orbital on Al in AlX₃. This results in the formation of the Lewis adduct, where a new σ bond between X and Al has formed. This Lewis adduct is a highly electrophilic species that is sufficiently electrophilic rendering its susceptibility to nucleophilic attack by benzene (Figure 19).

Figure 16. 
Role of Lewis acidic AlCl₃ in Friedel-crafts alkylation of benzene.

Figure 17. 
Examples of Friedel-crafts alkylation of benzene.

Figure 18. 
Friedel-crafts acylation of benzene.
The electrophilic Lewis adduct formed can be envisioned to undergo dissociation to a highly electrophilic acylium cation intermediate. Thus, the stage is set for a facile Friedel-Crafts acylation reaction (Figure 19). The figure below shows examples of Friedel-Crafts acylation of benzene (Figure 20).

2.4 Electrophilic aromatic substitution: Halogenation

Halogenaion of benzene using a halogen in the presence of FeX₃ is an example of electrophilic aromatic substitution reactions (Figure 21). In the reaction, FeX₃ acts as a Lewis acid, which is essential for the reaction [22].

The Lewis basic halogen, X₂, donates an electron pair from X to an empty orbital on Fe in FeX₃ to form an electrophilic Lewis adduct (Figure 22). This electrophilic intermediate is susceptible to nucleophilic attack by benzene at the terminal halogen (X) of the polarized X-X bond. This electrophilic Lewis adduct can be envisioned to undergo dissociation of the polarized X-X bond to give X⁺ as an equivalent electrophilic intermediate (Figure 22). Thus, the stage is set for a benzene nucleophilic attack.

The Figure below shows examples of the halogenation of benzene (Figure 23).
2.5 Hydroboration-oxidation

Hydroboration-oxidation is an electrophilic addition of borane, BH$_3$, to alkenes or alkynes. In the case of hydroboration of alkenes, the product is alcohol that ends at the less sterically hindered or more accessible C of C=C bond of the alkene (Figure 24) [23]. This method is a complementary method to the oxymercuration of alkenes that leads to the more substituted alcohol. Unlike oxymercuration, which follows Markovnikov’s rule, hydroboration-oxidation is an anti-Markovnikov’s alcohol formation. BH$_3$ acts as a Lewis acid/electrophile that utilizes its empty p orbital to accept an electron pair from the nucleophilic double bond in an alkene. The hydroboration addition takes place in a concerted manner, thus governed by steric control. As a result, the BH$_2$ group of the electrophilic BH$_3$ ends up at the less sterically hindered (more accessible) C of the C=C bond, while H bonds to the more sterically hindered C (less accessible).

2.6 Diels-Alder reaction

The Diels-Alder reaction is an electrocyclic [4 + 2] cycloaddition reaction between a diene and a dienophile [24, 25]. It is a robust and well-established C-C formation method. Typically, the diene is bonded with an electron-donating group (EDG), such as alkoxy (OR) or amino groups (NR$_2$), and thus electron-rich. The dienophile is...
typically electron-poor, because of attachment with an electron-withdrawing group (EWG), such as an ester (CO$_2$R), cyano (CN), or nitro (NO$_2$) groups (Figure 25). The regioselectivity is governed by proper interactions between the HOMO of the diene and the LUMO of the dienophile (Figure 26).

Diels-Alder reactions that do not meet the proper electron-demand/match involving an electron-rich diene and electron-poor dienophile may require Lewis acid catalysis. The role of Lewis acids lies in their activation of the Lewis basic dienophile by binding with it. Formation of the Lewis adduct results in lowering the LUMO of the dienophile (Figure 26). The result is a smaller energy gap between the HOMO of the diene and the LUMO of the dienophile, setting the stage for stronger orbital interactions and thus enhancement of reaction rates. Lewis acids, such as AlCl$_3$, BF$_3$, ZnCl$_2$, and TiCl$_4$, have been found to be efficient catalysts for the Diels-Alder reaction.

2.7 Alder-ene reaction

The Alder-ene reaction is an electrocyclic cycloaddition reaction between an ene and an enophile (Figure 27) [26, 27].

Figure 25.
Diels-Alder reaction.

Figure 26.
Role of Lewis acids in activation of dienophiles as reaction partners in Diels-Alder reactions.
The role of Lewis acids in the Alder-ene reaction lies in their activation of the enophile by binding with it thus lowering the LUMO of the enophile (Figure 28). As a result, the energy gap between the HOMO of the ene and the LUMO of the enophile is lowered. Therefore, the resultant stronger interactions facilitate the ene reaction.

2.8 Mukaiyama aldol reaction

The aldol reaction, which is a reaction between an enolate of a carbonyl compound and an aldehyde or ketone to form β-hydroxy carbonyl compound or α,β-unsaturated carbonyl compound. The Mukaiyama aldol reaction is a variant of the aldol reaction that employs a silyl enol ether, an enolate equivalent, as a nucleophile, an aldehyde or a ketone as an electrophile in the presence of TiCl₄ as a Lewis acid catalyst (Figure 29) [28].
The role of the TiCl$_4$ Lewis acid catalyst lies in its coordination with the electrophilic aldehyde or ketone. The Lewis basic O of the carbonyl group employs one of its lone pairs for donation to an empty orbital on the Lewis acidic Ti in TiCl$_4$. The result is the formation of a Lewis adduct that is an activated aldehyde with enhanced electrophilicity. The highly electrophilic aldehyde-TiCl$_3$ Lewis complex sets the stage for subsequent nucleophilic attack by the silyl enol ether (Figure 30). The reaction continues to ultimately give the $\beta$-hydroxy carbonyl compound.

2.9 C-F bond functionalization

The synthetic utility of Lewis acids has been extended to C-F bond functionalization reactions [29]. Lewis acids based on B, Si, and Al have affected the hydrodefluorination of alkyl fluorides, which is the transformation of C-F bond into C-H bond (Figure 31). Lewis acids based on B, Al, and Si (Figure 30) have achieved the ultimate functionalization of C-F bonds. Functionalization of C-F bonds has been achieved due to the high Lewis acidity of B, Al, and Si and to the high fluoride affinity, especially in the case of Si.

3. Green Lewis acids

3.1 Uses in various organic reactions

Typical Lewis acids, such as BF$_3$ and AlCl$_3$, are highly reactive with water. Thus, they are non-recoverable and end up as waste at the end of reactions. Catalysis is one of the 12 principles of green chemistry and this is due to the minimization of waste at the end of the reaction. Prevention of waste is another principle of the 12 principles of green chemistry. Therefore, it is a viable strategy to seek and develop green Lewis acid.

Figure 30. The role of the Lewis acidic TiCl$_4$ in the Mukaiyama aldol reaction.

Figure 31. Lewis acid-assisted C-F bond functionalization.
alternatives to the highly water-sensitive Lewis acids, such as BF$_3$ and AlCl$_3$ [30]. From a green chemistry point of view, the alternative should still function as a catalyst and it should not be water-sensitive. The idea is to minimize waste that is obtained at the end of reactions that employ BF$_3$ and AlCl$_3$. Lanthanide triflates (trifluoromethanesulfonate) are water-soluble and recyclable. The triflate group is a strongly electron-withdrawing group that imparts or enhances the Lewis acidity of the lanthanide. Thus, they are considered green Lewis acids. Examples of lanthanide triflates are Yb(OTf)$_3$, Sc(OTf)$_3$, and Ln(OTf)$_3$, which have been in various organic reactions (Figure 32) [31].

Developments of green alternatives to the classical stoichiometric oxidants, such as CrO$_3$ and MnO$_2$, that employ heavy metals producing metal waste, thus posing environmental problems, are sought. Ideal oxidants should be stable, active, and selective and ideally based on green oxidants, such as air or dilute H$_2$O$_2$. An example of green Lewis acidic oxidant is TS-1 (titanium silicate) (Figure 33) [32]. TS-1 is especially useful for oxidation reactions using H$_2$O$_2$ where the only by-product is water. Examples of its use include its catalytic conversion of cyclohexanone into cyclohexanone oxime, which is elaborated into caprolactam, a nylon 6 precursor (Figure 33).

A green Lewis acid-based zeolite, Sn-beta, was developed. Sn-beta [33] has been found to catalyze various oxidation methods/processes such as Baeyer-Villiger
oxidation reaction of ketones to produce the corresponding esters. Typical oxidations of alkylbenzene or aromatic compounds involve HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} oxidation method (Figure 34). A green alternative to the harsh Lowry-Bronsted acidic method is using mild Lewis acid. An oxidation method that employs V\textsubscript{2}O\textsubscript{5} and TiO\textsubscript{2} is found to oxidize 3-methyl pyridine into nicotinic acid [34]. TPAP (tetrapropylammonium perruthenate), vide supra, a Lewis-acidic oxidizing agent for alcohols to aldehydes and ketones, has been heterogenized by reaction of KRuO\textsubscript{4} with NH\textsubscript{4}Cl functionalized polystyrene [35]. Heterogenization is an environmentally benign process that converts a homogenous catalyst into a heterogeneous one by attaching the catalyst to a metal support, such as SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, graphite, or zeolite. The process permits the separation and recovery of the Lewis acid and thus setting the stage for recycling and reuse. Hence, heterogenized Lewis acids fulfill the requirements of green Lewis acids.

3.2 Aqueous Diels-Alder reaction

The Diels-Alder reaction is one of the great C-C bond formation reactions. Its great utility in organic synthesis has been extended to its ability to take place in the presence of water in organic solvents or in water as the sole solvent [36–38]. Rates of Diels-Alder reactions have been tremendously accelerated in water/aqueous media. The enhancement of reaction rates is attributed to the association of water molecules with each other forcing organic molecules to come in proximity with each other and thus close contact commencing reactions. Lewis acid-catalyzed Diels-Alder reactions that have been carried out in water/in the presence of water have demonstrated the hydrophobic effect. Examples are shown below (Figure 35). Lewis acid-catalyzed aqueous Diels-Alder reactions manifest themselves as green organic reactions by fulfilling some great green chemistry principles, such as catalysis, prevention of waste, and use of environmentally benign solvents.

3.3 Aqueous aldol reaction

The aldol reaction is one of the great C-C bond formation reactions in organic synthesis. Their ability to take place in the presence of water has extended their utility/versatility in organic synthesis. Lewis acid-catalyzed aqueous aldol reactions have been possible employing silyl enol ether as masked nucleophilic enolates and a wide range of metal chloride, perchlorate of triflate (Figure 36) [31, 38].

3.4 As ionic liquids

Ionic liquids are produced from large, non-coordinating asymmetric ions with one of them being organic. Usually, the organic ion is a bulky heterocyclic cation that interacts with a small inorganic anion. Due to difference in size, the ion
packing in ionic liquids is poor, which makes them liquids at room temperature. Examples of ionic liquid include \[(emim)AlCl_4\], \[(bmim)BF_4\], and \[(bmim)PF_6\] (Figure 37) [39]. The positive/electrophilic character of the bulky organic ion imparts Lewis acidity to ionic liquids. Thus, they are used as catalysts. Ionic liquids Lewis acidic catalysts that are not miscible with organic solvents are separable from reaction mixtures, thus recoverable and recyclable/reusable. Therefore, catalytic Lewis acidic ionic liquids are green Lewis acids. Reactions involving ionic liquids may result in simpler workup procedures, especially if the organic product is immiscible with the ionic liquid. This allows easy and simple product separation and purification. \[(emim)AlCl_4\] has been used as a catalyst in oligomerization/polymerization reactions that occurred with a
high reaction rate and conversions. The Lewis acidity of ionic liquids can be enhanced by increasing the amount of the Lewis acid, the counter anion, in the formation process. Ionic liquids have been immobilized for uses and applications in alkylation reactions of aromatic compounds, such as benzene, toluene, and naphthalene with olefins [39].

3.5 Oil refining

Cracking of heavy oil fractions is required for the efficient production of gasoline. Original catalytic cracking methods were carried out thermally employing AlCl₃ as a Lewis acid. Such processes were considered inefficient due to their high-energy intensive feature and also due to the use of wasteful, corrosive, and environmentally non-friendly Lewis acid. Catalytic cracking currently and commonly employs zeolites such as zeolite Y. Zeolites are made of three-dimensional frameworks of crystalline hydrated aluminosilicates consisting of TO₄ (T: tetrahedral, Si or Al). Zeolites are hydrated, which imparts significant Brønsted acidity (Figure 38) [40].

The exact nature of zeolite is determined by important parameters, such as reaction conditions and silica-to-alumina ratio. ZSM-5 is an aluminosilicate mineral that is used to alkylate benzene with ethane to give ethylbenzene selectively. Many zeolites are not stable at high temperatures in the presence of water, due to the dealumination process (Figure 39). SiO₂ is added to obtain high silica zeolites, which are used in the bulk chemical industry.

![Figure 37. Examples of ionic liquids.](image1)

![Figure 38. The structure of zeolites.](image2)

![Figure 39. Dealumination of zeolites and formation of high silica zeolites.](image3)
High silica zeolites result in reactions with high yields and better selectivity. Green development is the Asahi process, hydration of cyclohexene to cyclohexanol (applications toward nylon 6 (via adipic acid) and nylon 6.6 (via caprolactam)) using high silica ZSM-5 with SiO$_2$/Al$_2$O$_3$ ratio of 25 (Figure 40) [40].

4. Concluding remarks

Due to their electron-pair affinity, Lewis acid catalysts have catalyzed various and numerous organic reactions, and C-C bond formation methods and processes. Their utility has been extended to their compatibility with water as a reaction medium. The catalytic feature of Lewis acids and the ability to use them in aqueous media make them environmentally benign and thus green catalysts. Applications of Lewis acids have been demonstrated by their ability to catalyze various organic transformations/reactions and in the ultimate and constantly sought reaction medium, water. The power of Lewis acids has affected the challenging C-F bond functionalization reactions. Lewis acids have seen applications in green processes/methods, such as ionic liquids, and in industrial processes, such as catalytic cracking in oil refining. It is envisioned that Lewis acids will have the potential to further contribute in the field of C-X bond functionalization reactions and other green transformations/processes.

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