Chapter-1

General Introduction
1.1 Introduction

The concept of green chemistry has been playing an important role in recent years for meeting the fundamental scientific challenges of protecting the living environment. One of the thrust areas for achieving this target is to explore alternative reaction conditions and reaction media to accomplish the desired chemical transformation with almost negligible byproducts and waste generation as well as elimination of the use of volatile and toxic organic solvents. It is therefore of utmost importance to evolve a simple and effective methodology for the different organic transformations that cover the concept of green chemistry\(^1\). Novel processes should encounter several requirements such as high chemo- regio- and stereoselectivity, one pot reactions or multi-component reactions instead of multi-step procedures, use of non-toxic solvents or solvent-free reactions, elimination of toxic and/or hazardous reagents, improvement of atom economy, etc.

A reasonable working definition of green chemistry can be formulated as follows: “Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products”.

An alternative term, which is currently favoured by the chemical industry, is sustainable technologies. Sustainable development has been defined as “meeting the needs of the present generation without compromising the ability of future generations to meet their own needs”\(^2\).
1.2 Heterogeneous catalysis

A powerful tool to enhance the sustainability of chemical processes is undoubtedly catalysis. Certain organic reactions are generally carried out in presence of a catalyst. Main features of frequently used homogeneous catalysts are having great activity and selectivity. Furthermore, forming catalyst are able to increase reaction and product specificity. However they have some disadvantages: some of them needs specific condition i.e. inert atmosphere, water free solvents, needs expensive ligands; they are unstable thereby strongly or cannot separate from the reaction mixture thus hinder it’s from reusability. The heterogenization of the catalysts can eliminate these disadvantages. Furthermore; heterogeneous catalysis allows a few more improvements over the homogeneous one that can contribute to develop cleaner, safer and more economically feasible processes.

However, heterogeneous catalysts, in order to be practical, have to meet some requisites as:

- the catalyst preparation should be simple, efficient and of general applicability

- the performance of the immobilized catalyst should be comparable to (or better than) its homogeneous counterpart.

- the separation of the heterogeneous catalyst from the reaction mixture after reaction should be possible via a simple filtration in which more than the 95% of the catalyst should be recovered.
• the leaching of the active species from the heterogenized catalyst should be minimal.

• the recycling of the catalyst for several cycles should be possible without loss of activity.

• the supports carrying the catalyst should be mechanically, thermally and chemically stable; they should be compatible with the solvent and commercially available in a good quality.

• from an environmental (increasing disposal costs) and economical (cost of raw materials and of downstream separation) viewpoint, the catalyst selectivity might sometimes become more important than its activity or lifetime.

In recent years two preferential tendencies have been developed: that of the polymer-supported catalysts and that of the inorganic oxides heterogenized catalysts.\textsuperscript{4,5} In particular the general area of cross-linked polymer supports has shown an explosive growth connected with the development of new macroporous materials, which are characterized by a rigid porous matrix that persists even in the dry state.\textsuperscript{6} These polymers are typically produced as spherical beads by a suspension polymerization process, which is based on the mixture of cross-linking monomer, inert diluent and the porogen. It has been reported that the preparation of “moulded” porous materials with high characteristics for catalysis and asymmetric catalysis too. On the other hand, inorganic oxides show several
advantages, such as more mechanical stability, easier handling and a wider range of solvents that can be used.

Another class of solid catalysts that has generated a particular interest is that of the supported homogeneous catalysts, that combine the potential versatility and selectivity of homogeneous catalysts with the practical advantages of solid materials, such as easy catalyst separation from the reaction medium, recovery, and use of a large variety of reaction conditions. However the creation of the ideal supported catalyst is related to the need of new technologies and new supports since they play an important role in the outcome of the process. In fact, normally, the heterogenization procedure causes a decreasing in stereoselectivity and activity in comparison with the homogeneous counterpart. Besides, the solid support determines limited diffusion of reactants to the active sites and these results in lower reaction rates. The support surface and the catalyst site surrounding can also influence the extent of the reaction.

The focus of this dissertation regards the immobilization of inorganic acids onto solid supports for the production of fine chemicals in batch and continuous flow conditions.
1.3 Solid supports

The development of supported catalysts for heterogeneous reactions prompted research groups all over the world to investigate many different solid supports as these play an important role in the outcome of the process. Solid supports can be roughly divided in two classes: inorganic materials and organic polymers.

(i) Inorganic materials

Many different types of inorganic supports are known for the preparation of heterogenized catalysts. The most used can be divided mainly in three categories: a) amorphous materials (e.g. amorphous silica and alumina), b) mesoporous materials (e.g. MCM-41, MCM-48 and MSU silicas) and c) crystalline materials (e.g. zeolites). Inorganic materials described in this dissertation are mainly amorphous silica.

(a) Amorphous silica

Amorphous silica has a non-ordered structure with irregular channels and pore diameter that can broadly vary. The amorphous silica utilized in the present work is commercially available (Merck) with an average pore diameter of 60 Å. This material has the advantage to be readily available and economically advantageous. However, due to the irregular pore sizes, part of the catalyst can penetrate into small pores during the supporting procedure with the consequence that this part of the catalyst is not easily accessible from reactants.
(b) Mesoporous synthetic silicas (MCM-41)

Ordered mesoporous (alumino) silicates offer interesting catalytic properties. These materials are synthesized with the help of surfactant micelle templates. Exemplified by the Mobil M41S materials, of which MCM-41 is the most familiar, they possess uniform channels with tunable diameters in the range 1.5-10 nm. M41S family is composed by three types of materials which have a very high surface area (often more than 700 m²/g) and which differ for the mesoporous spatial organization:

- MCM-41 with a mono-dimensional array of hexagonal channels
- MCM-48 with a three-dimensional network of cubic channels
- MCM-50 with a lamellar, but not very stable, organization of channels.

(c) Crystalline materials

A crystalline material or microporous material is a material containing pores with diameters less than 2nm. Examples of microporous materials include zeolites and metal-organic frame works. Porous materials are classified into several kinds by their size.

(ii) Organic Polymers

Organic polymers as solid phases for heterogeneous catalysis are mainly of three types: soluble polymers (linear non cross-linked), cross-linked insoluble polymers and macroreticulated resins. The term “macroporous” resin is used to indicate a
class of polymers which have a permanent well-developed porous structure even at the solid state.\textsuperscript{11}

### 1.4 Solid-supported reagents for organic synthesis

The utility of solid-supported reagents has been proven by application in a large number of diverse and interesting chemical manipulations\textsuperscript{12}. The practical advantages and novel synthetic properties of these reagents have created extensive demand for additional chemical entities to supplement the existing chemistry. Solid-supported reagents have more advantages like; easy preparation, commercial availability, removal from reactions by simple filtration, Excess reagents can be used to drive reactions to completion without introducing difficulties in purification, Recycling of recovered reagents is economical, environmentally-sound and efficient.

**Inorganic Supports: Alumina**

**Alumina — Al\textsubscript{2}O\textsubscript{3}· (H\textsubscript{2}O)\textsubscript{n}, n=0-3**

Alumina is thermally-stable, high-surface-area forms lead to use as acid or base catalysis or as supports for other catalytic materials (e.g. metals, oxides, sulphides, etc.). Alumina composition depends on precursors, temperature, and mode of heating, thermolysis combines hydroxyls to generate water which is driven from the solids. Alumina used as a drying agent, catalyst, catalyst support, and for column chromatography among other applications.
Common reagents on alumina

KF/Al$_2$O$_3$

Potassium fluoride on alumina (KF/Al$_2$O$_3$) was originally introduced in 1979 by Ando et al. as a useful agent for inducing alkylation reactions$^{13}$. KF/Al$_2$O$_3$ is strongly basic, which allowed it to replace organic bases in a number of reactions including selective N-alkylation of amides$^{14}$, epoxidation$^{15}$, diazetizations$^{16}$, Sonogashira couplings$^{17}$, Suzuki couplings$^{18}$, Knoevenagel reactions$^{19}$, and Horner – Emmons chemistry$^{20}$.

Preparation of KF/alumina$^{21}$:

To a stirred solution of potassium fluoride (20g) in water (150 ml) is added neutral alumina (60-80 mesh, 30 g) in water (150 ml). After 30 minutes, the water was removed using a rotary evaporator at ~60$^\circ$C. When most of the water has been removed, the remaining mixture was heated to 140-150$^\circ$C and maintained at that temperature under vacuum (5 mmHg) for 6h to give 50g of KF-alumina reagent.

J. M. Fralie et al.$^{15}$ reported that epoxidation of α-isophorone with tert-butyl hydroperoxide/KF-Al$_2$O$_3$ in toluene leads to the highest quantitative yield.
Kabalka et al.,\textsuperscript{17} accomplished a tandem process for Sonogashira coupling with KF/Al\textsubscript{2}O\textsubscript{3} under solvent-free conditions. Aryl iodides were found to undergo Sonogashira couplings with various terminal alkynes in the presence of KF/Al\textsubscript{2}O\textsubscript{3}, Copper (I) iodide, powdered palladium, and triphenylphosphine under solvent free conditions with microwave irradiation. The reaction times were very short (2.5 min) and yields were high in most cases.

\[
\text{ArI} + \text{R} = \text{H} \xrightarrow{\text{Kg/Al}_2\text{O}_3, \text{CuI}} \text{R} = \text{n-aryl} X
\]

Kabalka et al.,\textsuperscript{18} reported Suzuki coupling with KF/Al\textsubscript{2}O\textsubscript{3} under solvent-free conditions. Aryl bromides and iodides with a series boronic acids to produce the cross coupled products at elevated temperatures in high yields.

\[
\text{R-X} + \text{R}_1\text{B(OH)}_2 \xrightarrow{\text{Kg/Al}_2\text{O}_3, 5\% \text{Pd}} \xrightarrow{100^\circ\text{C}, 4\text{h}} \text{R}_1\text{-R}
\]

\textbf{NaBH}_4/\text{Al}_2\text{O}_3

R. S. Varma \textit{et al.},\textsuperscript{22} reported a simple and rapid method for the reduction of carbonyl compounds which can be conducted under solvent less ‘dry’ conditions using NaBH\textsubscript{4}-Alumina and microwave irradiation.
CuBr$_2$/Al$_2$O$_3$

B. S. Park et al.,$^{23}$ reported a convenient method for conversion of methylene ketones to 1,2-diketones using CuBr$_2$ adsorbed onto alumina. The ketonization turned out to go through bromo ketones and alumina seemed to play an important role in the oxidation step.

Inorganic Supports: Silica

Silica gel is an amorphous inorganic polymer composed of internal siloxane groups (Si–O–Si) with silanol groups (Si–OH) distributed on the surface$^{24,25}$. The active hydrogen atom of the silanol groups of silica gel has the ability to react with agents containing organosilyl functions, to give some organic nature to the precursor inorganic support$^{26}$. These covalently bonded groups are resistant to removal from the surface by organic solvents or water.
The principal success of such inorganic solid surfaces modified with organofunctional groups is the immobilization of the desired reactive atomic group, which causes a great versatility of this surface in developing various functions\textsuperscript{27,28}. Thus, chemically modified silica gel can be used in various areas of chemistry such as heterogeneous catalysis\textsuperscript{29}, and ion-exchange\textsuperscript{30–32}, as a stationary phase in chromatography\textsuperscript{33}, and for enzyme catalysis\textsuperscript{34}, biotechnology\textsuperscript{35}, electrochemistry\textsuperscript{36} and metal ion preconcentration\textsuperscript{37}.

**Common reagents on silica**

During the last decade many academic and industrial processes shifted towards the development of new technologies in synthetic organic chemistry using solid acid catalysts. Adsorption onto solid supports is known to cause a change in the chemical properties of many reagents\textsuperscript{38}. The most striking examples of such a change in chemical reactivity that has been reported to date is with the well-known reagents on silica supports like KMnO\textsubscript{4}, FeCl\textsubscript{3}, sodium meta periodate, NaHSO\textsubscript{4}, poly phosphoric acid, chloro sulphonic acid. Silica supported catalysts described in this dissertation are mainly on silica supported sodium hydrogen sulphate.

**Silica supported permanganate**

Hajipour et al.,\textsuperscript{39} reported that wet silica-supported potassium permanganate was used as an inexpensive and efficient reagent for conversion of semicarbazones and phenyl hydrazones to the corresponding carbonyl compounds under solid-state conditions.
Wet silica gel was prepared by shaking silica gel (20 g, 230-400 mesh) with distilled water (5 mL). The reagent was prepared by mixing KMnO₄ (3 mmol, 0.48 g) with wet silica gel (3 g) using a pestle and mortar until a fine, homogeneous, and purple powder was obtained.

**Silica supported ferric chloride**

Iranpoor et al.,⁴⁰ reported that FeCl₃·6H₂O adsorbed on chromatographic silica gel can act as an efficient catalyst for alcoholyis, hydrolysis and acetolysis of epoxides. Methanolysis of (R)-styrene oxide proceeds with high stereospecificity and in excellent yield. This catalyst can also convert epoxides to their corresponding β-halohydrins and β-nitrato alcohols in the presence of chloride, bromide and nitrate ions respectively.
**Silica supported sodium metaperiodate**

*Preparation of NaIO₄-SiO₂*: Sodium metaperiodate (2.57 g, 12mmol) was dissolved in hot water (5mL). To the hot solution, silica gel (230-400 mesh, 10 g) was added with vigorous swirling and shaking. The resultant silica gel coated with NaIO₄ was in a powder form and was free flowing.

Sivabalan et al.,⁴¹ reported that 1,2-5,6-di-O-isopropylidine-D-mannitol oxidized with silica supported sodium meta periodate in DCM was obtained 2,3-O-isopropylidene 1-propanal in excellent yield.

![Chemical structure](image)

**Silica supported sodium hydrogen sulphate**

*Preparation of silica supported sodium hydrogen sulphate*: To a solution of 4.14 g (0.03 mol) of NaHSO₄.H₂O in 20 mL of water in a 100 mL beaker containing a stir bar was added 10 g of SiO₂ (column chromatographic grade, 230-400 mesh). The mixture was stirred for 15 min and then gently heated on a hot plate, with intermittent swirling, until a free-flowing white solid was
obtained. The catalyst was further dried by placing the beaker in an oven maintained at 120°C for at least 48 h prior to use.

G.W. Breton,\textsuperscript{42} reported that silica supported sodium hydrogen sulphate was an attractive catalyst for selective mono acetylation of unsymmetrical diols.

\textbf{H. R. Shaterian et al.,\textsuperscript{43}} described an efficient method for preparation of amidoalkyl naphthols from condensation of aryl aldehydes, 2-naphthol, and acetamide in presence of silica supported sodium hydrogen sulphate under solvent-free conditions.

\textbf{U. V. Desai et al.,\textsuperscript{44}} reported o-Aminoaryl ketones underwent smooth condensation with a variety of α-methylene ketones in the presence of NaHSO₄-SiO₂ as a solid acid catalyst to afford 1,2,3-trisubstituted quinolines in excellent yields.
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M. A. Chari *et al.*,\(^{45}\) reported the synthesis of 3,4-dihydropyrimidinones from three component condensation reaction of aldehydes, β-ketoesters and urea in refluxing acetonitrile in presence of silica supported sodium hydrogen sulphate.

L. Zhou *et al.*,\(^{46}\) reported that silica supported sodium hydrogen sulphate as a good catalyst for debenzylation of aromatic benzyl ethers under thiophene reflux condition to get excellent yields.

[16]
B. Das et al., reported that silica supported sodium hydrogen sulphate as a heterogeneous catalyst and they are used in many organic transformations like deprotection of TBDMS ethers\textsuperscript{47}, MOM ethers\textsuperscript{48}, trityl ethers\textsuperscript{49}, cleavage of prenyl esters\textsuperscript{50}, synthesis of \textit{gem}-dihydro peroxides\textsuperscript{51}, conversion of alcohols to ethers\textsuperscript{52}, α-bromination of carbonyl compounds\textsuperscript{53} and conversion of camptothecin to mappicine ketones\textsuperscript{54}.

t-Butyldimethylsilly (TBDMS) ethers have been efficiently and selectively deprotected using this silica supported sodium hydrogen sulphate as a heterogeneous catalyst at room temperature in dichloromethane solvent condition to regenerate the parent alcohols in high yields.

\[
\text{R-OTBDMS} \xrightarrow{\text{NaHSO}_4\cdot\text{SiO}_2, \text{CH}_2\text{Cl}_2, \tau, 30 \text{ mi}} \text{R-OH}
\]

Phenolic methoxy methyl (MOM) ethers are selectively deprotected with this silica supported sodium hydrogen sulphate as a catalyst at room temperature in high yields.

\[
\text{Ar-OMOM} \xrightarrow{\text{NaHSO}_4\cdot\text{SiO}_2, \text{CH}_2\text{Cl}_2, \tau, 1-1.5 \text{ h}} \text{Ar-OH}
\]
Chemoselective deprotection of trityl ethers were also reported with this silica supported sodium hydrogen sulphate.

Prenyl esters were selectively cleaved under slightly acidic reaction conditions using silica supported sodium hydrogen sulphate as a heterogeneous catalyst at room temperature to regenerate the parent carboxylic acids in very high yields.

NaHSO₄-SiO₂ was used as catalyst for the synthesis of gem-dihydroperoxides from ketones and aqueous H₂O₂ under mild conditions at room temperature.
Silica supported sodium hydrogen sulphate is a catalyst for conversion of \( p \)-hydroxybenzyl alcohols to \( p \)-hydroxy benzyl ethers and thioethers at room temperature.

\[
\text{HO-}R_1\text{OH} \xrightarrow{\text{RXH}} \xrightarrow{\text{NaHSO}_4\text{-SiO}_2} \text{HO-}R_1XR\text{R}_2
\]

\( \text{r.t., 1-1.5 h} \)

\( X \) O,S

\( \alpha \)-Bromination of carbonyl compounds (cyclic and acyclic ketones, amides and \( \beta \)-ketoesters) are achieved efficiently by treatment with \( N \)-Bromosuccinimide (NBS) and catalyzed by silica supported sodium hydrogen sulphate.

\[
\text{R}_1\text{R}_2\text{CO} \xrightarrow{\text{NBS}} \xrightarrow{\text{NaHSO}_4\text{-SiO}_2} \text{BrR}_1\text{R}_2\text{CO}
\]

\( \text{Ether or CCl} \)

Conversion of camptothecin and 9-methoxycamptothecin to mappicine ketone was also reported with this catalyst.
Silica supported poly phosphoric acid

Preparation of silica supported poly phosphoric acid:

PPA (2.1 g) was charged in the round bottom flask and CHCl₃ (100 mL) was added. After the mixture was stirred at 50°C for 1 hr, SiO₂ (230-400 mesh, 4.9 g) was added to the solution and mixture was stored for another 1 hr. The CHCl₃ was removed with rotary evaporator and the resulting solid was dried in vacuum at room temperature for 3 hr.

H. R. Shaterian et al.,⁵⁵ reported that silica supported poly phosphoric acid as a heterogeneous catalyst for the synthesis of 2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione derivatives from the three-component condensation reaction of phthalhydrazide, dimedone, and aromatic aldehydes under solvent-free conditions in good to excellent yields and short reaction times.
M. T. Maghsoodlou et al.,\textsuperscript{56} reported the preparation of α-amino phosphonates, employing a one-pot three-component condensation reaction between aldehydes, amines, and trialkyl phosphites in the presence of silica supported poly phosphoric acid under solvent-free conditions at 80°C.

Montazeri et al.,\textsuperscript{57} reported for the synthesis of tetra substituted imidazole, including four components condensation of 1,2-diketones, aromatic aldehydes, primary amines and ammonium acetate in presence of silica supported poly phosphoric acid in high yields under solvent-free and microwave irradiation conditions.
Silica sulfuric acid

**Preparation of silica sulfuric acid:**

A 500 mL suction flask equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (23.3 g, 0.2 mol) and a gas inlet tube for conducting of HCl gas over adsorbing solution (i.e. water) was used. Then 60.0 g of silica gel was charged in to the flask. Chlorosulfonic acid was added drop wise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately. After the addition was complete, the mixture was shaken for 30 min. SSA was obtained (76 g) as a white solid.

M. A. Zolfigol et al.,\(^{58}\) reported that a mixture of ethyl formate and a catalytic amount of silica sulfuric acid or Al(HSO\(_4\))\(_3\) as a suitable formylating systems can formylate various alcohols to their corresponding formate ester derivatives under mild, nearly neutral and heterogeneous conditions at room temperature with good to excellent yields.
Minoo Dabiri et al.,\textsuperscript{59} described that silica sulfuric acid as a heterogeneous reagent catalyzed eco-friendly synthesis of 2,3-dihydroquinazolinones by the reaction of isatoic anhydride, a primary amine or ammonium acetate and an aromatic aldehyde in water or under solvent-free conditions.

\[
\text{O}_2\text{C} + \text{R}_1\text{-CHO} + \text{R}_2\text{-NH}_2 \xrightarrow{\text{Silica sulfuric acid}} \text{O}_2\text{C} + \text{R}_2\text{N} + \text{R}_1\text{-CHO} \\
\xrightarrow{\text{Water or Solvent-free} \atop 80^\circ} \text{O}_2\text{C}
\]

H. R. Shterian et al.,\textsuperscript{60} reported that silica sulfuric acid as an efficient and reusable heterogeneous catalyst for the preparation of 2\textit{H}-indazolo[2,1-\textit{b}]phthalazine-1,6,11(13\textit{H})-trione derivatives from the three-component condensation reaction of phthalhydrazide, dimedone, and aromatic aldehydes under solvent-free conditions in good to excellent yields and short reaction times.

\[
\text{O}_2\text{C} + \text{ArCHO} + \text{NH}_2\text{C} = \text{NH} \xrightarrow{\text{Silica-SO}_2\text{H}} \text{O}_2\text{C} + \text{NH}_2\text{C} = \text{NH} \text{N} + \text{ArCHO} \\
\xrightarrow{\text{Silica-SO}_2\text{H}} \text{O}_2\text{C} + \text{N} + \text{N} + \text{ArCHO}
\]
Silica chloride

Preparation of silica chloride:

To an oven-dried (120°C, vacuum) sample of silica gel (10 g) in a round bottomed flask (250 mL) equipped with a condenser and a drying tube, was added thionyl chloride (40 mL) and the mixture was refluxed for 48 h. The unreacted thionyl chloride was distilled off. The resulting white-grayish powder was flame-dried and stored in a tightly capped bottle.

L. Q. Wu et al.,\textsuperscript{61} reported for the synthesis of 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-ones has been accomplished by the one-pot condensation of β-naphthol, aldehydes, and 2H-indene-1,3-dione under solvent-free conditions in the presence of silica chloride as a heterogeneous catalyst.

![Reaction Equation]

Inorganic Supports: Zeolites

Zeolites are crystalline microporous minerals, built up of silicon, aluminum and oxygen atoms. Natural zeolites contain a mixture of cations (e.g. Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+} and
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Ca^{2+}) which can be ion-exchanged. Zeolites are inorganic crystalline solids with small pores (1-20 Å diameter) running throughout the solid. Zeolites are used as drying agents for solvents, shape selective catalysis and also for selective ion exchangers.

Das et al.,\textsuperscript{62} reported that HY-Zeolites have been found to be an efficient catalyst for selective monoacetylation of symmetrical diols and selective monodeaetylation of symmetrical diacetates to form the products in high yields.

| HO-(CH\textsubscript{2})\text{n-}OH | AcOH or EtOAc | HY-Zeolite | heat | HO-(CH\textsubscript{2})\text{n-}OAc | MeOH | HY-Zeolite | heat | AcO-(CH\textsubscript{2})\text{n-}C\text{Ac} |

Inorganic Supports: Clays

Clays are solid acidic catalysts which can function as both Bronsted and Lewis acids in their natural and ion-exchanged form. They are also known to act as radical catalysts. Modified smectite (swelling) clays can be very selective catalysts for a wide range of organic transformations. Clays are a class of soil with a particle size of <2 mm in diameter (~ 7.2 \times 10^{11} particles per gram of clay, which implies a surface area of about 23000 cm\textsuperscript{2} per gram). Their characteristic physical features are, they are sticky and plastic when moist, but hard and cohesive when dry. Structurally, they are crystalline hydrous aluminosilicates, and also contain various other cations.
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The range of reactions that have been successfully performed on clay catalysts includes addition, elimination, addition-elimination, substitution, rearrangement, Diels–Alder reactions, oxidation-reduction and others.

Braibanate et al.,\(^63\) reported that NBS supported on montmorillonite (K-10) as a heterogeneous catalyst for bromination reaction in good yields.
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**Main objective of the present work**

In view of the applicability of different solid supported heterogeneous catalysts, the present work was undertaken to develop the methodologies for various organic transformations by using silica supported sodium hydrogen sulphate as a heterogeneous catalyst.

The thesis comprises of four chapters in all, describing the present research work. Chapter 1 is introductory, describing the solid supported heterogeneous catalysts and their applications in organic synthesis. Second chapter reveals the synthesis of 2-substituted benzoazole, benzimidazole and benzothiazole derivatives by using NaHSO$_4$-SiO$_2$ as a catalyst. Tetrahydropyranylation (THP) of alcohols and phenols and their regeneration by catalytic silica supported sodium hydrogen sulphate has been discussed in chapter three and chapter four deals with the synthesis of acylals from aldehydes by using NaHSO$_4$-SiO$_2$ as a heterogeneous and chemoselective catalyst.
1.5 References


[28]


