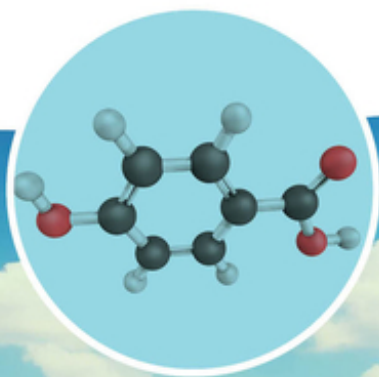


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and Ramesh Chandra

Solid Base Catalysts

Synthesis, Characterization, and Applications



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Edited by Ravi Tomar, K. K. Pant, and Ramesh Chandra

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Preface

In 1958, Pines and Haag conducted a series of investigations on solid base catalysts. They found that alkali metal-supported alumina can catalyze double-bond isomerization of alkenes via carbanions as intermediates. Subsequently, in the 1970s, other metal oxides were also discovered to have catalytic activity for base-catalyzed reactions. The advantages of using solid base catalysts over liquid base catalysts in industrial processes are numerous, such as not requiring neutralization of the reaction mixture, allowing high-temperature reactions, employing flow reactor systems for highly productive processes, and facilitating easy separation of catalysts from products. The rapid development of material chemistry and catalysis chemistry has ignited significant interest in the heterogeneous catalysis field, with sophisticated arrangements and the production of solid basic catalysts. In contrast, homogeneous catalysts have several drawbacks, such as being nonrecyclable, producing low-quality side products, and generating a large amount of waste that leads to energy and chemical waste. Solid basic catalysts play a crucial role in many base-catalyzed industrial procedures, offering opportunities for aiding separation, minimizing corrosion, and resolving pollution issues. This book provides a comprehensive overview of the latest advanced studies in the synthesis and characterization of solid base catalysts, along with their applications in various fields such as industrial, catalytic, biomedical, among others. The book focuses on how advanced techniques can be applied to characterize various types of solid base catalysts. It can serve as a valuable educational resource for students and professionals in the field of material and organic synthesis, providing insights and knowledge from experts in the industry.

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1

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, CO₂ 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 ZrO₂, 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 were fabricated by Wei et al. by heating a porous hydroxyapatite doped with Sr(NO₃)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 CO₂ 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 Li₂CO₃ 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-SiO₂ 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].

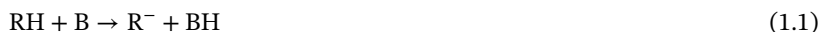
Ye et al. synthesized Mg-Al hydrotalcite catalyst using bottom-up approach. Characterization was performed via DFT and FTIR studies. These were applicable in glucose to fructose isomerization, and experimental data confirm conversion through base-catalyzed route. The interaction between catalyst and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

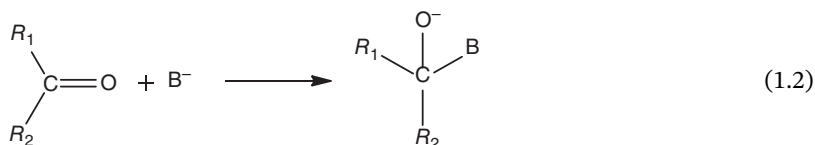
Mg-Al-based hydrotalcites were fabricated by Park and his research team employing various approaches including coprecipitation, simple, and urea methods. The results exemplified that synthesis method strongly affects catalytic properties of catalyst. Coprecipitation method-based catalysts were best ones 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^-).



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).



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 fraily 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 $\text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$. 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

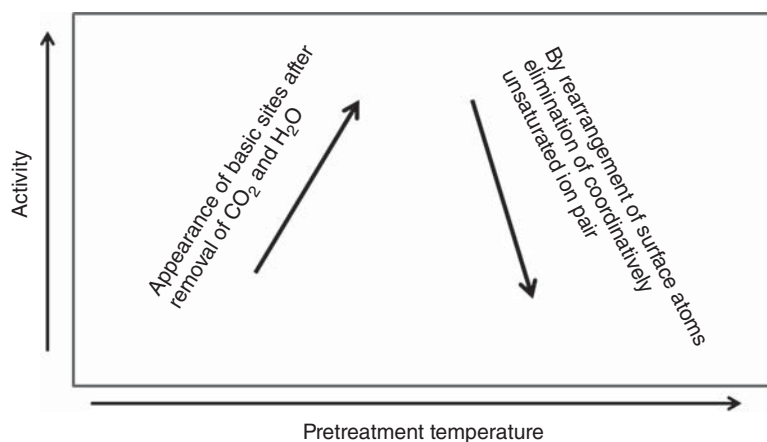


Figure 1.1 Volcano shape in catalysis as a function of temperature in solid base catalysis. Reprinted with permission Ref. [29] © Elsevier, 2015.

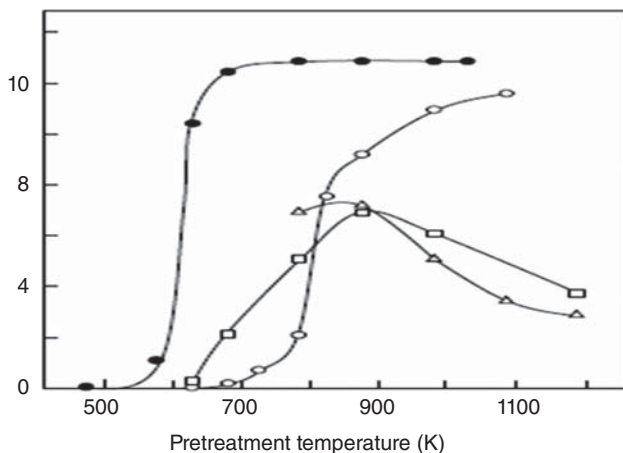


Figure 1.2 Variations in (●) amount of water evolved. (Δ) surface area/100 m² g⁻¹. (□) Activity of 1-butene isomerization/a.u. as a function of pretreatment temperature of CaO. (○) Amount of CO₂ evolved/20 mmol g⁻¹. Reprinted with permission Ref. [18] © Springer Nature, 2011.

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 CO₂ 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-D₂ 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 ZrO₂ catalyzes numerous base-catalyzed reactions, still its functions are highly different from other alkali-based oxides. The acid–base bifunctional characteristics of ZrO₂ 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]

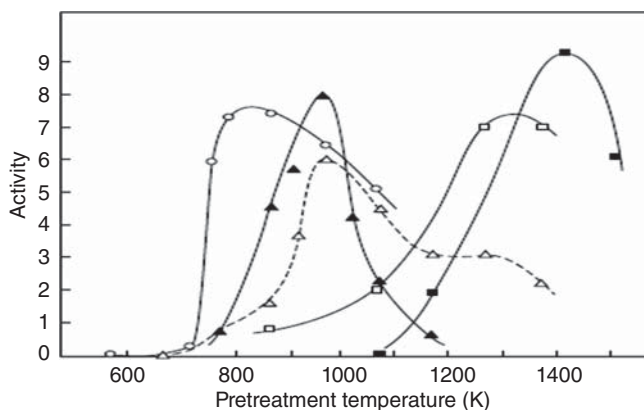


Figure 1.3 Variations in MgO activities with various reactions versus pretreatment temperature as a function. (○) 1-Butene isomerization at 303 K, (□) 1,3-butadiene hydrogenation at 273 K, (Δ) 1,3-butadiene amination at 273 K, (▲) methane-D₂ exchange at 673 K, (■) ethylene hydrogenation at 523 K. Reprinted 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 ZrO₂ is produced from hydrous ZrO₂ 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 H₂-D₂ 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 m² 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 La₂O₃ 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

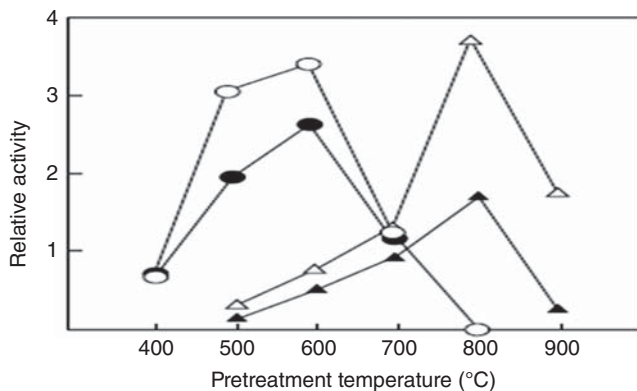


Figure 1.4 Catalytic activity of ZrO_2 at various pretreatment temperatures. (Δ) Isomerization of 1-butene; (o) 1,3-butadiene hydrogenation with H_2 ; (\bullet) equilibration of H_2 - D_2 ; (\blacktriangle) 1,3-butadiene hydrogenation with cyclohexadiene. Reprinted with permission Ref. [38] © Elsevier,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

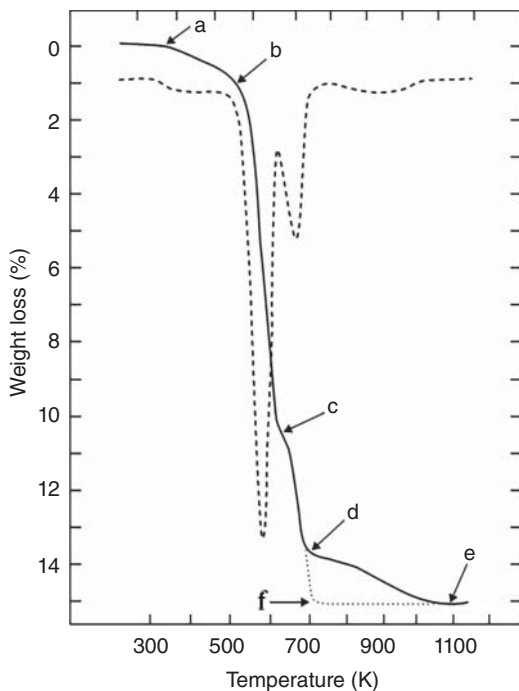


Figure 1.5 TG curve of La(OH)_3 procured at 2 K min^{-1} in vacuum. Dotted line (...) path followed by rehydrated La_2O_3 sample throughout 2nd step of dehydration; broken line (- -) represents time/temperature derivative; solid line (-) represents weight loss curve. Reprinted with permission Ref. [37] © 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 polymorphs, i.e. rutile, brookite, and anatase. Among them, rutile and anatase are most frequently utilized in catalyzing reactions as revealed by literature study.

Anatase (TiO_2) \rightarrow Rutile (TiO_2) 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 ($\text{AlO}(\text{OH})$) and hydroxide ($\text{Al}(\text{OH})_3$) 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

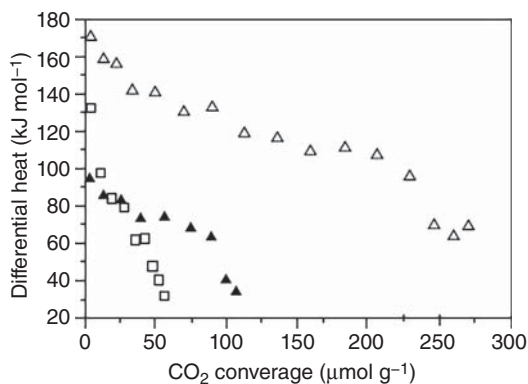
Two distinct categories of metal oxides are amalgamated to generate mixed oxides. Alkali metal oxide containing mixed oxides and the Al–Mg oxides generated through calcination of hydrotalcite are the most extensively researched mixed oxides possessing basic characteristics. Certainly, one of the component 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 CO₂ on gamma-Al₂O₃ (□) 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 CO₂ adsorption, which happens when alkali compounds are introduced to Al₂O₃. The incorporation of K⁺ ions into γ-Al₂O₃ and subsequent calcination at 873 K resulted in the production of extreme basic sites. For γ-Al₂O₃ loaded with K⁺ ions, the heat of adsorption was 170 kJ mol⁻¹, whereas it was 100 kJ mol⁻¹ for pure γ-Al₂O₃ [55] reflects the categorization of the various types of metal oxides (Figure 1.7).

1.5.2 Zeolites

Zeolites are aluminosilicates fabricated from SiO₄ and AlO₄ 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].

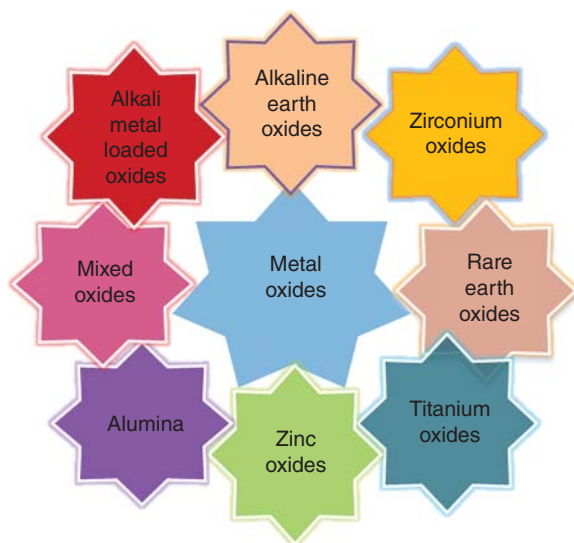


Figure 1.7 Metal oxides categorization.

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 possess 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 CO₂ to be retained as bidentate carbonate at temperatures as high as 573 K. After CO₂ poisoning the active sites, the activity starts to recuperate by deaeration at 573 K and at 673 K, the previous activity is fully reinstated [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 Mg₆Al₂(OH)₁₆CO₃·4H₂O 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 sub-categories: 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 $\text{MgO-Al}_2\text{O}_3$. 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 Ruitter first synthesized silicon oxynitride, $\text{Si}_2\text{N}_2\text{O}$, 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 , $\text{Ca}_3(\text{PO}_4)_2$, 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).