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# A prospective study on Silica based heterogeneous catalyst as modern organic synthesis tool

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## ABSTRACT

*The objective of this tutorial review is to summarize some of the recent advances in a specific class of silica based multifunctional, heterogeneous catalysis. We are focusing on recent advances have led to the preparation of silica materials containing multiple, different functional groups that can be used as catalyst in organic synthesis. In this review we summarizes the recent used silica based catalyst in synthesis of different organic compounds their preparation, reaction schemes and procedures. This review will help the reader to understand the preparation and use of silica based catalyst in both theoretical and practical aspect.*

**Key words:** Silica based catalyst, Heterogeneous catalyst, Green synthesis, Organic synthesis

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## INTRODUCTION

In present world of medicinal chemistry we are focusing on the science of chemical compound which are pharmacologically active. Science of chemical compound means to study about the production and properties of new compounds. Nature and synthesis are the two main sources of obtaining a new chemical compound. In chemistry, chemical synthesis is a purposeful execution of chemical reactions to obtain a product, or several products. Many strategies and methods implanted in Synthesis of different compounds and one of them is the use of catalyst to speed up the chemical synthesis process.

A substance that increases the rate of a chemical reaction without itself being changed in the process is called as Catalyst. In general, there are heterogeneous, homogeneous and biological catalysts. Heterogeneous catalysis is a type of catalysis in which the catalyst occupies a different phase than the reaction mixture. But running a reaction under heterogeneous catalytic conditions has several advantages compared to other catalytic processes (Figure1).

Solid acid catalysts play a prominent role in organic synthesis under heterogeneous conditions[1] . In general, solid acid catalysts are mainly based on clay and silica[2]. Silica-based materials are commonly used as heterogeneous catalysts. Hybrid inorganic–organic materials comprising organic functional groups bonded from silica surfaces are versatile, heterogeneous catalysts. Recent advances have led to the preparation of silica materials containing multiple, different functional groups that can be used as catalyst in organic synthesis, that is, these functional groups can act together to provide catalytic activity and selectivity superior to what can be obtained from either mono-functional materials or homogeneous catalysts. Organic functionalization of amorphous, mesoporous, and zeolitic silica materials leads to a vast array of catalytically active materials[3].

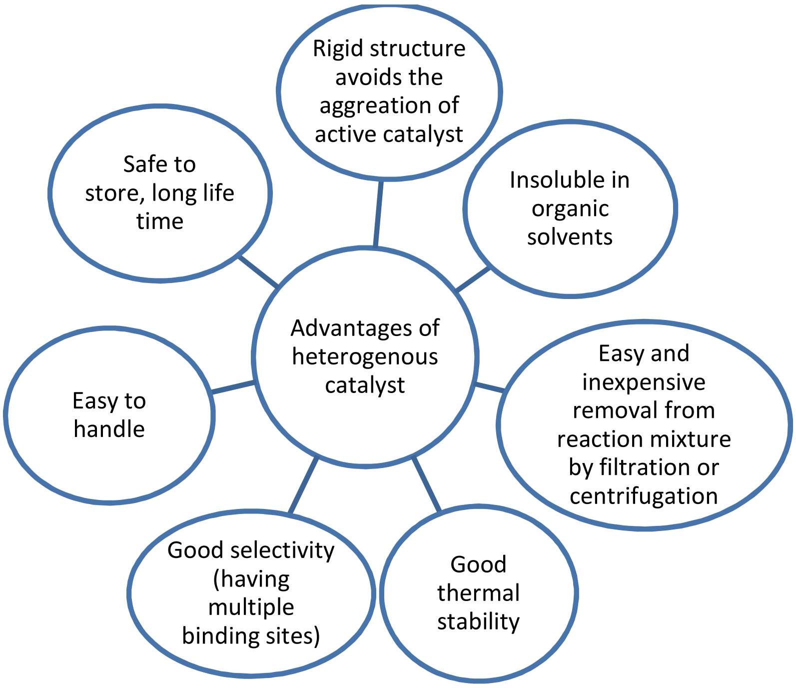


**FIGURE 1: Advantages of heterogenous catalyst**

As the literature survey reviles that silica based catalyst shown good applicability in modern synthetic procedure so we are trying to explore some important and frequently used silica based catalyst, their preparation and synthetic uses in this review.

### Preparation of some silica based catalyst

### Preparation of $SiO_2$-$ZnCl_2$

To a mixture of anhydrous zinc chloride (3g) and activated silica (10 g) in a round bottom flask (100 ml), sodium dried toluene (60ml) was added and the reaction mixture was refluxed for 12 hr, $SiO_2$-$ZnCl_2$ was obtained as a free flowing powder after filtration under reduced pressure and drying at 110$^0$C for 12 hr. and store in desicater[4].

### Preparation of silica-supported antimony (III) chloride

A mixture of 1 g antimony trichloride ($SbCl_3$), 6 g SiO2 and 15mL dried dichloromethane solvent were stirred at room temperature for 120 min. HCl gas evolved from the reaction vessel immediately. The solvent was then removed on a rotary evaporator under reduced pressure to afford white powder of silica-supported antimony (III) chloride (6.44 g). It was applied in the next stage[5].

### Preparation of nano-$SiO_2$

The synthesis of nano-$SiO_2$ was achieved by the ammonia-catalysed hydrolysis of tetraethyl orthosilicate (TEOS) in a mixed solvent of deionized water and ethanol using PEG as the surfactant agent in the process at room temperature. In a typical procedure, 100mL ethanol and 20mL deionized water were mixed together in a beaker, and then 1.0 g of PEG (MW 6000) was dispersed into the mixture by ultrasonication. After adding ammonia water (2.5 mL), tetraethyl orthosilicate (TEOS, 2mL) was added to the reaction solution. The resulting dispersion was under mechanically stirred continuously for 20 h at room temperature. The resultant products were collected and washed with ethanol and deionized water in sequence, and then dried under vacuum at 60◦C for 2 h for further use[6].

### Preparation of Ni/$SiO_2$ catalysts

The catalyst was prepared by the impregnation method by dissolving nickel nitrate hexa hydrate (2.5107 g) in distilled water (20.0 mL) and adding it to silica gel (5.0 g) and stirring for 2 h using a magnetic stirrer at room temperature (20 ±1 $^0$C) and ageing at room temperature overnight. The excess water is removed by heating the mixture on water bath and using a rotavapor under vacuum to evaporate the water. The catalyst material is dried in an oven at 100–120 $^0$C for 12 h[7].

### Preparation of $HClO_4/SiO_2$ catalyst

Seventy percent aqueous perchloric acid (1.8 g, 12.5 mmol) was added to a suspension of $SiO_2$ (230–400 mesh, 23.7 g) in ether (70 ml). The mixture was concentrated and the residue was heated at 100 ◦C for 72 h under vacuum to give $HClO_4$–$SiO_2$ (0.5 mmol/g) as free flowing powder[8].

### Preparation of PPA/$SiO_2$

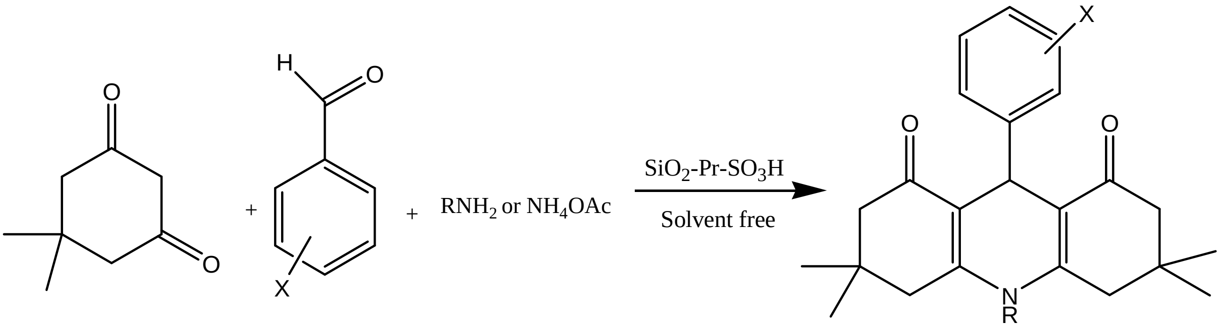
PPA (4.0 g) was charged in the round-bottom flask, and $CHCl_3$ (100 mL) was added. After the mixture was stirred at 50 °C for 1 h, followed by $SiO_2$ (16.0 g, 70–230 mesh) was added to the solution, and the mixture was stirred for another 1 h. $CHCl_3$ was removed by evaporation, and the resulting solid was dried in vacuo at room temperature for 3 h. Used PPA/$SiO_2$ was regenerated as follows: PPA/$SiO_2$ was recovered by filtration from the reaction mixture, and then it was put in the 50 mL round-bottom flask and dried in vacuum at 100 °C for 2 h[9].

### Preparation of 3-mercaptopropylsilica (MPS)

To 20 g of $SiO_2$ in dry toluene, 25 ml of (3-mercaptopropyl)trimethoxysilane was added, and the mixture of the reaction was refluxed for 24 h. After this period, the mixture was filtered to obtain 3-mercaptopropylsilica (MPS) which was washed with acetone and dried. 3-Mercaptopropylsilica (MPS) was oxidized with $H_2O_2$ (excess) and 2–3 drops of $H_2SO_4$ (conc) in methanol (20 ml) for 24 h at rt and then the mixture was filtered and washed with $H_2O$, and then acetone to obtain $SiO_2$-Pr-$SO_3$H catalyst. The modified $SiO_2$-Pr-$SO_3$H was dried and used as a solid acid catalyst in the organic synthesis[10].

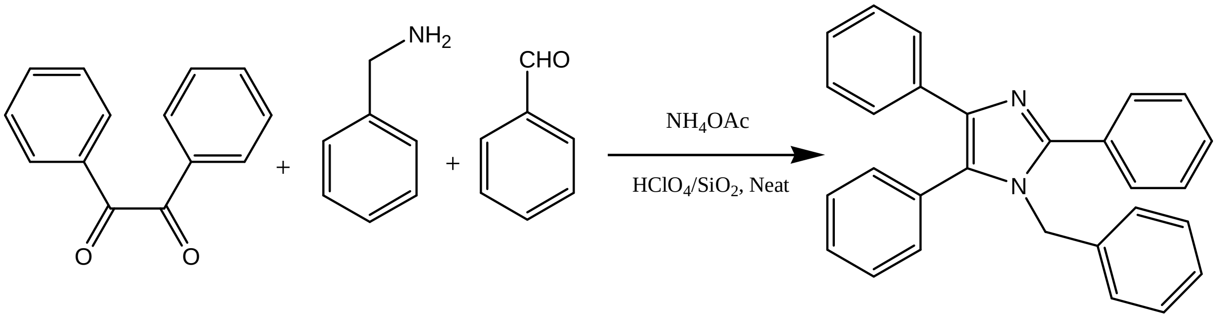
### Recent synthetic Applications of Silica based catalyst

Ziarani et al. reported a facile, efficient method for the preparation of 1,8-dioxo-decahydroacridines in excellent yields using silica-based sulfonic acid as a heterogeneous solid acid catalyst, which makes this reaction clean, safe and high-yielding process. The reaction was carried out under solvent free conditions at 120 $^0$C for 2 h by taking a 1:1.2:2 mol ratio mixture of an aromatic aldehyde, an amine and 5, 5-dimethyl- 1,3-cyclohexanedione to give the desired products (Scheme 1). After dissolving the crude product in hot ethanol, the catalyst was removed from the reaction mixture by simple filtration and then, after cooling the filtrate, the pure products were obtained as yellow crystals[10].



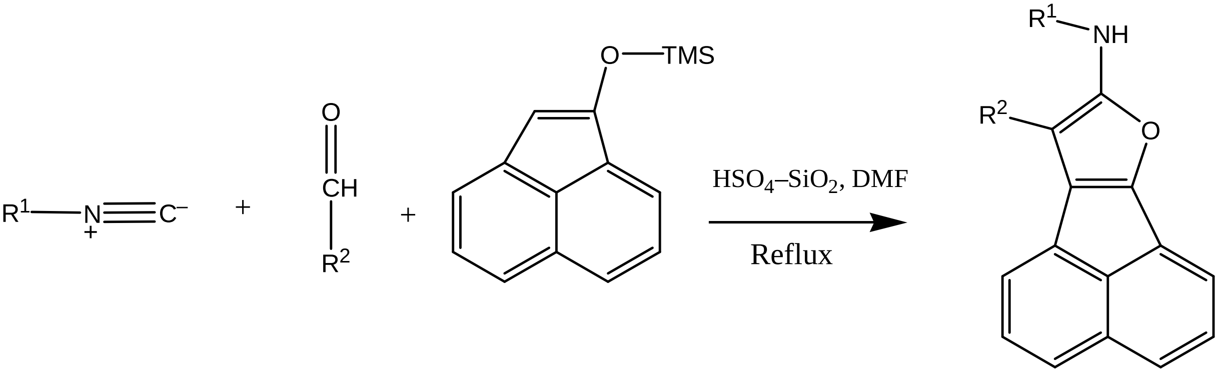
**Scheme 1**

Kantevari et al. developed a highly efficient, one-pot, four-component synthesis of 1,2,4,5- tetrasubstituted imidazoles by the condensation of various aldehydes, benzil, aliphatic or aromatic primary amines and ammonium acetate under solvent free conditions using perchloric acid adsorbed on silica gel ($HClO_4$–$SiO_2$) as catalyst in excellent yields. $HClO_4$–$SiO_2$ exhibited remarkable catalytic activity with respect to the reaction time (2–20 min), amount of catalyst. (Scheme 2). Present protocol with $HClO_4$–$SiO_2$ catalyst is convincingly superior to the recently reported catalytic methods[11].



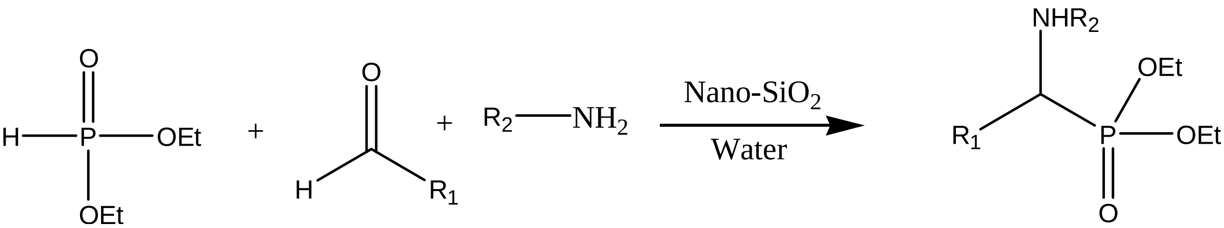
**Scheme 2**

Some new derivatives of acenaphtho[1,2-b]furan efficiently synthesized by one-pot reaction of (acenaphthylen-1-yloxy)trimethylsilane, various aldehydes and isocyanides at the presence of silica-supported ionic liquid by Sandaroos et al (Scheme 3). To a magnetically stirred mixture of aldehyde (1 mmol) and catalyst (0.01 mmol) in DMF (40 mL) at 0◦C was drop-wise added to a solution of (acenaphthylen-1-yloxy)trimethylsilane (1 mmol) in DMF (10 mL) over a 30 min period. Then, the mixture was allowed to warm to room temperature and treated with a solution of isocyanide (1.0 mmol) in DMF (10 mL). The mixture was refluxed for 10 h, cooled to room temperature, and filtered. The filtrate was extracted with dichloromethane (4 × 15 mL). After evaporation of solvent, the residue was washed with ether and crystallized from acetonitrile to give analytically pure product[12].



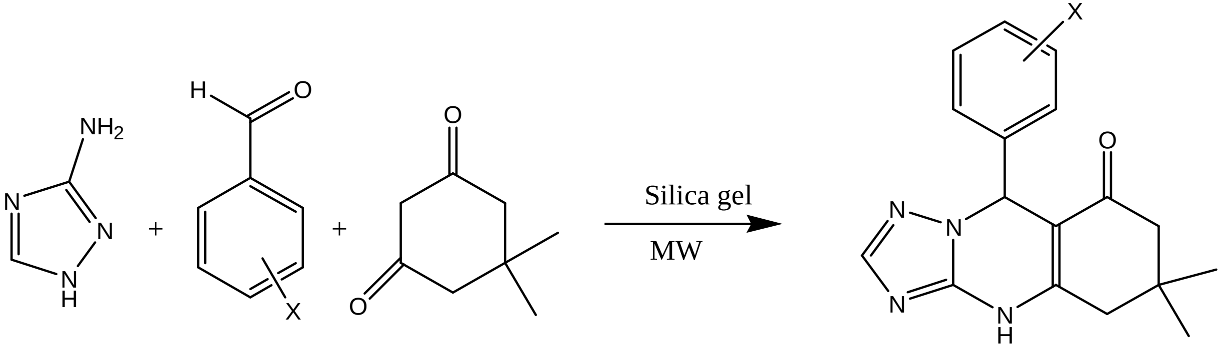
**Scheme 3**

Nasseri and Sadeghzadeh prepared nano-SiO2 catalyst from inexpensive starting materials in aqueous media which catalysed the synthesis a-aminophosphonates from aldehydes, amines and diethylphosphate under ultrasonication in water (Scheme 4). A mixture of aldehydes (1 mmol), amines (1 mmol), diethylphosphate (1 mmol) and nano-$SiO_2$ (0.0007 g) in water (5 ml), at room-temperature was irradiated by ultrasound for 10–20 min (the progress of the reaction was monitored by TLC). After completion, the catalyst was filtered and washed with $H_2O$ (5 ml) and EtOH (5 ml). The reaction mixture was cooled to ambient temperature and extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and the solvent removed under reduced pressure[13].



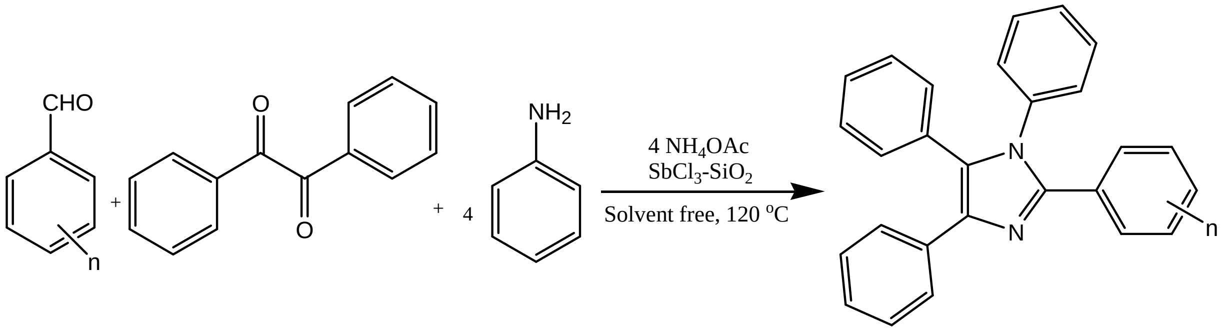
**Scheme 4**

Krishnamurthy and Jagannath Prepared derivative of triazolo/benzimidazoquinazolinones via silica-promoted solvent-free method using microwave irradiation with an excellent yield (Scheme 5). A Slurry of equimolar quantities of 3-amino-1,2,4- triazole/2-amino benzimidazole, dimedone and benzaldehyde in a minimum quantity of ethanol/MDC was allowed to adsorb over silica gel. The solvent is removed by evaporation and the impregnated silica gel was irradiated with Microwaves of 150W at 120◦C and pressure of 100 psi till the completion of the reaction. After completion of the reaction (as monitored by TLC), it was cooled to room temperature and the product was extracted with methylene chloride (3 × 15 ml). The crude product was recrystalised to get a pure compound[14].



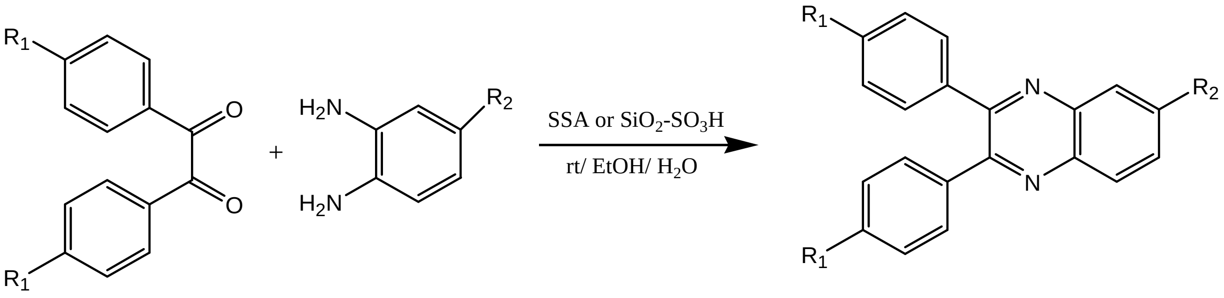
**Scheme 5**

Antimony trichloride based silica gel ($SbCl_3/SiO_2$) was developed and studied by Safari et al. which efficiently catalyses the four-component cyclocondensation of 1,2-diketone, aldehyde, ammonium acetate, and primary amine under solvent-free conditions to afford the corresponding tetrasubstituted imidazoles in high yields (Scheme 6). A mixture of 1 g antimony trichloride ($SbCl_3$), 6 g $SiO_2$ and 15mL dried dichloromethane solvent were stirred at room temperature for 120 min. HCl gas evolved from the reaction vessel immediately. The solvent was then removed on a rotary evaporator under reduced pressure to afford white powder of silica-supported antimony (III) chloride (6.44 g). It was applied in the next stage. In a 50mL round bottom flask mixture of benzyl (1 mmol), ammonium acetate (4 mmol), benzaldehyde (1 mmol) and primary amine (4 mmol) in the presence of 0.1 g $SbCl_3/SiO_2$ catalyst was stirred at 120◦C for appropriated time. The progress of the reaction was monitored by TLC. After cooling, the reaction mixture was dissolved in acetone and filtered. The filtrate was concentrated on a rotary evaporator under reduced pressure and the solid product obtained was washed with water and recrystallized from acetone–water[15].



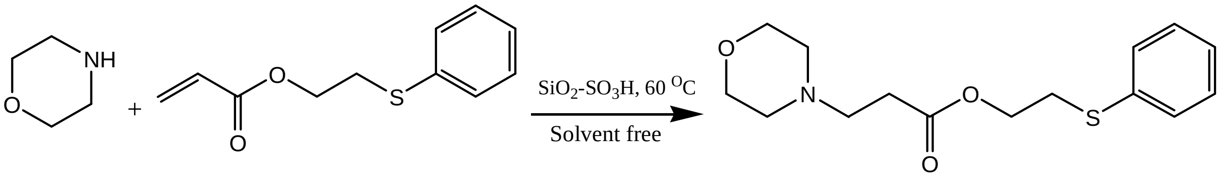
**Scheme 6**

Niknam et al. studied the reaction of 3-mercaptopropylsilica (MPS) and chlorosulfonic acid in chloroform afforded silica bonded S-sulfonic acid (SBSSA), which was used as a catalyst for the room temperature synthesis of quinoxaline derivatives from 1,2-diamino compounds and 1,2-dicarbonyl compounds (Scheme 7). The catalyst could be recycled and reused several times without any loss of efficiency[16].



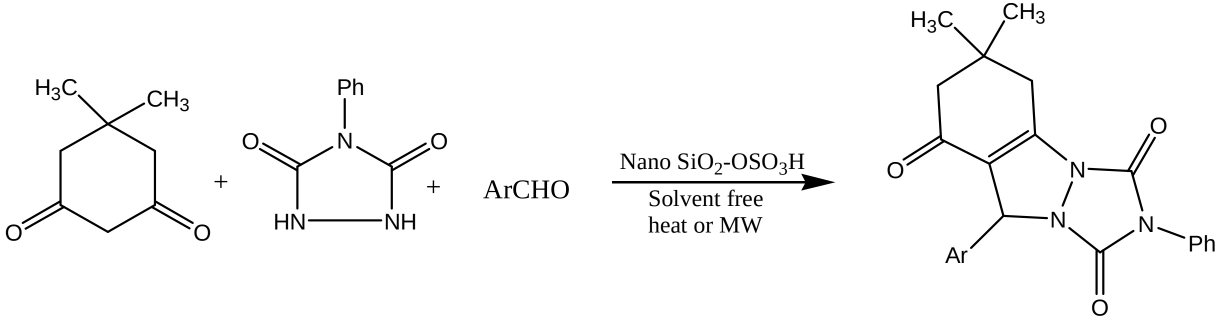
**Scheme 7**

Wang et al. developed a highly efficient, inexpensive, recyclable, convenient, and green protocol for chemoselective aza-Michael addition reactions of amines/thiols to α,β-unsaturated compounds using silica sulfuric acid (SSA or $SiO_2$-$SO_3H$) was developed. This method is simple, convenient and the title compounds are produced in good to excellent yields (Scheme 8). acrylic acid 2-phenylsulfanyl-ethyl ester（PTEA）was allowed to react with morpholine in the presence of a varying quantities of $SiO_2$-$SO_3H$. The results show that an excellent yield of the Michael adduct can be achieved by reacting a mixture of morpholine (1.2 equiv.) and PTEA (1.0 equiv) in the presence of $SiO_2$-$SO_3H$ (SSA, 100 mg) at room temperature [17].



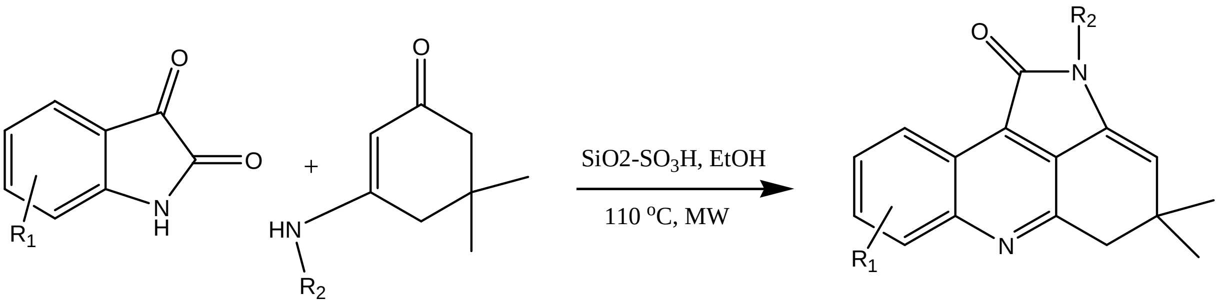
**Scheme 8**

A novel synthesis of triazolo[1,2-a]indazole-1,3,8-trione derivatives by reaction of urazole, dimedone and aromatic aldehydes under conventional heating and microwave irradiation and solvent-free conditions using silica nanoparticles prepared from rice husk ash as catalyst was developed by Hamidian et al (Scheme 9). A mixture of dimedone (1, 5 mmol), urazole (2, 5 mmol), aldehyde (6 mmol) and nanosilica sulfuric acid (125 mg) was heated at 80 °C in a round-bottom flask for the appropriate time. After completion of reaction (monitored by TLC) the mixture was cooled to room temperature, then EtOAc (10 mL) was added to the mixture, which was filtered to remove the catalyst. The washing step was repeated twice. After evaporation of the solvent, the residue recrystallized from ethyl acetate/hexane (1:3) to afford pure product[18].



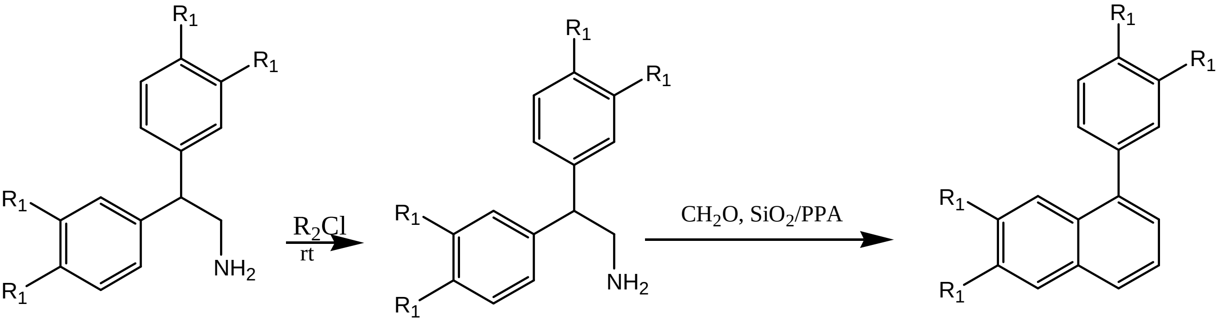
**Scheme 9**

Cao et al. developed an improved synthesis of multifunctionalized pyrrolo[2,3,4-kl]acridine derivatives with different substituted patterns using silica sulfuric acid (SSA) as a heterogeneous catalyst under microwave irradiation conditions (Scheme 10)[19].



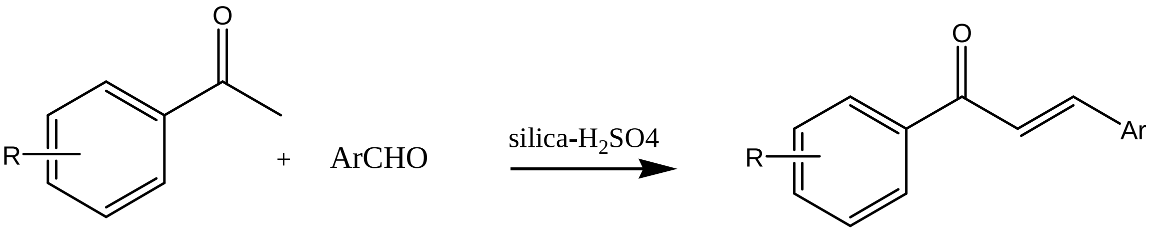
**Scheme 10**

Manolov et al. reported an application of an α-amidoalkylation reaction, as an alternative efficient synthesis of 4-aryl- and 4-methyl-1,2,3,4-tetrahydroisoquinoline derivatives. The amides required for this purpose would result from reaction of aminoacetaldehyde dimethylacetal with different substituted benzenes in polyphosphoric acid, followed by acylation of the obtained amines with different acid chlorides or sulfochlorides. They compared the cyclisation step using conventional (milieu of acetictrifluoracetic acid = 4:1) and solid supported reagents ($SiO_2$/PPA), as recovered, regenerated and reused without loss of its activity catalyst (Scheme 11). And found that in comparison to conventional methods, the yields of the reaction was greater and the reaction time was shorter[20].



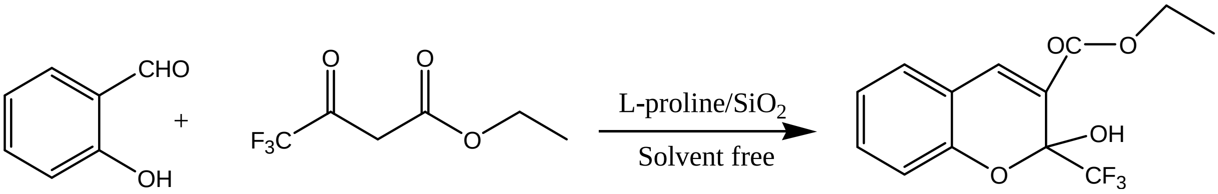
**Scheme 11**

An efficient silica-$H_2SO_4$ mediated synthesis of a variety of chalcones was reported by Sultan et al. which afforded the targeted compounds in very good yield compared to base catalyzed solvent free conditions as well as acid or base catalyzed refluxing conditions. When substituted PhAc and ArCHO were condensed in the presence of different reagents, the capricious yield of the products depends upon the nature of reagent used (Scheme 12). In general, the base- catalyzed reaction under refluxing conditions gave the lowest yields in almost all cases. The effect was more pronounced when either substrate contains –I and +R groups (such as OH, $NMe_2$) or –I and –R groups (such as $NO_2$). The acid catalyzed reaction also suffered the problem of low yields. The low yield with base-catalyzed refluxing conditions was attributed to the oxidation of aldehydes to their corresponding carboxylic acids via the Cannizarro reaction, which results in an overall decrease in the active concentration of aldehyde. The oxidation of aldehydes to carboxylic acids was much pronounced with para-substituted. The solvent free (SF) conditions led to quite a high yield of the product; however, the yields were quite low when either or both of the reactants contains –I and +R/–R groups. The yields of such substrates under SSA conditions are quite higher[21].



**Scheme 12**

Xu et al. studied an efficient synthesis of 2-hydroxy-2-(trifluoromethyl)-2H-chromene-3-carboxylates which was carried out under solvent-free conditions in an oven or microwave oven via the Knoevenagel condensation of salicylaldehydes with ethyl trifluoroacetoacetate followed by intramolecular cyclization in the presence of silica-immobilized L-proline (Scheme 13)[22].



**Scheme 13**

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