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ORIGINAL PAPER

High Yield Silica-Based Emerging Nanoparticles Activities for Hybrid Catalyst Applications

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Abstract

Today is the era of catalysis, which has a spectacular range of influence in every field of research as they brought about many exciting developments. Among the varieties of catalysts studied, nanocatalysts, in particular, have grabbed the attention of many researchers worldwide since they facilitate environmentally sustainable catalytic processes. Currently, hybrid nanocatalysts made up of organic–inorganic nanomaterials are used for various transformation reactions. Including this, a remarkable number of reports in the literature describe the use of silica N.P.s as solid support for the fabrication of hybrid nanocatalysts. Because of its high natural abundance, unique chemical and physical properties, and easy synthesis and separation, it is considered a promising candidate for the immobilization process. Moreover, it can be used in the bare form and as solid support material for the active catalytic species' adsorption, enhancing the nanocatalysts' stability, reactivity, selectivity, recovery, and recyclability. Through this review, the authors attempt to briefly summarize the recent progress made by the heterogeneous Si-based hybrid nanaocatalysts in developing a diverse range of transformation reactions, including coupling, oxidation, reduction multicomponent reaction, and CO_2 conversion.

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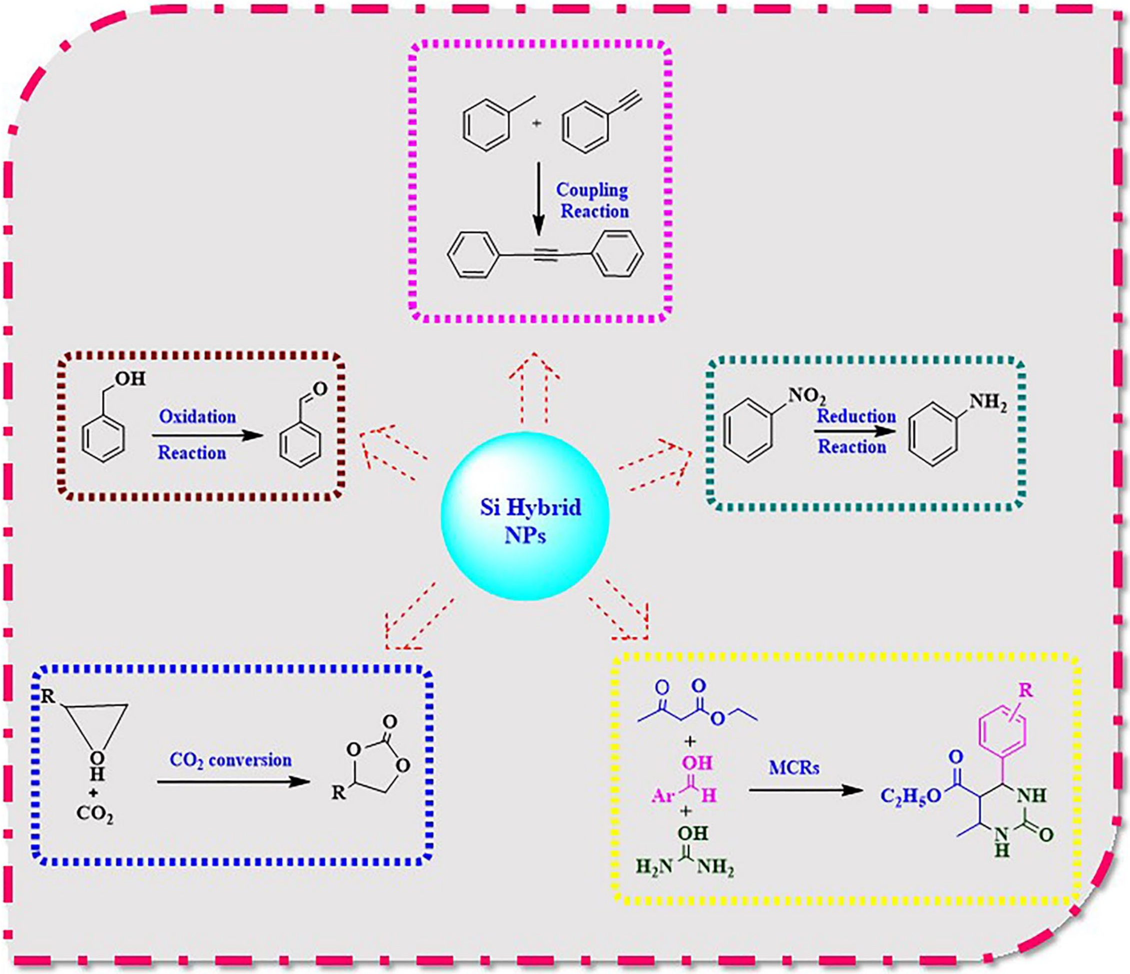
Graphical Abstract



Keywords Hybrid nanocatalyst · Oxidation · Coupling · Multicomponent reaction · Reduction

1 Introduction

Recently, nanotechnology has been standing as one of the most advanced and studied fields of science and technology for manipulating and describing matter's properties on the nanoscale [1]. R. P. Feynman first introduced this technology in the year 1959 in his Nobel prize-winning speech, i.e., "There's a Plenty of Room at the Bottom," in the annual gathering of APS (American Physical Society) at CIT, California [2]. Nanomaterial has gained significance in the galaxy of research and development and has also caught the eyes of industrial and pharmaceutical persons throughout the world [3, 4]. Primarily it can be defined by its associated tremendous functional properties, which suggest its interaction with other branches of science. [5]. In the current era, it has become a developing platform in materials processing technology, material science, mechanics, optics, electronics, medicine, textiles and plastics, aerospace and energy, etc. [6]. These technologies create a multidisciplinary field that includes engineering, chemistry, and physics [7] and contribute to disease diagnosis, better treatment options, and significantly decreased health care costs [8].

A hybrid nanomaterial is a composite made up of two or more different materials, typically inorganic elements such as metal clusters or particles, metal ions, oxides, salts, sulfides and other nonmetal components or derivatives, and organic elements such as organic molecules or groups, ligands, polymers, biomolecules, and other pharmaceutical components. These materials are integrated through direct interaction, resulting in the improvement of their functional properties. The various interactions involved in the construction of hybrid materials may be π-complexations, covalent

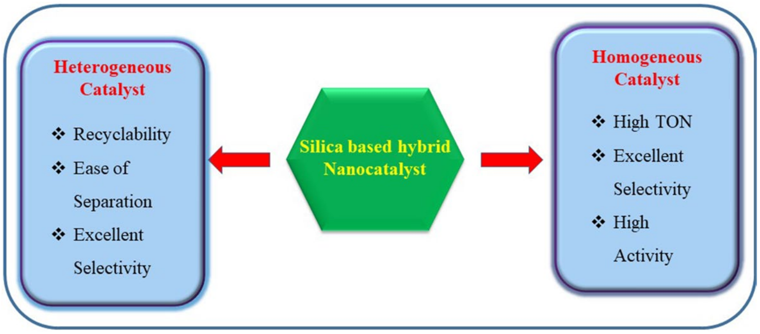


Fig. 1 Dual behavior of nano catalyst

bonds, a wide variety of non-covalent interactions, including H-bonding, electrostatic interactions, Van der Waal's interaction, dispersion, and other cooperative interactions involving multiple modes. The grouping of diverse parts and structural elements accompanying different interactions results in an almost endless diversity of elements specific to a particular task. [9]

The organic molecules chosen to form hybrid materials include simple organic entities to advanced molecular frameworks and polymers of organic origin [10–12]. Similarly, the inorganic component of the hybrid may be composed of a wide range of simple inorganic entities that can be tuneable at their atomic level ranges, including materials of monometallic elements to clusters and from nanosized inorganic particles up to extended phases form particles [9, 11, 12]. The process of merging inorganic components into organic polymers represents a simple and straightforward approach to the development of versatile materials with innovative extendable properties [11, 12]

The use of hybrid systems in catalysis, environmental protection, and adsorption is very important and challenging. The shape and size of nanoparticles, i.e., the type of "core–shell" or their decoration with other sub-nanoparticles and matrix interactions, significantly impact catalyst performance, i.e., its stability, activity, and selectivity [13–15].

Catalytic processes are essential in the industrial production of products derived from cheap raw materials (e.g., transport fuels, bulk chemicals, and pharmaceuticals) and catalysts [16]. Among the various types of catalysts, chemical industries specifically rely on heterogeneous catalysts (where the reaction of a liquid or gas phase is formed over a solid supported catalyst) for several reasons such as easy separation of catalyst, consistent performance, and longevity. However, because of their complex morphology and limited idea about the active centers, the derivation of the rational framework of a solid catalyst is not that much easy and straightforward process [17]. This information is essential for generating qualitative amounts of solid heterogeneous catalysts in a repetitive manner. Though a huge number of advancements are made in the field of the generation of catalysis, there is still a limitation. Therefore, the development of catalytic systems with a multidimensional application, often known as an art of science, is the most important call of the day [18].

Therefore, the desire to produce a stable, efficient and the selective catalytic system allows scientists to use nanoparticles in the catalytic process. The main advantageous feature associated with the nanoparticles as a catalyst is their large size to volume ratio, resulting in a large surface area with a number of surface-active particles and ultimately leading to a highly efficient catalytic environment. Overall, the effect of a large, highly active catalytic surface area, dispersibility, quantum confinement, durability, and stability are the main parameters possessed by the N.P.s play a vital role in developing dynamic, efficient, and eco-friendly catalytic systems [19].

Additionally, the surface-associated features of the N.P.s can also be modified accordingly with respect to functionalization by different organic (surfactant, polymers) as well as inorganic (Silica, carbon, metals, and its oxides) components [20]. Nanocatalysts have superior performance, selectivity, and stability and have convenient separation and recovery. So, nanocatalyst fills up the space between homogeneous and heterogeneous catalysis and maintains both systems' desirable characteristics, as shown in Fig. 1 [20–22].

The functionalization of silica-based hybrid N.P.s with organic moieties has been a long-enduring focus of research, i.e., to get an extendable version of the heterogeneous form of silica from inactive silica following hybridization possessing a broad range of applicability, particularly in the area of catalysis. Today, numerous reports of SiO_2 NPs are available describing their practical use to build up the exceedingly active, prominent, selective, and recyclable catalyst for many organic conversions [23].

SiO_2 NPs are usually affordable to manufacture on a large scale, are hydrophobic, have a large surface area, pore-volume, and are biocompatible, therefore, they have a wide range of applications. For example, SiO_2 NPs have been used for medication administration because of their non-toxic nature and high adsorption ability [24, 25]. Researchers have recently effectively used SiO_2 NPs as cargo loading for a variety of cargo, ranging from medicines to macromolecules like RNA, DNA, and proteins [26, 27]. Biomedicine, biotechnology, medication delivery, food, personal care items, insecticides, adsorption, semiconductors, and ceramics are now just several fields where silica nanoparticles have been used [28]. SiO_2 NPs have recently been used to absorb oil spills during oil exploration, transportation, and storage [29, 30]. The research to investigate and exploit the new conceivable applicability of silica nanoparticles is still ongoing [28]. This review article focuses on Silica-based hybrid nanoparticles' advancements and their application in catalysis.

2 Silica-Based Hybrid Nanoparticle

Silicon is a widely explored element among many other plentiful elements on the earth core. Most of the silicon properties generally resemble "carbon" as both belong to the similar family of the periodic desk. "Si" is commonly considered chemically inert; however, it has a great affinity for oxygen and other high electronegative elements. Among the different compounds of Si, Si–O compounds are generally the most studied and familiar. Si's most common available compounds include clay, silica, silicates, and POSS (polyhedral oligomeric silsesquioxanes) [31]. Recently, Si and SiO_2 have been found to be fabricated over various sizes ranging from micro size up to nanoscale. The main feature found in them is their large surface by volume ratio. Because of this unique and marvelous aspect, N.P.s of Si and its derivatives were found to possess a profound number of popularities in different sectors, i.e., from catalysis to electronics and other pharmacological purposes [32]. Similarly, the hybrid materials of Si can also be formulated by incorporating Si with some other organic and inorganic materials. The hybridization process makes the nanomaterials more divergent with multiple applications in single-core, which found to exhibit extensive job in catalysis due to their more durable and improved thermal and chemical stability and selectivity. [20]

The earth's crust is rich with Si or SiO_2, which may occur either in amorphous or crystalline forms [33]. It possesses a 3D-network like structure, made up [SiO_4] as a packing unit and a bulk structure that terminates near the surface via two different paths, that is, by -O- on the surface through -Si–O–Si- (siloxane) functional or by -Si–OH (silanol) functional. Three different kinds of -Si–OH functionals, namely vicinal (H-bonded -Si–OH), geminal (one Si-atom firmed with two silanol groups), and isolated (there are no H-bonds possible at -Si–OH sites), as presented in Fig. 2.

A wide range of techniques has been invented to prepare SiO_2 NPs, such as flame synthesis, sol–gel method, hydrothermal synthesis, and the reverse microemulsion technique.

The reason for supporting the active form in SiO_2 NPs is to construct a heterogeneous catalytic process that can cite the transition metal-based catalyst's reusability by resisting its unaltered performance. Variation of SiO_2 NP by combining certain active groups can make them appropriate for the catalytic exploit accomplished by chemical and physical treatment. Chemical treatment alters the chemical properties of the SiO_2 surface, while physical treatment changes the ratio of Si–OH to –Si-O-Si- groups. In addition, it has been demonstrated that the physical interaction between the solid supports and the modifier occurs by the insertion of the supporting material or by an electrostatic process [34]. Surfactants usually get adsorbed to silica through electrostatic interactions through a polar group, ultimately reducing the interaction between each SiO_2 NPs and preventing their agglomeration[35].

The substantial adsorption of molecules over SiO_2 can be illustrated by the pioneering work disclosed by Zidki et al., which incorporates a well stable and efficient water-oxidation catalyst using pH-controlled Co(II) adsorption on SiO_2 NPs with 10 nm diameter [36]. The catalyst showed both enhanced selectivity and water oxidation function. However, the process of adsorption was found to be reversible, as the interaction between them was the weak physical forces.

Since metal leaching is a significant problem in an industrial sense, such a practice is far from ideal. Thus, modification of nano-silica surfaces has now been observed via chemical bonding. It may lead to strong chemical interactions

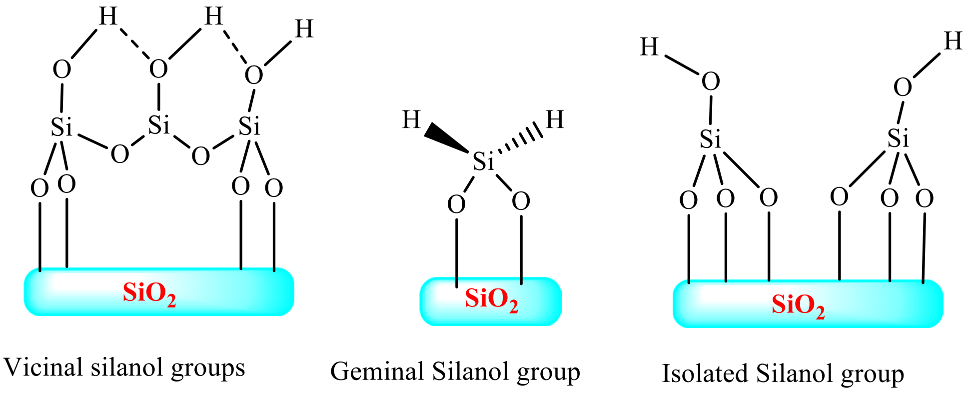


Fig. 2 Different ways of attachment of silanol groups on the surface of silica

between the modifiers and SiO2, thereby ultimately decreasing the leaching of active catalytic species used to alter the surface of SiO_2 NPs [37]. Various altering and grafting polymers are being used to transform the surface of SiO_2 NPs chemically. The traditional process of alteration using the chemical route includes silane blend agents, which are the familiar altering mediators, as they usually have hydrolyzable organo-functional assemblies. These silylating groups react with –Si–OH group of SiO_2, allowing the surface to get the targeted functional entities by acting as precursors for more immobilization of molecules of choice.

These connecting reagents are usually cited as $RSiX_3$ (X = any hydrolyzable group such as -Cl, -OMe, or -OEt groups, and R = different functionals selected to meet the requirements of the polymer) Fig. 3. Functionals of X react with -O.H. group of SiO_2 NPs, and the alkyl chain may interact with polymer. If there are three leaving groups attached with the silylating agent, anchoring can be possible by exchanging one or two groups.

Silane with $–NH_2$ groups such as 3-aminopropyltriethoxysilane (APTS) [38, 39] can participate in polycondensation and uncontrolled hydrolytic reaction in the aqueous medium. Thus, a non-aqueous medium is generally chosen to avoid hydrolysis during the grafting of APTS on Silica. On the other hand, in an aqueous environment that allows for large-scale manufacture, alkoxy groups get first hydrolyzed by contact with H_2O, following a self-condensation reaction between the hydrolyzed silanes molecules. After that, the silane molecules get adsorbed on the SiO_2 surface by forming –Si–O-Si- bonds between the –Si–OH and hydrolyzed silane groups by removing water molecules. Apart from the silylating agents, additives such as 2-(methacryloyloxy) ethyl isocyanate, epichlorohydrin, octadecylamine, glycidyl phenyl ether, and others have also been used for surface alterations.

3 Silica-Based Hybrid Nanoparticle Catalysed Reaction

The unique properties of nanosized materials, due to their nano size, large surface area, large pore volume, and stability, are ideal candidates for every chemical reaction's catalytic application. A specific catalyst is required for a specific reaction. Often the use of catalysts can increase the rate and selectivity of a reaction. [20]

As previously stated, the primary need of a catalyst is its stability, ease of separation, and recycling. To facilitate the recovery of catalyst easier, the production of active magnetic nanocatalyst was developed by Kaur et al. and used in various organic transformations reactions [40]. The use of silica N.P.s in various organic transformation reactions has increased significantly in recent years, owing to their unique properties, which include nanoscale size, large surface area, large pore volume, excellent thermal and mechanical stability, and the presence of silanol groups on their surfaces, which enable an extremely broad range of functionalities to be achieved. SiO_2 NPs have risen as flexible supports for anchoring metal complexes, heteropolyacids, etc., therefore opening the way for the development of hybrid nanocatalysts. While the interactions between the functional groups of silica and metals play an essential part in making efficient and versatile catalysts were previously discussed. [23]

Therefore, all these factors and the significance of various types of hybrid silica N.P.s based catalysts for promoting diverse reactions, including coupling, oxidation, reduction, and multicomponent reactions (MCR), have been reported recently. This review discussed the current significant development in this regard.

3.1 Coupling Reaction

The coupling reactions are the essential synthetic tools widely used in industry to synthesize valuable chemicals. These are mainly employed to synthesize C–C, C-N, and C-S bonds. Sonogashira cross-coupling reaction [41] is the most commonly used reaction in natural product synthesis to synthesize C–C bonds. This coupling reaction was applicable

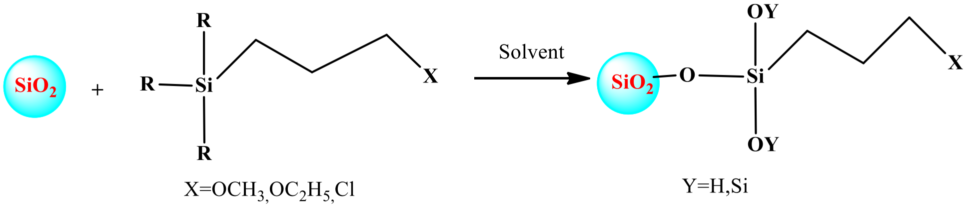
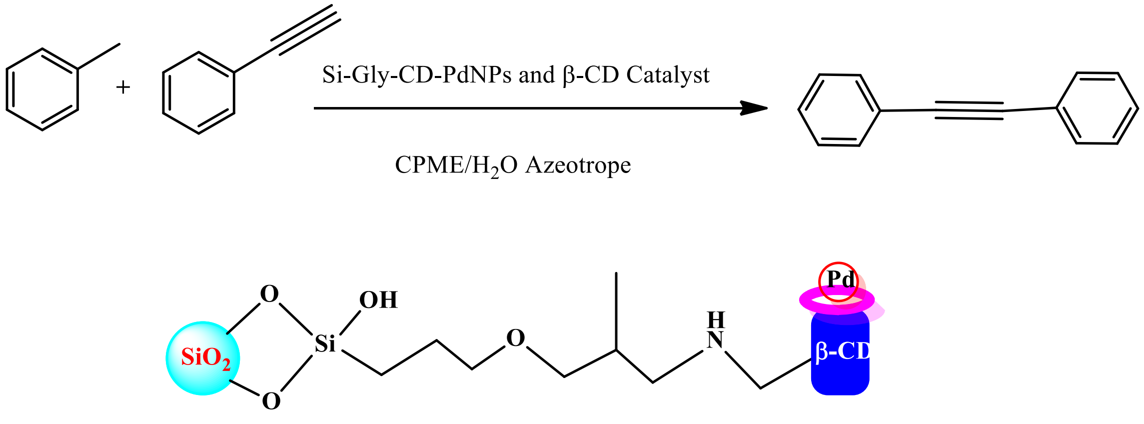


Fig. 3 Modification of surface of silica nanoparticle



Si-Gly-CD-PdNPs and β-CD Catalyst

Fig. 4 Si-Gly-CD-PdNPs and β-CD catalyzed Sonogashira cross-coupling reaction

for the synthesis of active pharmaceutical compounds and optoelectronic substances [42]. The original Sonogashira cross-coupling is carried out in Palladium and copper as a co-catalyst [43] which is economical. Then Cassar and Heck developed a copper-free Sonogashira cross-coupling reaction [44, 45]. However, an efficient catalytic system and new techniques have been developed to improve the Sonogashira cross-coupling reaction's efficiency [46–48]. Nowadays, diverse hybrid catalysts have been used for coupling reaction, which exhibits good stability and recoverability and shows good activity towards the coupling reaction [49, 50].

Ferlin et al. prepared a Si-Gly-CD-PdNP hybrid catalyst for the Sonogashira cross-coupling reaction. Here, the catalyst's efficiency was improved by using the β-Cyclodextrin (β-CD) ligand due to their hydrophilicity, allowing cyclopentyl methyl ether (CPME)/water azeotropic mixture. The reaction method enhanced the stability and durability of the catalyst, as shown in Fig. 4 [51].

Sudharsan et al. has demonstrated benzoyl chloride and phenylboronic acid cross-coupling reaction using K$_2$CO$_3$ in methanol catalyzed by Pd-TPMO catalyst. The co-condensation method prepared the Thiazoline functionalized mesoporous organosilica (TPMO). The palladium nanoparticle (Pd N.P.s) was immobilized on TPMO using a double solvent to form a (Pd-TPMO) catalyst. The catalytic efficiency of Pd-TPMO was tested for cross-coupling reaction, as shown in Fig. 5 [52].

Veisi and his co-worker investigated the use of green tea extract in catalysis and reported green tea extracted-encapsulated silica gel nanocomposite catalyzed coupling reaction. The reducing properties of the green tea open the door for the anchoring of Pd N.P.s on the green tea surface. The SiO$_2$@green tea/Pd nanocatalyst was deployed for the amination reaction, the Buchwald Hartwig reaction used to form a C-N bond. This is a green method for synthesizing the C-N bond [53]. This catalyst exhibits excellent yield, easy separation of products, and excellent reusability with less loss in its efficiency, as shown in Fig. 6.

However, glycerol functionalized Fe$_3$O$_4$@SiO$_2$ immobilized copper complex was an efficient catalyst for synthesizing the C-S and C-O bond. The Fe$_3$O$_4$@SiO$_2$-Glycerol-Cu(II) catalyst exhibits excellent reusability. The C-O bond formation is essential in the cosmetic, medicine, and dye industries and critical for various organic reactions, as shown in Fig. 7 [54].

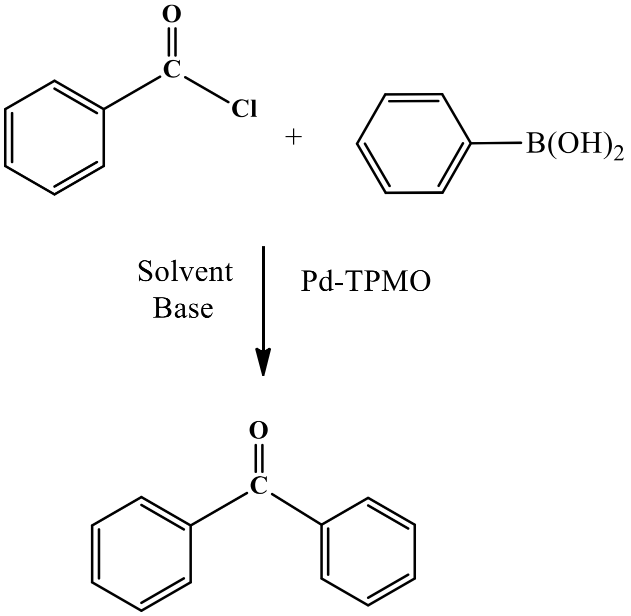


Fig. 5 Coupling reaction using Pd-TPMO catalyst

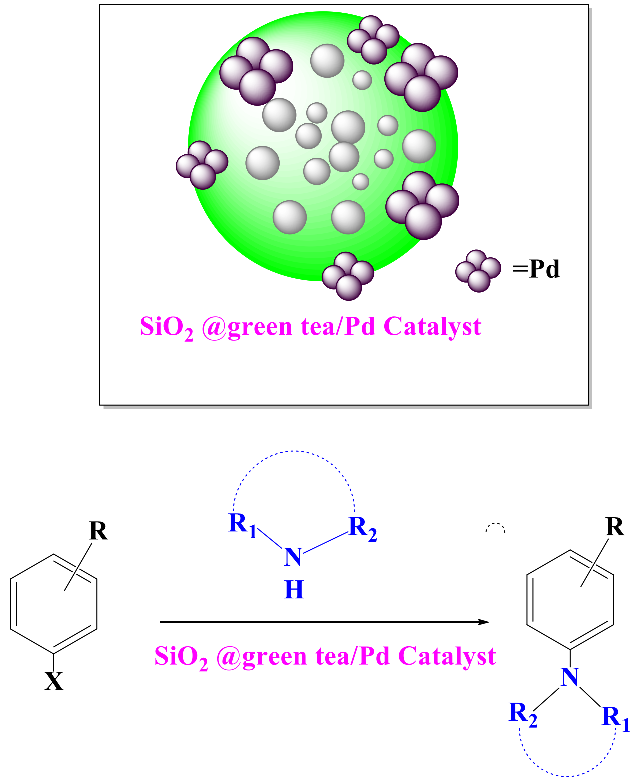


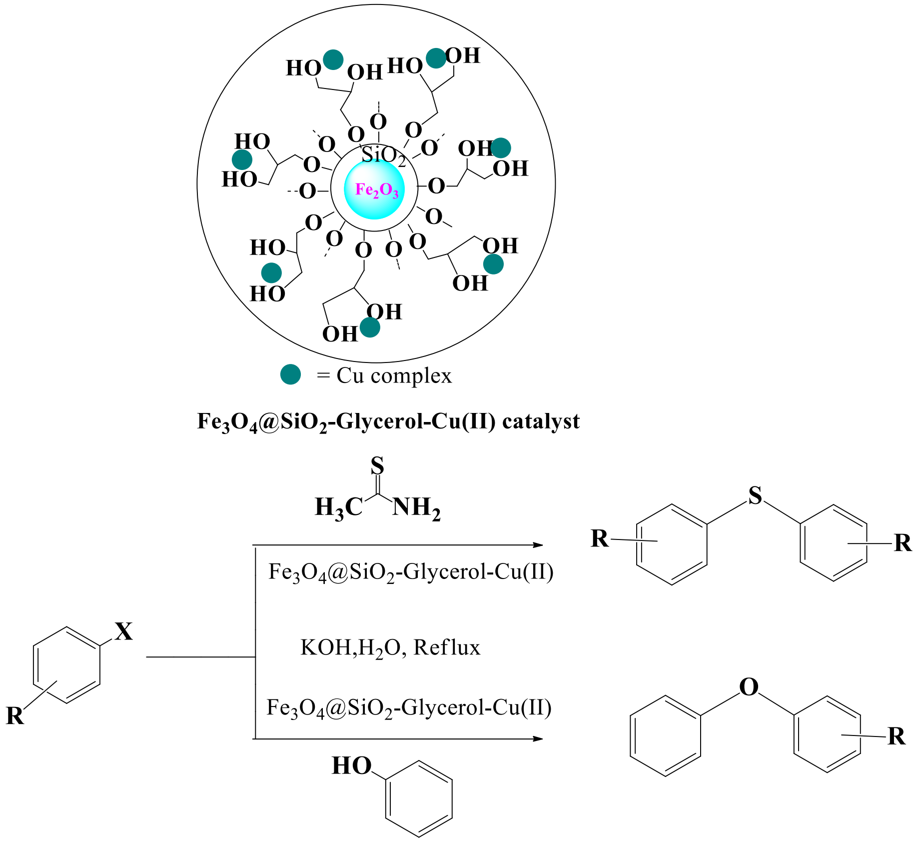
Fig. 6 SiO_2@green tea/Pd catalyzed C-N cross-coupling reaction

3.2 Oxidation Reactions

Oxidation reactions in chemistry play a crucial role in designing and synthesizing various value-added products. The traditional oxidant used in stoichiometric quantities generates toxic and hazardous waste. Instead, modern oxidation reactions are carried out using molecular oxygen or hydrogen peroxide as oxidant and recyclable catalysts and green solvents, thus promoting green processes [55–58].

Jia and his co-worker have reported that Ag-doped hexagonal mesoporous silica catalyzed oxidation reaction, with excellent yield (96%) at 240 °C. Still, the main demerit of the catalyst was its use at high temperature [59]. To overcome this drawback, Thomas et al. reported novel silver nanoparticles (AgNPs) anchored mesoporous silica SBA−15/copolymer hybrid catalyst. The *N,-N*-dimethylaminoethyl methacrylate and 2-hydroxyethyl acrylate (p(DMAEMA-*co*-HEA)) grafted modified SBA−15 (M.S.) was prepared then the AgNPs were dispersed on grafted SBA−15. The catalytic activity of the prepared catalyst was tested for oxidation of various alcohols to carbonyl compounds, which shows the highest activity for oxidation of alcohol, as shown in Fig. 8 [60].

Fig. 7 Fe_3O_4@SiO_2-Glycerol-Cu(II) catalyzed cross-coupling reactions



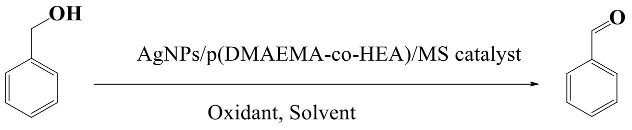


Fig. 8 oxidation of benzyl alcohol using AgNPs/p(DMAEMA-*co*-HEA)/MS

3.3 Multicomponent Reaction

Multicomponent reactions (MCRs) are powerful tools for constructing molecular architecture from readily available raw materials. These reactions are economical, require less time and energy, and are carried out in one step. It is one of the newest strategies for making chemical processes more environmentally friendly. The advantages of MCRs over other chemical reactions include their atom economy and efficiency, which lowers the byproduct. MCRs would be more frugal and greener using various heterogeneous catalysts. Several MCRs have been reported using silica-based nanohybrids as catalysts [61].

Due to the diverse biological properties of dihydropyrimidinones (DHPMs) and their derivatives, they have been the subject of research in medicinal chemistry [61–64]. At the same time, traditional synthesis methods involve Brønsted or Lewis acids catalysts by the Biginelli reaction [65–69]. Among the different catalysts, the supported catalysts like silica-supported catalysts enhanced the rate and selectivity of the response [66–70]. However, research should be carried out to develop new versatile catalysts for MCRs. [70–77].

Valiey and his co-worker have reported the synthesis of novel hybrid catalyst MCM-41 -functionalized sulfamic acid and pyromellitic diamide denoted as MCM-41-APS-PMDA-$NHSO_3H$. This catalyst was an efficient nanocatalyst for the preparation of 3,4-dihydropyrimidin-2-(1H)-one derivative using solventless environments. This catalyst is acidic and provides a large surface area, which initiates the Biginelli reaction to prepare 3,4-dihydropyrimidin-2-(1H)-ones which is an active molecule in the Pharma industry, as shown in Fig. 9 [79].

In another example, Sharma and his co-worker reported the preparation of TiO_2 SiO_2 NPs by immobilized TiO_2 Nano Particles on SiO_2 Nanoparticles using the “sol–gel” technique. This catalyst was efficient for one-pot synthesis of 2,3-diaryl- 3,4-dihydroimidazo[4,5-b] indole scaffolds via reaction between isatin and anilines aldehydes and ammonium acetate using methanol, as shown in Fig. 10 [78].

Kohzadian et al. introduced an effective way for one-pot synthesis of pyrido[2,3-d:6,5-d’]dipyrimidines. The one-pot synthesis involves using aryl aldehydes, 2-thiobarbutaric acid, and NH_4OAc under solvent-less conditions. The mesoporous silica based nanocatalyst denoted as Nano-[SiO_2-R-NMe_2SO_3H] [Cl] were employed for preparation of pyrido [2,3-d:6,5-d’] dipyrimidines via one-pot method as shown in Fig. 11. The key features of this catalyst were the mild reaction condition, less reaction time, high product yield, and ease of separation [79].

3.4 Reduction Reaction

The reduction reactions are a powerful tool for the chemical industry. These are extensively used to synthesize many organic compounds and useful chemicals. However, the traditional reduction reactions are carried out using transition metal catalysts. So the separation and recyclability of these catalysts can be challenging. Various types of heterogeneous catalysts have been developed for reduction reaction using mild reducing agents [80, 81].

Zao and his co-worker prepared a size-uniformed mesoporous Ag@SiO_2 nanospheres’ catalyst. This catalyst was prepared in a one-pot step via reducing $AgNO_3$ with various aldehyde via one-pot synthesis that controls the size of Ag@SiO_2 NPs. The performance of the nanocatalyst was tested in the hydrogenation of nitrobenzene, as shown in Fig. 12. It serves as a highly active catalyst for the reaction [82].

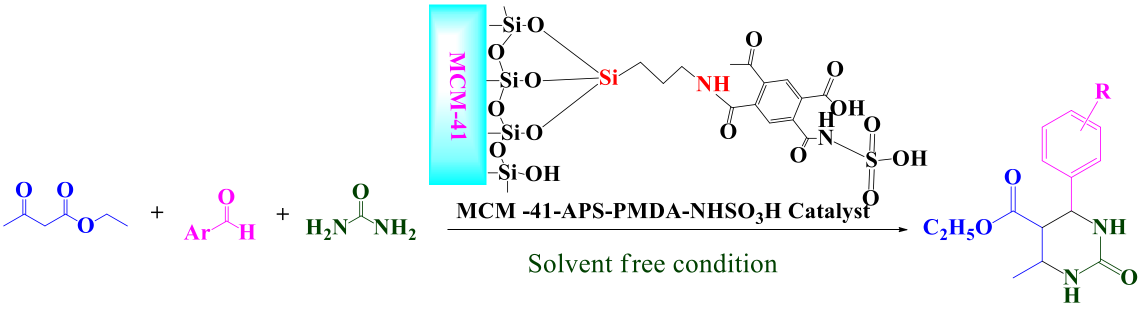


Fig. 9 Preparation of 3,4-dihydropyrimidin-2-(1*H*)-one derivatives using MCM-41-APS-PMDA-$NHSO_3H$ catalyst

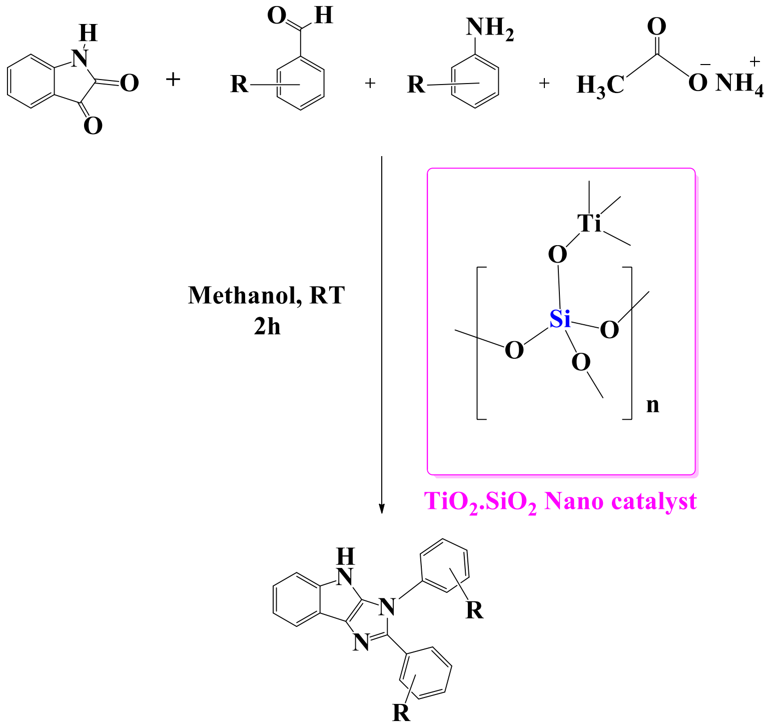


Fig. 10 $TiO_2.SiO_2$ NPs as catalyst for one-pot synthesis of 2,3-diaryl-3,4-dihydroimidazo[4,5-b] indole derivatives MCRs

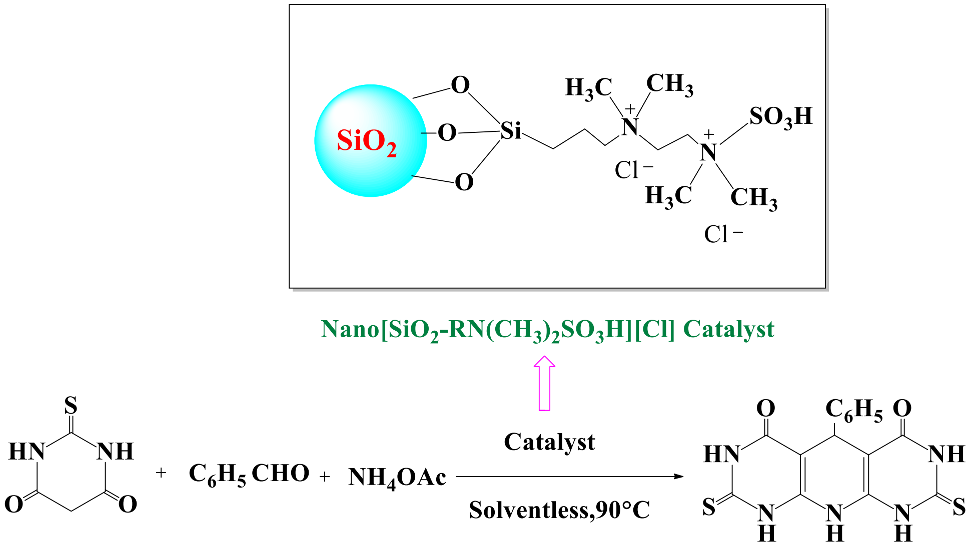


Fig. 11 Nano-[SiO_2-R-NMe_2SO_3H][Cl] catalyzed One-pot synthesis of pyrido[2,3-d:6,5-d0] dipyrimidines

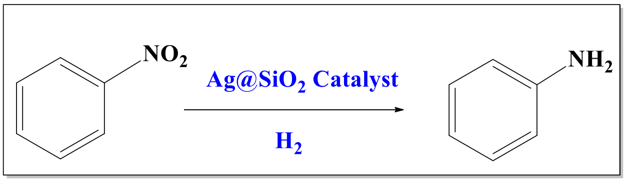


Fig. 12 Ag@SiO_2 Catalyzed Reduction of nitrobenzene

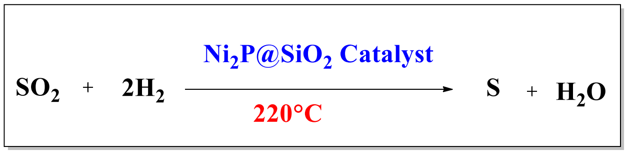


Fig. 13 Reduction of SO_2 using Ni_2P@ SiO_2 Catalyst

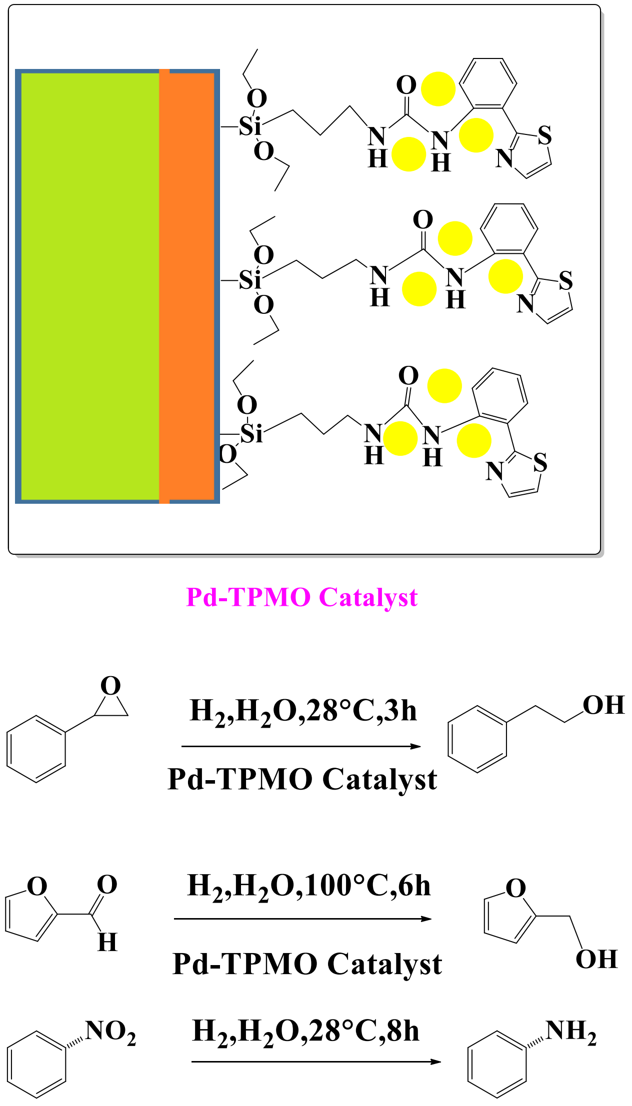


Fig. 14 Pd-TPMO Catalyzed Reduction reaction

Lu et al. synthesized nickel phosphide (Ni_2P) nanoclusters functionalized mesoporous SiO_2 catalyst in a two-step synthetic process that regulates the size of Ni_2P. "The process of functionalization of Ni onto the MCM-41 matrix was carried out via one-pot synthesis, followed by phosphorization reaction between oleylamine and trioctylphosphine, which transform Ni to Ni_2P". The Ni_2P@SiO_2catalyst can serve as an efficient catalyst for reducing SO_2, as shown in Fig. 13 [83].

Sudharsan et al. introduced another application of Pd-TPMO for the catalytic reduction reaction. Thiazoline fabricated mesoporous organosilica (TPMO) anchored metal nanocatalyst was employed to hydrogenation of Phenylethylene oxide, Furfural, and nitrobenzene as shown in Fig. 14, shows better yields and selectivity [52].

3.5 Carbon Dioxide Conversion

Due to anthropogenic emissions, carbon dioxide (CO_2) concentration increases day by day. Decreasing the concentration of CO_2 in the atmosphere is currently a serious environmental issue recently. Increasing research has been done to design a new approach to solve this issue [84, 85]. Nowadays synthesis of value-added chemicals from carbon is an effective method for the utilization of CO_2. A diverse range of homogeneous and heterogeneous catalysts was developed to utilize CO_2. Cyclic carbonates are well known in the chemical industry due to their applications as fuel additives, electrolytes in batteries, reagents, solvents, the monomer for polymer, etc. Thus the cyclic carbonates synthesis by the reaction between CO_2 and epoxide has witnessed enormous attention for the utilization of CO_2. Several recent works have explored the development of numerous catalysts (homogeneous and heterogeneous) that are efficient for converting CO_2 to cyclic carbonate. [86]

Tan and his co-worker recently designed functionalized benzotriazolium ionic liquid functionalized periodic mesoporous organosilica nanoparticles (PMOs) as a catalyst denoted as PMO-ILTiCl$_5$. This nanocatalyst was successfully employed to transform CO_2 to cyclic carbonates without any solvents and co-catalysts. Figure 15 The PMO-ILTiCl$_5$ was an excellent catalyst for the synthesis of cyclic carbonates from CO_2 with high yields and selectivities. The synthesized PMO-ILTiCl$_5$ nanocatalyst showed remarkable recovery, activity, and reusability (used five times with no significant decrease in its efficiency). This is because of the intramolecular synergic effect between active hydroxyl sites, and TiCl$_5$which provide the most stable catalytic sites [87].

4 Conclusion and Outlook

This review has highlighted current improvements in methods for the production of silica nanoparticles due to their widespread use as a catalyst in response to various

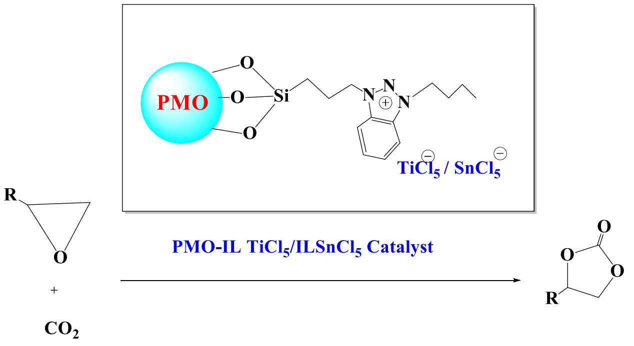


Fig. 15 Conversion of CO_2 to Cyclic Carbonate using PMO-ILTiCl$_5$ catalyst

transformation reactions. This protocol provides a large surface area, excellent stability, and nanoscale size of silica. Its surface contains silanol groups that promote the fabrication of different groups to the surface of silica. The hybrid nanocatalysts were a burgeoning tool for synthesizing valuable added products in chemical and pharma industries. This review aims to provide information about the recently published work on silica-based hybrid Nanocatalyst for various organic reactions, such as coupling reaction, oxidation, reduction, multicomponent reaction, and CO_2 conversion reaction. The essential features of this hybrid nanocatalyst were its excellent activity, selectivity, reasonable recovery, and excellent reusability. While numerous works have been done to synthesize hybrid nanocatalysis, there is still a requirement to develop a more promising, Green, and viable hybrid catalyst for the organic reaction. These nanoparticles have made significant contributions to agricultural production, preservation of food, biomedical research, and catalytic reactions, among other domains. SNPs have been proved to be effective encapsulating agents for a wide range of bioactive compounds, and they have already been proven to be safe for targeted medication delivery. Furthermore, the ability of SNPs to combine with various polymeric and non-polymeric materials to generate hybrid composites has broadened the range of functionalities. MSNPs (mesoporous Silica nanoparticles) have already demonstrated outstanding carrier qualities, allowing them to be used in chemotherapy to target specific cancer cells.

As a result, additional study is needed to develop a flexible, environmentally friendly, recyclable, and recoverable silica-based nanohybrid catalyst that can catalyze the green reaction and serve as a critical step toward developing a more environmentally friendly method. The Nanohybrids catalyst is an emerging field of research and less explored with vast potential for the future. Yet, this type of material will remain at the forefront for decades.

References

1. Sahoo M, Vishwakarma S, Panigrahi C, Kumar J (2021) Nanotechnology: current applications and future scope in food. Food Frontiers 2:3–22
2. Sobolev K, Gutierrez MF (2021) How nanotechnology can change the concrete world successfully mimicking nature's bottom-up construction processes is one of the most promising directions. Am Ceram Soc Bull 84:15–17
3. Mohajerani A, Burnett L, Smith JV, Kurmus H, Milas J, Arulrajah A, Horpibulsuk S, Abdul Kadir A (2019) Nanoparticles in construction materials and other applications, and implications of nanoparticle use. Materials 12:3052
4. Pokrajac L, Abbas A, Chrzanowski W, Dias GM, Eggleton BJ, Maguire S, Maine E, Malloy T, Nathwani J, Nazar L, Sips A, Sone J, Berg A, Weiss PS, Mitra S (2021) Nanotechnology for a sustainable future: addressing global challenges with the international network4sustainable nanotechnology. ACS Nano 15:18608–18623
5. Tang W, Zhang Y, Zhu G (2022) Pulmonary delivery of mucosal nanovaccines. Nanoscale 14:263–276
6. Shah MA, Pirzada BM, Price G, Shibiru AL, Qurashi A (2022) Applications of nanotechnology in smart textile industry: a critical review. J Adv Res 38:55–75
7. Muñoz-Écija T, Vargas-Quesada B, Rodríguez ZC (2019) Coping with methods for delineating emerging fields: Nanoscience and nanotechnology as a case study. J Inf 13:100976
8. Satalkar P, Elger B, Shaw D (2015) Defining nano, nanotechnology and nanomedicine: why should it matter? Sci Eng Ethics 22:1255–1276
9. Ananikov VP (2019) Organic-inorganic hybrid nanomaterials. Nanomaterial 9:1197–1203
10. Ananikov VP, Eremin DB, Yakukhnov SA, Dilman AD, Levin VV, Egorov MP, Karlov SS, Kustov LM, Tarasov AL, Greish AA et al (2017) Organic and hybrid systems: from science to practice. Mendeleev Commun 27:425–438
11. Gomez-Romero P (2001) Hybrid organic-inorganic materials in search of synergic activity. Adv Mater 13:163–174
12. Gon M, Tanaka K, Chujo Y (2017) Creative synthesis of organic-inorganic molecular hybrid materials. Bull Chem Soc Jpn 90:463–474
13. Schubert U (2011) Cluster-based inorganic–organic hybrid materials. Chem Soc Rev 40:575–582
14. Rao CNR, Cheetham AK, Thirumurugan A (2008) Hybrid inorganic–organic materials: a new family in condensed matter physics. J Phys Condens Matter 20:083202
15. Kustov LM (2021) Catalysis by hybrid nanomaterials. Molecules 26:352
16. Fechete I, Wang Y, Vedrine JC (2012) The past, present and future of heterogeneous catalysis. Catal Today 189:2–27
17. Coperet C, Allouche F, Chan KW, Conley MP, Delley MF, Fedorov A, Moroz IB, Mougel V, Pucino M, Searles K, Yamamoto K, Zhizhko PA (2018) Bridging the gap between industrial and well-defined supported catalysts. Angew Chem Int Ed 57:6398–6440
18. Amrute AP, De Bellis J, Felderhoff M, Schuth F (2021) Mechanochemical synthesis of catalytic materials. Chem Eur J 27:6819–6847
19. Chaturvedi S, Dave PN, Shah NK (2012) Applications of nanocatalyst in new era. J Saudi Chem Soc 16:307–325
20. Pratibha, K. and Rajput, J. (2022) Ch.10—application of silicon-based hybrid nanoparticles in catalysis. In Micro and nano technologies, silicon-based hybrid nanoparticles. Elsevier, pp Pages 199–246. ISBN 9780128240076
21. Knezevic NZ, Trewyn BG, Lin VS (2011) Functionalized mesoporous silica nanoparticle-based visible light responsive controlled release delivery system. Chem Commun 47:2817–2819
22. Moro AJ, Schmidt J, Doussineau T, Lapresta- Fernandez A, Wegener J, Mohr GJ (2011) Surface-functionalized fluorescent silica nanoparticles for the detection of ATP. Chem Commun 47:6066–6068
23. Ou B, Yang G, Xiao Y, Zeng X, Zhou Z, Liu Q, Zhang X, Li D (2013) Covalent functionalization of silica nanoparticle with poly(glycidyl methacrylate) *via* ATRP at ambient temperature. J Macromol Sci A 50:25–28
24. Sharma RK, Sharma S, Dutta S, Zboril R, Gawande MB (2015) Silicananosphere-based organic-inorganic hybrid nanomaterials: synthesis, functionalization and applications in catalysis. Green Chem 17:3207–3230
25. Wang Y, Zhao Q, Han N, Bai L, Li J, Liu J, Che E, Hu L, Zhang Q, Jiang T, Wang S (2015) Mesoporous silica nanoparticles in drug delivery and biomedical applications. Nanomedicine 11:313–327
26. Li Z, Barnes JC, Bosoy A et al (2012) Mesoporous silica nanoparticles in biomedical applications. Chem Soc Rev 41:2590–2605

27. Isa EDM, Ahmad H, Rahman MBA, Gill MR (2021) Progress in mesoporous silica nanoparticles as drug delivery agents for cancer treatment. Pharmaceutics 13:1–33
28. Dayana E, Isa M, Ahmad H et al (2021) Pharmaceutics progress in mesoporous silica nanoparticles as drug delivery agents for cancer treatment. mdpi.com. https://doi.org/10.3390/pharmaceutics13020152
29. Jeelani PG, Mulay P, Venkat R, Ramalingam C (2020) Multifaceted application of silica nanoparticles. Rev Silicon 12:1337–1354
30. Bera A, Shah S, Shah M et al (2020) Mechanistic study on silica nanoparticles-assisted guar gum polymer flooding for enhanced oil recovery in sandstone reservoirs. Colloids Surfaces A Physicochem Eng Asp 598:124833
31. Hadia NJ, Ng YH, Stubbs P, Torsaeter O (2021) High salinity and high temperature stable colloidal silica nanoparticles with wettability alteration ability for EOR applications. mdpi.com. https://doi.org/10.3390/nano11030707
32. Gogoi S, Barua S, Khan R, Karak N (2019) Silicon-Based Nanomaterials and Their Polymer Nanocomposites. Nanomater and Polymer Nanocomposites. https://doi.org/10.1016/B978-0-12-814615-6.00008-4
33. McInnes SJP, Voelcker NH (2009) Silicon-polymer hybrid materials for drug delivery. Future Med Chem 1:1051–1074
34. Napierska D, Thomassen LC, Lison D, Martens JA, Hoet PH (2010) The nanosilica hazard: another variable entity. Part Fibre Toxicol 7:39
35. Li X, Niitsoo O, Couzis A (2013) Electrostatically driven adsorption of silica nanoparticles on functionalized surfaces. J Colloid Interface Sci 394:26–35
36. Rovani S, Santos JJ, Corio P, Fungaro DA (2018) Highly pure silica nanoparticles with high adsorption capacity obtained from sugarcane waste ash. ACS Omega 3(3):2618–2627
37. Zidki T, Zhang L, Shafirovich V, Lymar SV (2012) Water oxidation catalyzed by cobalt(II) adsorbed on silica nanoparticles. J Am Chem Soc 134:14275–14278
38. Corma A, Garcia H (2006) Silica-bound homogenous catalysts as recoverable and reusable catalysts in organic synthesis. Adv Synth Catal 348:1391–1412
39. Li W, Xu Y, Zhou Y, Ma W, Wang S, Dai Y (2012) Effects of crystallization and dopant concentration on the emission behavior of TiO2: Eu nanophosphors. Nanoscale Res Lett 7:1–7
40. Gude K, Narayanan R (2010) Synthesis and characterization of colloidal-supported metal nanoparticles as potential intermediate nanocatalysts. J Phys Chem C 114:6356–6362
41. Singh H, Pratibha KA, Kaur Rajput A (2021) Urea chelated autocombused synthesis of $BiFeO_3$ nanoparticles: application as magnetically retriable heterogeneous catalyst for synthesis of pyrano [2,3-c] pyrazoles. Ferroelectrics 583(1):125–142
42. Chinchilla R, Nájera C (2014) Chemicals from alkynes with palladium catalysts. Chem Rev 114:1783–1826
43. Chinchilla R, Nájera C (2011) Recent advances in Sonogashira reactions. Chem Soc Rev 40:5084–5121
44. Sonogashira K, Tohda Y, Hagihara N (1975) A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes and bromopyridines. Tetrahedron Lett 16:4467–4470
45. Dieck HA, Heck FR (1975) Palladium catalyzed synthesis of aryl, heterocyclic and vinylic acetylene derivatives. J Organomet Chem 93:259–263
46. Cassar L (1975) Synthesis of aryl- and vinyl-substituted acetylene derivatives by the use of nickel and palladium complexes. J Organomet Chem 93:253–257
47. Cortes-Clerget M, Yu J, Kincaid JRA, Walde P, Gallou F, Lipshutz BH (2021) Water as the reaction medium in organic chemistry: from our worst enemy to our best friend. Chem Sci 12:4237–4266
48. Mohajer F, Heravi MM, Zadsirjan V, Poormohammad N (2021) RSC Adv 11:6885–6925
49. Tan LM, Sem ZY, W.-Y. Chong WY, X. Liu, Hendra, W. L. Kwan and C.-L. Ken Lee, (2013) Continuous flow sonogashira c-c coupling using a heterogeneous palladium-copper dual reactor. Org Lett 15:65–67
50. Newton MA, Ferri D, Mulligan CJ, Alxneit I, Emerich H, Thompson PBJ, Hii KK (2020) In situ study of metal leaching from Pd/Al2O3 induced by K2CO3. Catal Sci Technol 10:466–474
51. Mohr Y, Alves-Favaro M, Rajapaksha R, Hisler G, Ranscht A, Samanta P, Lorentz C, Duguet M, Mellot- Draznieks C, Quadrelli EA, Wisser FM, Canivet J (2021) Heterogenization of a molecular Ni catalyst within a porous macroligand for the direct C-H arylation of heteroarenes. ACS Catal 11:3507–3515
52. Ferlin F, Sciosci D, Valentini F, Menzio J, Cravotto G, Martina K, Vaccaro L (2021) Si-Gly-CD-PdNPs as a hybrid heterogeneous catalyst for environmentally friendly continuous flow Sonogashira cross-coupling. Green Chem 23:7210
53. Sudharsan M, Subramanian S, Amali AJ, Suresh D (2020) Palladium nanoparticles incorporated thiazoline functionalized periodic mesoporous organosilica: efficient catalyst for selective hydrogenation & Csp2–Csp2 bond formation reactions. Chem Select 5:6131–6140
54. Veisi H, Tamoradi T, Karmakar B, Hemmati S (2020) Green tea extract-modified silica gel decorated with palladium nanoparticles as a heterogeneous and recyclable nanocatalyst for Buchwald-Hartwig C-N cross-coupling reactions. J Phys Chem Solids 138:109256
55. Ashraf MA, Liu Z, Peng WX, Zhou L (2020) Glycerol Cu(II) complex supported on Fe3O4 magnetic nanoparticles: a new and highly efficient reusable catalyst for the formation of aryl-sulfur and aryl-oxygen bonds. Catal Lett 150:1128–1141
56. Nagaraju P, Pasha N, Prasad PSS, Lingaiah N (2007) Iron and vanadium containing molybdophosphoric acid catalyst for selective oxidation of alcohols with molecular oxygen. Green Chem 9:1126–1129
57. Shi Z, Zhang C, Tang C, Jiao N (2012) Recent advances in transition-metal catalyzed reactions using molecular oxygen as the oxidant. Chem Soc Rev 41:3381–3430
58. Guo Z, Liu B, Zhang Q, Deng W, Wang Y, Yang Y (2014) Recent advances in heterogeneous selective oxidation catalysis for sustainable chemistry. Chem Soc Rev 43:3480–3524
59. Gawande MB, Rathi A, Nogueira ID, Ghumman CAA, Bundaleski N, Teodoro OMND, Branco PS (2012) A recyclable ferrite–co magnetic nanocatalyst for the oxidation of alcohols to carbonyl compounds. ChemPlusChem 77:865–871
60. Jia L, Zhang S, Gu F, Ping Y, Guo X, Zhong Z, Su F (2012) Highly selective gas-phase oxidation of benzyl alcohol to benzaldehyde over silver containing hexagonal mesoporous silica. Micropor Mesopor Mat 149:158–165
61. Thomas AM, Peter J, Mohan A, Nagappan S, Selvaraj M, Ha C (2021) Dual stimuli-responsive silver nanoparticles decorated SBA-15 hybrid catalyst for selective oxidation of alcohols under ‘mild’ conditions. Micropor Mesopor Mater 311:110697
62. Dekamin MG, Alikhani M, Emami A, Ghafuri H, Javanshir S (2016) An efficient catalyst- and solvent-free method for the synthesis of medicinally important dihydropyrano[2,3-c]pyrazole derivatives using ball milling technique. J Iran Chem Soc 13:591–596
63. Matos LHS, Masson FT, Simeoni LA, Homem-de-Mello M (2018) Biological activity of dihydropyrimidinone (DHPM) derivatives: a systematic review. Eur J Med Chem 143:1779–1789
64. Fard MAD, Ghafuri H, Rashidizadeh A (2019) Sulfonated highly ordered mesoporous graphitic carbon nitride as a super active

heterogeneous solid acid catalyst for Biginelli reaction. Microporous Mesoporous Mater 274:83–93

65. Elhamifar D, Hosseinpoor F, Karimi B, Hajati S (2015) Ionic liquid-based ordered mesoporous organosilica-supported copper as a novel and efficient nanocatalyst for the one-pot synthesis of Biginelli products. Micropor Mesop Mater 204:269–275
66. Sharma V, Chitranshi N, Agarwal AK (2014) Significance and biological importance of pyrimidine in the microbial world. Int J Med Chem 2014:1–13
67. Wan JP, Liu Y (2010) Synthesis of dihydro pyrimidinones and thiones by multicomponent reactions: strategies beyond the classical Biginelli reaction. Synthesis 2010:3943–3953
68. Heravi MM, Asadi S, Lashkariani BM (2013) Recent progress in asymmetric Biginelli reaction. Mol Divers 17:389–407
69. Huang Y, Yang F, Zhu C (2005) Highly enantioseletive biginelli reaction using a new chiral ytterbium catalyst: asymmetric synthesis of dihydropyrimidines. J Am Chem Soc 127:16386–16387
70. Jadhav CK et al (2019) Efficient rapid access to Biginelli for the multicomponent synthesis of 1, 2, 3, 4-tetrahydropyrimidines in room temperature diisopropylethyl ammonium acetate. ACS Omega 4:22313–22324
71. Dekamin MG, Mehdipoor F, Yaghoubi A (2017) 1,3,5-Tris(2-hydroxyethyl) isocyanurate functionalized graphene oxide: a novel and efficient nanocatalyst for the one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones. New J Chem 41:6893–6901
72. Alirezvani Z, Dekamin MG, Davoodi F, Valiey E (2018) Melamine-functionalized chitosan: a new bio-based reusable bifunctional organocatalyst for the synthesis of cyanocinnamonitrile intermediates and densely functionalized nicotinonitrile derivatives. ChemistrySelect 3:10450–10463
73. Alirezvani Z, Dekamin MG, Valiey E (2019) Cu (II) and magnetite nanoparticles decorated melamine-functionalized chitosan: a synergistic multifunctional catalyst for sustainable cascade oxidation of benzyl alcohols/Knoevenagel condensation. Sci Rep 9:17758
74. Alirezvani Z, Dekamin MG, Valiey E (2019) New hydrogen-bond-enriched 1, 3, 5-tris (2-hydroxyethyl) isocyanurate covalently functionalized MCM-41: an efficient and recoverable hybrid catalyst for convenient synthesis of acridinedione derivatives. ACS Omega 4:20618–20633
75. Banakar SH, Dekamin MG, Yaghoubi A (2018) Selective and highly efficient synthesis of xanthenedione or tetraketone derivatives catalyzed by ZnO nanorod-decorated graphene oxide. New J Chem 42:14246–14262
76. Dekamin MG, Arefi E, Yaghoubi A (2016) Isocyanurate-based periodic mesoporous organosilica (PMO-ICS): a highly efficient and recoverable nanocatalyst for the one-pot synthesis of substituted imidazoles and benzimidazoles. RSC Adv 6:86982–86988
77. Valiey E, Dekamin MG, Alirezvani Z (2019) Melamine-modified chitosan materials: An efficient and recyclable bifunctional organocatalyst for green synthesis of densely functionalized bioactive dihydropyrano [2, 3-c] pyrazole and benzylpyrazolyl coumarin derivatives. Int J Biol Macromol 129:407–421
78. Sam M, Dekamin MG, Alirezvani Z (2021) Dendrons containing boric acid and 1,3,5-tris(2-hydroxyethyl) isocyanurate covalently attached to silica-coated magnetite for the expeditious synthesis of Hantzsch esters. Sci Rep 11:4820
79. Valiey E, Dekamin MG, Alirezvani Z (2021) Sulfamic acid pyromellitic diamide-functionalized MCM-41 as a multifunctional hybrid catalyst for melting-assisted solvent-free synthesis of bioactive 3,4-dihydropyrimidin-2-(1H)-ones. Sci Rep 11:11199
80. Geedkar D, Kumar A, Reen GK, Sharma P (2020) Titania-silica nanoparticles ensemblies assisted heterogeneous catalytic strategy for the synthesis of pharmacologically significant 2,3-diaryl-3,4-dihydroimidazo [4,5-b] indole scaffolds. J Heterocycl Chem 57:1963–1973
81. Kohzadian A, Zare A (2020) Effective and rapid synthesis of pyrido[2,3-d:6,5-d'] dipyrimidines catalyzed by a mesoporous recoverable silica-based nanomaterial. SILICON 12:1407–1415
82. Naseem K, Begum R, Farooqi ZH (2017) Catalytic reduction of 2-nitroaniline: A review. Environ Sci Pollut Res 24:6446–6460
83. Zeynizadeh B, Karami S (2019) Synthesis of Ni nanoparticles anchored on cellulose using different reducing agents and their applications toward reduction of 4-nitrophenol. Polyhedron 166:196–202
84. Zhao B, Dong Z, Wang Q, Xu Y, Zhang N, Liu W et al (2020) Highly efficient mesoporous core-shell structured ag@sio$_2$ nanosphere as an environmentally friendly catalyst for hydrogenation of nitrobenzene. Nanomaterials 10(5):883
85. Lu X, Baker MA, Anjum DH, Basina G, Hinder SJ, Papawassiliou W, Pell AJ, Karagianni M, Papavassiliou G, Shetty D, Gaber D, Gaber S, Wahedi YA, Polychronopoulou K (2021) Ni$_2$P nanoparticles embedded in mesoporous SiO$_2$ for catalytic hydrogenation of SO$_2$ to elemental S. ACS Appl Nano Mater 4:5665–5676
86. Khdary NH, Abdelsalam ME (2020) Polymer-silica nanocomposite membranes for CO$_2$ capturing. Arab J Chem 13:557–567
87. Nath N (2020) Conversion of CO$_2$ to high value products. Adv Chem Mater Eng. https://doi.org/10.4018/978-1-5225-8033-1.ch002
88. Pescarmona PP (2021) Cyclic carbonates synthesised from CO$_2$: applications, challenges and recent research trends. Curr Opin Green Sustain Chem 29:100457
89. Tan J, Wang L, Hu YL (2020) Multifunctional periodic mesoporous organosilica supported benzotriazolium ionic liquid as an efficient nanocatalyst for synergistic transformation of CO$_2$ to cyclic carbonates. Chem Select 5:4893–4897