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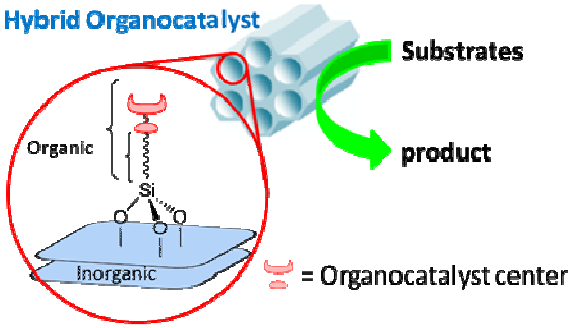

Nanoporous-silica supported organocatalyst: A heterogeneous and green hybrid-catalyst in organic transformations

Sadegh Rostamnia,* Esmail Doustkhah

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Abstract: Nowadays, organically modified hybrid silica mesostructures are increasingly developing as the promising candidate in catalysis of various kinds of organic reactions and green chemistry. Among them, organic moieties with amine and sulphonic acid basis have taken a major part of this class. In this review, we have discussed recent advances of most common types of organically modified hybrid materials which act as organocatalyst in organic transformations and processes.

Keywords: Hybrid nanomaterial; Green chemistry; Organocatalyst; Mesoporous support.

1. Introduction

Green chemistry aims to eliminate pollution by preventing it from happening in the first place and by using resources for chemical products that are renewable [1]. The "greening" of global chemical processes has become a major issue in the chemical industry both in terms of selection of reactions and for the study catalyst effects or reaction mediums [1]. The development of new strategies for recycling catalysts, which minimizes the consumption of auxiliary substances in achieving separations can result in significant economic and environmental benefits [1,2]. On the other hand, incorporating acid or base functionality into the mesoporous silicas are of particular interest in organic synthesis, green chemistry and industry because of its high selectivity and high yielding abilities, and also heterogeneity and reusability capacities based on green chemistry desires [2].

Hybrid nanoporous materials have been widely developed particularly in areas of adsorption, chromatography, catalysis, sensor technology, and gas storage, since first discovery of nanoporous materials [3,4]. These materials surpassed the zeolite molecular sieves in which the pore size limitations were resolved. By incorporation of specific organic moieties on or within the porewalls of mesostructures, their features can vary in a vast domain [3,4]. In addition, synthesis conditions and template, type of structure directing agent (SDA) of silica mesostructure which has self-assembling nature determines the shape, thickness, pore diameter of mesostructure [5-8]. On the other hand, organocatalytic reactions are becoming powerful tools in the organic synthetic chemistry. The growing interest in environmental-friendly and metal-free reactions has led to great progress in organocatalysis [9-12]. Moreover, many efforts have been performed for the heterogenizing organocatalysts by immobilizing them [13-15] to enable their recyclability and easy recovery. This system can deliver a green product and metal-free waste which favors environmentally compatible processes. The purpose of this review is to discuss the scope and application of hybrid nanoporous organocatalyst as a heterogeneous reusable green catalyst in organic transformations. Hence, we have overviewed recent advances and developments in the organocatalyst supported hybrid materials within the silica mesostructures (Fig. 1).

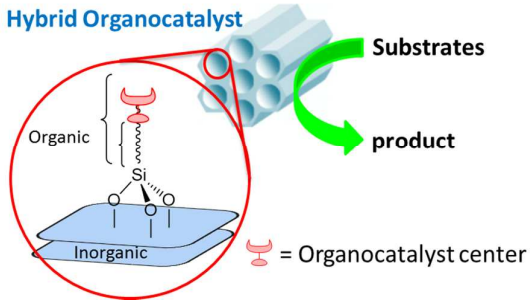


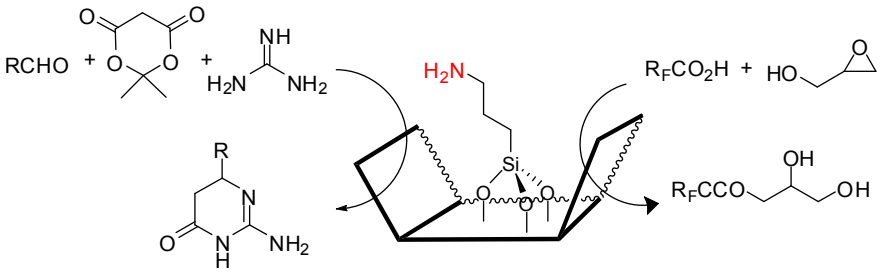
Figure 1. Components and structure of hybrid organocatalyst.

2. Primary, secondart and tertiary organoamine-based mesostructures

Amine-based organocatalysis are suitable and major part of organocatalyzing agents due to their inherent versatility in the most organic reactions. They can mediate the reaction over their nucleophilic or basic nature. On the other hand, they can proceed the reactions by imine or enamine formation. They can be a suitable case to catalyze the C-C and C-N bonds formation. Kubota and coworkers [16] reviewed and reported the applications of amine-based silica mesopores in adsorption, separation, chromatography, *etc*. In that study, they

overviewed the recent developments of various kinds of amino-grafted mesopores and they also mentioned to amino-grafted mesoporous materials as solid base catalyst and adsorbent.

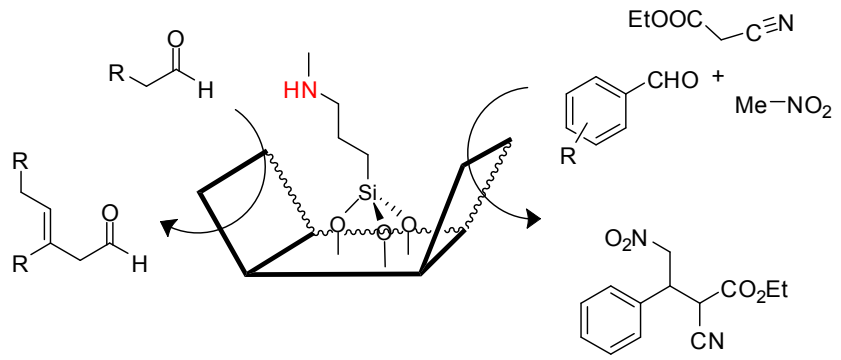
In 1977, Brunel *et al.* [17] were the first to report the hybrid amino-grafted MCM-41 as catalyst. In that work, they investigated a series of amine-based organocatalysts including pipyridine, (3-aminopropyl)trimethoxysilane (ATPS) loaded MCM-41 in the synthesis of monoglyceride. Mirza-Aghayan's group [18] developed the catalytic activity of ATPS modified MCM-41 the preparation of 2-amino-5,6-dihydropyrimidin-4(3*H*)-one from the cyclocondensation of Meldrum's acid, aldehydes and guanidinium carbonate (Scheme 1). Advantages of this method included good to high yields generation, being completed in short reaction times and ease of isolation (Scheme 1).



Scheme 1.

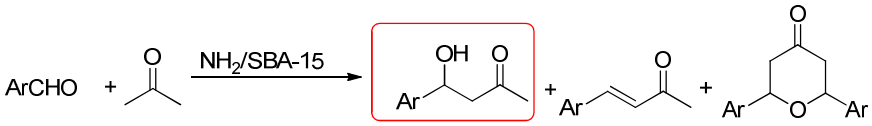
In comparison, secondary amines are more efficient than primary amines in the catalysis of organic reactions [19,29]. In 2002, Shimizu and coworkers used FSM-16 modified by secondary amine in the catalysis of self-aldol condensation of aldehydes and acetone, whose activity was higher than that of homogeneous amine catalyst [20].

Komura et al. used amiofunctionalized MCM-41 mesoporous silica as a heterogeneous solid base catalyst, in which 3-methylaminopropyl moiety inside the mesoporous silica, was responsible to catalyze three-component one-pot reaction of Knoevenagel condensation of aldehyde with the active methylene compound to yield an electron deficient alkene (scheme 2) which underwent Michael addition of nitromethane to form trisubstituted primary nitro compound [21].



Scheme 2.

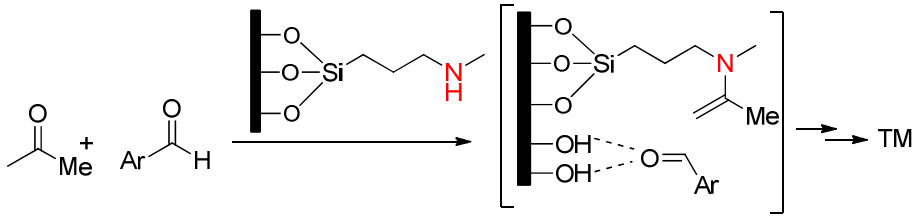
Silanol groups can act as an acidic functionality which can form an acid-base system to cooperate the catalytic performance of amine based heterogeneous mesoporous silica materials [22,23,29]. Kubota *et al.* [22] applied SBA-15-NH_2 as catalyst in the aldol reaction of 4-nitrobenzaldehyde and acetone (Scheme 3). They claimed that addition of this catalyst caused to a significant increase in the rate of reaction in high yield. This observation demonstrated that the physical proximity and the relative positions of two catalytic groups within the mesopores have key role in performing these reactions. Silanol groups on the surface of mesoporous materials have weak acidic feature and therefore, they are relatively active functionality.



Scheme 3.

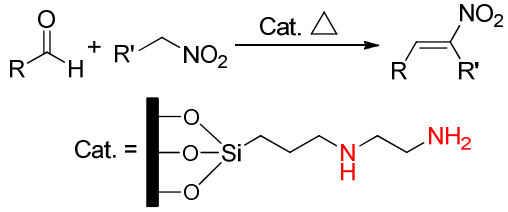
In 2009, Asefa *et al.* reported the aldol condensation reaction using MCM-41 grafted by site-isolated secondary amines onto the channel walls of mesopores [23]. They found that site-isolated organoamines accompany with silanol groups and generate a pair feature which exhibit an acid-base cooperativity during the aldol condensation reaction with high turnover number (TON) and selectivity (alcohol products over alkene products). In addition, when amine based groups were grafted in a polar-protic solvent, isopropanol, it showed higher catalytic activity towards aldol reaction than those grafted in a non-polar solvent, toluene, due to the fact that the later conditions cause to generate a less dense amino-grafted material which are loaded onto the surface of mesopore. To elucidate the role of surface silanols as acidic sites and their ability to activate the substrates in aldol condensation, control experiment with diethyl amine as a homogeneous catalyst in the presence of MCM-41, silica microspheres, methyl-capped MCM-41 or methyl-capped catalyst was carried out. Amino-

grafted MCM-41 with free silanols resulted in significant enhancement in the catalytic activity compared to the corresponding reactions conducted in the absence of MCM-41, or in the presence of methyl-capped catalysts or silica spheres. By testing materials with different grafted organoamine groups as catalysts, they also found that secondary amine functionalized sample produced the best acid and base pairs and most efficient catalytic activity in aldol reaction. This was followed by primary amines, while the tertiary amine functionalized samples showed negligible catalytic property (Scheme 4).



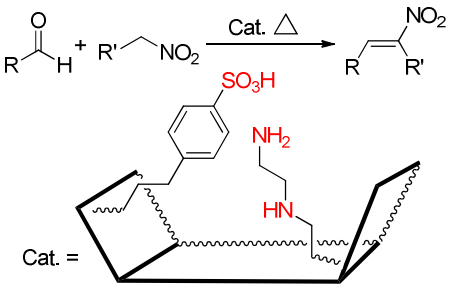
Scheme 4.

Later, Choudary *et al.* [24] reported Knoevenagel and aldol condensations by diamino-based MCM-41 which was furnished by grafting the *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPTS) on MCM-41. Then, Kantam's group reported the synthesis of nitroalkenes [25] in a one-pot liquid-phase procedure using the same diamino-functionalized MCM-41 as catalyst (Scheme 5).



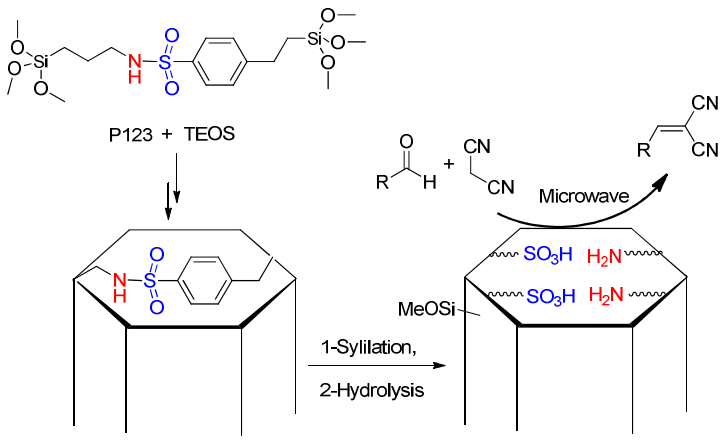
Scheme 5.

Thiel *et al.* [26] prepared and studied a series of organomodified hybrid mesostructures by ATPS and AAPTS in nitroaldol condensation. They found that when these amine based mesostructrures are bifunctionalized by arenesulfonic acid, it causes to form a cooperative acid-base system which raises the catalyst efficiency (Scheme 6). They also compared these two amine based functionalities in cooperative system and found that the best yields and selectivities for nitroaldol condensation were obtained by AATPS and CSES bifunctional cooperative system.



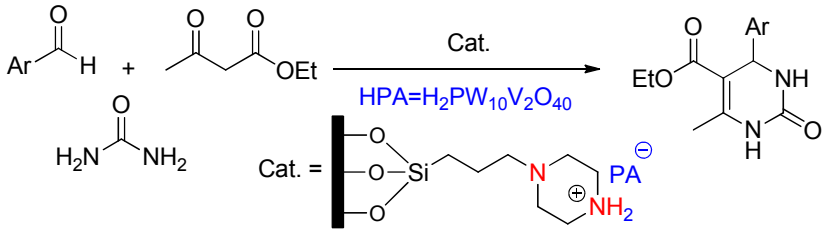
Scheme 6.

Liu *et al.* [27] prepared the same system with a controllable acid-base bifunctionalized mesoporous catalyst with acidic sites and basic sites in adjacent arrangements via an in situ cleavage of sulfonamide bond on synthetic process (Scheme 7). During Knoevenagel condensation reaction of aromatic aldehydes and ethyl cyanoacetate under microwave irradiation in solid media, the bifunctionalized mesoporous catalyst Me-A/B-SBA-15 exhibited higher catalytic activity than those of the corresponding amine-functionalized catalyst and the randomly-arranged acid-base catalyst, showing obvious acid-base cooperativity.



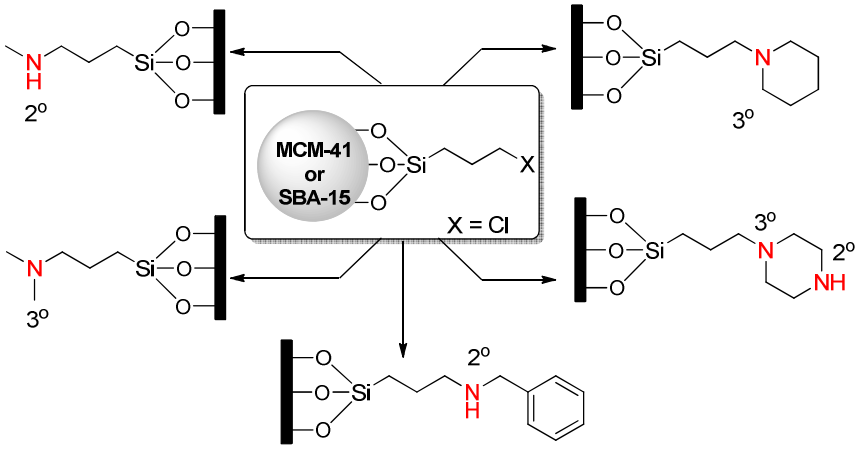
Scheme 7.

Based on catalytic study of acid-base bifunctionalized systems on the mesoporous by Liu [27], Tayebee *et al.* synthesized the heteropoly acids immobilized amine content mesoporous as HPA/amine-SBA-15 ($H_5PW_{10}V_2O_{40}$/Pip-SBA-15 and HPA=$H_5PW_{10}V_2O_{40}$). HPA/Pip-SBA-15 heterogeneous solid catalyst were used in solvent-free condition for Biginelli reaction (Scheme 8). The functional groups may enhance the interactions of heteropoly acids with the supporting material via hydrogen bonding, electrostatic interactions, and chemical bonding, result a higher and more stable immobilization. [28].



Scheme 8.

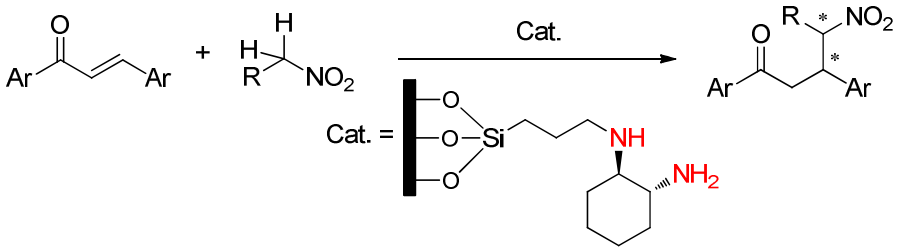
Shantz and coworkers [29] prepared a series of amine-based MCM-41 materials and studied their catalytic properties in nitroaldol reaction. They investigated the effects of organoamine type (primary, secondary, tertiary), amine density, and the presence of silanol groups on the catalytic activity and product selectivity (Scheme 9). High selectivity to the nitroalcohol product was achieved by introducing secondary and tertiary amine groups on the MCM-41 surface, while the nitroalkene was the dominant product for primary amines. The authors also claimed that when the secondary amines were applied, best results were obtained. They also found that an increase in the amount of amine loading cause to decrease the catalytic activity. One noteworthy was that the capping of silanols with trimethylsilyl groups reduces the catalytic activity for nearly all samples, indicating the cooperative effect of surface silanols with amine groups.



Scheme 9.

Park and coworkers [30] prepared mesoporous supported organocatalyst by a simple procedure. That is, *trans*-1,2-diaminocyclohexane was supported to mesoporous silica (Scheme 10) for asymmetric Michael addition of various nitroalkane derivatives. They attributed the enhancement of stereoselectivity the plugs and short channels presenting on the

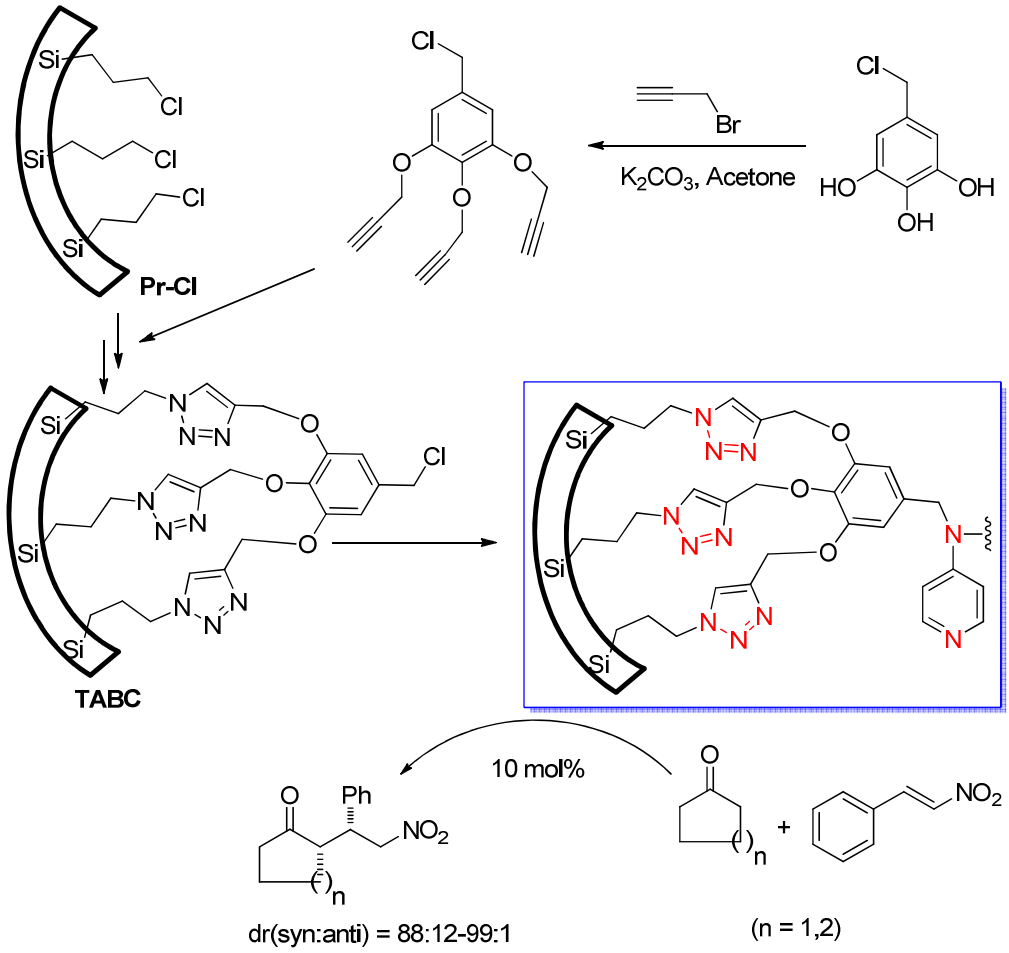
surface of mesoporous silica. They claimed that short channels and plug effect result in higher enantioselectivity in the addition of nitroalkanes to *α,β*-unsaturated ketones. This reaction was performed at room temperature during 24 h with *ee* value of 31-79%.



Scheme 10.

Jain and Bhaumik's research groups [31] prepared an interesting heterogeneous mesoporous silica supported organocatalyst *via* click method. It was very efficient and recyclable mesoporous silica grafted organocatalyst with bifunctional acid-base nature in Michael addition of ketones to *β*-nitrostyrenes affording the products with excellent diastereoselectivity. They found a remarkable enhancement in the reaction rates with respect to the corresponding monofunctional organocatalyst.

Preparation of mesoporous supported organocatalyst begins with functionalization of mesopore with CPTS and substitution of azide with –Cl and then reaction with propargylated 5-(chloromethyl)benzene-1,2,3-triol produce TABC was subsequently undergo reaction with *p*-aminopyridine and generate the final organocatalyst (Scheme 11).

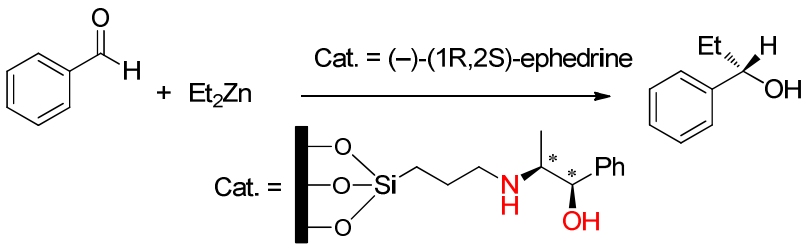


Scheme 11.

3. Ephedrine, proline and proline-type supported mesostructures

Ephedrine is a *β*-aminoalcohol which acts as a chiral auxiliary and moreover, it behaves organocatalytic property. Its asymmetric organocatalysis has attained an interest. Abramson's group [32] used (-)-ephedrine supported Al-MTS to obtain an enantioselective catalyst to induce the enantioselectivity in alkylation of benzaldehyde with diethylzinc. (-)-ephedrine is a chiral aminoalcohol anchored through covalent bonding of 3-chloropropyltrimethoxysilane (CPTS) and substitution of the halogen by (-)-ephedrine (Scheme 12).

They also studied the effect of CPTS density and free silanol groups on the surface of the support. They investigated the two kinds of and the effect of the uncovered mineral surface on activities and enantioselectivities.



Scheme 10.

Next group which has wide range of applications in organocatalysis is proline and its related compounds [33,34]. Gruttadauria and coworkers reviewed recent recyclable supported proline and proline-derivatives as organocatalysts [35]. In the literature, they discussed variety of supports including the silica supported, dendrimer supported, polymer supported, ionic liquid supported, cyclodextrin supported, and DNA supported prolines. Conventionally, proline can be supported by either of covalently bond or electrostatic interaction.

Cheng *et al.* [36] studied the enantioselectivity of mesoporous supported chiral (*S*)-(-)-*α,α*-diphenyl-2-pyrrolidinemethanol (Fig. 2) on the same addition of diethylzinc to benzaldehyde to form (*S*)-1-phenyl-propanol. Proline derivative was supported to SBA-15-Pr-Cl. Enantioselective addition of diethylzinc to benzaldehyde to form (*S*)-1-phenyl-propanol was increased from *ee* of 66 to 75% by adding a small amount of n-butyl lithium. The reaction rate and the enantioselectivity increase was attributed to the chiral proline species in the mesopores and the hydrophobicity (methylating silanol groups) around the active sites. Moreover, this chiral supported proline SBA-15 was recoverable and reusable through the next cycles.

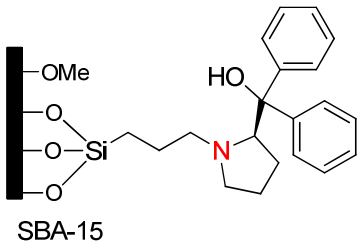


Figure 2. (*S*)-(-)-*α,α*-diphenyl-2-pyrrolidinemethanol**.**

An independent research group [37] studied the same reaction of diethylzinc addition to aldehyde with a similar chiral proline derivative (Fig. 3) which was supported to SBA-15, MCM-15 and amorphous silica. A similar results were obtained in enantioselectivity to that of Cheng *et al.* they also increased the *ee* value up to 75% by adding small amount of *n*-butyl lithium and capping free silanols with trimethylsilyl groups.

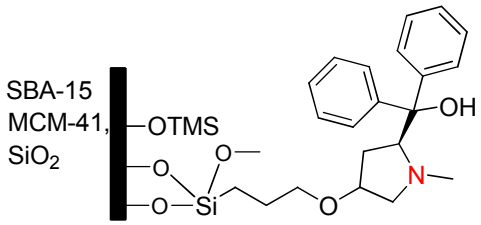
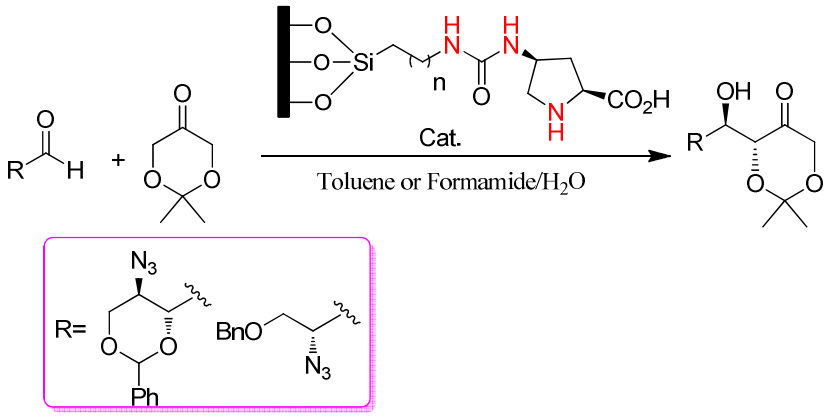


Figure 3. diphenyl-2-pyrrolidinemethanol.

Fernandez *et al.* [38] reported the asymmetric aldol reaction of cyclic ketone and aldehydes via heterogeneous *L*-proline grafted silica MCM-41. In their report, they investigated the influence of a series solvents on the catalysis of the asymmetric aldol reaction. Observations showed that the result depends on the nature of the solvent. Reactions proceeded more efficiently in hydrophilic polar solvents while a small amount addition of water causes an increase in the rate and the stereoselectivity of the reaction performed in hydrophobic toluene. The reaction under heterogeneous conditions furnished useful intermediates of azasugars (Scheme 13).



Scheme 11.

Dhar *et al.* [39] prepared and compared functionalized proline into MCM-41 with benzylpenicillin derivative (Fig. 4) as catalysts for direct, asymmetric aldol reaction between acetone and activated aromatic aldehydes. In the reaction of 4-nitro and 4-fluoro benzaldehyde, the aldol products were obtained in *ee* and yield of 36% and 59%, respectively. The catalysts were reusable with neither significant drop in enantioselectivity nor loss of mesostructure. Characterization of catalysts was achieved by FT-IR, ^{13}C CP MAS solid state NMR, XRD and TEM techniques. Moreover, these catalysts contain no metal in their structures. Therefore, the problem of leaching encountered with many metallic catalysts

does not arise. Results from comparing confirmed proline derivative as a high efficient catalyst rather than benzylpenicillin one in yield and stereoselectivity.

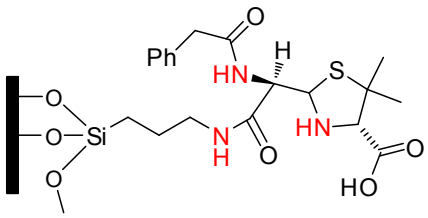


Figure 4. Proline derivative functionalized MCM-41.

Yang *et al.* [40] reported a similar catalyst for the asymmetric aldol reaction of cyclohexanone and *p*-nitrobenzaldehyde with *L*-prolinamide within SBA-15. This catalyst was obtained by co-condensation of TEOS, Na_2SiO_3, and prolineamide group (Fig. 5). These differences are in the route of functionalization. The procedure includes the co-condensation of silica precursors with *L*-prolinamide modified organosilane (PCA) in HOAc–NaOAc buffer solution (*p*H = 4.4) using block copolymer P123 as a template. The highly ordered 2D hexagonal mesostructure was obtained through one-pot co-condensation of TEOS, Na_2SiO_3 and PCA as silica source. The disordered foam-like mesostructure was also obtained when TEOS and PCA were used as silicon sources. In asymmetric aldol reaction of cyclohexanone with 4-nitrobenzaldehyde, the materials with highly ordered mesostructure exhibit higher enantioselectivity (91% *ee*) than that with disordered foam-like mesostructure (75% *ee*), suggesting that the ordered pore structure imparts improved enantioselectivity. The *L*-prolinamide functionalized materials were also synthesized by grafting PCA onto mesoporous silica nanoparticle (MSNs), which showed catalytic efficiencies similar to the materials synthesized by the co-condensation method.

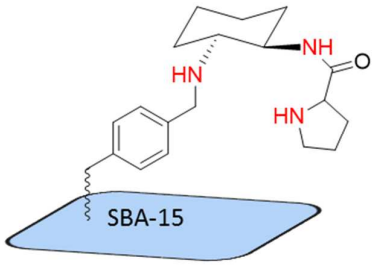
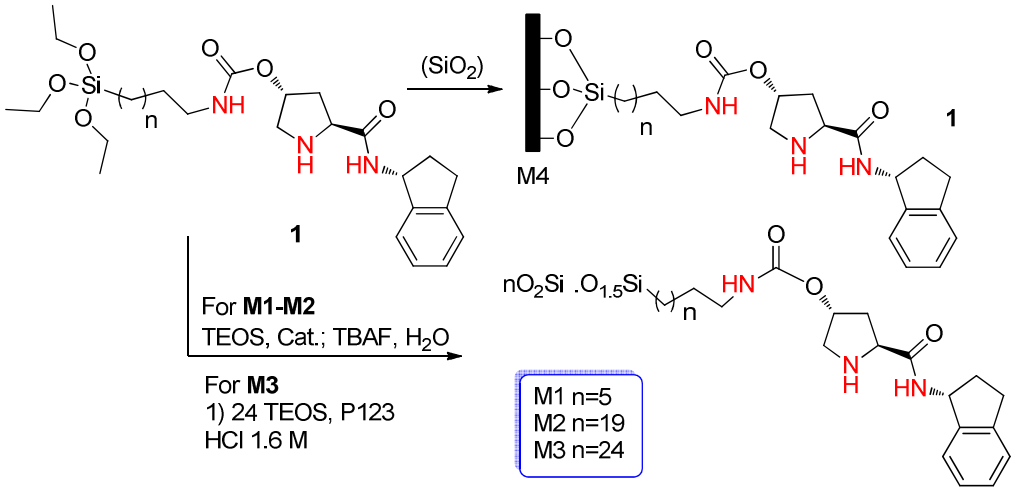


Figure 5. Chiral prolinamide modified organosilane.

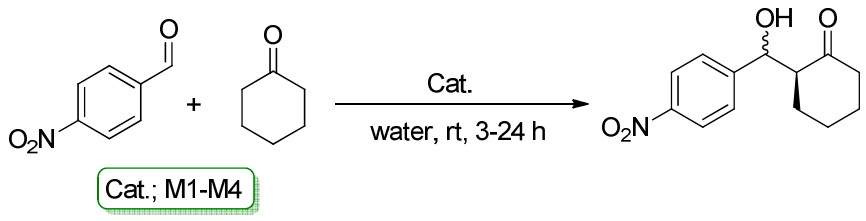
In 2012, Pleixats and coworkers [41] demonstrated that amidation of carboxylic acid moiety in proline with a suitable group can improve the obtained results such as

enantioselectivity. They prepared a series of catalysts (**M1**–**M4**) and tested them in aldol reaction. They first prepared prolinamide **1** and then, in different conditions, they obtained four kinds of catalysts. **M1** was prepared by sol–gel method and grafting on SBA-15 type mesostructured silica. **M2** and **M3** were obtained by sol-gel co-condensation of prolineamide **1** with different amounts of TEOS (molar ratios of 1:5 and 1:19 respectively) under nucleophilic conditions using a fluoride salt (TBAF) as catalyst. Template-assisted hydrolytic polycondensation of **1** with TEOS under acidic conditions (1.6 M HCl, P123, EtOH as co-solvent with several drops of DMF) afforded **M4** ([P123]:[TEOS]:[3]:[H_2O]:[HCl]:[EtOH] = 0.37:24:1.0:4390:126:106) (Scheme 14).



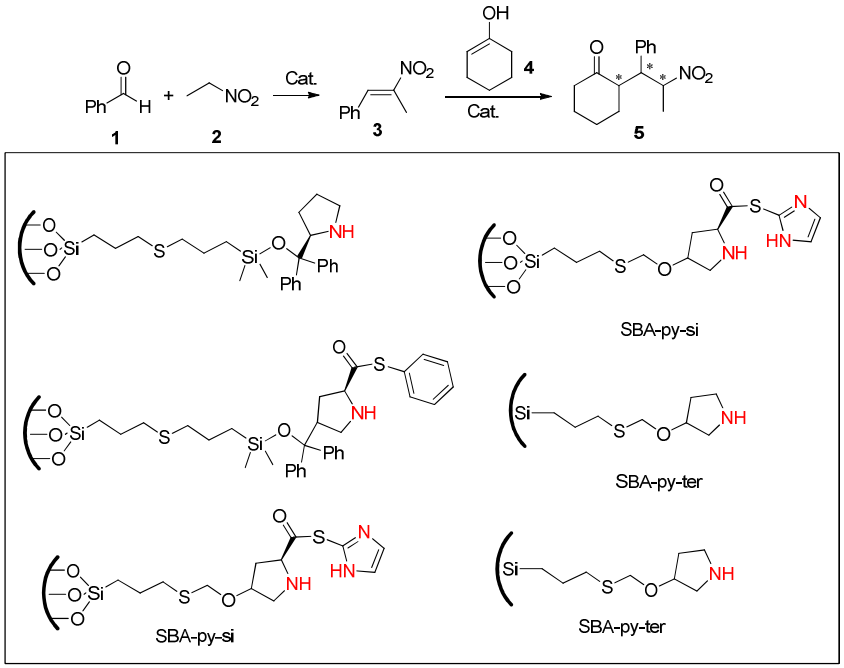
Scheme 12

The best catalytic results obtained from a simple co-condensation without structure-directing agent. Simple and green conditions are used for the aldol reaction, the process being performed in water at room temperature, with relatively low amounts of supported organocatalysts and in the absence of an acid co-catalyst. Good recyclabilities are observed without the need for catalyst regeneration, with enantioselectivities (*ee* of 82-88%) higher than that of the former free carboxylic acid prolines anchored onto MSNs (Scheme 15).



Scheme 13

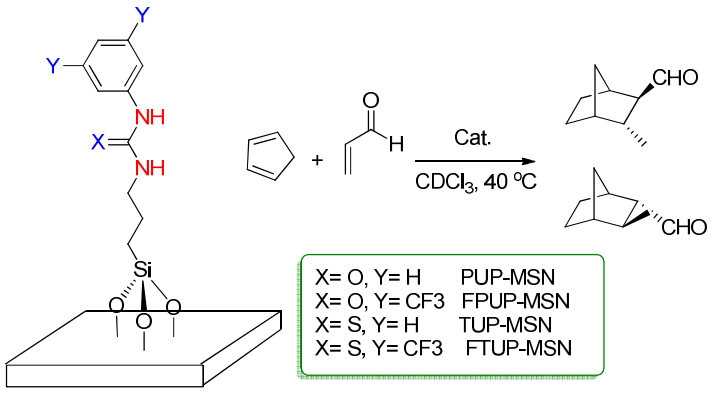
He and coworker [42] designed the next acid-base system of hybrid catalyst for one-pot asymmetric enantioselective Henry-Michael tandem reaction. They used inherent achiral hydroxyls as acidic sites and immobilized chiral amines as basic sites in their bifunctional heterogeneous catalysts. Highly efficient and enantioselective asymmetric Henry–Michael reaction, a type of aldol reaction, has been achieved in one-pot condition using this system. Final products were obtained in yields of up to 85% and *ee* of 99%. (*S*)-2-(((Allyldimethylsilyl)oxy)diphenylmethyl)pyrrolidine, (*S*)-2-(((allyldimethylsilyl)oxy)methyl)pyrrolidine, (*S*)- (2-amino-phenyl)-4-(allyloxy)pyrrolidine-2-carbothioate and (*S*)-(1-methyl-1*H*-imidazol-2-yl)-4-(allyloxy)pyrrolidine-2-carbothioate, all with pyrrolidine structure, were selected as the amine moiety. SBA-py-si-diphin catalyzed both Henry and Henry–Michael one-pot reaction. Thus it was supposed that hydroxyl groups as acidic sites with the grafted pyrrolidine as basic sites had synergy effect. Without the steric hindrance of the two phenyl groups as in SBA-py-si-diph, SBA-py-si afforded 99% conversion of **1** in the heterogeneous Henry reaction and 66% yield of **5** in the heterogeneous Henry–Michael one-pot reaction. SBA-py-pri afforded a yield of **5** similar to SBA-py-si, with 74% conversion of 1 in the Henry reaction and 85% conversion of **3** in the Michael reaction. SBA-py-ter catalyzed the Michael reaction, similarly to SBA-py-pri, while catalyzing the Henry reaction more effectively than SBA-py-pri. A yield of up to 85% for 5 is afforded on SBA-py-ter. Especially amazing and encouraging, an *ee* of 98% for anti -isomers and an *ee* of 71% f or syn-isomers were afforded on SBA-py-si-di ph, and >95% *ee* was observed for both syn- and anti-configured product on SBA-py-si, SBA-py-pri and SBA-py-ter (Scheme 16).



Scheme 14.

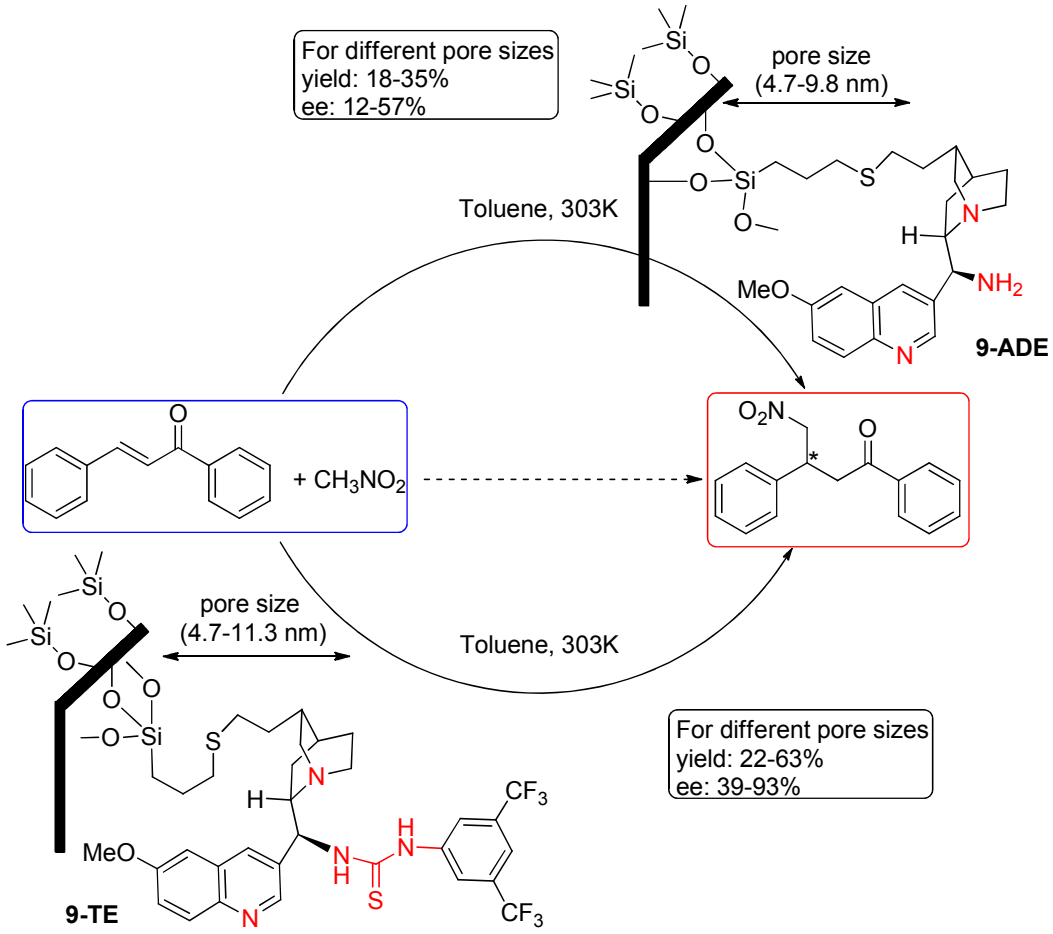
4. Urea, thiourea and guanidine supports mesostructures

Urea and urea type compounds form effective catalyzing agents when are supported to mesostructures. They are considered as supported organocatalysts which have been interestingly used in the catalysis of organic reactions. Lin and coworkers [43] prepared a series of urea and thiourea functionalized MSNs and investigated their catalytic performance in Diels-Alder reaction. In this case, the prepared catalysts exhibited a superior catalytic activity to Diels-Alder reaction than those of homogeneous analogues. The reaction was between crotonaldehyde and cyclopentadiene (Scheme 17). They attributed the enhancement in the catalytic activity to cooperative acid-base system. They also compared four urea- and thiourea- supported MSNs and found that among them, the strong electron-withdrawing group (CF_3) containing urea and thiourea structures could increase the Lewis acidity of these heterogeneous organocatalysts and thus, the best result can be obtained.



Scheme 15.

He *et al.* [44] extensively studied enantioselectivity in Michael addition of nitromethane and chalcone. In this case they prepared several mesoporous with variable pore sizes which their outer surfaces were capped by trimethylsilyl- groups and inner surfaces were modified by propylthiols. Then they grafted two species of organocatalysts (family of epiquinine) inside the mesopores. In this research they compared heterogeneous **9-ADE** and **9-TE** catalysts together and also with their corresponding homogeneous versions. They understood that **9-TE** in the catalytic activity is superior to **9-ADE** (*ee* and yield). They also found a relationship between the catalytic activity of supported organocatalysts and pore size of mesopores. The best pore size for **9-TE** was 6.3 nm and for **9-ADE** in the yield was 5.8 and in *ee* was 4.7 nm (Scheme 18).



Scheme 16.

Urea groups in adjacent with amine based groups on the silica surface act as an acid and amines act as a base. Therefore, they form an efficient cooperative catalytic system. Lin's group [45] simultaneously incorporated the AAPTS with urea function on the surface of MSN and investigated it in aldol reaction. They used 3-ureidopropyl group as an acid and AAPTS as a base to perform aldol, Henry and cyanosilylation reactions. TONs of the bifunctionalized MSN in these reactions were higher than those of physically mixed functions (Fig. 6).

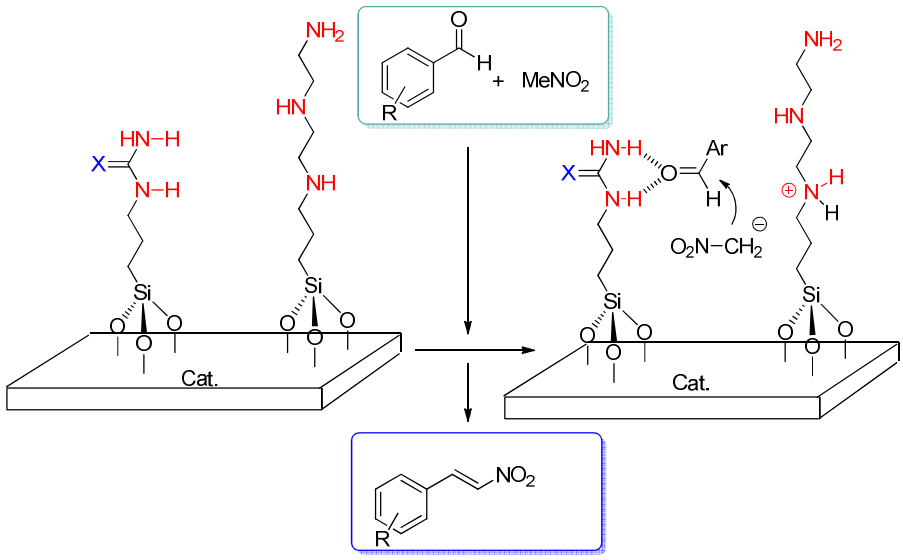
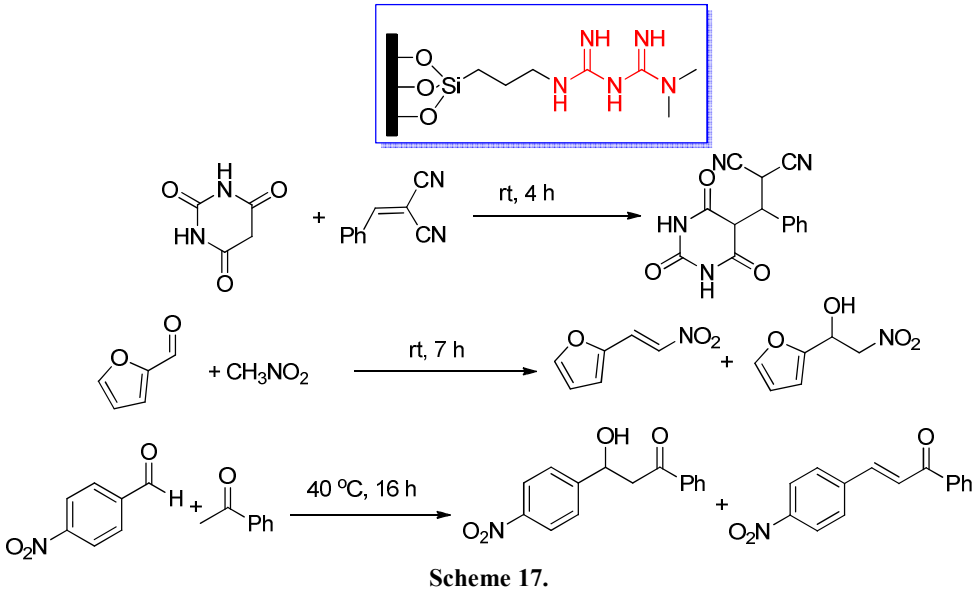


Figure 6. Cooperative catalysis by acid and base bifunctionalized MSN.

The successful synthesis of a series of novel biguanide-functionalized mesoporous silica of SBA-15 catalysts was developed by Alizadeh *et.al* [46]. Various amounts of a biguanide, termed metformin, was immobilized onto the silica surface through a covalent attachment. They investigated the structural and surface characteristics of these catalysts by various techniques such as TEM, SEM, TGA. Then they studied the catalytic behavior of it in aldol and nitroaldol coupling and Michael-addition reactions. They proved that it acts as efficient and recoverable catalysts in aqueous solution with excellent reactivity combined with considerable recyclability (Scheme 19).



Scheme 17.

Ronconib and coworkers [47] prepared a new amine based heterogeneous mesoporous silica, MCM-41, and compared it with piperazine and ATPS based MCM-41 in the production of biodiesel, transesterification of soybean oil in the presence of methanol. This new amine based MCM-41 (Fig. 7) which was a guanidine-derived compound (1,5,7-triazabicyclo [4,4,0] dec-5-ene) had higher activity rather to later piperazine and ATPS based catalysts in this reaction. Up to 99% yield this production at 70 °C and 3h of reaction were furnished by the guanidine-derived catalyst, while the other amine-derived catalysts were less active for the production of biodiesel, generating lower yields under more severe reaction conditions [42].

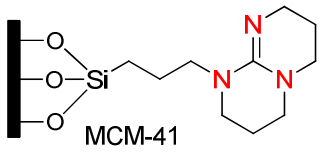
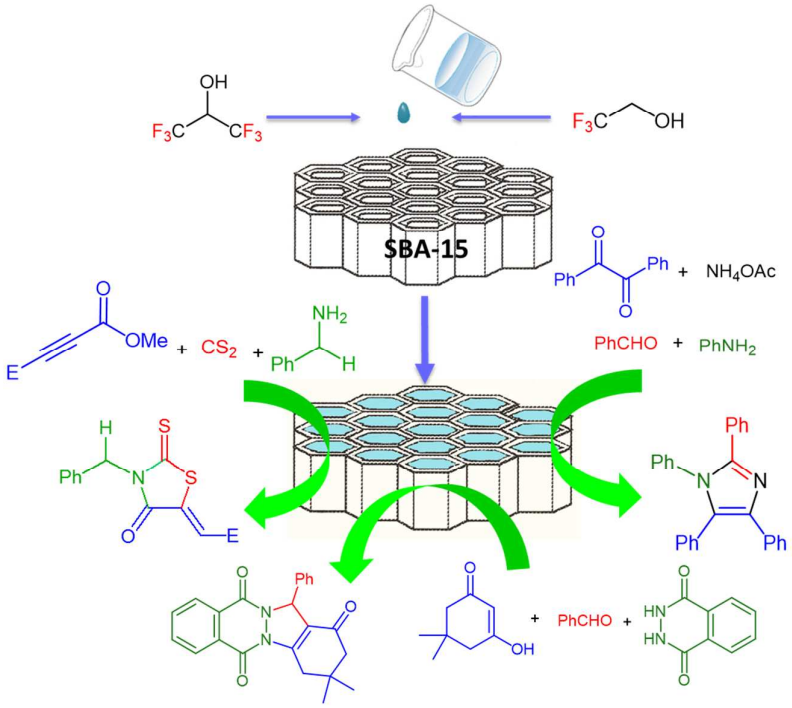


Figure 7. Amine based MCM-41.

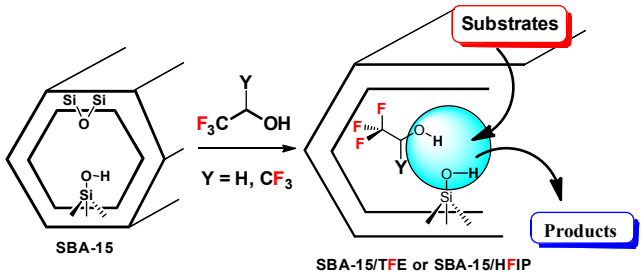
5. Fluorinated alcohol/SBA-15 adducts

One of our research interests is to develop the catalytic applications of confined fluorinated alcohols in mesoporous materials [48-50]. We found that the adduct of mesoporous SBA-15 and 2,2,2-trifluoroethanol (SBA-15/TFE) exhibit catalytic activity in the reaction of aldehydes, amines, and ammonia with benzil which causes to provide highly substituted classes of imidazoles. In this method, imidazoles which are synthetically potential and pharmaceutically interesting compounds were obtained via one-pot multicomponent method. We also performed the synthesis of indazolophthalazinetrione skeletons via three-component coupling reactions in the presence of SBA-15/TFE as a green conditions [50]. This method carries the advantages of being performed under the neutral conditions without catalyst activation or modification step (Scheme 20). This new catalytic system which is developed by our group can be recovered and reused without a significant loss of the catalytic activity [48].



Scheme 20.

Later, we developed a similar catalytic system for the synthesis of rhodanine scaffolds which are synthetically valuable in pharmaceutical and industry (Scheme 21). The catalyst (SBA-15/HFIP) was obtained by confining the hexafluproisopropanol (HFIP) inside SBA-15 at room temperature with adding no further solvent. The other advantages of this method was its low catalyst loading, simple procedure, waste-free and direct synthetic entry to excellent yields of rhodanines, high reusability of the catalyst, and short reaction time. We have not already established a mechanism process for the synthesis of imidazoles or rhodanine over the SBA-15/TFE or SBA-15/HFIP adduct in an experimental manner. A possible explanation [48-50] is proposed in Scheme 21.



Scheme 21.

6. Organosulfonic acids

Organosulfonic acid supported mesostructures (OSASMs) are a class of hybrid mesopores material which have extensively applied and investigated in catalysis during the recent years. The first pioneering reports on OSASMs were in 1998 [51-53]. Preparing the earliest versions of OSASMs is generally performed by two alternative routes. Post-functionalization of 3-mercaptopropyltrimethoxysilane (MPTS) into mesoporous silica and co-condensation of MPTS with silica source, such as TEOS or TMOS, during the synthesis of mesoporous silica which is called direct synthesis of OSASMs.

Since first discovery of OSASMs, many types of OSASMs are prepared and proposed by researchers. In this case, propylsulfonic acid modified mesostructures are most common type of OSASMs. However, many types of OSASMs are synthesized and introduced by researchers. These OASMSs have opened a great path of researches in this area. In 2006, Melero and coworkers [55] reviewed and discussed advances, developments, and catalytic applications of OSASMs. They also overviewed new types of OSASMs which had other had other key precursor for synthesis of OSASMs instead of MPTS. In addition to these primary advances in OSASMs, many catalytic applications are developed for these hybrid catalysts. Some of them are depicted in Figure 8.

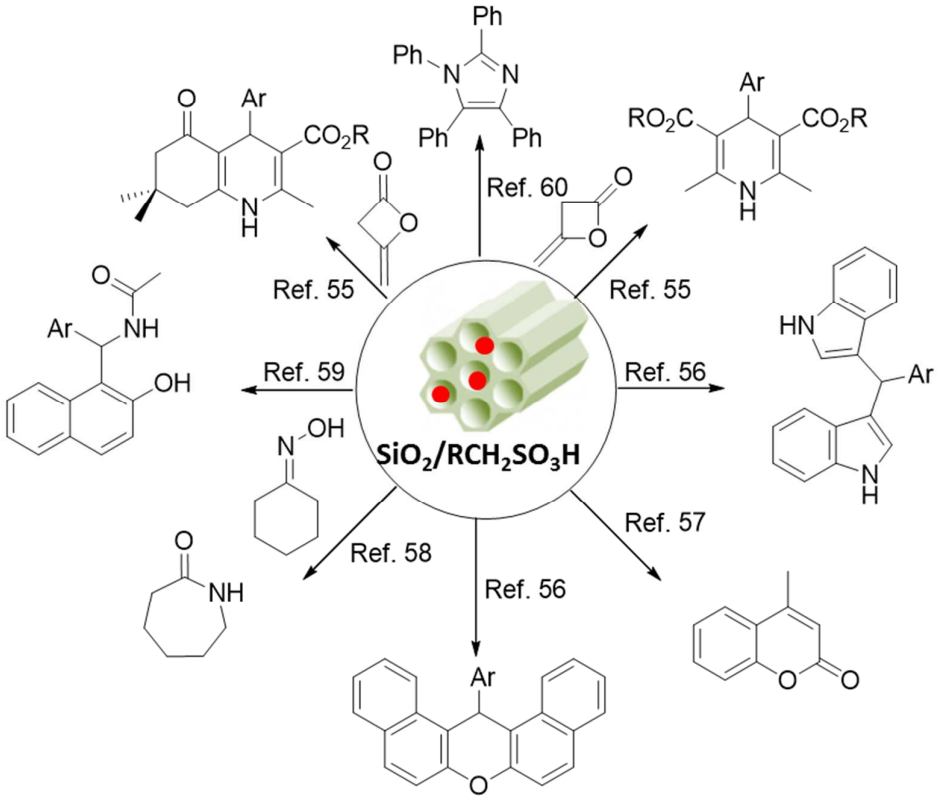


Figure 8. OSASMs as organocatalyst.

Because the silica frameworks in mesostructures have intrinsic hydrophilicity and therefore, adsorption of water may cause a catalyst surface deactivation for mass transfer of organic molecules as substrates during reaction times. Recently in our group, we have developed the simultaneous application of ultrasound (US) system with propylsulfonic acid grafted SBA-15 to increase its efficiency and mass transfer within the pores of SBA-15 [61]. In this regard, we investigated the catalytic performance of SBA-15-Pr-SO_3H in three separate biologically interest reactions including the syntheses of 2*H*-indazolo[2,1-*b*]phthalazine-triones, *α*-aminophosphonates, and polyhydroquinolines (Fig. 9) under sonication. Results showed higher selectivity and yield toward the products in very short reaction times (4-25 min).

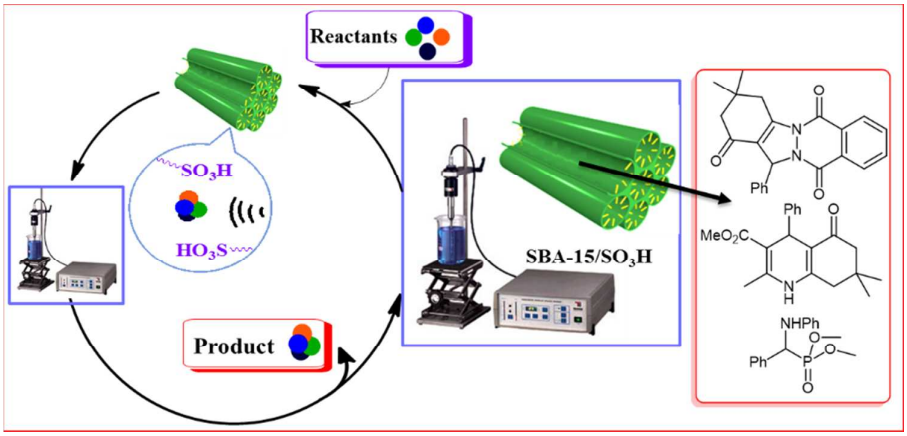
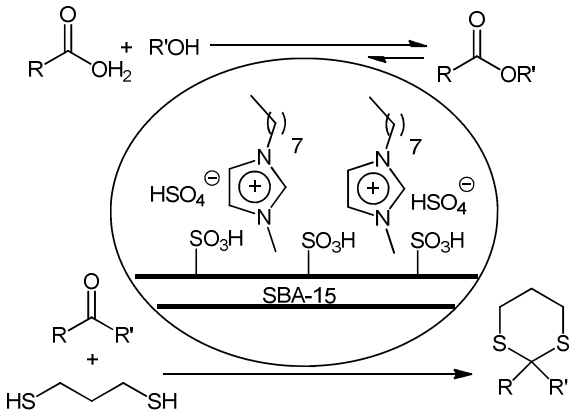


Figure 9. US/SBA-15-SO3H system as simultaneous method.

Other method to increase their efficiency is simultaneous application of microwave irradiation. They first [62] prepared ATPS modified MCM-41 (NH_2-MCM-41) and then, they reacted this substrate with 1,4-butane-sultone to give MCM-41-$NHSO_3H$. Afterward, this catalytic system was used to catalyze the *tert*-butylation of hydroquinone under microwave irradiation in which the microwave irradiation had cooperative role. Moreover, amine and sulfonic acid together can also create a cooperative system. MCM-41-$NHSO_3H$ showed a high conversion of hydroquinone (88.0%) selectivity (93.1%) to 2-*tert*-butylhydroquinone (2-TBHQ) after 8 min.

Karimi and Vafaeezadeh took another strategy to enhance the efficiency of OASMSs [63,64]. They confined a hydrophobic and acidic ionic liquid (IL) within SBA-15/PrSO_3H to increase its mass transfer and hydrophobicity. Moreover, this confinement caused to increase the Brønsted acid strength as a result of an acid site cooperativity mechanism. Their suggested catalytic system showed excellent performance in direct esterification of alcohols

and carboxylic acids at ambient temperature under solvent-free conditions [63]. They also successfully incorporated this efficient catalytic system in solvent-free thioacetalization of carbonyl compounds, one of the most popular methods for protecting aldehydes and ketones, at room temperature [64]. The catalyst was recoverable and reusable at least for 7 runs without a significant loss in the yields and IL (Scheme 22).



Scheme 182.

7. Conclusion

In summary, most of silica mesostructure supported organocatalysts act have drastic properties in catalysis, stereoselectivity, and green reaction delivery. Silica is the most suitable support due to its stability, functionalizing nature, and biocompatibility. Moreover, its efficiency increases when its structural property is an ordered mesostructure. In this case, its mesochanels can either act as nanoreactors. Therefore, its catalytic behavior, stereoselectivity, and chemoselectivity will be improved. On the other hand, by developing such heterogeneous organocatalysts, it opens a gateway to metals free, stereoselective, and green chemical processes.

Abbreviations

TMOS = tetramethyl orthosilicate
TEOS = tetraethyl orthosilicate
MPTS = 3-mercaptopropyltrimethoxysilane
AAPTS = *N*-(2-aminoethyl)-3-aminopropyl trimethoxysilane
MPTS = 3-mercaptopropyltrimethoxysilane
TM = Target Molecule
SDA = structure directing agent
CPTS = 3-chloropropyltrimethoxysilane
OSASMs = Organosulphonic acid supported mesostructures
MSN = Mesoporous silica nanosphere
MSNs = Mesoporous silica nanoparticles

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