Application of silica supported heterogeneous catalysts in one-pot multicomponent reactions
1. Introduction

Fundamental and applied research is done by the research institutions, industries and university research laboratories to find out how catalysts work and to improve their effectiveness. If catalytic activity can be improved, it may be possible to lower the temperature and/or the pressure at which the process operates and thus save fuel which is one of the major costs in a large-scale chemical process. Further, it may be possible to reduce the amount of reactants that are wasted forming unwanted by-products.¹

In the present century, it is predicted that 80% of the industrial chemical processes are mainly dependent on the catalytic processes,² because of that, catalysts generate annual global sales of about $1.5 trillion, and contribute directly or indirectly to approximately 35% of the world's GDP. Most catalytic processes are heterogeneous in nature.³ Catalysis is a strategic field of science relying on many disciplines. It has emerged as an essential avenue in modern chemistry because it signifies an innovative way to meet the challenges of energy and sustainability.⁴

Existence of a catalyst is primarily required in both modern organic syntheses as well as in chemical industries.⁵ The growth of industries mainly depends on the use of catalysts, since catalysts reduce the time and are economically viable.

The advent of industrial catalytic technologies in the last century has most often resulted from a sequential interaction between chemists and chemical engineers, both communities developing their own fundamental and applied sciences, i.e., a multidisciplinary process. In recent years, environmental and economic considerations have promoted process innovation towards cleaner technologies therefore; it is desirable to use heterogeneous catalysts that can perform under milder reaction conditions.

**Heterogeneous catalysis in organic synthesis**

Heterogeneous catalysts cover almost 90% of the industrial catalytic processes. Due to their definite technical advantages, like production process, competitiveness and economy, heterogeneous catalysts are gaining more and more importance to the world’s economy, to convert inexpensive raw materials into value added fine chemicals and fuel in an economic and environmentally efficient manner. These challenges are becoming the main concerns of the global vision of societal challenges and world economy.
New methods should give noteworthy advantages as well as high selectivity, increased productivity and it should be inexpensive. By considering the importance of catalysts, national laboratories, academic institutions, chemical industries and R & D centers all around the world are pursuing research in the field of catalysis, to develop new catalysts that are environmentally benign, more efficient and highly accurate.

1.1 Catalyst
Catalyst by definition is a substance which increases the rate of a chemical reaction by reducing the activation energy, and is left unchanged by the reaction. If the catalyst is in the same phase as the reactants, it is referred to as a homogeneous catalyst. A heterogeneous catalyst on the other hand is in a different phase to the reactants and products, and is often favoured in industry, being easily separated from the products.

1.2 Classification
Catalysts can be classified as homogeneous, heterogeneous, electrocatalysts, organocatalysts and biocatalysts (enzymes which, are often seen as a separate group). Another way of classifying the catalysts are: (i) Positive catalyst: The catalyst which increases the rate of a reaction. (ii) Negative catalyst: Chemical reactions are sometimes retarded by the presence of a foreign substance the substance is known as a negative catalyst. (iii) Auto catalysis: In this type of catalysis, one of the substrates or intermediates of the reaction catalyses the reaction.  

1.2.1 Homogeneous catalyst
A homogeneous catalyst refers to the form of a catalyst where the catalyst and reactants are in the same phase.

1.2.2 Brief outlook on the heterogeneous catalysts
The term a heterogeneous catalyst refers to the form of a catalyst where the phase of the catalyst differs from that of the reactants. The first heterogeneous catalytic reaction, that is, the dehydration of ethanol in active clay, was studied by Priestley in 1778; later VanMarum in 1796 used a metallic catalyst for the dehydrogenation of ethanol. In 1813, Thenard revealed that ammonia is decomposed into nitrogen and hydrogen when passed over different burning metals. In 1823, Dulong found that the activity of different metals such as iron, copper, silver, gold and platinum for decomposing ammonia decreased in the given order. In 1817, H. Davy and E. Davy reported the oxidation of hydrogen by air over platinum, then onwards the use of heterogeneous catalysts in research and industries are ever expanding. In
heterogeneous catalysis, the reactants adsorb on the catalyst surface, after the completion of the reaction, the product desorbs from the surface and diffuse away. Understanding the transport phenomena and surface chemistry such as dispersion is important. If diffusion rates are not taken into account, the reaction rates for various reactions on surfaces depend solely on the rate constants and reactant concentrations. For solid heterogeneous catalysts, the surface area of the catalyst is critical since it determines the availability of catalytic sites. Heterogeneous catalysts are the workhorses of the chemical and petrochemical industry, some of the important catalysts that are very popularly used are: 1) Iron oxide on alumina in the well known Haber Bosch process for ammonia synthesis which consumes 1% of world’s industrial energy budget. 2) Mo–Co on alumina in the desulfurization of petroleum products. 3)V in the contact process to get sulfuric acid, and many more industrially important reactions are carried out using heterogeneous catalysts. 9

1.2.3 Differences between heterogeneous and homogeneous catalysts

<table>
<thead>
<tr>
<th>Property</th>
<th>Heterogeneous</th>
<th>Homogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst recovery</td>
<td>Easy and inexpensive</td>
<td>Difficult and expensive</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Number of active site</td>
<td>Multiple active site</td>
<td>Single active site</td>
</tr>
</tbody>
</table>

**Heterogeneous catalysts**

- Bulk metal
- Supported metals
- Metal oxides and sulfides
- Supported inorganic metal compounds
- Supported organometallic complexes

**Homogeneous catalysts**

- liquid acids and bases
- solid acids and bases soluble in suitable solvents
- Organometallic complexes (Wilkinson’s catalyst)

**Biological catalysts**

- Enzymes
1.3 Introduction to solid supported catalysts

In heterogeneous catalysis solid support is an essential component. The solid supported acid catalysts may be used in native state or loaded on a solid support. In the case of unsupported catalysts the active species is present on the surface of the material. Thus the atoms present on the surface will only be participating in the catalysis rather than the remaining atoms present inside the bulk of the supporting system which will not take part in the reaction. Solid support provides uniform dispersion of the active component, good accessibility and stability. Therefore the porous materials which have high surface area are preferred as solid supports. The porous nature of catalysts may also control the transport of the reactant and product molecules affecting the overall conversion, in addition to this, the support reduces the amount of the active components needed and increases the surface area of the catalyst. The support holds on its surface the microcrystalline particles of the active component and prevents its sintering.

1.3.1 Solid supported /solid silica supported catalysts in organic synthesis

Solid supported catalysts are used as a heterogeneous catalyst for a variety of organic reactions, which can be summarized under the following sub headings:

1. Synthesis of heterocyclic compounds.
2. Protection–deprotection of functional groups.
3. Alkylation/acylation/sulfonation reactions.
4. Oxidation reactions.
5. Miscellaneous reactions.

Solid silica supported substances have emerged as successful solid catalysts for a number of organic reactions. A brief note about the silica supported catalysts is presented in this part.

Silica gel came into existence as early as 1640s; it was used in World War I for the adsorption of vapors and gases in gas mask canisters. The synthetic route for producing silica gel was patented by Walter A. Patrick at Johns Hopkins Univeristy, Baltimore, Maryland, USA in 1919. In World War II, silica gel was indispensable in the war; effort for keeping penicillin dry, protecting military equipment from moisture damage. Silica gel is used as fluid cracking catalyst for the production of high octane gasoline, as a catalyst support for the manufacture of butadiene from and feedstock for the synthetic rubber program.¹⁰
Reactions on solid-supports under solvent-free conditions are currently the subject of interest; they provide an attractive and practical means of exploring organic synthesis. The advantages of using these silica supported catalysts instead of their solution phase counterparts in organic synthesis are that they are (a) Less toxic and easier to prepare and to handle; (b) After the completion of the reaction, these solid catalysts can be separated from the product by a simple filtration, thus the purification protocols including chromatography and liquid-liquid extractions, which are time consuming, are not required; (c) The catalyst is cheap hence large quantity of reagent can be used, thus driving the reaction to completion; hence it is easy to scale up; (d) One-pot multiple step/multi-component reactions are easier to carry out using silica supported catalysts. The silica–supported reagents also have a number of advantages over the polymeric counterparts, such as, (a) Silica neither shrinks nor swells in any solvent and, it does not partially dissolve in any solvent either; (b) It is free flowing and thus easy to weigh out and handle; (c) It does not require extensive washing for high recoveries and it won't stick to glassware; (d) Most silica bound reagents and scavengers can withstand temperatures of over 200 °C and are suitable for use in microwave synthesizers.  

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2. Explorative study on the application of silica supported heterogeneous catalysis in organic synthesis

1. Hamid Reza Shaterian and coworkers\textsuperscript{12} have developed a direct protocol for the preparation of α-amido alkyl naphthols employing a multi-component and one-pot condensation reaction of 2-naphthol, aromatic aldehydes and acetonitrile or acetamide using HClO$_4$-SiO$_2$ as a efficient catalyst in the presence of a solvent, solvent-free, and microwave irradiation conditions.

\begin{center}
\begin{tikzpicture}
\node (n1) [circle, draw] at (0,0) {X, H, H, OMe, NO$_2$, Me};
\node (n2) [circle, draw] at (1,0) {X, H, H, OMe, NO$_2$, Me};
\node (n3) [circle, draw] at (1,1) {X, H, H, OMe, NO$_2$, Me};
\node (n4) [circle, draw] at (0,1) {X, H, H, OMe, NO$_2$, Me};
\node (n5) [circle, draw] at (1,2) {X, H, H, OMe, NO$_2$, Me};
\node (n6) [circle, draw] at (0,2) {X, H, H, OMe, NO$_2$, Me};
\node (n7) [circle, draw] at (1,3) {X, H, H, OMe, NO$_2$, Me};
\node (n8) [circle, draw] at (0,3) {X, H, H, OMe, NO$_2$, Me};
\node (n9) [circle, draw] at (1,4) {X, H, H, OMe, NO$_2$, Me};
\node (n10) [circle, draw] at (0,4) {X, H, H, OMe, NO$_2$, Me};
\node (n11) [circle, draw] at (1,5) {X, H, H, OMe, NO$_2$, Me};
\node (n12) [circle, draw] at (0,5) {X, H, H, OMe, NO$_2$, Me};
\node (n13) [circle, draw] at (1,6) {X, H, H, OMe, NO$_2$, Me};
\node (n14) [circle, draw] at (0,6) {X, H, H, OMe, NO$_2$, Me};
\node (n15) [circle, draw] at (1,7) {X, H, H, OMe, NO$_2$, Me};
\node (n16) [circle, draw] at (0,7) {X, H, H, OMe, NO$_2$, Me};
\node (n17) [circle, draw] at (1,8) {X, H, H, OMe, NO$_2$, Me};
\node (n18) [circle, draw] at (0,8) {X, H, H, OMe, NO$_2$, Me};
\node (n19) [circle, draw] at (1,9) {X, H, H, OMe, NO$_2$, Me};
\node (n20) [circle, draw] at (0,9) {X, H, H, OMe, NO$_2$, Me};
\node (n21) [circle, draw] at (1,10) {X, H, H, OMe, NO$_2$, Me};
\node (n22) [circle, draw] at (0,10) {X, H, H, OMe, NO$_2$, Me};
\node (n23) [circle, draw] at (1,11) {X, H, H, OMe, NO$_2$, Me};
\node (n24) [circle, draw] at (0,11) {X, H, H, OMe, NO$_2$, Me};
\node (n25) [circle, draw] at (1,12) {X, H, H, OMe, NO$_2$, Me};\end{tikzpicture}
\end{center}

Scheme I.1

2. Mahmoud Nasrollahzadeh and coworkers\textsuperscript{13} described an efficient method for the preparation of 5-substituted-1H-tetrazole derivatives reported using FeCl$_3$-SiO$_2$ as an effective heterogeneous catalyst, it can be recovered by simple filtration and reused delivering good yields.

\begin{center}
\begin{tikzpicture}
\node (n1) [circle, draw] at (0,0) {R, H, H, OMe, NO$_2$, Me};
\node (n2) [circle, draw] at (1,0) {R, H, H, OMe, NO$_2$, Me};
\node (n3) [circle, draw] at (1,1) {R, H, H, OMe, NO$_2$, Me};
\node (n4) [circle, draw] at (0,1) {R, H, H, OMe, NO$_2$, Me};
\node (n5) [circle, draw] at (1,2) {R, H, H, OMe, NO$_2$, Me};
\node (n6) [circle, draw] at (0,2) {R, H, H, OMe, NO$_2$, Me};
\node (n7) [circle, draw] at (1,3) {R, H, H, OMe, NO$_2$, Me};
\node (n8) [circle, draw] at (0,3) {R, H, H, OMe, NO$_2$, Me};
\node (n9) [circle, draw] at (1,4) {R, H, H, OMe, NO$_2$, Me};
\node (n10) [circle, draw] at (0,4) {R, H, H, OMe, NO$_2$, Me};
\node (n11) [circle, draw] at (1,5) {R, H, H, OMe, NO$_2$, Me};\end{tikzpicture}\end{center}

Scheme I.2

3. Ali Khalafi-Nezhad and coworkers\textsuperscript{14} demonstrated a simple and practical synthetic strategy for the preparation of a novel silica-supported organocatalyst system l-proline (SSLP). The efficiency of the catalyst was evaluated in a three-component synthesis of spirooxindole derivatives via the condensation reaction of isatins and dicarbonyl compounds in water.

\begin{center}
\begin{tikzpicture}
\node (n1) [circle, draw] at (0,0) {R, H, H, OMe, NO$_2$, Me};
\node (n2) [circle, draw] at (1,0) {R, H, H, OMe, NO$_2$, Me};
\node (n3) [circle, draw] at (1,1) {R, H, H, OMe, NO$_2$, Me};
\node (n4) [circle, draw] at (0,1) {R, H, H, OMe, NO$_2$, Me};
\node (n5) [circle, draw] at (1,2) {R, H, H, OMe, NO$_2$, Me};
\node (n6) [circle, draw] at (0,2) {R, H, H, OMe, NO$_2$, Me};\end{tikzpicture}\end{center}

Scheme I.3
4. Hossein Eshghi and coworkers\textsuperscript{15} reported the preparation of a series of substituted β-enaminones through a one-pot reaction of dicarbonyl compounds with various amines in the presence of silica ferric hydrogen sulfate under solvent free conditions at room temperature. The reactions proceed smoothly in excellent yield with high chemoselectivity.

\[
\text{R}_1\text{C}=\text{O} + \text{ArNH}_2 \xrightarrow{\text{Fe(HSO}_4\text{)}_3\cdot\text{SiO}_2\text{, solvent-free, r.t.}} \text{R}_1\text{C}=\text{O} + \text{NH}\text{Ar}
\]

**Scheme I.4**

5. M. Kooti and coworkers\textsuperscript{16} described that, Phosphotungstic acid (PTA) can be used on the surface of silica coated cobalt ferrite core to obtain a new nanocomposite (CoFe$_2$O$_4$@SiO$_2$-PTA). The catalyst is efficient for the N-formylation of various amines under solvent-free condition at room temperature.

\[
\text{NH}_2\text{CH}_2 + \text{HO} = \text{CHO} \xrightarrow{\text{CoFe}_2\text{O}_4\text{@SiO}_2\text{-PTA, solvent-free, r.t.}} \text{NH}_2\text{CHO}
\]

**Scheme I.5**

6. Amol. B. Atar and coworkers\textsuperscript{17} demonstrated a mild, efficient and expeditious method for the synthesis of 3,5-dispirosubstituted piperidines via a three component, one-pot cyclocondensation reaction of aromatic amines, formaldehyde, and dimedone using Silica supported tungstic acid as an effective heterogeneous catalyst.

\[
\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2 + \text{R}_1\text{C}=\text{O} + \text{HO} = \text{CHO} \xrightarrow{\text{Silica tungstic acid, DCM, r.t.}} \text{R}_1\text{C}=\text{O}
\]

**Scheme I.6**
7. Ali Keivanloo and coworkers\textsuperscript{18} reported the use of silica-supported zinc bromide (SiO\textsubscript{2}–ZnBr\textsubscript{2}) as an efficient heterogeneous catalyst for the rapid synthesis of yrones by cross-coupling of acid chlorides with terminal alkynes in good to excellent yields under solvent-free condition.

![Scheme I.7](image)

8. Wenhu Duan and coworkers\textsuperscript{19} described an efficient synthesis of triarylmethanes \textit{via} bisarylation of aryl aldehydes with arenes catalyzed by silica gel-supported sodium hydrogen sulfate in a solvent-free system.

![Scheme I.8](image)

9. Asit K. Chakraborti and coworkers\textsuperscript{20} reported the use of Fluoroboric acid adsorbed on silica-gel (HBF\textsubscript{4}–SiO\textsubscript{2}) as a new and highly efficient heterogeneous catalyst for thia-Michael addition to α,β-unsaturated carbonyl compounds under solvent-free condition.

![Scheme I.9](image)
10. Hojat Veisi and coworkers\textsuperscript{21} reported that, a variety of N-substituted pyrroles can be synthesized by reacting γ-diketones with amines, diamines or triamine in the presence of silica sulfuric acid at room temperature under solvent-free condition.

\[ \text{RNH}_2 + \begin{array}{c} \text{SSA} \\ \text{Solvent-free, r.t} \end{array} \rightarrow \begin{array}{c} \text{N} \\ \text{R} \end{array} \]

Scheme I.10

11. Animesh Pramanik and coworkers\textsuperscript{22} described a highly efficient protocol for the synthesis of biologically important 3\textit{H}, 3′\textit{H}-spiro[benzofuran-2,1′-isobenzofuran]-3,3′-diones by SSA as a solid acid supported catalyst under solvent-free condition.

\[ \begin{array}{c} \text{OH} \\ \text{OH} \end{array} + \begin{array}{c} \text{SSA} \\ 800 \, ^\circ\text{C}, 3\text{h} \end{array} \rightarrow \begin{array}{c} \text{R} \\ \text{R} \end{array} \]

Scheme I.11

12. Shahram Tangestaninejad and coworkers\textsuperscript{23} reported the epoxidation of alkenes with hydrogen peroxide catalyzed by [PZnMo, ZnPOM], supported on ionic liquid-modified silica (Im-SiO\textsubscript{2}) the immobilized catalyst [ZnPOM@Im-SiO\textsubscript{2}].

\[ \text{[PZnMoW@SiO\textsubscript{2}-Im], reflux} \]

Scheme I.12

13. Atul Chaskar and coworkers\textsuperscript{24} demonstrated the coupling of 4-Hydroxycoumarin with a carbonyl compound in the presence of a heterogeneous catalyst
(NaHSO$_4$/SiO$_2$/Indion 190 resin) to get bis-(4-hydroxycoumarin-3-yl) methanes in good to excellent yields.

**Scheme I.13**

14. Yeon Tae Jeong and coworkers$^{25}$ described the synthesis of Aminophosphonates, by a simple and efficient one-pot three-component condensation reaction of 5-amino-2,2-difluoro-1,3-benzodioxole, aromatic aldehydes and diethyl phosphate by silica-supported boron trifluoride (BF$_3$-SiO$_2$) in ionic liquid ([bmim][HCl]) under solvent-free condition at room temperature in good to excellent yields and in short reaction duration.

**Scheme I.14**

### 2.1 Brief introduction on heterocycles

Heterocycles having oxygen, nitrogen and sulfur moiety are the important targets in the field of synthetic organic chemistry, since this fragment is a key structure in many biologically active compounds.$^{26}$ Innumerable innovations in methodologies and development of new heterocycles are still undergoing today. These heterocycles play a key role as drugs for curing numerous diseases, as well as in the synthesis of new materials.

Heterocyclic compounds, making up to more than half of all known organic compounds are widely spread in nature and show numerous applications as drugs, antioxidants, dyes, preservatives, corrosion inhibitors, polymer material,$^{27-32}$ found many natural products, most vitamins, biomolecules, and in biologically active
compounds. They serve as antitumor, antibiotic, anti-inflammatory, antidepressant, antimalarial, anti-HIV, antimicrobial, antibacterial, antifungal, antiviral, antidiabetic, herbicidal, fungicidal, and insecticidal agents. They have been frequently found as key structural units in synthetic pharmaceuticals and agrochemicals. Some of these compounds exhibit a significant photochromic, solvatochromic and biochemi-luminescence properties also in addition; they have applications in supramolecular and polymer chemistry, especially in conjugated polymers. Moreover, they act as organic conductors, semiconductors, molecular wires and find application in photovoltaic cells, and organic light-emitting diodes (OLEDs), light harvesting systems, optical data carriers, chemically controllable switches and serve as liquid crystalline compounds. Heterocycles are also of considerable attention because of their synthetic utility as synthetic intermediates, chiral auxiliaries, organocatalysts, protecting groups, and metal ligands in asymmetric catalysis in organic synthesis. Hence, substantial attention has been paid to develop efficient new methods and new catalysts to synthesize heterocycles.

3. Brief introduction to the Nano materials

Materials having a dimension in the range of 1–100 nm are said to be nano materials. Nano materials are classified into compact materials and nano dispersions. The use of nanomaterials as catalysts have gained much attention compared to normal catalysts during the past few decades both in homogeneous and heterogeneous catalysis due to their high surface-to-volume ratio compared to bulk materials. The key objective of nano catalyst is to produce 100% selectivity, high activity, low energy consumption and long lifetime. Nanoparticles naturally occur as volcanic ash, ocean spray, fine sand and dust, and even biological species as viruses. Due to its high surface area and porous material nature, they are widely used as catalysts in organic synthesis, electromagnetic materials, optoelectronic, photonic crystals, gas sensors and also in biomedical field as biosensors, controlled drug liberation and in the detection of cancer cells in tissues.
3.1 Nano metal oxides in catalysis

Metal oxides have emerged as a significant class of heterogeneous catalysts, which are widely used in native state as solid supports. Metal oxides can be acidic or basic and their redox properties make them a large family of catalysts. Metal oxides such as alumina, silica, zirconia and Titania have been widely used as catalysts in various transformations due to their diverse spectrum of catalytic activity. Modifications of these metal oxides have given new methods in the field of catalysis as well as in chemical industry. Mixed metal oxides are generally obtained in the form of powder. They have wide spectrum of applications in the field of ceramics, electronics, nuclear research and in catalysis.
4. Explorative study on the application of nano heterogeneous catalysis in organic synthesis

1. M.P. Kaushik and coworkers developed a general synthetic route to 1,2-dihydro-1-arlylnaphtho[1,2-e][1,3]oxazine-3-ones and 14-substituted-14H-dibenzo[a,j]xanthenes using ZnO-NPs under thermal and solvent-free conditions.

![Scheme I.15](image)

2. B. V. Subba Reddy and coworkers reported a one-pot three component synthesis of α-aminophosphonates using super magnetic nano iron oxide at 50 °C under solvent-free conditions in excellent yields.

![Scheme I.16](image)

3. Ayoob Bazgir and coworkers have developed magnetically recoverable nano copper ferrite and used as an efficient catalyst for the one-pot three-component synthesis of spirooxindoles in water.

![Scheme I.17](image)
4. Jayashree Nagarkar and coworkers \(^{52}\) reported synthesis of a series of substituted benzimidazoles, benzothiazoles, and benzoxazoles by combining 1,2-phenylenediamine, 2-aminothiophenol or 2-aminophenol with aryl, heteroaryl, aliphatic, \(\alpha,\beta\)-unsaturated aldehydes in the presence of nano ceria (CeO\(_2\)) as an efficient heterogeneous catalyst.

![Scheme 1.18](image)

**Scheme 1.18**

6. Julie Banerji and coworkers \(^{53}\) reported an efficient and eco-friendly method for the synthesis of spirooxindoles with fused tetrahydrochromenes using basic nanocrystalline MgO catalyst under aqueous condition. The method has been applied for the synthesis of a range of compounds with variable functionalities in excellent yield and selectivity.

![Scheme 1.19](image)

**Scheme 1.19**
7. N. Karade and coworkers reported that, a wide range of Biginelli 4-aryl-3,4-dihydro(pyrimidin-2(1H)-thiones undergo ligand-free C–S cross coupling with diaryliodoniumtriflates in the presence of CuO nanoparticles with the concomitant oxidative aromatization to form highly substituted 2-(thioaryl)pyrimidine. The nano CuO catalyst can be recycled and reused three times without any significant loss of catalytic activity.

![Scheme I.20]

7. Sadegh Rostamnia and coworkers demonstrated that, water dispersed magnetic nanoparticles (DMNPs) of γ-Fe₂O₃ represents a simple and green catalyst for the rapid one-pot three-component synthesis of tetrahydro-4H-chromene and hexahydroquinoline carboxylate skeletons via single-pot domino Knoevenagel–Michael-cyclization reaction.

![Scheme I.21]

8. Animesh Pramanik and coworkers reported that, the bimetallic ZnFe₂O₄ nano powder a dual Lewis acid–base combined catalyst can efficiently catalyse a four-component reaction for the synthesis of functionalized tetrahydrospiro[indoline-3,2quinoline] derivatives from arylamines, dialkylacyclenedicarboxylates, isatin derivatives and cyclohexane-1,3-diones in water medium at room temperature.

![Scheme I.22]
9. Kulathu I. Sathiyanarayanan and coworkers\textsuperscript{57} reported a synthesis of xanthene derivatives catalysed by Nano-ZnAl\textsubscript{2}O\textsubscript{4} blended with metal-citrate complex-acrylamide polymer.

Scheme I.23

10. Muthusamy Boominathan and coworkers\textsuperscript{58} have demonstrated that, nanoporous titania-supported gold nanoparticles can be used for a green synthesis of 1,2,3-triazoles, by 1,3-dipolar cycloaddition of organic azides with a variety of terminal alkynes in aqueous medium.

Scheme I.24

25. Diwan S. Rawat and coworkers\textsuperscript{59} reported the synthesis of novel 3-substituted indoles via Yonemitsu-type condensation of indole, aromatic aldehydes and dimedone, catalysed by nano MgO in water.

Scheme I.25
26. Maasoumeh Jafarpour and coworkers\textsuperscript{60} have described a monoclinic zirconia nanoparticles catalyzed synthesis of quinoxalines and pyridopyrazines derivatives by the condensation of 1,2-diamines with 1,2-dicarbonyl compounds under mild reaction conditions.

![Scheme I.26](image)

**Scheme I.26**

4.1 Preparation of the nanocatalysts

The preparation of nanocatalysts mainly depends on their surface area, chemical composition and other properties of the catalyst. In the present work we have used normal filtration method for the solid supported catalyst and combustion method to prepare nano heterogeneous catalyst.

4.1.1 Characterization of catalysts

4.1.1.1 P-XRD

Powder X-ray Diffraction (P-XRD) technique is used to determine the crystalline nature of nano materials. The scattering of X-rays from atoms produce a diffraction pattern which contains information about the atomic arrangement in the crystals.

For a given set of lattice plane with an inter-planar distance of \( d \), the condition for a diffraction (peak) to occur can be calculated by the Bragg’s law.

\[
\eta \lambda = 2dsin\theta \quad \text{(1)}
\]

Where \( n \) is contained in \( d\text{hkl} \) and \( (hkl) \) refers to the Miller indices of the reflecting planes. The interplanar distance in \( n \) times is smaller than that between real planes.

\[
d\text{hkl} = n\text{dhnknkl}
\]

The above equation is referred to Bragg’s law.
Chapter 1

Introduction

Powder XRD arguably the most widely used X-ray diffraction method for characterizing powder samples, and thin films. In PXRD, the sample which is in the form of fine grains of single crystalline material is studied in liquid suspension, and also Polycrystalline solids may be studied using this technique. The particle size in powder is measured by using the formula given below.

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

(2)

where \(d\) is the average grain size of the crystallites, \(\lambda\) is the incident wavelength, \(\theta\) is the Bragg angle and \(\beta\) is the diffracted full-width at half-maximum (FWHM) in radians caused by the crystallites.

4.1.1.2 Fourier transforms Infrared Spectroscopy (FT-IR)

Infrared spectroscopy gives information about the adsorbed molecules bonded to the surface as well as the structural information of solids. In recent years infrared spectroscopy is frequently employed to study the nature of acid sites present on the solid acid materials.

4.1.1.3 SEM

Scanning electron microscopy (SEM) is largely used for studying solid surface of particles in size, shape, texture, porosity and dispersion of one phase in another. The magnification and resolution of the SEM is used for examining crystallites in the size range from 1 to 50 nm.

4.1.1.4 TEM

Transmission electron microscopy is widely used for material characterization by metallurgists and materials scientists. The direct observation of catalyst morphology with a TEM resolution can go down to the resolution tunable in the range \(10^{-4} - 10^{-10}\) m and TEM is used for obtaining the structural information by lattice imaging and micro diffraction techniques.
5. Conclusion and outlook
As illustrated through the selected reports in the literature survey, we conclude that, the use of heterogeneous catalysts has received considerable interest in various disciplines including organic synthesis of a variety of biologically and pharmacologically important molecules.
6. References


