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Introduction to Solid Base Catalyst

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1.1 Introduction

With the expeditious growth of material chemistry and catalysis chemistry, the sophisticated arrangement and manufacture of solid base catalysts have sparked stupendous interest in the heterogeneous catalysis field. Moreover, there is an array of shortcomings for the homogeneous catalysts: they are nonrecyclable, produce low-quality side products, and generate a large amount of waste that leads to energy and chemical waste that still needs to be addressed. The principal supremacy of heterogeneous catalysts over homogeneous catalysts is their harmless nature and highly basic nature. In the context of catalyst regeneration and the potential to be reused in ongoing processes, heterogeneous catalysts reduce the drawbacks of homogeneous catalysis. The heterogeneous catalytic process has been reported to have greater economic potential than the homogeneous one, as reported in the literature. For example, the solvent role is very different in solid base catalysis in comparison to homogeneous catalysis because in solid catalysis the reaction can be executed without the use of a solvent [1]. As a consequence, when the reaction occurs entirely, there is no incentive to separate the solvents. Evidently, no solvent waste is emitted and solid catalysts could potentially be used in additional reactions [2, 3]. For instance, heterogeneous catalysts have 4–20% lower refinery expenses as compared with homogeneous catalysts [4, 5]. Overall, solid base catalysts have a number of incentives encompassing effectiveness in separating their components from the reaction mixture, the potential to be reutilized, stability in challenging reaction conditions and the ability to proceed in a shorter time [6–8]. They are often involved in a variety of industrial processes, notably hydrogenation, aldol condensation, transesterification, Henry reaction, Knoevenagel, Wittig reaction, Michael addition and Cannizzaro reaction. These catalysts facilitate the reaction pathways by having basic sites on their surfaces that can receive protons (H^+) or donate lone pairs of electrons to reactants [9]. Solid base catalysts are present in a different phase, generally a solid, while the reactants are in a different phase, typically a

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liquid or a gas. This is in contrast to conventional homogeneous catalysts, which are present in the similar phase as the reactants [10]. In essence, solid base catalysts ought to replace the role of homogeneous base catalysts in industrial processes for the purpose of streamlining procedures and sustaining the environment. For the purpose of elucidating their catalytic properties in solid base catalysts, their basic properties must be scrutinized. It depends on the locality of basic sites, the definite count of basic sites and their basic dominance factors.

The fundamental constituents of solid base catalysts are the poisoning of the active site by acidic molecules such as HCl, CO_2 and water, which persuades the firmness of the basic sites. Characterization methods and several kinds of other techniques, such as the variation in color of acid–base indicators and the adsorption of acidic molecules, signify the presence of basic sites on surfaces [11]. The reaction pathway includes the inclusion of anionic intermediates, as evidenced by spectroscopic analyses and the reaction proceedings are extremely comparable to base-catalyzed reactions that are prominent in homogeneous systems. Since the beginning of the twentieth century, it has been discovered that plenty of reactions are possible using various solid base catalysts. Numerous studies on solid base catalysts suggest that their catalytic behavior was principally determined by structure, property and the existence of active basic sites on surface [12–14].

1.2 History and Main Facts on Solid Base Catalysts

Pines and Haag conducted the foremost work on the heterogeneous base catalyst, demonstrating that sodium metal dissolved in alumina acted as a potent catalyst for the double-bond isomerization of alkenes [15]. "Solid Acids and Bases" written by Professor Kozo Tanabe was an innovative work that popularized the concept of "solid base" in the catalysis world in 1970 [2]. The work addressed significant research on solid acid and base catalysis carried out throughout the 1950s and 1960s. As a sequel to "Solid Acids and Bases," Tanabe, Misono, and other authors published "New Solid Acids and Bases" in 1989, providing an overview of the advances in the area during the 1970s and 1980s [16]. It described contemporary advances in the field throughout the 1970s and 1980s. Both solid acids and solid bases were covered in the two publications, but the focus was primarily on the former, which was typical for those decades. Significant strides have been made in solid base-catalyzed processes and catalytic materials since the early 1990s. This is because solid base catalysts has been proven to be environmentally benign. Consequently, there is an expanding utilization of solid base catalysts in organic reactions.

Until that time, research on solid bases has advanced significantly in terms of catalyst materials and catalytic processes, but with greater slack than research on solid acids. When the catalysts were prepared under vacuum, Tanabe and colleagues reported in 1972 that magnesium oxide and calcium oxide demonstrated extraordinarily high catalytic activity for 1-butene isomerization [4, 17]. This research elucidated the significance of the base catalyst pretreatment and preparation techniques.

Tanabe and his colleagues conducted a thorough investigation of the fundamental characteristics of different metal oxides, combined metal oxides, and the wide range of processes that these substances catalyzed in the 1970s. A family of solid bases for new materials entered the market in the interim period. Different approaches to identifying the reaction intermediates and describing the fundamental characteristics of solid surfaces were also developed [18].

1.3 Literary Perspective of Solid Base Catalyst

The coprecipitation approach was adopted to fabricate heterogeneous solid catalysts made of mixed oxides of CaO and ZrO_2, containing various Ca-to-Zr ratios. Temperature-programmed desorption, Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy(XPS) were employed for the characterization by Dehkordi and Ghasemi. The increase in catalyst activity with an uptick in the Ca-to-Zr ratio is corroborated by the results of the experiment. These chemically synthesized mixed oxides were tested as catalysts in the transesterification of residual cooking oil and methanol at 65°C to yield biodiesel fuel [19].

Wang et al. designed Mg–Al oxides, which were utilized as catalysts for the transesterification of ethanol and dimethyl carbonate. Mg–Al-layered double hydroxide was crushed without the assistance of a solvent. Fourier transform infrared (FTIR), scanning electron microscopy (SEM), XPS, and XRD were employed to validate the surface properties. With moderate basic sites and high BET surface areas, a molar ratio of 2.0 was shown to yield satisfactory catalytic activity [20].

The solid base catalysts was fabricated by Wei et al. by heating a porous hydroxyapatite doped with $Sr(NO_3)_2$ at 873 K. The thermogravimetric analysis (TGA), XRD, FTIR, SEM, BET, and indicator techniques were implemented for the characterization. With an 85% conversion rate, these innovative solid base catalysts demonstrate use in the transesterification of soybean oil [21].

Magnesium oxide/carbon mesoporous composites were fabricated utilizing potassium chloride as the salt template and alkali lignin as the carbon source, resulting in a range of Mg-doping ratios by Wang and research team. For characterization, the BET, FTIR, SEM, and transmission electron microscopy (TEM) were employed. To optimize the fructose yield during glucose isomerization, these chemicals were employed as base catalysts [22].

Na-modified graphite carbon nitrides were synthesized by Kim et al. and used to transesterify soybean oil and methanol. Melamine and sodium hydroxide were polymerized co-thermally to produce the catalyst. Carbon dioxide diffuse reflectance, SEM, FTIR, and XRD were employed for the characterization. The density functional theory (DFT) theory and CO_2 diffuse reflectance infrared Fourier transform spectroscopy verified the basicity produced by the electron transfer from the sodium to nitrogen atoms [23].

Lithium-doped Li/NaY zeolite materials were designed using microemulsion-assisted impregnation with varying Li_2CO_3 to NaY molar ratios by Li and research group. Several alkali species were added to the zeolites, which increased the strength and catalytic property of Li/NaY catalysts in the ethanol-castor oil transesterification reactions [24].

The TiO_2-based Na–SiO_2 heterogeneous base catalysts were synthesized and characterized with SEM, XPS, FTIR, and BET measurements by Naeem et al. This catalyst was successfully implemented in production of biodiesel from waste cooking oil with 98% yield. Another important potential of these catalysts is their ability to be reused after five successive runs in reactions [25].

Ye et al. synthesized Mg–Al hydrotalcite catalyst using bottom-up approach. Characterization was performed via DFT and FTIR studies. These were applicable in glucose to fructose isomerization, and experimental data confirm conversion through base-catalyzed route. The interaction between catalyst and glucose rises with increase in Mg–Al molar ratio [26].

A two-dimensional (2D) nanoporous carbonaceous solid base catalyst was synthesized by one-step carbonization method utilizing chitosan by Kong and his team. They were tested for their applicability in transesterification to generate biodiesel and Knoevenagel condensation reactions. The result suggests their adequate potency in these reactions. The literature also claims their use in biodiesel production [27].

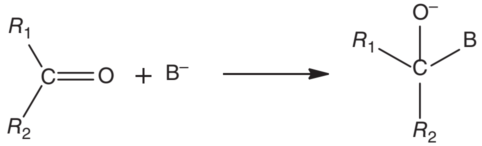
Mg–Al-based hydrotalcites were fabricated by Park and his research team employing various approaches including coprecipitation, simple, and urea methods. The results exemplified that synthesis method strongly affects catalytic properties of catalyst. Coprecipitation method-based catalysts were best ones that are utilized for glucose isomerization due to their small crystalline size [28].

1.4 Solid Basic Sites

Solid basic sites are some discrete sites present on surface of solid bases, which can act as a base. These basic sites can extract protons from reactant species (RH) and lead to formation of carbanions (R^-).

$$RH + B \rightarrow R^- + BH \tag{1.1}$$

In this reaction (1.1), the basic center on the surface of solid behaves as Brønsted base. In some cases, such as in carbonyl groups (aldehyde and ketones), these basic sites can act as Lewis base (1.2), as observed in aldol condensation and Knoevenagel reactions. As observed in many reactions, these basic sites can simultaneously act as Lewis base (e-donor) and Brønsted base (proton acceptor).



(1.2)

For most of the basic catalysts, banishing oxygen and water molecules over the surface and pretreating them at extremely high temperatures is the most crucial step to exhibit the ability to illustrate basic characteristics that foster base-catalyzed reactions. The temperature required for pretreatment mainly depends on decomposition temperature of adsorbed oxides and hydroxide molecules. The molecules that are attached frailly are detached at lower temperatures and the sturdy molecules are sequestrated at high-temperature conditions. In infrequent instances, with increasing pretreatment temperature repositioning of bulk and surface particles eventuates, which expedites the unusual change in nature of basic center on surface, and this alteration reflects in their catalytic power on variation with temperature [17].

1.5 Types of Solid Base Catalysts

To remove acidic impurities adsorbed on surfaces of basic sites pretreatment is essential and this treatment generally follows volcanic-type variation as a function of temperature. The left side in Figure 1.1 points toward emergence of basic site and right side focuses on deliberation of basic sites by surface realignment of atoms [29].

1.5.1 Metal Oxides

1.5.1.1 Alkaline Earth Oxides

With some anomalies, this type of catalyst catalyzed almost every base-catalyzed reaction. MgO, CaO, BaO, and SrO are examples of alkaline earth metal oxides but among all, MgO is the most extensively explored owing to its definite structure with large surface area and synthesizes effortlessly as compared to CaO, SrO, and BaO preparation. Because of structural similarity of CaO, SrO, and BaO with magnesium oxide, their catalytic properties can be clarified with the study of MgO catalytic activity. The basicity trend followed by alkaline oxides is BaO > SrO > CaO > MgO. CaO and MgO can be prepared smoothly from thermal decomposition of their hydroxide salts. SrO and BaO active sites are synthesized from their carbonate salts, as their

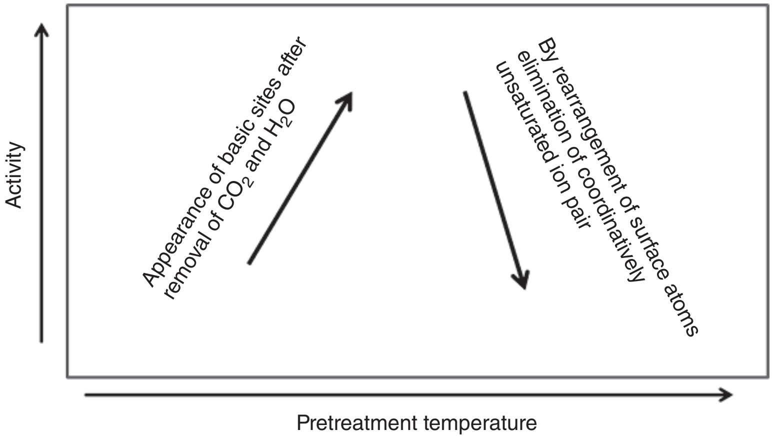


Figure 1.1 Volcano shape in catalysis as a function of temperature in solid base catalysis. Reprinted with permission Ref. [29] © Elsevier, 2015.

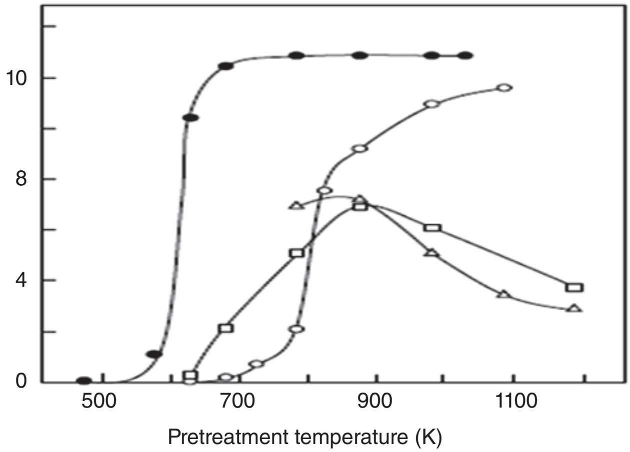


Figure 1.2 Variations in (●) amount of water evolved. (Δ) surface area/100 $m^2\ g^{-1}$. (□) Activity of 1-butene isomerization/a.u. as a function of pretreatment temperature of CaO. (○) Amount of CO_2 evolved/20 mmol g^{-1}. Reprinted with permission Ref. [18] © Springer Nature, 2011.

hydroxide salt melts at a certain temperature range. Figure 1.2 represents that with deaeration temperature the active sites of CaO are produced by detachment of water and CO_2 gases [30, 31].

To determine how effortless it is to eradicate protons from the reactant under the reaction conditions deployed, differing basic sites need to be met for base-catalyzed reactions. When a proton is easily extracted from a reactant, the reaction is feasible even on a weak basic site, whereas if a proton is laborious to remove, the reaction will only occur on a strongly basic site. The exact kind of reaction and the particular form of alkaline earth oxide ascertain the pinnacle of pretreatment temperature. Figure 1.3 emphasizes how the activity of MgO produced from hydroxide by decomposition in a vacuum fluctuates based on the pretreatment temperature for different processes [32]. Depending on the type of preparedness, various temperatures are recommended for pretreatment. The temperatures for MgO demonstrating the most stringent instances of reactivity are 800 K just for 1-butene isomerization, 973 K for methane–D_2 exchange, and 1300 K for 1,3-butadiene hydrogenation. The dominance of the basic site needed to trigger the reaction is depicted in the variance in the optimum pretreatment temperature. Proceeding from 1-butene isomerization toward 1,3-butadiene hydrogenation necessitates more formidable basic sites.

1.5.1.2 Zirconium Oxides

Although ZrO_2 catalyzes numerous base-catalyzed reactions, still its functions are highly different from other alkali-based oxides. The acid–base bifunctional characteristics of ZrO_2 are extensively utilized for deciphering the catalytic characteristics that distinguish it from other solid base catalysts. Some industrial reactions in which zirconium oxides are utilized as catalysts are:

- Hydrogenation of carboxylic acids (aromatic) to aromatic aldehydes [33]
- Conversion of isobutyraldehyde into diisopropyl ketone [34]

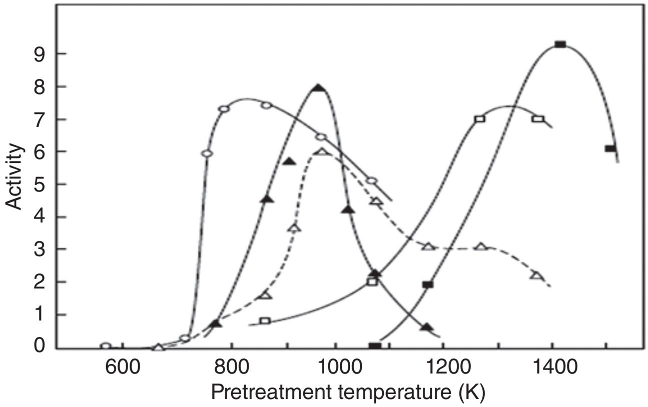


Figure 1.3 Variations in MgO activities with various reactions versus pretreatment temperature as a function. (○) 1-Butene isomerization at 303 K, (□) 1,3-butadiene hydrogenation at 273 K, (Δ) 1,3-butadiene amination at 273 K, (▲) methane-D_2 exchange at 673 K, (■) ethylene hydrogenation at 523 K. Reprinted with permission Ref. [18] © Springer Nature, 2011.

- Dehydration reaction of 2-hydroxypropylamine [35]
- Production of cyclohexylethylene from 1-cyclohexylethanol dehydration [36, 37].

The temperature at which ZrO_2 is produced from hydrous ZrO_2 influences its catalytic activity. The sort of reaction dictates the temperature at which the highest activity emerges. Figure 1.4 provides examples of the hydrogenation of 1,3-butadiene and the H_2–D_2 equilibration, both demonstrate optimal activity at 873 K for pretreatment and the activities vanish at 1073 K for pretreatment. However, the activity maxima for isomerization of 1-butene and transfer hydrogenation of 1,3-butadiene with cyclohexadiene occur at a temperature of 1073 K during the pretreatment phase. As the pretreatment temperature rises, the surface area reduces, and the fraction of monoclinic phase is enhanced. Tanabe and Yamaguchi hypothesize that the bond gap between Zr and O varies with pretreatment temperature, which, in consequence, creates fluctuations in the activity [38].

1.5.1.3 Rare Earth Oxides

Rare earth oxides have not been frequently used in base-catalyzed processes despite having strong basic characteristics. The oxides are also endowed with an innate capacity to oxidize. Rare earth oxides are created from the hydroxides either through air calcination or high-temperature vacuum decomposition. By hydrolyzing aqueous nitrates with aqueous ammonia, hydroxides can be generated [37].

The conditions under which hydroxides decompose, including temperature and environment, affect the surface areas of the rare earth oxides that are produced. The oxides produced by hydroxide breakdown at 873 K in a vacuum have certain surface areas between 10 and 50 $m^2\,g^{-1}$. The synthesis of oxides from hydroxides typically transpires through three different stages. Figure 1.5 displays the thermogram of $La(OH)_3$ to La_2O_3 in a vacuum [37]. The initial step of $La(OH)_3$ decomposition was obtained in the temperature range of 523–623 K and led to the generation of a distinct

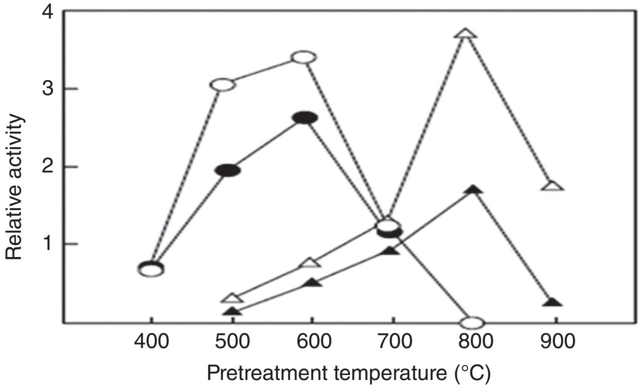


Figure 1.4 Catalytic activity of ZrO_2 at various pretreatment temperatures. (Δ) Isomerization of 1-butene; (○) 1,3-butadiene hydrogenation with H_2; (•) equilibration of H_2-D_2; (▲) 1,3-butadiene hydrogenation with cyclohexadiene. Reprinted with permission Ref. [38] © Elsevier, 1994.

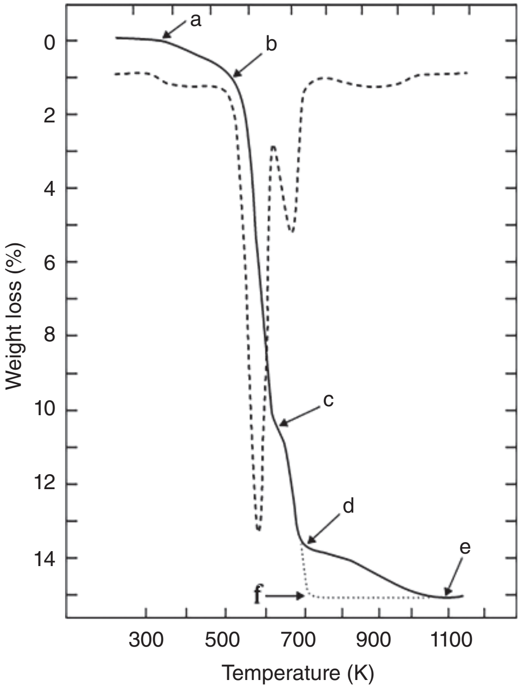


Figure 1.5 TG curve of $La(OH)_3$ procured at 2 K min^{-1} in vacuum. Dotted line (.….) path followed by rehydrated La_2O_3 sample throughout 2nd step of dehydration; broken line (- - -) represents time/temperature derivative; solid line (-) represents weight loss curve. Reprinted with permission Ref. [37] © Elsevier, 1977.

hexagonal LaO(OH) intermediate, delineated by the point c break in the integral thermogravimetric curve. This is after a primary small weight loss at 373–473 K (a–b) attributed to the eradication of adsorbed water and crystallization water. At 523–693 K (c–d), oxyhydroxide undergoes subsequent dehydration to La_2O_3, which is finished at that temperature. When the highly basic trihydroxide precursor interacts with the atmospheric CO_2 during formation and handling, carbonate species that always exist in the oxide undergo decomposition, which results in the eventual weight loss that happens in the temperature range of 723–1073 K (d–e) and results in generation of active site.

1.5.1.4 Titanium Oxides

Titanium oxides exist in three stable polymorphforms, i.e. rutile, brookite, and anatase. Among them, rutile and anatase are most frequently utilized in catalyzing reactions as revealed by literature study.

$$\text{Anatase } (TiO_2) \rightarrow \text{Rutile } (TiO_2) \text{ at 1073 K temperature range}$$

Both the anatase and the rutile polymorphs of titanium dioxide exhibit acidic and basic characteristics on their surfaces and they catalyze methods in which acidic and/or basic sites are significant. The basic character of ZrO_2 is higher than TiO_2's basic nature [39].

Inevitably, titanium oxides can be generated by hydrolyzing and then calcining titanium chlorides or alkoxide salts. Some examples where $TiO_2$is used as catalyst:

- Dehydration of 2-propanol to propene and finally to acetone by dehydrogenation reaction [40]
- Acetaldehyde aldolization to form crotonaldehyde occurs faster on rutile than anatase polymorph of TiO_2[41]
- Isomerization of 1-butene [42].

Butene isomerization occurs at 473 K over TiO_2. In a vacuum, the pretreatment temperature impacted both the activity of TiO_2 and the reaction process. The activity began to become apparent at 473 K and accelerated as the pretreatment temperature rose, eventually culminating at 673 K. The activity dropped as the temperature rose over 673 K, while the cis/trans ratio of the 2-butenes that were generated increased. Ti^{3+} also increased as the pretreatment temperature climbed [42].

1.5.1.5 Zinc Oxide

Despite it being apparent that acidic sites have a stake in the reactions, ZnO serves as a catalyst that fosters base-catalyzed reactions. Experimental evidence bears out the prevalence of both basic and acidic properties in zinc oxide, thereby hypothesizing it to be amphoteric. By introducing ammonium hydroxide to a simple aqueous solution of zinc nitrate and scorching the resultant mixture to 353 K until almost completely precipitated, zinc oxide can typically appear [43]. The precipitate gets filtered, rinsed with water, patted dry, and calcined in air between 673 and 773 K. ZnO acts as solid base catalysts in:

- Acetone formation from dehydrogenation of 2-propanol [44]
- Formation of *cis*- and *trans*-butene from 1-butene isomerization [45, 46]
- Cis–trans isomerization of 1,3-pentadiene [47].

By altering ZnO by alkylsilylation, the isomerization of 1-butene, 1-pentene, and 1,3-pentadiene was increased. Specifically, the addition of triethylsilane increased the activity of 1,3-pentadiene by a ratio of 89. The improvement was attributed to the reactant's irreversible adsorption being averted with the goal of preventing self-poisoning of the active sites [47].

1.5.1.6 Alumina

In spite of its tremendous mechanical strength and beneficial liaisons with metals and metal oxides, which foster widespread dispersion across the supported compounds, Al_2O_3 is frequently employed as a support for commercial catalysts. By dehydrating at high temperatures, oxyhydroxide (AlO(OH)) and hydroxide ($Al(OH)_3$) are converted to alumina. While referring to surface characteristics, alumina is usually considered acidic rather than basic. However, the relevance of fundamental sites in alumina's catalytic activity is undoubtedly exaggerated. Alumina (Al_2O_3) is implemented as a support for metals and metal oxides in addition to serving as a catalyst for an assortment of processes. Al_2O_3 serves as a catalyst in an ordinary reaction

- wherein alcohols are dehydrated to yield alkenes
- Al_2O_3-specific operation called the H–D exchange between CH_4 and D_2 transpires even at ambient temperature [48].

This is the mechanism through which alcohol is activated [49, 50]. It is thought that proton oscillations between the surface enable the activation and the adsorbed alcohol molecules, which can cause the molecule to polarize. It is proposed that the alcohol molecule itself has some rotational or vibrational freedom in comparison to the surface, allowing the β-H to go closer to a basic O^{2-} ion when the alcohol is in its antiperiplanar conformation. The major isotope effect is noticed when D substitutes for the H linked to β–C is employed for estimating the removal of H connected to β–C by the basic site on Al_2O_3 (O^{2-}), which is the step that establishes the rate [51].

1.5.1.7 Mixed Oxides

Two distinct categories of metal oxides are amalgamated to generate mixed oxides. Alkali metal oxide containing mixed oxides and the Al–Mg oxides generated through calcination of hydrotalcite are the most extensively researched mixed oxides possessing basic characteristics. Certainly, one of the component oxides has basic characteristics, especially when it pertains to mixed oxides that reflect these characteristics. In most instances, the addition of the second component oxide modifies the basicity of the first component oxide to certain extent. Different techniques, including coprecipitation, sol–gel, quick combustion, kneading, impregnation, and molten mixture are employed for manufacturing mixed oxides. The coprecipitation approach is the most prevalent [18].

ZnO can dehydrogenate cyclohexanol and transfer hydrogenate cyclohexanone with 2-propanol. When CeO_2 was incorporated, the activity of both reactions increased. When ZnO was blended with CeO_2, its strong basicity was reduced and its acidity was increased, which increased the activity of the two processes [52].

1.5.1.8 Alkali Metal-Loaded Metal Oxides

Alkali metal compounds can change the surface properties for a sort of reason, and it can be exigent to pinpoint the exact cause of the increased activity in each situation. Some reasons are:

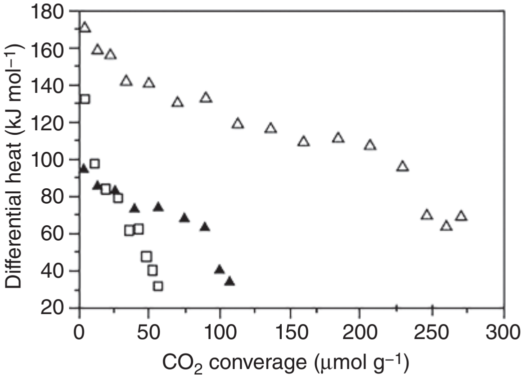


Figure 1.6 Differential heat versus adsorbate coverage for absorption of CO_2 on gamma-Al_2O_3 (□) at 873 K (Δ) and 1273 K (▲). Reprinted with permission Ref [53] © Elsevier, 2003.

- Alkali metal reduces the reaction ability of acidic sites by neutralizing the acidic sites present on surface.
- These alkali metal compounds are converted into its oxides, which display basic characteristics.
- The alkali can react with surface compounds and assist the inception of active sites that can act as catalysts.

The catalytic activity of the alkali metal-loaded metal oxides varies with variation in metal compounds. Incorporation of alkali metals on different metal oxides enhances activity, which was reported in these examples:

(a) Addition of metal oxide in alumina [53]
(b) 1-Butene isomerization in which addition of alkali metal on MgO [54]

Figure 1.6 illustrates the increase in the heat of CO_2 adsorption, which happens when alkali compounds are introduced to Al_2O_3. The incorporation of K^+ ions into γ-Al_2O_3 and subsequent calcination at 873 K resulted in the production of extreme basic sites. For γ-Al_2O_3 loaded with K^+ ions, the heat of adsorption was 170 kJ mol^{-1}, whereas it was 100 kJ mol^{-1} for pure γ-Al_2O_3 [55] reflects the categorization of the various types of metal oxides (Figure 1.7).

1.5.2 Zeolites

Zeolites are aluminosilicates fabricated from SiO_4 and AlO_4 tetrahedra that share an apical oxygen atom with their neighboring tetrahedral. These are frequently implemented as solid acid catalysts, as is well established, but in the early decades, they were employed as base catalysts in their ion-exchanged forms [56, 57]. Zeolites that have been subjected to alkali cations exchanged with them result in weak bases; however, zeolites that offer alkali cations in excess of their ion exchange capacity, rendering them stronger bases. Zeolites become more basic when alkali metals are infused into them, as contrasted with zeolites that are solely loaded with alkali metal oxide. Many research investigations have assessed the catalytic characteristics of these zeolites incorporating alkali metals in numerous ways [58–63].

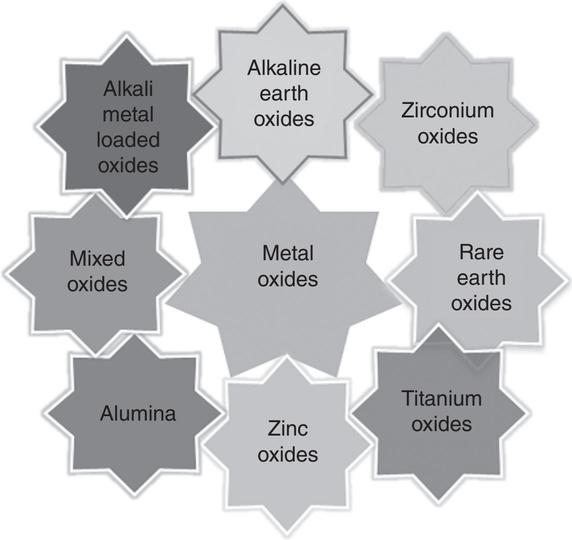


Figure 1.7 Metal oxides categorization.

According to assessments, X- and Y-type zeolites, additionally recognized as faujasites, exchange with alkali cations and facilitate side-chain alkylation reactions. For instance, styrene and ethylbenzene are the products of the reaction of toluene with formaldehyde in the occupancy of alkali cations exchanged from zeolites. As a whole, basic category of catalysts contributes to the side-chain alkylation reaction, while acidic-type catalysts induce ring alkylation. Until then, the fundamental and catalytic properties of alkali cation-exchanged zeolites, particularly those of the faujasite type, have been thoroughly investigated [64]. The delicate basic nature and narrow pore structure are the distinctive properties of the catalysis by alkali cation-exchanged zeolites. These types of exchanged zeolites obsess weak basic sites as compared with alkaline earth oxides and alkali loaded (excess) ion-exchanged zeolites.

Strong solid base catalysts derived from different basic zeolites with caged alkali metals have been explored. Ionic or neutral metal clusters can be generated via imbibing zeolite with NaN_3 or CsN_3, subsequently permitting the alkali azide to decompose under controlled ambient temperatures. First, occluded metallic sodium zeolites were developed by Martens and colleagues by thermally decomposing sodium azide that had been adsorbed on the zeolite. These catalysts were active in the hydrogenation of acetylene, benzene, and *cis*-2-butene as well as the isomerization of *cis*-2-butene [65–67]. Some reactions that were reported to be catalyzed by basic zeolites are:

- Alkylation of toluene with methanol [68]
- Double bond isomerization [69]
- Aldol condensation [70]
- Cycloaddition reactions [71]
- Alcohol dehydrogenation [72]
- Knoevenagel condensation reactions [73].

In the reaction 1-butene isomerization, the catalytic activity clearly demonstrates the production of extreme base sites on alkali metal oxide-loaded zeolites as contrasted to those on alkali cation-exchanged zeolites. Strong active sites for 1-butene isomerization allow CO_2 to be retained as bidentate carbonate at temperatures as high as 573 K. After CO_2 poisoning the active sites, the activity starts to recuperate by deaeration at 573 K and at 673 K, the previous activity is fully reinstituted [69].

1.5.3 Mesoporous Materials

Zeolites having basic nature have been utilized in a wide range of processes; however, in some instances, their employment in the production of fine compounds is restricted due to their narrow pore orifices, which prohibit large molecules from accessing the active sites in zeolite cages. Due to their tunable bigger pore sizes, novel categories of mesoporous silicas, such as MCM-41 [74] and SBA-15 [75], provide fresh avenues for support. The following methods can be exploited for fabricating basic mesoporous materials:

(a) Cation exchange with alkali metal ions (such as Na^+, K^+, and Cs^+);
(b) Impregnation with alkali salt solution and calcination; and
(c) Organic group functionalization.

The first two types of mesoporous materials can be prepared in a manner that is comparable to that used for basic zeolites. Mesoporous catalysts are frequently employed in green catalytic chemistry, owing to its primacy of anticorrosive nature, facile separation, and rapid mass transport. Despite this, these catalysts are also utilized in fabrication of organics and fine chemicals via catalytic ways and engaged in environmental catalysis field. These mesoporous solids have made significant strides during the past several decades.

An abundance of emphasis has been devoted to developing basic sites on mesoporous materials. These mesoporous hosts rarely exhibit basic features, so it is necessary to get acquainted with basic guests. Because the surfactants have obscured their pores, the as-synthesized samples have a low surface area. Typically, these samples are extracted or calcined to detach the surfactants, facilitating guest species to be introduced to the supports with open mesopores. Remarkably for the Knoevenagel condensation reaction, the as-synthesized mesoporous silica MCM-41 was discovered to be an effective basic catalyst [76].

1.5.4 Clay Minerals (Hydrotalcite)

Catalysts and catalyst precursors crafted from hydrotalcite and other comparable elements are crucial. Numerous publications have reviewed the creation, composition and catalytic employability of hydrotalcite [77, 78]. A naturally occurring mineral referred to as hydrotalcite has the approximated chemical formula $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ and the structure of hydrotalcite is dimorphous, positively charged, comprised up of brucite-like hydroxide layers surrounding negatively charged interlayers, possessing anion exchange capabilities. In brucite, hydroxyl groups are positioned octahedrally around the magnesium cation, forming sheets of unlimited thickness from the resulting octahedral sharp edges. Al^{3+} ions are isomorphously substituted for some of the magnesium ions in the brucite layer of hydrotalcite. The interlayers of hydrotalcite naturally embrace CO_3^{2-} ions. These materials are frequently utilized as base catalysts for various organic reactions [79–83]. The base catalysis originating from hydrotalcite is categorized into subcategories: first one is, the hydrotalcite layer structure was retained and interlayer anions are changed and second one, by calcination of materials with hydrotalcite structure produced mixed oxides catalysts. Hydrotalcite catalyst is active against these reactions:

- Michael's addition of 2-acetylcyclopentanone
- 2-Methylcyclo-hexane-1,3-dione to methyl vinyl ketone [84]

The Mg/Al ratio influences the catalytic activity and basic characteristics of $MgO–Al_2O_3$. According to a titration procedure, the number of basic sites reaches its maximum when $Mg/Al = 3$. The highest percentage was detected at a calcination temperature of around 773 K. The basicity is equally dependent on the calcination temperature [18].

1.5.5 Oxynitride

Lednor and Ruiter first synthesized silicon oxynitride, Si_2N_2O, through the execution of a gas–solid reaction of amorphous silica with NH_3 at 1373 K and noticed that the obtained substance showcased a solid base catalysis in the Knoevenagel condensation reaction [85–88]. Following that, aluminophosphateoxynitrides (AlPON), generated by nitriding high-surface-area amorphous aluminophosphate precursors under NH_3 at about 1073 K, were identified as a novel class of solid base catalysts [89, 90]. These catalysts communicated highly intriguing activities in the methyl isobutyl ketone synthesis and in Knoevenagel condensation reactions. The surface acid–base characteristics of the precursors can be tweaked through the inclusion of nitrogen in the aluminophosphate anionic framework, especially by minimizing the quantity of acid sites and raising the proportion of basic sites. Recognition of oxynitrides' basic sites is quite difficult due to presence of various species on surface that can behave as basic sites. The catalytic characteristics of oxynitrides are more commonly investigated for Knoevenagel condensation reactions.

1.5.6 Calcined Metal Phosphates

Metal phosphates that were reported most frequently are K_3PO_4, $Ca_3(PO_4)_2$, and Na_3PO_4 and among them potassium phosphate possesses great base strength. Calcium phosphate is most commonly employed in methylation reaction of phenol to *o*-cresol and 2,6-dimethylphenol [91]. The natural phosphates are widely investigated for numerous base catalysis reactions such as:

- Knoevenagel reaction and
- Michael addition reaction as reported [102, 103]. Numerous reaction has been catalyzed by various kinds of catalyst and some of them are reported here (Table 1.1).

Table 1.1 Different types of catalyst are used in different reactions as base catalysts.

Types of catalysts	Reaction catalyzed	Temperature condition (K)	Ref.
Alkaline earth oxide	(a) Alkene hydrogenation	—	[30]
	(b) Tischenko reaction	—	[92]
Rare earth oxide	(a) Dehydration of alcohol	623–700;	[93]
	(b) Hydrogenation of ethylene	195	[94]
ZrO_2	(a) Isomerization of 1-butene	373	[95]
	(b) Dehydration of 2-butanol	473	[96]
	(c) Conjugated dienes dehydrogenation	323	[96]
	(d) Alkylamine decomposition to nitriles	673	[97]
	(e) Formation of diisopropyl ketone from isobutyraldehyde	733	
	(f) Meerwein–Ponndorf–Verley reduction of ketones, aldehydes, carboxylic acids, nitriles, anhydrides and lactones	573	
TiO_2	(a) Dehydration of 2-propanol to yield propene (anatase)	423–523	[40]
	(b) Aldolization of acetaldehyde to form crotonaldehyde	313 (rutile)	[41]
	(c) Alkylation of phenol	753 (rutile)	
	(d) Isomerization of 1-butene	473	[48]
	(e) Dehydration of glucose to produce 1,6-anhydroglucose	473 (anatase)	
	(f) Isomerization of glucose to form fructose and further dehydration occurs	473 (anatase)	
ZnO	(a) Dehydrogenation of 2-propanol into acetone	483	[44]
	(b) Production of acetone, acetylene (1:1) from 2-methyl-3-butyn-2-ol (MBOH)	453	
	(c) Double bond isomerization of 1-butene to form *cis*/*trans*-2-butene	Room temp.	[48]
	(d) Isomerization of *cis*-1,3-pentadiene into *trans* form	293	
Alumina	(a) Co-isomerization of 1-butene and *cis*-2-butene d_0/d_8	300	[48]
Mixed oxides with MgO	(a) Ortho selective alkylation of phenol over MgO-CeO_2	723–823	[98]
	(b) Conversion of 1-propanol into 3-pentanone	723	[99]
KF/Al_2O_3	(a) Isomerization of 1-pentene	473	[100]
	(b) Tischenko reaction of benzaldehyde	473	[101]

(Continued)

Table 1.1 (Continued)

Types of catalysts	Reaction catalyzed	Temperature condition (K)	Ref.
KNH_2/Al_2O_3	(a) Double bond isomerization of alkenes (b) Production of enamines from unsaturated amine	— —	[48]
Hydrotalcite	(a) Aldol condensation of benzaldehyde and acetone	723	[70]
Zeolites	(a) Meerwein–Ponndorf–Verley reduction of aldehydes with 2-propanol (b) Nitroaldol condensation of aromatic aldehydes with nitroalkanes	373 and 453 413	[73]
ZrPON (zirconium phosphate oxynitride)	(a) Knoevenagel condensation of benzaldehyde with malononitrile	323	[48]
VAlPON (alumino-vanadate oxynitride)	(a) Knoevenagel condensation of benzaldehyde with malononitrile	323	[48]

1.6 Why Solid Base Catalysts Have Fascinated the Scientific Community?

Base-catalyzed reactions, a significant area of synthetic chemistry with numerous industrial applications, have garnered a lot of fascination since they yield a wide range of compounds with added value. Currently, liquid alkali (such as aqueous NaOH, KOH, and triethylamine) has been broadly implemented as a homogeneous catalyst in the fabrication of fine compounds because of its high activity and affordability. However, a number of issues are yet unresolved, including the production of copious amounts of waste liquid, atmospheric contamination, and appliance erosion. In addition, the process of isolating the product from the liquid alkali catalyst is exceptionally challenging and frequently leads to further side reactions. Solid base catalysts are therefore important since they can help with separation, prevent corrosion, and reduce pollution in profuse base-catalyzed industrial procedures [104–107]. Additionally, in terms of the recycling of catalysts, solid base catalysts expedite the easy separation and retrieval of products from reaction systems [108–111]. Basic oxide catalysts with substantial specific surface area and a high concentration of accessible basic sites on their surface are considered to have significant catalytic activity. But solid base catalysts are able to achieve the equivalent yield in less time and at lower temperatures. Hence, for a variety of base-catalyzed processes, solid base catalysts provide an affordable and environmentally safe approach.

Considering several examples of industrial environmental effects, one of the main disruptions to the aquatic ecosystem is wastewater from different industrial activities that contains organic contaminants. The need for heterogeneous solid base catalysts to be used in the treatment of such wastewater is growing along with their growth. Numerous catalysts, including those based on copper, aid in the remediation of solid waste as well as the breakdown of organic contaminants [112]. In order to remove dyes from contaminated water in the textile industry, a number of metal oxides, including solid base catalysts such as lanthanum oxide and calcium oxide, are also employed [113]. However, in spite of this, solid base heterogeneous catalysts recognizes application in an assortment of other processes, including amination, polymerization, alkylation and isomerization.

1.7 Advantages and Disadvantages of Solid Base Catalysts Over Inorganic/Organic Bases

- **Advantages**
  - **Minimize wastes**: The utilization of hazardous chemicals such as methyl iodide and dimethyl sulfate was reduced in case of solid base catalysis turning the reaction more efficient and productive.
  - **Solvent selection**: Solid bases have a significant solvent advantage over homogeneous bases. Both the reactants and the base catalyst need to dissolve in the solvent during homogeneous phase reactions. This significantly limits the solvent selection. Hazardous solvents such as methyl chloride and dimethyl sulfoxide (DMSO) are therefore frequently used. Otherwise, a phase-transfer system must be employed, just like in the reaction example (1.3). This could lead to tedious complications with workup procedures such as separation. Solvents in solid-base-catalyzed processes are only required to dissolve reactants and products. This greatly broadens the choice of solvent [15, 114]. For example, water and hydrocarbons such as pentane perform as alternate solvents in the Knoevenagel condensation of 2-furaldehyde with ethyl cyanoacetate on calcium silicate [104]. Moreover, there is no need for a solvent to conduct the reactions [16]. The reactions can even proceed in the vapor phase, as demonstrated by the case above. This makes the process less complicated, considering there is obviously no requirement for separating the solvents when the reactions have concluded. There are no solvent-based wastes generated, such as organic solvent-containing alkaline water or organic solvent-containing water.

$$\mathrm{PhCH_2CN + NaOH + CH_3I \rightarrow PhCH(CH_3)CN + H_2O + NaI} \tag{1.3}$$

  - **Corrosion resistance**: The reactor and disposal device must be made of corrosion-resistant materials since solutions containing bases, such as sodium hydroxide are corrosive in the case of acid–base catalysts. Solid base catalyst reaction systems rarely experience this kind of issue.
  - **Reaction smoothness**: Furthermore, solid base catalysts can occasionally be the only ones that can accomplish eminent activity and selectivity for an assortment of reactions. Many reactions can occur without mishap when acid

and basic sites work together. The major issue in acid-catalyzed reactions is coking, which basic catalysts typically do not encounter. When compared to acidic sites, functionalized organic molecules such as amines have less interaction with basic sites. As a result, these molecules desorb from the surface more readily and do not become trapped there. Consequently, over solid bases, reactions involving these molecules proceed more easily. Examples of this type of reaction include aldol condensation, hydrogenation, and transfer hydrogenation.

- **Catalytic efficiency**: Furthermore, the use of organometallic reagents must be stoichiometric. Solid bases provide more convenient and environmentally friendly paths for the same products. Both of these reactions are catalytic and occur well in the existence of KF/Al_2O_3 and KNH_2/Al_2O_3, respectively [115, 116].

$$H_2SiEt_2 + tBuC \equiv CH \rightarrow tBuC \equiv C - SiEt_2H + H_2 \tag{1.4}$$

$$H_2SiEt_2 + C_6H_5CH_3 \rightarrow C_6H_5CH_2 - SiEt_2H + H_2 \tag{1.5}$$

- **Reusability**: These solid base catalysts are reusable and can be regenerated easily after completion of a reaction.
- **Bifunctional characteristics**: Having dual-purpose catalytic properties that permit basic and acidic sites to coexist on the surface of solid base catalysts, which, in the case of liquid basic catalysts, is not attainable.
- **Energy efficiency**: The reaction with solid base catalysts can occur even at mild conditions. These catalysts are less energy-intensive as reported.

- **Disadvantages**
  - **Poisoning**: When exposed to external surrounding or when coming in contact with air particles these catalysts turn into poison.
  - **Sensitivity**: These catalysts are sensitive to free fatty acid (FFA) content present in the oils owing to their basic nature.
  - **Leaching**: Leaching of catalyst active sites can occur and lead to contamination in the products.
  - **Decreased yields**: If FFA content in feedstocks exceed 2 wt% then it leads to excess soap formation in reaction thus decreasing the yield of the reaction.

1.8 Role of Solid Base Catalysts in Green Chemistry

Green chemistry's primary objective is to synthesize organic molecules more effectively and in an environmentally friendly way. Synthesizing solid base catalysts that enable cleaner, more effective chemical reactions with the goal of producing zero waste in industrial processes is one of the significant challenges confronting academia nowadays.

Biodiesel production: Biodiesel is a green fuel made by transesterification of oil and alcohol with a catalyst, which renders it cost-effective and environmentally friendly. It is a potential diesel fuel extender that is speculated to comprise fatty acid methyl esters extracted from vegetable oil. Triglycerides are transesterified with methanol with the assistance of an acid or base catalyst to yield methyl esters of fatty acids. This transesterification method is preferred owing to its mild conditions for reaction and fewer byproducts compared to biodiesel production. The characteristic of the feedstock and the kind of reactions has a major impact on the transesterification process's efficiency and the catalyst's effectiveness is crucial to the formulation of biodiesel [117–119]. For the production of biodiesel, a variety of heterogeneous base catalysts have been employed extensively, comprising base zeolites, hydrotalcite, base-doped alumina, and base earth metal oxides [120]. Owing to its many benefits and higher biodiesel output, heterogeneous catalyst use in catalyzed transesterification reactions is becoming more and more prevalent. Furthermore, by calcining the ashes from these residues, which are regarded as wastes, heterogeneous catalysts have been produced from a variety of agricultural residues. Consequently, because of its renewable, recoverable and reusable character, producing biodiesel is somewhat less expensive than using a homogeneous catalyst [121, 122].

Dimethyl carbonate (DMC) synthesis: DMC has long been fabricated by reacting methanol with phosgene. An enormous amount of study has been attempted in pursuit of non-phosgene, environmentally conscious methods to synthesize DMC. Utilizing a Cu or Pd catalyst DMC manufactured from methanol, CO, and oxygen has been industrialized. Dimethyl carbonate is a significant methylation and carbonylation agent in addition to being an essential step for polycarbonate resins. Due to DMC's minimal toxicity, it presents a viable alternative to the hazardous and caustic phosgene dimethyl sulfate or methyl iodide [45, 123, 124]. It might potentially be used as an octane enhancer for petrol. Solid base catalysts, on the other hand, have drawn a lot of interest because homogeneous basic catalysts, including trialkylamine and alkali alkoxides, produce complications with separation of the product and catalyst reuse.

Isoeugenol synthesis: Eugenol was utilized to produce isoeugenol, which is employed in medications and a wide range of floral compositions in perfumes. The isomerization reaction generally precedes as-synthesized hydrotalcite materials. The higher effectiveness was reported by a combination of Mg–Al and Ni–Al hydrotalcite [125].

Anethole synthesis: An effective way to fabricate an anethole is by isomerizing estragole, which is used in mouthwash and alcoholic beverages. It was revealed that compounds such as hydrotalcite that had been synthesized using combinations of Mg–Al, Ni–Al, and Mg–Ni–Al were also effective in isomerizing estragole to anethole. With a cis/trans ratio of 15/85, Mg–Ni–Al hydrotalcite yielded a 99% conversion of estragole [126].

Flavanone synthesis: A common intermediary for many medicinal and fine chemical products is flavanone. A typical pathway leading to flavonone involves the Claisen–Schmidt condensation process. However, research revealed that this solvent-free condensation reaction can occur in the presence of MgO–Al_2O_3 mixed oxides generated from calcining hydrotalcite [127].

Synthesis of phytosterol esters: The food and cosmetics sectors can benefit from phytosterol esters, which can be produced through esterification or transesterification reactions. Solid bases such as MgO, ZnO, and La_2O_3 facilitate the transesterification of β-sitosterol and methyl dodecanoate, which produce phytosterol ester [128, 129].

1.9 Future Prospects for Solid Base Catalysts

The following significant solid base catalysts challenges require deeper study.

(i) **Clarification of the fundamental sites**: The majority of solid-base-catalyzed reactions begin with the removal of a proton from the reactant, which results in the constitution of an anionic species. It is necessary to stabilize the anionic species somewhere, presumably on the conjugate acid sites. It is a crucial step to dictate the location of the conjugate acid sites.
(ii) **Shape-selective catalysts**: The fabrication of shape-selective solid catalysts is a crucial step in the catalysis of solid acids, but no shape-selective solid base catalysis has been discovered yet. Materials with both fundamental and shape-selective characteristics are readily synthesized. These substances may pave the way for new developments in solid base catalysis.
(iii) **Characterization of basic sites**: In order to get more accurate information, more techniques should be used to analyze basic sites. To enhance characterization, new techniques for characterization should be created.
(iv) **Theoretical computation**: In comparison to acid-catalyzed reactions, the theoretical computation for solid-base-catalyzed reactions is inadequate. Solid base catalysts would advance significantly if theoretical calculations could describe the parameters controlling the basic site's strength and the reactant's interaction with the surface to start the base-catalyzed reaction.
(v) **Clarification of the unique characteristics of alumina-supported alkalis**: High activity is exhibited by alumina-supported alkalis in a variety of processes. Even yet, nearly five decades ago, Pines et al. introduced Na metal supported by alumina as the first solid base catalyst. It is yet uncertain whether alumina contributes to the creation of the fundamental sites.

1.10 Conclusion

Overall, solid base catalysts are a promising area of research in the field of catalysis that has numerous avenues for use. The technology's significance stems from its knack for furnishing effective and sustainable substitutes for existing liquid-base catalysts. Several prominent movements and opportunities will shape the direction of solid base catalysts. Alkali metal and alkaline earth oxides, aside from other salts, either in their pure form or on an adequate carrier, are the heterogeneous base catalysts that have been researched most thoroughly. They provide a reasonably quick reaction rate and are not prohibitively costly. The specific surface area and distribution of pore size serve an essential role in defining the activity of these catalysts since the active sites on the surface ultimately determine their activity. Thus, preparation and pretreatment procedures are extremely important, as the catalyst is poisoned by the existence of water, carbon dioxide and free fatty acids. Zeolites are covered with alkali and alkaline earth metals since they are ineffective as catalysts on their own. As catalysts, clays and organic solids have also been produced, but all of these are still in the laboratory. In its entirety, the foreseeable future of solid base catalysts will ultimately be governed by a dynamic interaction of basic research, technological advancements and practical implementations. The field is intended to advance environmentally friendly and efficient chemical processes across several kinds of areas as it keeps expanding.

References

1 Laszlo, P. (1986). *Accounts of Chemical Research* 19: 121. https://doi.org/10.1021/ar00124a004.

2 Wang, X., Tseng, Y.H., Chan, J.C.C., and Cheng, S. (2005). *Journal of Catalysis* 233: 266.

3 Climent, M.J., Corma, A., Iborra, S., and Velty, A. (2004). *Journal of Catalysis* 221: 474.

4 Boro, J., Deka, D., and Thakur, A.J. (2012). *Renewable and Sustainable Energy Reviews* 16: 904.

5 Dube, M.A., Tremblay, A.Y., and Liu, J. (2007). *Bioresource Technology* 98 (3): 639.

6 Chen, X., Qian, W.W., Lu, X.P., and Han, P.F. (2012). *Natural Product Research* 26 (13): 1249.

7 Li, E. and Rudolph, V. (2008). *Energy & Fuels* 22: 145.

8 Liu, X., Piao, X., Wang, Y., and Zhu, S. (2008). *Energy & Fuels* 22: 1313.

9 Bing, W. and Wei, M. (2019). *Journal of Solid State Chemistry* 269: 184. https://doi.org/10.1016/j.jssc.2018.09.023.

10 Sharma, Y.C., Singh, B., and Korstad, J. (2010). *Fuel* 90 (4): 1309.

11 Liu, Z., Li, W., Pan, C. et al. (2011). *Catalysis Communications* 15: 82.

12 Ge, J., Zeng, Z., Liao, F. et al. (2013). *Green Chemistry* 15: 2064.

13 Lei, X., Lü, Z., Guo, X., and Zhang, F. (2012). *Industrial and Engineering Chemistry Research* 51: 1275.

14 Frey, A.M., Bitter, J.H., and de Jong, K.P. (2011). *Chemical Catalysis Chemistry* 3: 1193.

15 Pines, H. and Haag, W. (1958). *The Journal of Organic Chemistry* 23: 328.

16 Tanabe, K., Misono, M., Ono, Y., and Hattori, H. (1989). *New Solid Acids and Bases*, 51, 0-444-98800-9. Kodansha-Elsevier.

17 Che, M. and Bond, G.C. (1985). *Adsorption and Catalysis on Oxide Surface*, 319, 9780080960555. Elsevier.

18 Ono, Y. and Hattori, H. (2011). *Solid Base Catalysis*. Springer Series in Chemical Physics https://doi.org/10.1007/978-3-642-18339-3.

19 Dehkordi, A.M. and Ghasemi, M. (2012). *Fuel Processing Technology* 97: 45.

20 Wang, H., Liu, W., Wang, Y. et al. (2020). *Industrial and Engineering Chemistry Research* 59: 5591.

21 Wei, C., Zhiliang, H., Yu, L., and Qianjun, H. (2008). *Catalysis Communications* 9: 4.

22 Wang, S., Guo, D., Kang, R. et al. (2023). *International Journal of Biological Macromolecules* 232: 123341.

23 Kim, S.E., Kim, J.H., Kim, D.K. et al. (2023). *Fuel* 341: 127548.

24 Li, Z., Ding, S., Chen, C. et al. (2019). *Energy Conversion and Management* 192: 335.

25 Naeem, A., Khan, I.W., Farooq, M. et al. (2021). *Bioresource Technology* 328: 124831.

26 Ye, X., Shi, X., Li, J. et al. (2022). *Chemical Engineering Journal* 440: 135844.

27 Kong, W., Liu, F., and Liu, Y. (2020). *Green Chemistry* 3: 903.

28 Park, S., Kwon, D., Kang, J.Y., and Jung, J.C. (2019). *Green Energy & Environment* 4 (3): 287.

29 Hattori, H. (2015). Solid base catalysts: fundamentals and their applications in organic reactions. *Applied Catalysis A: General* 504: 103–109. https://doi.org/10.1016/j.apcata.2014.10.060

30 Hattori, H., Yoshii, N., Tanabe, K. (1972). Proceedings of the 5th International Congress on Catalysis, Miami Beach, 233.

31 Utiyama, M., Hattori, H., and Tanabe, K. (1978). *Journal of Catalysis* 53: 237.

32 Yokoyama, T., Setoyama, T., Fujita, N. et al. (1992). *Applied Catalysis A* 88: 149.

33 M. Fukui, S.Hayashi, K. Okamoto, I. Koga, T. Inoi, US Pat. 3966822 (1976).

34 K. KagakuEur. Pat. 0433959 (1991).

35 M. Araki, K.Takahashi, T.Hibi, Eur. Pat. 0150832 B1 (1985).

36 Takahashi, K., Hibi, T., Higashio, Y. et al. (1993). *Catalysts* 35: 12.

37 Rosynek, M.P. and Magnuson, D.T. (1977). *Journal of Catalysis* 46: 402.

38 Tanabe, K. and Yamaguchi, T. (1994). *Catalysis Today* 20: 185.

39 Busca, G. (1999). *Physical Chemistry Chemical Physics* 1: 723.

40 Haffad, D., Chambellan, A., and Lavalley, J.C. (2001). *Journal of Molecular Catalysis A* 168: 153.

41 Rekoske, J.E. and Barteau, M.A. (1999). *Langmuir* 15: 2061.

42 Hattori, H., Ito, M., and Tanabe, K. (1975). *Journal of Catalysis* 38: 172.

43 Huffman, J.R. and Dodge, B.F. (1929). *Industrial and Engineering Chemistry* 21: 1056.

44 Lahousse, C., Bachelier, J., and Lavalley, J.C. (1994). *Journal of Molecular Catalysis* 87: 329.

45 Chang, C.C., Conner, W.C., and Kokes, R.J. (1973). *The Journal of Physical Chemistry* 77: 1957.

46 Dent, A.L. and Kokes, R. (1971). *The Journal of Physical Chemistry* 75: 487.

47 Imizu, Y., Narita, T., Fujito, Y., and Yamada, H. (2000). *Studies in Surface Science and Catalysis* 130: 2429.

48 Saunders, P.C. and Hightower, J.W. (1970). *The Journal of Physical Chemistry* 74: 4323.

49 Knozinger, H., Buehl, H., and Kochloefl, K. (1972). *Journal of Catalysis* 24: 57.

50 Knozinger, H. and Scheglila, A. (1970). *Journal of Catalysis* 17: 252.

51 Kraus, M. (1997). *Handbook of Heterogeneous Catalysis* (ed. G. Ertl, H. Knozinger, and J. Weitkamp), 1051. Wiley-VCH.

52 Mishra, B.G. and Rao, G.R. (2006). *Journal of Molecular Catalysis A* 243: 204.

53 Zou, H., Ge, X., and Shen, J. (2003). *Thermochemica Acta* 397: 81.

54 Matsuda, T., Sasaki, Y., Miura, H., and Sugiyama, K. (1985). *Bulletin of Chemical Society Japan* 58: 1041.

55 Berteau, P., Kellens, M.-A., and Delmon, B. (1991). *Journal of the Chemical Society, Faraday Transactions* 87: 1425.

56 Weitkamp, J., Hunger, M., and Rymsa, U. (2001). *Microporous and Mesoporous Materials* 48: 255.

57 Corma, A. (1995). *Chemical Reviews* 95: 559.

58 Pines, H., Vesely, J.A., and Ipatieff, V.N. (1955). *Journal of the American Chemical Society* 77: 347.

59 Barthomeuf, D. (1996). *Catalysis Reviews: Science and Engineering* 38: 521.

60 Dartt, C.B. and Davis, M.E. (1994). *Catalysis Today* 19: 151.

61 Ono, Y. (1997). *Catalysis Today* 38: 321.

62 Weitkamp, J. and Hunger, M. (2007). *Studies in Surface Science and Catalysis* 168: 787.

63 Davis, R.J. (2003). *Journal of Catalysis* 216: 396.

64 Yashima, T., Sato, K., Hayashi, T., and Hara, N. (1972). *Journal of Catalysis* 26: 303.

65 Xu, B. and Kevan, L. (1991). *Journal of the Chemical Society, Faraday Transactions* 87: 2843.

66 Xu, B. and Kevan, L. (1992). *The Journal of Physical Chemistry* 96: 2642.

67 Martens, L.R.M., Grobet, P.J., Vermeiren, W.J.M., and Jacobs, P.A. (1986). *Studies in Surface Science and Catalysis* 28: 935.

68 Engelhardt, J., Szanyi, J., and Valyon, J. (1987). *Journal of Catalysis* 107: 296.

69 Yagi, F., Tshji, H., and Hattori, H. (1997). *Microporous Materials* 9: 237.

70 Ballini, R., Bigi, F., Gogni, E. et al. (2000). *J. Catal.* 191: 348.

71 Tu, M. and Davis, R.J. (2001). *Journal of Catalysis* 199: 85.

72 Hathaway, P.E. and Davis, M.E. (1989). *Journal of Catalysis* 116: 263.

73 Corma, A., Martin-Aranda, R.M., and Sanchez, F. (1991). *Studies in Surface Science and Catalysis* 59: 503.

74 Kresge, C.T., Leonowicz, M.E., Roth, W.J. et al. (1992). *Nature* 359: 710.

75 Zhao, D., Feng, J., Huo, Q. et al. (1998). *Science* 279: 548.

76 Kubota, Y., Nishizaki, Y., Ikeya, H. et al. (2004). *Microporous and Mesoporous Materials* 70: 135.

77 Cavani, F. and Trifiro, T. (1991). *Catalysis Today* 11: 173.

78 Vaccari, A. (1998). *Catalysis Today* 41: 53.

79 Tomar, R., Singh, N., Rathee, G. et al. (2017). Synthesis and Characterization of Hybrid $Mg(OH)_2$ and $CeCO_3OH$ Composite with Improved Activity Towards

Henry Reaction. *Asian Journal of Organic Chemistry* 6 (12): 1728–1732. Portico. https://doi.org/10.1002/ajoc.201700485.

80 Tomar, R., Ebitani, K., and Chandra, R. (2019). Hydrotalcite-Supported Ceria Nanoparticles as a Heterogeneous Catalyst for One-Pot Synthesis of Imines under Atmospheric Air. *ChemistrySelect* 4 (12): 3577–3581. https://doi.org/10.1002/slct.201900750.

81 Tomar, R., Singh, N., Kumar, N. et al. (2019). Base-Free Suzuki–Miyaura Coupling Reaction Using Palladium(II) Supported Catalyst in Water. *Catalysis Letters* 149 (6): 1589–1594. https://doi.org/10.1007/s10562-019-02723-9.

82 Tomar, R., Rathee, G., Chandra, I. et al. (2018). Synthesis and Characterization of Magnesium Hydroxide & Cerium Oxide Composite: Application in Organic Transformation. *ChemistrySelect* 3 (6): 1645–1649. Portico. https://doi.org/10.1002/slct.201702947.

83 Kumar, L., Verma, N., Sehrawat, H. et al. (2022). *New Journal of Chemistry* 46 (7): 3472–3481. https://doi.org/10.1039/d1nj05690e.

84 Prescott, H.A., Li, Z.J., Trunschke, A. et al. (2005). *Journal of Catalysis* 234: 119.

85 Lednor, P.W. and de Ruiter, R. (1989). *Journal of the Chemical Society, Chemical Communications* 5: 320.

86 Lednor, P.W. and de Ruiter, R. (1991). *Journal of the Chemical Society, Chemical Communications* 22: 1625.

87 Lednor, P.W. (1992). *Catalysis Today* 15: 243.

88 Benitez, J.J., Odriozola, J.A., Marchand, R. et al. (1995). *Journal of the Chemical Society, Faraday Transactions* 91: 4477.

89 Massinon, A., Odriozola, J.A., Bastians, P. et al. (1996). *Applied Catalysis A* 137: 9.

90 Nozaki, F. and Kimura, I. (1977). *Bulletin of Chemical Society Japan* 50: 614.

91 Sebti, S., Solhy, A., Tahir, R. et al. (2003). *Journal of Catalysis* 213: 1.

92 Lundeen, A.J. and van Hoozen, R. (1967). *The Journal of Organic Chemistry* 32: 3386.

93 Minachev, K.M., Khdakov, Y.S., and Nakhshunov, V.S. (1977). *Journal of Catalysis* 49: 207.

94 Yamaguchi, T., Sasaki, H., and Tanabe, K. (1973). *Chemistry Letters* 2: 1017.

95 Xu, B.-Q., Yamaguchi, T., and Tanabe, K. (1991). *Applied Catalysis* 75: 75.

96 Takahashi, K., Shibagaki, M., and Matsushita, H. (1992). *Bulletin of Chemical Society Japan* 65: 262.

97 Sato, S., Koizumi, K., and Nozaki, F. (1998). *Journal of Catalysis* 178: 264.

98 Kamimura, Y., Sato, S., Takahashi, R. et al. (2003). *Applied Catalysis A* 252: 399.

99 Tsuji, T., Kabashima, H., Kita, H., and Hattori, H. (1995). *Reaction Kinetics and Catalysis Letters* 56: 363.

100 Handa, H., Baba, T., Sugisawa, H., and Ono, Y. (1998). *Journal of Molecular Catalysis* 134: 171.

101 Kantam, M.L., Choudary, B.M., Reddy, C.V. et al. (1998). *Chemical Communications* 1033: 163.

102 Abouki, Y., Zahouly, M., Rayadh, A. et al. (2002). *Tetrahedron Letters* 43: 8951.

103 Seki, T., Kabashima, H., Akutsu, K. et al. (2001). *Journal of Catalysis* 204: 393.

104 Faba, L., Diaz, E., and Ordonez, S. (2013). *ChemSusChem* 6: 463.

105 Boukha, Z., Fitian, L., López-Haro, M. et al. (2010). *Journal of Catalysis* 272: 121.

106 Keller, T.C., Isabettini, S., Verboekend, D. et al. (2014). *Chemical Science* 5: 677.

107 Shen, W., Tompsett, G.A., Hammond, K.D. et al. (2011). *Applied Catalysis A* 392: 57.

108 Kandel, K., Althaus, S.M., Peeraphatdit, C. et al. (2012). *Journal of Catalysis* 291: 63.

109 Bai, R., Liu, P., Yang, J. et al. (2015). *ACS Sustainable Chemistry & Engineering* 3: 1292.

110 Bai, R., Zhang, H., Mei, F. et al. (2013). *Green Chemistry* 15: 2929.

111 Radhakrishan, R., Do, D.M., Jaenicke, S. et al. (2011). *ACS Catalysis* 1: 1631.

112 Basumatary, S., Nath, B., and Kalita, P. (2018). *Journal of Renewable and Sustainable Energy* 10 (4): 043105.

113 Mogha, N.K., Gosain, S., and Masram, D.T. (2020). *Arabian Journal of Chemistry* 13 (1): 1367.

114 Tanabe, K. (1970). *Solid Acids and Bases*. Kodansha/Academic Press.

115 Baba, T., Kato, A., Yuasa, H. et al. (1998). *Catalysis Today* 44: 271.

116 Baba, T., Yuasa, H., Handa, H., and Ono, Y. (1998). *Catalysis Letters* 50: 83.

117 Costantini, A. and Califano, V. (2021). *Catalysts* 11: 629.

118 Nguyen, H.C., Wang, F.M., Dinh, K.K. et al. (2020). *Energies* 13: 2167.

119 Nguyen, H.C., Liang, S.H., Li, S.Y. et al. (2018). *Journal of the Taiwan Institute of Chemical Engineers* 85: 165.

120 Borges, M.E. and Díaz, L. (2012). *Renewable and Sustainable Energy Reviews* 16: 2839.

121 Olatundun, E.A., Borokini, O.O., and Betiku, E. (2020). *Renewable Energy* 166: 163.

122 Dhawane, S.H., Kumar, T., and Halder, G. (2016). *Renewable Energy* 89: 506.

123 Ono, Y. (1996). *Pure and Applied Chemistry* 68: 367.

124 Tundo, P. (2001). *Pure and Applied Chemistry* 73: 1117.

125 Kishore, D. and Kannan, S. (2004). *Applied Catalysis A* 270: 227.

126 Kishore, D. and Kannan, S. (2006). *Journal of Molecular Catalysis A* 244: 83.

127 Climent, M.J., Corma, A., Iborra, S., and Primo, J. (1995). *Journal of Catalysis* 151: 60.

128 Pouilloux, Y., Courtols, G., Boisseau, M. et al. (2003). *Green Chemistry* 5: 89.

129 Vallange, S., Beauchaud, A., Barrault, J. et al. (2007). *Journal of Catalysis* 251: 113.