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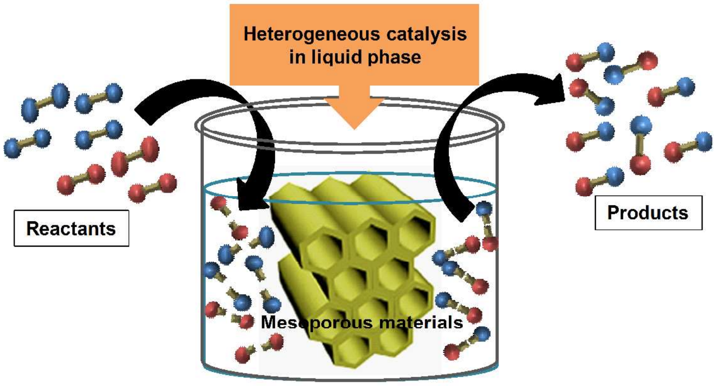
This review article provides an overview of the literature reported for several important liquid phase heterogeneous catalytic transformations performed over a wide range of mesoporous materials along with a brief outline of their surfactant-assisted synthesis and its pivotal role in the environment-friendly green catalysis.



Mesoporous material: a versatile support in heterogeneous catalysis for the liquid phase catalytic transformations

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ABSTRACT: Due to their unprecedented intrinsic structural features, like tunable pore diameter of nanoscale dimensions, huge BET surface areas, good flexibility to recognize/accommodate various functional groups and metals onto the surface an inevitable linkage between nanoporous materials and catalysis has been built-up over past few decades. As a result of which a huge numbers of communications and articles dealing with these materials with nanoscale porosity have came to light. In this review, our objective is to provide a comprehensive overview on mesoporous solids, most remarkable member of nanoporous family of materials, the general strategy for their syntheses and application of those functionalized porous materials in the liquid phase catalytic reactions. In the latter part, role of catalytic centres in various organic transformations over these functionalized mesoporous materials and their economical, environmental and industrial aspects are described in detail.

KEYWORDS: Mesoporous materials; organic transformations; heterogeneous catalysis; liquid phase reactions; green chemistry.

1. INTRODUCTION

Today, worldwide over 60% of the industrially important chemical products are produced by different chemical process and the majority of these processes are accelerated by using the suitable catalysts.[1] Wilhelm Ostwald rightly said that “there is probably no chemical reaction which cannot be influenced catalytically”.[2] Catalysts play the crucial role in the manufacturing process for the synthesis of fine chemicals, pharmaceuticals, commodity chemicals, energy resources, fuels, biofuels and so on. The extraordinary advantage of heterogeneous catalysis over that of homogeneous one is the separation, recovering and recycling capability, which leads to the compliance to green synthetic pathways involving minimum environmental pollution.

Porous nanostructured materials with huge BET surface area are suitable for catalytic reactions and in most cases the nature of the catalytically active components (e.g. metals, organic functional groups etc.) are most crucial in the heterogeneous catalysts. Hence, researchers are very keen to design hierarchical porous nanomaterials bearing catalytically active centers at its surface. A number of reviews by Pérez-Ramírez et al.,[3] Pal et al.,[4] Lopez-Orozco et al.[5] and others on the synthesis and applications of porous solids are reported in recent times. The introduction of microporous solids particularly zeolites in industrial manufacturing process has brought an enormous economical and environmental revolution.[6] These microporous materials play key role in shape-selective catalysis at the industrial scale.[7] However, their small pore opening has motivated the researchers to focus their attention to design materials with pores of still larger dimensions in nanoscale regime. And this ultimately leads to the discovery of ordered mesoporous silicas through supramolecular templating pathways.[8] Later, other mesoporous supports like mesoporous oxides, phosphates, carbons, etc. have been invented and they play significant role in industrial manufacturing process for the fine chemicals. Liquid phase catalytic transformations in heterogeneous media over mesoporous solids are more favorable, which lead to minimum diffusion than the other materials belonging to the porous categories.

A number of comprehensive reviews in the literature related to the catalytic application of mesoporous solids by Corma,[9] Taguchi et al.,[10] Perego et al.,[11] Martín-Aranda et al.[12] have come-up, which mainly discussed about the catalysis over ordered mesoporous silica based materials. The other mesoporous materials like oxides, phosphates, carbons, polymers and organic-inorganic hybrid periodic mesoporous organosilicas,[13] which are of parallel importance as far as industrial catalysis is concerened, have got less emphasis there. The present review illustrates an overall picture of heterogeneous catalytic reactions mediated by wide range of mesoporous materials invented so far and their environmental aspects for clean chemical synthesis.

2. WHAT ARE MESOPOROUS MATERIALS?

Traditional porous materials, more commonly used term 'nanoporous' materials are defined as a continuous and solid network material filled through voids of 'nanoscale pores' of the order of say 100 nm or smaller. International Union of Pure and Applied Chemistry (IUPAC) have classified nanoporous solids into three categories according to the pore size they possess. Microporous with pore diameter less than 2 nm, mesoporous having pore diameter in the range of 2-50 nm and macroporous with great than 50 nm pore size.[14] Though there are some recent reports on the catalytic activity over macroporous materials,[15,16] but owing to low surface area this category of nanoporous materials is not so demanding for the liquid phase heterogeneous catalysis. Also many microporous zeolites, aluminophosphates, organic-inorganic hybrid phosphonates, metal organic frameworks (MOF) are quite useful for environmentally benign green catalytic reactions,[17,18] but those are out of the scope of this review, where our discussion will be focused on mesoporous solids and their potentials in heterogeneous catalysis.

The history of mesoporous molecular sieves (where, '*meso'* the Greek prefix, meaning "in between", adopted by IUPAC for having dimension of pores typically between 2 and 50 nm) begins from the last decades of twentieth century when materials like MCM (Mobil Composition of Matter)-type materials[8] were successfully synthesized by Mobil scientists. The discovery of M41S family of ordered mesoporous materials with pore dimension 2-10 nm, high surface area (~1000 m^2g^{-1}) and large pore volume (~1.0 cm^3g^{-1}) by using quaternary alkylammonium surfactants (e.g. cetyltrimethylammonium bromide, $CH_3(CH_2)_{15}N(CH_3)_3^+Br^-$) as template, can be considered one of the most important milestones in the history of porous world, suggesting huge expectations to apply them as heterogeneous catalysts.[19,20]

Among ordered mesoporous materials discovered initially mesoporous silica for e.g. MCM-41, MCM-48, MCM-50, FSM-16,[21] SBA-15[22] etc. are well-known. Though there is some difference in the synthesis conditions and structural properties of these silicas, basic strategy of synthesis is similar in all cases, which is based on the supramolecular self-assembly of the surfactants (or templates).[23] Rather than a small organic molecules as the single molecule template (SDA), long chain cationic surfactant molecules, like CTAB (cetyltrimethylammonium bromide), CPC (cetylpyridinium chloride) etc. or anion surfactants like SDS (sodium dodecyl sulphate) are used during the synthesis of the highly ordered silica based materials.[8] In solution co-operative self-assembly of surfactant molecules takes place at concentration higher than CMC when spherical or rod shaped geometry is obtained around which hydrolyzed inorganic silica precursors (say tetraethyl orthosilicate or TEOS) arranged themselves in order to form organic-inorganic metal-template composites under highly basic medium. Through ageing for a particular time further condensation occurs and the composites take an ordered arrangement such as cubic, hexagonal etc. After the removal of the the surfactants from the composite materials through calcination or solvent-extraction we can obtain the final mesoporous solids free from organic templates. A detail synthesis strategy of mesoporous silica and other mesoporous solids in surfactant-templated route based on the selection of different types of surfactants has been extended in the review published recently.[4] Typical synthesis scheme of highly ordered 2D hexagonal pure mesoporous silica MCM-41 mediated by surfactant is shown in Figure 1. Depending upon the type of surfactant used, surfactant-silica ratio, pH of the solution, the structure and mesopore size of the silica can be varied from hexagonal (e.g. MCM-41), cubic (e.g. MCM-48) to lamellar (e.g. MCM-50). Mesoporous SBA-15 type materials is another family of silica with large mesopores, synthesized using non-ionic block copolymer surfactants under highly acidic condition.[22] In addition to the co-operative pathways, nanocasting using already formed ordered mesoporousmaterials as hard templateshas been developed to synthesize mesoporous materials.[24] This method of nanocasting is highly effective for the synthesis of other non-siliceousporous oxide and carbon materials with ordered pore arrangements which are difficult to prepare directly by surfactant-assisted route.[25]

Non-siliceous mesoporous materials like oxides, mixed oxides,[26] metal sulphides,[27] metal phosphates,[28] polymers,[29] carbons,[30] carbon nitrides[31] and have also been synthesized successfully using surfactant templating routes. The long range applications of these materials extend from gas adsorption, ion-exchange, magnetism, sensing, catalysis, electrochemical to many versatile fields of research. Some of these mesoporous materials are purely inorganic; some are organic-inorganic hybrid materials while the others are completely organic based. Types of mesoporous solids commonly known in these three categories are shown in Table 1.

3. CATALYSIS: HOMOGENEOUS VS HETEROGENEOUS

The phenomenon called ‘catalysis’ was known from very ancient centuries, even though people know nothing about the underlying mechanism and chemical process involved in it. The making of soap, the fermentation of wine to vinegar, and the leavening of bread are all processes involving catalysis.The name ‘catalysis’, first proposed in 1835 by Swedish chemist Jöns Jakob Berzelius (1779-1848), was taken from the Greek words *kata* which means ‘down’ and *lyein* meaning ‘loosen’. In a short paper summarising his concepts on ‘catalysis’ as a new force, Berjelius wrote: “*It is, then, proved that several simple or compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of their elements and different recombination of these same elements to which they remain indifferent.*” He called this new force as ‘catalytic force’.[32] Actual basic role of a catalyst is to offer an alternating pathway of lower activation energy than the respective uncatalyzed reaction, resulting a faster reaction rate without hampering the overall thermodynamics of the reaction. Enzymes are the most common and efficient catalyst found in nature. Not a single reaction in our body is possible without the aid of these biocatalysts. They are also used as catalysts in food industries for many years. In case of laboratory and industrial use, catalytic oxidation using oxygen, hydrogenation using metal catalysts and many well known reactions are worthy to mention. Day by day imperative role of catalysis in the manufacturing of majority of chemicals used by our society is increasing rapidly. According to the survey report, in 2005, catalytic processes has generated about $900 billion products worldwide.

Catalytic reactions are usually categorized as either homogeneous or heterogeneous. Biocatalysis (enzymatic reactions) are often considered as a separate group. A homogeneous catalysis reaction is one where both the catalyst, the reactants on which it works and the products, all are in the same phase (solid, liquid, or gas), generally in liquid phase. The first formal example of this type is the reaction involving the decomposition of starch into glucose in boiling water in presence of sulphuric acid catalyst studied by Russian chemist Gottlieb Sigismund Constantin Kirchhoff (1764-1833) in 1812. Both the sulfuric acid and the starch were in aqueous solution during the reaction.[33]. Organometallic catalysts are another example of homogeneous catalysts.[34] On the other hand, heterogeneous catalysis is that where the catalyst is generally solid and remains as distinct phase from the liquid or gaseous reaction media on which it acts. Most of the reactions occurs in industry are driven by heterogeneous catalysts. Role of finely divided iron in Haber process for synthesis of ammonia or vanadium oxide for the production of sulphuric acid in contact process, etc. are well-known example of this type. In fact, with the production of sulphuric acid in “contact” process solved by Knietsch in the year 1898in Europe, the idea of industrial catalysis was developed.[35] Today porous materials are recognized as one of the most important materials in heterogeneous catalysts and they play the major role in industrial fine chemical synthesis.[9]

Homogeneous catalysis has some important properties like high selective of the products, good accessibility to catalytically active sites, etc. but with increasing public awareness regarding environmental issues, heterogeneous catalysis has become much more important over homogeneous ones.[36] This is because, some major problems like corrosions, toxicity, the difficulty of catalyst separation, its recovery, regeneration and reuse, high cost, creation of huge solid waste, etc. in case of homogeneous catalyst, make it unsuitable for application in industrial purposein these environmentally conscious and economically pressured world. Though, homogeneous catalysts are used in some industries like food, fine chemicals, pharmaceuticals, agrochemicals etc. but in this century heterogeneous catalysis has been proved to be the ultimate goal of industrial catalysis and engineering field. The industrial process which are highly dependent on homogeneous catalysts are recommended to use only by 'heterogenization' that means, immobilization of those catalysts on a solid insoluble support, which possess all the properties of homogeneous counterparts, and also the advantage of recyclability like heterogeneous.[37]

Catalytic reaction on heterogeneous support involves the fundamental steps like diffusion and adsorption of the reactants on solid surface, successful reaction on it, then desorption of the products to bulk with regeneration of the catalyst for next cycle. The schematic representation of heterogeneous catalytic cycle taking place through different steps is shown in Figure 2. Since the surface of catalyst plays a pivotal role in the related process, materials having high surface area are more desirable than nonporous to put on a significant part in industrial catalysis.[1,9] Although most of the chemical industries generally use zeolites or activated carbon based microporous materials as stable support for catalysis, but the number of fascinating organic transformations successfully carried out over different mesoporous supports are growing very rapidly today. In light of this a systematic brief discussion on mesopore mediated various important heterogeneous catalytic transformations under liquid phase reaction conditions has been made and illustrated in the following part of this review.

4. HETEROGENEOUS CATALYSIS OVER MESOPOROUS MATERIALS

The most important feature of the mesoporous material for which they show great potential for catalytic applications, is the possibility of controlling the morphology and local environment at the catalytic site depending upon the requirement of a particular reaction. Basically the reasons for which mesoporous materials act as a promising candidate for heterogeneous catalysis are, (i) high surface area and narrow pore size distribution essential for acting as catalyst bed, (ii) the dimension of pores can be tuned on varying the functional groups and ligands to control good selectivity for the product of interest, (iii) well adsorption property, which allow facile diffusion of reactant and products molecules during reactions, (iv) variation of the type and concentration of surface functionality to change the textural property and (v) the polarity/hydrophobicity/hydrophilicity of the surface which can be tailored in order to influence the yield of a catalytic reaction. Moreover, they are more or less non-toxic, non-corrosive, non-air sensitive, highly reusable, completely pollution-free, environment benign support for catalytic transformation in liquid phase.[10] The role and function of the mesoporous silica and other non-siliceous materials mediated sustainable liquid phase reactions for e.g. acid-base, redox, polymerization, condensation and other organic coupling reactions, etc. are discussed herein.

4.1 Redox reactions over mesoporous materials

Although pure mesoporous silica surface has high BET surface area (*ca.* 800-1400 m^2g^{-1}) and tunable pore diameter (2-50 nm), the material is not so effective for doing any catalytic reactions. Introduction of one or more heteroatom and metal complex in the silica framework (metal doped silica) or often by suitable immobilization of organic functionalities (organosilica or organic-inorganic hybrid silicas) the desired catalytic activity of the material could be achieved. The advantage of choosing mesoporous silica as support for incorporating other foreign atoms or functionalities is the inertness of the inorganic silica walls, where tetravalent Si atom can be replaced by the other reactive metal centers retaining considerably good surface area and porosity.[10] In spite of these benefits, silica structures like SBA-15, KIT-6 etc. have the limitation of losing porosity at elevated temperature, which restricted their application in large scale heterogeneous catalysis. Metal incorporated mesoporous silica can be prepared in both direct (or one step) or by post synthesis method.[4] A number of related reports of mesoporous metal doped silica as heterogeneous catalysts can be mentioned in this connection, for e.g. Zn-silica,[20] Cr-MCM-41,[37] CeO_2-silica,[38] Ti-MCM-41,[39] Ce-Fe-SBA-15,[40] Mn doped CeO_2-silica,[41] Pt and Rh nanoparticles supported silica[42] and so on. Periodic mesoporous silica (PMO) prepared by immobilizing organic moieties to inorganic silica surface by direct synthesis method can also act as good redox catalyst when grafted with transition metals like V, Ti, Au, Mo etc.[43]

Further, additional advantage of mesoporous transition metal oxides and mixed oxide catalysts are their high crystallinity and also their capability of existing in various oxidation states due to having the vacant *d* orbitals, which can take part in electron transfer from reactants during a given catalytic process.[44] Thus, these metal oxides or metal doped silica based materials are attracting wide-spread attention in recent times as non-toxic and environment friendly mild catalysts replacing conventional homogeneous hazardous oxidants like chromate, permanganate or periodide. Following section we are summarizing some redox reactions mediated by the mesoporous solids.

a. Oxidation of hydrocarbons

Oxidation, partial oxidation and epoxidation of hydrocarbons specially olefins (Figure 3) using peroxides or molecular oxygen under mild conditions are very important organic synthesis from both academic and industrial points of view, since a variety of highly demanding chemicals like polyurethanes, nylons, unsaturated resins, glycols etc. are manufactured by this pathway.[9] Due to several over oxidation products, satisfactory conversion and isolation of epoxides from alkene is quite difficult in many cases. Recently, a number of scientists have dealt with this difficulty and reported the epoxidation of various alkenes like styrene, cyclohexene, cyclooctene, norbornene etc. over Ti-PMO materials[45] under mild condition. Ti-PMO, Ti-containing periodic mesoporous organosilica, was obtained by a co-synthesis method using a organosilica, inorganic silica precursor (TEOS) and Ti-precursor in presence of CTAB surfactant under hydrothermal condition. This mesoporous Ti-silica was tested for epoxide preparation under liquid phase condition in presence of tert-butylhydroperoxide (TBHP) oxidant. On the contrary, Cu-complex embedded MCM-41 was prepared by post-synthesis method by surface modification of MCM-41 and then applied for epoxidation of various substrates in presence of TBHP.[46] Along with epoxide formation, partial oxidation of olefins sometimes produces other industrially used fine chemicals over various metal doped mesoporous silica supports. Another Cu(II)-complex grafted SBA-16 catalyst synthesized in a similar way like Jana et al.[46] has been used for oxidation of cyclohexene in presence of mild oxidant H_2O_2, when other oxidation products like cyclohexanol, cyclohexanone etc. are produced in significant amount along with epoxide.[47] Liquid phase allylic oxidation of highly stained α-pinene, β-pinene is also feasible over UO_2^{2+}/MCM-41 producing a number of products along with respective epoxides.[48] In this connection, styrene oxidation to produce benzaldehyde as major product over Fe and Ti-SBA-1 mesoporous silica using H_2O_2, reported by Tanglumlert et al. can also be mentioned.[49] Instead of using any oxidant, oxidation of hydrocarbons using air or O_2 under mild condition is more environment-friendly and highly demanding. Mesoporous silica acts as good support for Au nanoparticles which efficiently catalyze the selective oxidation of cyclohexane in presence of molecular O_2, as reported by Wu et al.[50]

Adipic acid is a industrially important dicarboxylic acid, which can be produced exclusively from catalytic oxidation of cyclohexane, cyclohexene or cyclohexanone over mesoporous materials like WO_3/SiO_2,[51] and core-shell Fenton catalyst (Fe_2O_3/Al_2O_3),[52] respectively in presence of H_2O_2 oxidant. In Figure 3 step by step formation of adipic acid from these hydrocarbons are shown. Over core shell Fenton catalyst, the process occurs through formation of a hydroxyl radical by the reaction of Fe^{3+} with H_2O_2 and that $OH^{\bullet}$ helps to oxidize cyclohexanone to adipic acid through intermediacy of caprolactone and 6-hydroxyhexanoic acid. Cr(VI) grafted mesoporous polyaniline synthesized by radical polymerization of aniline with Cr precursor exhibits good conversion in liquid phase oxidation of alkane, alkene in non-toxic green solvent, water with reusing capability for more than five times.[53] Highly selective oxidation of cyclohexane to produce cyclohexanone is very challenging task since cyclohexanol is always obtained as a major side product. Very recently, another porous co-ordination polymer is reported by Zhang et al. who have employed atmospheric O_2 as oxidant.[54] This catalytic pathway provides an useful route for the selective conversion of β-isophorone to ketoisophorone, a significant reaction for the synthesis of vitamin E.

Porous carbon based materials are also utilized as effective support for the oxidation of hydrocarbons under liquid phase reaction conditions. N doped nanoporous carbon with supported Pd nanoparticles has showed high catalytic efficiency for the selective aerobic oxidation of indane, diphenyl methane, ethyl benzene etc. and thus providing a potential route for large scale fine chemical synthesis.[55] A new kind of boron- and fluorine-enriched polymeric mesoporous carbon nitride with high surface area has been prepared by Wang et al. who illustrate the potential of the material for selective cyclohexane to cyclohexanone conversion under mild conditions.[56] This organic semiconductor with controlled mesopore structures and narrow pore size distribution highly facilitates this selective oxidation reaction with reusability for several times without losing any activity. Heterogeneous organocatalysts are particularly demanding as they are devoid of toxic metal and thus free from the possibility of metal-leaching during the catalytic reactions. In this context porous graphitic carbon nitride (g-C_3N_4) has showed high catalytic activity in the selective oxidation of many branched hydrocarbons under mild environment-friendly conditions.[57,58]

b. Oxidation of alcohols and sulfides

The aldehydes and ketones obtained from oxidation of primary and secondary alcohols respectively are very essential intermediates in organic synthesis, pharmaceuticals, agricultural industries etc. Aerobic oxidation of long chain primary alcohol like 1-octanol with excellent yield has been obtained using small Au nanoparticle deposited on ceria or iron oxide doped hexagonal mesoporous silica (HMS) materials.[59] Synthesis of high grade benzaldehyde is particularly attractive to modern researchers for application in perfumery and food industries. A highly selective chlorine-free method of benzaldehyde production without formation of over oxidized products like acid or ester at room temperature is observed over highly ordered mesoporous ceria-silica composite which was able to convert above 50% of benzyl alcohol to benzaldehyde exclusively under solvent-free condition using TBHP. The silica supported catalyst was truly heterogeneous and stable to exhibit high recyclability up to three times towards this alcohol oxidation without minimum Ce leaching.[38] A detail study has also been undertaken by the authors to compare the product conversions at RT with that at elevated temperature. A schematic representation is given in Figure 4 to highlight the synthesis and catalysis condition for this ceria-silica catalyst. Mesoporous metal oxides are also efficient in the oxidation of primary and secondary alcohol which has been demonstrated by the catalytic potential of an interesting mesoporous nanocomposite of Cr_2O_3 and 12-phosphomolybdic acid (PMA), prepared via a “nanocasting” using mesoporous SBA-15 as hard template.[60] The catalyst Cr_2O_3-PMA solid-solution shows an extraordinary green oxidative pathway for oxidation of 1-phenylethanol to produce acetophenone with up to 85-87% yield using non-toxic H_2O_2 at very low temperature

(323 K). The synergetic interaction between the PMA clusters and Cr_2O_3 matrix via Cr-O-Mo bonds as well as dispersion of PMA over large efficient surface area of Cr_2O_3 play the key role for this selective oxidation of this secondary alcohol. Using molecular oxygen from air as a clean oxidant, oxidation of benzyl alcohol to benzaldehyde with 72% conversion and 100% selectivity is reported over highly dispersed mesoporous carbon supported iron oxide (FeO_x/H-CMK-3) under mild reaction conditions.[61] A Pd@core-shell nanosphere consisting of Pd metal clusters as core and microporous silica as outer shell also exhibits good catalytic efficiency and selectivity for the aerobic oxidation of long chain primary alcohols under solvent-free conditions.[62]

Oxidation of sulfides to obtain sulfoxide, sulfones; products playing an imperative role in organic and biological reactions as well as in anti-hypertension, cardiotonic agents etc. using industrially important heterogeneous and mesoporous catalysts replacing the homogeneous one like halogen compound, nitrates, transition metal oxides etc. has won good scientific interest.[63] Cr-grafted organic-inorganic hybrid mesoporous polymer synthesized using anionic surfactant, efficiently catalyze partial oxidation of different aromatic and aliphatic sulfides to the corresponding oxides with impressive yields having excellent recyclability and no significant loss in activity.[63] Almost selective oxidation of sulfide to sulfoxide using H_2O_2 oxidant in methanol solvent is reported over WO_3 nanoparticles supported MCM-48 heterogeneous catalyst in the year 2005.[64] The activity and stability of Mn and Cu oxo complexes have been increased to a great extent by ‘heterogenization’ of these homogeneous catalysts, i.e. by post-grafting onto mesoporous MCM-41 and the resulting supported catalysts was able to convert methyl phenyl sulphide to sulfoxide with high yield and up to five times excellent reusability in presence of TBHP.[65] Here, Mn^V=O species present in Mn-oxo salen complex stabilized in the mesoporous silica framework plays the active role for this sulphide oxidation. Mesoporous graphitic carbon nitride (g-C_3N_4) polymer has been established as green oxidation catalyst for the selective oxidation of various sulphides using visible light at room temperature.[66]

c. Oxidation of amines

Oxidation of primary amine, for *e.g.*, aniline and substituted anilines to the corresponding azoxybenzene derivatives is a very common and fundamental reaction in organic chemistry, because azoxybenzene and its derivatives have a high potential application in the synthesis of industrially important fine chemicals.[67] In 2009 a very interesting cobalt-bound polymer was prepared by Chang et al. group and the polymer was used as template to prepare mesoporous silica containing cobalt-oxide. The material exhibited good activity and reusability in the catalytic oxidation of aniline and its derivates to the respective azoxybenzenes with above 60% conversion at 298 K as well as 100% conversion at elevated temperature in presence of non-toxic H_2O_2 oxidant.[67] Apart from Co, Ti- and Zr-containing mesoporous silicas have been employed as catalysts for the oxidation of amines under variable reaction conditions.[68] An advanced approach has also been made at the end of 20th century when hexagonal mesoporous silica H_ISiO_2 was prepared using non-ionic surfactant, Brij 76 at room temperature and then modified with 3-(aminopropyltriethoxysilane) or APTES, a well-known organosilica precursor to form a NH_2-fuunctionalized organic-inorganic hybrid silica, which immobilized with various metal aqua complexes (e.g. Mn^{II}, Cu^{II}, Co^{II} and Zn^{II}). These metal complex loaded mesoporous silicas were tested for the oxidation of amine.[69] Amine oxidation follows first order kinetics and the rate of the reaction is highly dependent on the oxidizing potential of the metal complex used in the catalyst.[69] In Figure 5, the synthesis of Mn^{II}-aqua-NH_2 functionalized H_ISiO_2 catalyst and its oxidizing role for the oxidation of *o*-aminophenol is shown by a simple schematic diagram.

d. Ammoximation

Ammoximation of ketones with ammonia and dilute aqueous H_2O_2oxidant to produce oximes is a very crucial reaction in modern synthetic chemistry because oxime plays an intermediate role for fine chemical synthesis like lactam; amides etc. via secondary chemical reactions. Many metallosilicates like TS-1 have been employed as an efficient catalyst for the synthesis of oximes in the presence of NH_3 and aqueous H_2O_2.[70] The ammoximation of bulky ketones has been efficiently carried out over a Ti-grafted ethane bridged hybrid mesoporous silica support synthesized in a one pot surfactant assisted method.[71] Cyclic ketones like cyclohexanone, cyclodecanone exhibited outstanding catalytic conversion with 100% selectivity for oxime using *tert*-butanol as solvent at 353 K reaction temperature.

e. Hydroxylation of aromatics

Hydroxylation or introduction of –OH group into various aromatic substrates like benzene, toluene, phenol etc. is a commercially important chemical reaction, because the resulting phenol and substituted phenols products are used in fine chemical, agrochemical, photographic chemical, pharmaceutical and food industries.[72] Fe-incorporated mesoporous silica was prepared by simple co-precipitation method and employed for the catalytic hydroxylation of phenol to selectively produce dihydroxybenzene with proper optimization of the reaction conditions.[72] Phenol hydroxylation was also successful over a redox active group, ferrocene loaded nanocomposite made by mesoporous polymer and silica in a controlled co-polymerization route.[73] Hydroxylation of benzene to phenol is sometimes inhibited by the formation of by-products like catechol, hydroquinone etc. Very high selective conversion of benzene to phenol is reported over V-complex incorporated PMO prepared by direct co-condensation of metal grafted organo silica with inorganic silica precursor in presence of CTAB. In this fashion, $VO(acac)_2$, a well-known homogeneous catalyst 'heterogenized' by immobilizing onto silica surface,[74] catalyzes this benzene to phenol transformation in presence of H_2O_2 oxidant and the reaction is proposed to be mediated by peroxovanadyl radical (V^{5+}-O-$O^{\bullet}$) as main active species.[74] Another important example of heterogenization over a solid support is the loading of $FeCl_3$ over mesoporous carbon nitride (g-C_3N_4) and this hybrid catalyst shows up to 38% conversion of benzene to phenol with high selectivity (97%) under visible light irradiation and mild conditions.[75] In Figure 6, a schematic representation of the synthesis and catalytic role of mesoporous Zn doped aluminophosphate ($ZnAlPO_4$) is shown. Highly selective formation of phenol from benzene is observed over this Zn-doped mesoporous aluminophosphate with minor amount of hydroquinone as a by-product. The material has been synthesized by a method of physical mixing using tetrapropylammonium bromide as template (Figure 6).[76]

f. Hydrogenation and other reductions

Hydrogenation of unsaturated compounds via treatment with hydrogen or reduction in the presence of Pt, Ir, Ru, Ni, Pd nanoparticles etc. over heterogeneous support is an important chemical reaction industrially. An easy way to prepare a heterogeneous catalyst bearing the above mentioned reducing metals is via successful confinement of these metals into mesoporous support. Hydrogenation of alkene, ketones, phenol, nitro substrates etc. are some potential examples of this category and worthy to mention in this connection. Instead of reduction in gas phase under drastic condition as reported in case of Zr/Ni-doped mesoporous silica for hydrogenation and ring opening of tetralin at high temperature using H_2 gas,[77] liquid phase catalytic reactions under mild condition is more desirable from environmental view point. Asymmetric hydrogenation of various aryl substituted ketones and quinolones with high conversion was successful under very mild condition over chiral Ir and Ru complexes supported mesoporous silica, synthesized through co-condensation of an organosilica, organometallic complex $[Cp^*IrCl_2]_2$or $[RuCl_2(-C_6Me_6)]_2$ and inorganic silica precursor in presence of non-ionic Pluronic (P123) and CTAB surfactants, respectively.[78,79]

Mesoporous oxides or mixed oxides can also act as support similarly for □hioethe nanoparticles such as Au, Ni, Pt, Pd and these confined nanoparticles can catalyze the hydrogenation of aromatic nitro compounds. Mesoporous oxides like $TiO_2/Al_2O_3/SiO_2/ZrO_2$ with confined PtPd/AuPd/AuPt □hioetheri nanoparticles are synthesized under surfactant-assisted route and show highly selective synthesis of aniline from nitrobenzene under mild condition using hydrazine hydrate as hydrogenating agent.[80] On the contrary, mesostructure nickel-aluminium mixed oxides hydrothermally synthesized using lauric acid as structure directing agent, itself was efficient for a satisfactory reduction of nitrobenzene and its derivatives in 2-propanol solvent which acts as hydride donor to generate substituted anilines.[81] The synthetic pathway for the mesoporous self-assembled Ni-Al mixed oxide nanoparticles and its application for hydrogenation of nitrobenzene to aniline is shown in Figure 7. Hydrogenation of D-glucose over Ru nanoparticles impregnated mesoporous hypercrosslinked polystyrene is reported by Sapunov et al.[82] They also provided an elaborate mechanistic pathway and kinetics for the formation of D-sorbitol. In non-toxic solvent like water, selective hydrogenation of phenol to cyclohexanone over ultra-small Pd nanoparticles grafted mesoporous carbon is a highly demanding green synthesis. Pd supported N-functionalized ordered mesoporous carbon was prepared by nitration of a typical mesoporous carbon FDU-15 using NH_3 followed by treatment with aqueous solution of H_2PdCl_4.[83] The catalyst was highly heterogeneous in nature and showed reusability up to 6 times with good product yield each time.

The above mentioned redox reactions are few examples of a huge number of liquid phase catalysis that has been carried out over the years using mesoporous family of materials. In most of these cases the mechanisms of the reactions follow free radical pathway mediated by one or two radicals generated in situ.[53,74] In Table 2, we have summarized all the relevant reactions in tabular form for the convenience of the readers.

4.2 Acid-base reactions mediated by mesoporous materials

Lewis and Brønsted acid or basic sites present in a solid catalyst are the main reason of generation of acid-base property in a given solid. Lewis acidity origins due to metal ions coordinated to mesoporous support whereas –COOH, $-SO_3H$, $-NR_3^+$ etc. groups are generally responsible for Brønsted acidity. In the same way, $-NH_2$, $-NMe_2$ etc. and $–COO^-$ groups account for Lewis and Brønsted basicity, respectively. The number and strength of these sites determine the catalytic activity of the concerned materials and also their selectivity for the organic transformations. Moreover, surface property *i.e.* huge surface area and pore width of the mesoporous material gave an additional advantage compared to the other nonporous materials. Though, inherent weak acid sites restrict the application of mesoporous materials in many petrochemical reactions, but still they demonstrate a good potential for the reactions which require a lower level of acidity, for *e.g.* Friedel-Crafts alkylation of organics.[10] A lot of scientific reports such as mesoporous perovskite $ZnTiO_3$,[19] Zn-silica,[20] –COOH grafted functionalized mesoporous silica,[84] Mn-doped ceria-silica,[42] sulphonated zinc phosphonate,[85] zirconium oxophosphate,[86] and so on are published in literature till date regarding the acid-base catalytic reactions over mesoporous supports. In this section we shall illustrate some of those heterogeneous reactions carried out in liquid phase.

a. Friedel-Crafts reaction

Friedel-Crafts (FC) alkylation and acylation reactions are the set of organic reactions developed by Charles Friedel and James Crafts in 1877 to attach substituent to an aromatic ring and this is one of the most important chemical processes for laboratory synthesis and industrial production of value added organic fine chemicals.[87] These liquid phase reactions are proceeded by electrophilic aromatic substitution and usually catalyzed by Lewis acidic groups. Instead of using corrosive H_2SO_4 or solid acids like $AlCl_3$, $FeCl_3$, BF_3 etc. in homogeneous phase which suffers from the lot of environmental hazards and inconvenience due to metal leaching, non-recyclability etc. mesoporous based catalysts can be a good replacement as non-toxic, heterogeneous, low-cost catalysts. Mesoporous oxides such as, perovskite $ZnTiO_3$ was reported to be highly efficient for FC benzylation of p-xylene, toluene and benzene using benzyl chloride as alkylating agent at 343-348 K temperature to produce 1-(2,5-dimethylbenzyl)benzene, 2/4-methylbenzyl benzene, diphenyl methane, respectively with above 90% conversions.[19] The presence of strong Lewis acidic metal sites (Zn and Ti) in the perovskite material along with good surface area helps such excellent conversion to substituted aromatics. Zhang et al. has synthesized a new mesoporous iron phosphate Fe-P-O catalyst in four different methods and applied it for benzylation of benzene and other substrates.[88] The alkylation carried out using benzyl chloride, gives 100% selective formation of diphenyl methane after 3 h. On the contrary, acylation reaction using acetic anhydride, benzoyl chloride or *p*-toluoyl chloride has been observed very frequently over functionalized mesoporous materials, *e.g.* *p*-toluoyl chloride is used for liquid phase FC benzoylation of anisole at 393 K over silicotungstic acid loaded mesoporous alumina molecular sieve.[89] Instead of these hazardous acylating and alkylating agents, green non-toxic reagents like aliphatic and aromatic alcohols are also very popular to be used for FC reactions. Mesoporous Nb oxide when sulphated catalyzes benzylation of toluene and anisole in presence of benzyl alcohol to produce substituted aromatics.[90] Alkylation of toluene using benzyl alcohol has been carried out efficiently over Mo-embedded mesoporous carbon microsphere which results 100% conversion of benzyl alcohol to produce *p*-, *m*-, and *o*-benzyl toluene after just 1 h at 383 K reaction temperature and exhibits high reutilization up to three cycles without any decay in activity. High oxidation state Mo(VI) along with porous structure of carbon allowing free movement of reactants and products between embedded α-MoO_3 and liquid medium mainly accounts for this excellent catalytic performances.[91] Different FC products obtained from different substrates using different alkylating and acylating reagents are shown in Figure 8.

FC reactions are also very common over mesoporous silica based materials as revealed from many recent reports. A 3D network of mesoporous gallosilicate (GaSBA-1) was prepared in an acidic medium using cationic surfactant CTAB and appropriate amount of Ga salt. This material has been tested for the benzylation of various aromatics using benzyl chloride. The catalytic role of Ga species along with a schematic representation of suitable mechanism has been mentioned and explained by the authors.[92] A Cu(II) complex containing chiral bis(oxazoline) ligand has been immobilized on mesoporous silica and the catalyst was employed for asymmetric benzoylation of 1,2-diphenyl-1,2-ethanediol which produces highly enantioselective product using benzoyl chloride under mild condition.[93] There are many other reports of alkylation of aromatics using alcohols over metal doped mesoporous silica. Sulphated Zr-MCM-41 and –MCM-48 solid acid catalysts have successfully catalyzed attached substituent to aromatic ring of phenol in presence of tert-butyl alcohol to produce 4-*tert*-butyl phenol as major product with above 90% yield at 413 K temperature.[94]

b. Esterification and transesterification reactions

Esterification and transesterification reactions are widely employed today for the biofuel production, which is an alternative and renewable source of fuel in most of the developed countries. The condensation of carboxylic acid with alcohol in presence of any acid catalyst is named as esterification by German chemist Emil Fischer whereas the conversion of one ester to another carboxylic acid ester using alcohol and acid or base as catalyst is called transesterification (Figure 9). Generally, the reactions of triglycerides *i.e.* triesters of glycerol or any other fatty acids with short chain alcohols like methanol or ethanol are categorized as biodiesel reactions.[95]

Both Lewis and Brønsted acids are used as catalysts for the esterification of long chain fatty acids and the equilibrium of the reversible reaction can be right shifted towards the ester conversion by removing water from the reaction medium through azeotropic distillation or using molecular sieves or taking an excess of alcohol.[19] Replacing previously used strong Brønsted acids like H_2SO_4, *p*-TsOH various environmentally non-hazardous, recyclable functionalized mesoporous materials are designed and these are successfully employed as heterogeneous catalyst for the biodiesel production. The mechanism of esterification reaction over solid acid catalysts can proceed via activation of carboxylic acid by catalyst, then nucleophilic attack by alcohol on activated carbonyl carbon to form tetrahedral intermediate and finally formation of ester with elimination of one molecule water.[19] Esterification of long chain fatty acid with alcohol and vice versa is observed over mesoporous zirconium oxophosphate material which not only produces the corresponding ester in high yield but also shows high reusability up to 5th cycle, the catalytic activity being attributed to the large surface area and large number of acidic sites located at the surface of the phosphate material.[86] In Figure 10, a simple scheme for synthesis of this Zr-oxophosphate material is shown along with its application in the proposed mechanistic pathway for acid catalyzed reaction. The presence of the acidic sites necessary for catalytic activity in the Zr-catalyst has been investigated and quantitatively estimated by using the temperature-programmed desorption of ammonia (NH_3-TPD) measurement.[86] TPD result suggested that with the increase in surface Brønsted acidity the higher yield of the biodiesel products are obtained. Esterification over periodic mesoporous silica materials have been described in the review published by Yang et al. in 2009.[96] MCM-48 supported tungstophosphoric acid acts as highly potential heterogeneous catalyst for esterification of a number of fatty acids like palmitic, lauric, stearic, isostearic, myristic etc. with alcohols e.g. cetyl, butanol, hexanol, octanol etc. in 11 Mpa super critical CO_2 medium at 373 K temperature to produce esters in appreciable amount which increases with increasing chain length of fatty acids.[97]

Transesterification reaction involves acid or base mediated reaction, where increasing the electrophilicity of carbonyl carbon of fatty acids or the nucleophilicity of attacking alcohol can improve the reaction rate considerably.[95] Sulphonated porous zinc phosphonate is a example of the green catalyst, which provide eco-friendly route for the biodiesel production via transesterification of long chain fatty acids in presence of methanol at room temperature.[85] Thus, ordered Zn-doped mesoporous silica[20] or amine-functionalized mesoporous organosilica[98] or mesoporous polyoxometalate-tantalum pentoxide composite, $H_3PW_{12}O_{40}/Ta_2O_5$[99] are very active acid catalysts to give satisfactory yield of the respective esters under suitable conditions. In mesoporous $H_3PW_{12}O_{40}/Ta_2O_5$ composite, $(\equiv TaOH_2)_n^+[H_{3-n}PW_{12}O_{40}]^{n-}$ species formed at the catalyst surface of the composite *via* Ta-O-W bond, facilitate the electron transfer from the terminal oxygen atoms of W=O groups to Ta_2O_5; encouraging a well amount of proton release to ensure high Brønsted acidity of the catalyst responsible for the biofuel conversion.[99] On the contrary, transesterification using base catalysts has been efficiently carried out over Mn-doped ceria-silica;[41] MgO-functionalized mesoporous silicas,[100] etc. Mn doped ceria-silica catalyzes transesterification of methyl benzoate and ethyl cyanoacetate, ethyl chloroacetate with methanol, butanol and octanol under solvent-less mild reaction conditions. The basic sites present in the MgO-silica was determined by CO_2 sorption measurements and the sites helps to produce biofuel from vegetable oil in the presence of ethanol, achieving a conversion level of above 90% within 5 h reaction time.[100]

c. Acetalization reactions

Acetalization is widely used in the synthesis of natural product or industrially important chemicals, which are employed for the protection of active functional groups like aldehydes or ketones in a molecule and thus usuful in designing a multi-functional molecule. Acetal formation occurs through the nucleophilic addition of an alcohol to carbonyl compounds in presence of an acid.[101,102] Mesoporous solids are used extensively as acid catalysts for acetalization, for e.g. methanol was used to acetalize cyclohexanone at room temperature over mesoporous silica catalyst, which shows remarkable shape selectivity and a good correlation of catalytic activity with pore diameter of the corresponding mesopores.[103] Acetalization of cyclohexanone using methanol to produce dimethyl ketal is also successfully carried out over mesoporous zirconia functionalized with $–SO_4$ gr. and conversion over 90% with 100% selectivity is observed within very short reaction period (45 min)[101] Glycerol is also used for acetalization of acetone over stable Ni-Zr supported mesoporous carbon catalyst, when selectively two products, 5-membered solketal and six-membered acetal were obtained under solvent less condition (Figure 11).[104] Another interesting acetalization process is that of the reaction of heptanal with 1-butanol over various sulphonic acid functionalized mesoporous organosilica.[105] Three types of organosilica, *viz.* arene sulfonic acid ethane-silica (AS-MES), mercaptopropyl ethane-silica (Pr-SH-MES) and arene sulfonic acid functionalized SBA-15 were prepared using Pluronic non-ionic surfactant, P123 and then post-functionalized with $–SO_3H$ group via treatment with H_2O_2/H_2SO_4 solution.These acid sites in the organosilica help to acetalize heptanal with butanol to form the corresponding acetal.[105]

d. Aldol condensation

Carbon-carbon bond formation reaction in various large biomolecule and industrial fine chemical syntheses are largely dependent on aldol condensation reaction, a well-known organic reaction of enol or enolate ion with a carbonyl compound in order to form a β-hydroxyaldehyde or β-hydroxyketone or ‘aldol’ (aldehyde+alcohol), followed by dehydration of the intermediate to produce an α,β-unsaturated carbonyl compound. The reaction is catalyzed by both acid and base to form enol and enolate ion, respectively. Conventionally used Brønsted bases like NaOH, $Ca(OH)_2$, $Ba(OH)_2$, etc. and acids such as acetic acid, Lewis acids like $M(Otf)_n$ (M = Zn, Cu, Pb, Sc etc.) produce hazardous, toxic by-products causing a lot of environmental pollution. Hence, aldol reaction over mesoporous catalysts in heterogeneous media is highly demanding.[106]

Mesoporous carbon can act as good support for metal nanoparticles or metal oxide to improve the catalytic performances, for e.g. Mg-Zr mixed oxide supported on mesoporous carbon catalyzes cross-aldol reaction of furfural and acetone followed by hydrogenation-dehydration, to form C_8 and C_{13} alkanes at 323 K temperature, the conversion and selectivity being high enough than that with bulk Mg-Zr mixed oxide.[107] The reaction mechanism and the kinetic model of aldol condensation over the distributed basic sites of this supported catalyst are also explained by the authors. Bai et al. have synthesized mesoporous γ-Al_2O_3 based on cation–anion double hydrolysis method and the material was proved to be truly efficient for the aldol reaction of cyclohexanone carried out in a water-separating device in the form of water-cyclohexanone azeotrope at 438 K temperature for 2 h when the conversion was as high as

~70%. The remarkably high catalytic activity of crystalline γ-Al_2O_3 could be attributed to the huge surface area, precise mesopore diameter, absence of anionic species as well as surface basicity generated due to aluminium and oxygen vacancies.[108] Based on the experimental results they also proposed a suitable mechanism for the formation of α,β-unsaturated ketone involving the absorption of α-H of cyclohexanone by the aluminium vacancies. Aldol condensation of benzaldehyde and heptanal to form jasminaldehyde under solvent free condition is reported over novel Mg-Al mixed oxide supported on hexagonal mesoporous silica (Figure 12).[109] The bi-functional behaviour of this catalyst, where the weak acid sites activates the aldehyde by protonation and the basic sites favours the formation of enolate heptanal intermediate for carrying out the reaction successfully.[109] In this context a completely metal-free organocatalyst has been developed via heterogenizing (S)-proline on MCM-41, which catalyzes asymmetric aldol condensation of *p*-nitrobenzaldehyde and 2,2-dimethyl-1,3-dioxan-5-one under the influence of different solvents ranging from hydrophobic to hydrophilic proving hydrophilic polar media more suitable for catalysis.[110]

e. Knoevenagel condensation

Unlike aldol reaction involving the condensation of two carbonyl compounds, Knoevenagel condensation involves the reaction of a carbonyl compound with a compound containing active methylene group followed by the dehydration to form C-C bond resulting a α,β-unsaturated compound. The reaction is generally mediated by basic catalyst and claims to be one of the most important environment benign C-C bond formation reactions, because water is the only by-product produced in this condensation.[1] Instead of using soluble amine bases in homogeneous media, any amine based heterogeneous support or metal support with basic sites will be more suitable as non-toxic pollution free catalyst for such reactions.

Mesoporous $Ce_xZr_{1-x}O_2$ solids consisting nanometer sized particles have been synthesized via sol-gel method and it showed excellent chemoselectivity for the classical Knoevenagel condensation of benzaldehyde and malononitrile owing to the presence of large pore size (~10 nm) and both surface acidic and basic sites.[111] Knoevenagel reaction under mild condition is also reported over ordered mesoporous Ni-Al mixed oxide obtained from Ni-Al-layered double hydroxides (LDHs) by ultrasonic irradiation using Pluronic-F127 surfactant. The catalyst exhibits high selectivity for the product with well reusability without significant loss in activity.[112] Mesoporous oxides without basic sites can also be used for Knoevenagel reaction after proper functionalization of the oxide surface with amine groups. By co-condensation of 3-aminopropyltrimethoxy silane and zirconium precursors in CTAB surfactant solution mesoporous amine grafted zirconia can be prepared and used for condensation of benzaldehyde and malonic ester, diethyl malonate in methanol solvent at room temperature to produce cinammic acid exclusively.[113] Besides this, as a metal-free organocatalyst, guanidine base immobilized on mesoporous silica SBA-15 and urea embedded mesoporous polymer are highly recommended for Knoevenagel reaction.[114,115] Two types of Knoevenagel condensation, one between benzaldehyde and ethyl cyanoacetate, and another between cyclohexanone and benzylcyanide has been reported over basic guanidine functionalized silica at RT as well as elevated temperature.[114] On the contrary, mesoporous urea-functionalized polymers synthesized through non-ionic F127 surfactant-directed urea-phenol-formaldehyde oligomers self-assembly approach has been utilized for Knoevenagel reaction of aromatic aldehyde and ethyl cyanoacetate at mild temperature in non hazardous aqueous medium. In Figure 13, a simple pictorial representation for the synthesis of this mesoporous urea-polymer along with a proposed mechanism for the catalytic reaction over this polymer is shown. The synergic effect between urea active sites embedded on mesopore wall and its neighbouring surface phenolic–OH groups in the mesoporous support accounts for the success of this reaction along with good stability of the catalyst inhibiting the leaching of active species as documented through successful reuse up to six reaction cycles.[115]

f. Baeyer-Villiger oxidation

Baeyer-Villiger (BV) oxidation involves oxidative cleavage of a carbon-carbon bond adjacent to a carbonyl, which forms esters and lactones from acyclic ketone and cyclic ketones, respectively. This reaction is important for industrial production of bioactive chemicals and generally proceeds in the presence of peracids like $C_6H_5CO_3H$, CF_3CO_3H etc. or non-toxic, less hazardous hydrogen peroxide along with Lewis acidic or sometimes basic catalysts.[116] The reaction has been successfully employed for the conversion of cyclohexanone, cyclooctanone, ethyl methyl ketone and methyl isopropyl ketone to the respective to lactones and esters in presence of non-siliceous mesoporous Mg-Al mixed oxide catalyst using H_2O_2.[117] The high surface area and nanoscale porosity alone with considerably good amount of basic sites present in porous $MgAl_2O_4$ catalyst accelerate the reaction process. However, the above reaction was carried out in benzonitrile as co-solvent at elevated temperature (343 K) for which formation of benzamide is observed as a by-product and this minimises the selectivity of desired lactone and ester. The conversion and selectivity of cyclic and acyclic ketones with or without using benzonitrile is shown in Figure 14. A more convenient and mild condition has been employed by Jeong et al. who carried out the BV reaction over metal doped PMO at quite lower temperature (313 K) in presence of molecular oxygen (O_2)/benzaldehyde system. For highly selective conversion of cyclohexanone to ε-caprolactone they used different metalloporphyrin (Fe, Cu, Sn) bridged periodic mesoporous organosilica materials among which Fe-catalyst has been proved to be most promising and efficient catalyst for this reaction.[118] Using O_2/benzaldehyde as an oxidizing agent, environment benign green catalytic route has been reported over mesoporous zirconium phosphate material which exhibits strong ability to catalyze the conversion of cyclic ketones even bulkier one like adamantanone, to the corresponding lactones with high yield and 100% selectivity at RT under solvent-free condition.[119] A free-radical reaction pathway facilitated by the Lewis acidic sites present in this mesoporous Zr-phosphate catalyst has been suggested. The catalyst is chemically stable and showed good recyclability, suggesting the procedure economically advantageous for industrial purposes.

g. Beckmann rearrangement

Beckmann rearrangement, named after the German chemist Ernst Otto Beckmann, is another important acid-induced reaction in organic chemistry to form lactams and amide from cyclic and acyclic oxime, respectively. The reaction is generally catalyzed by strong acids like polyphosphoric acid, sulphuric acid etc. Though instead of using these corrosive acids there are some reports of Beckmann rearrangement over mesoporous acid catalysts, but most of those reactions proceed under drastic conditions like high temperature in vapor or gas phase.[120] Liquid phase rearrangement of cyclohexanone oxime to form ε-caprolactam (with about 50% yield) was observed in a series of solvents over acidic sites of Al doped mesoporous MCM-41 molecular sieves by Ngamcharussrivichai et al. although the conversion and selectivity level is low.[121] Few years later, sulphonic acid functionalized mesoporous organosilica with SBA-15 type nanostructure has been employed for this reaction, but the yield and selectivity of lactam did not improve so much. But the material is quite interesting as heterogeneous metal free organocatalyst mediated catalytic transformations are comparatively scare.[122] The above acid-base reactions are summarized in Table 3. These acid-base reactions mentioned here are few examples of wide range of mesoporous catalyst-mediated liquid phase organic transformations reported in literature.

4.3 Different coupling reactions over mesoporous catalysts

Involvement of mesoporous solids for hydrosilylation, cyanosilylation, Diels-Alder, Suzuki reactions etc. mediated C-C, C-N, C-H, C-S, C-O coupling and cross coupling reactions in heterogeneous media to synthesize various value-added organic fine chemicals is a widely recognized area of research now-a-days. Transition metals like Cu, Ni, Fe etc. or noble metal like Au, Pt, Pd etc. supported mesoporous siliceous and non-siliceous materials, polymers or carbons play an imperative role for these types of organic transformations.[123] A concise report on all these reactions are mentioned in the following sections and these are also summarized in Table 4.

a. Reactions involving C-C coupling

Replacing metal based homogeneous catalysts which suffer from the drawback of catalyst recovery, regeneration of the original activity, corrosiveness, metal based heterogeneous mesoporous support with exceptionally high surface area, tunable pore opening in nanoscale dimension are highly desirable for different C-C homo or cross coupling reactions[124] as mentioned below.

Sonogashira coupling reactions is a highly demanding reaction in organic synthesis, which is usually catalyzed by Pd metal to form C-C bond between a terminal alkyne and an aryl or vinyl halide in presence of amine base and with or without Cu co-catalyst.[124] Instead of using Pd metal directly, Pd-grafted mesoporous silica, polymer or carbons are highly appreciated as non-corrosive, stable, environment-friendly, highly reusable catalyst for production of aryl or vinyl substituted alkyne using Sonogashira reaction. Using Cu catalyst the mechanism is initiated with the simultaneous formation of copper acetylide complex when the copper ion catalyst attacks on the terminal alkyne in presence of base and oxidative addition of organic halides occurs to Pd(0) form a Pd(II) intermediate complex. The Pd(II) intermediate on reaction with copper acetylide followed by reductive elimination gives the final C-C coupled product with regeneration of Pd(0) catalyst.[125] The reaction is reported to be highly successful over Pd-grafted triazine functionalized ordered mesoporous polymer material,[125] Pd nanoparticles loaded mesoporous polysaccharide-derived material,[126] etc. The catalysis in former case (Pd-polysaccharide) were carried out without Cu co-catalyst in microwave condition at 403 K temperature, while later (Pd-triazine polymer) employs much lower temperature (363 K) and green solvent water for coupling of substituted aryl halides with phenylacetylene in presence of triethanol amine and Cu catalyst. Similar experiment was carried out very efficiently by Modak et al. with Pd-loaded periodic mesoporous silica catalyst in aqueous media at 393 K temperature using hexamine base and without any Cu catalyst.[124] The yield was very satisfactory in this Cu-free Sonogashira reaction and a suitable mechanism has also been proposed showing thecoupling between Pd(II) intermediate and alkyne to form an alkyne co-ordinated Pd complex which followed by the attack of base produced the final product with regeneration of catalyst.[124] A comparative mechanism of Sonogashira coupling without and with Cu co-catalyst over Pd@PMO material and mesoporous Pd@ triazine polymer, respectively has been proposed in Figure 15. An extraordinary approach has been made by Reddy et al. who tested acyl sonogashira coupling reaction using acyl halide (instead of aryl halide) over mesoporous tin silicate material (an alternative to Pd catalyst) synthesized in a simple surfactant assisted soft-templating route.[127] The reaction was performed at room temperature under solvent-free condition using triethyl amine as base as well as solvent and the catalyst was highly stable for reusing several cycles to produce a high yield of ynones.

Suzuki or Suzuki-Miyuara cross coupling reaction first published by Akira Suzuki 1979 is the organic reaction of an organoboronic acid with a aryl or alkyl halide in presence of Pd(0) to form C-C coupled product with or without using a base.[124] Compared to the homogeneous counterparts, Pd-grafted mesoporous catalysts provide an ease of product separation, catalyst recovery by simple filtration and excellent recycling efficiency. Recently, a number of reports have been revealed regarding this Suzuki coupling reaction studied in presence of Pd immobilized heterogeneous mesoporous silica or polymer using mild reaction conditions. The reaction proceeds through oxidative addition of halide to Pd(0) to form organopalladium(II) halide. This species on reaction with organic base followed by a nucleophilic attack by boronate species via transmetalation forms organopalladium(II) species. Finally reductive elimination of the desired biaryl or divinyl the original palladium(0) catalyst is restored.[128,129] Ordered mesoporous carbon with loaded Pd nanoparticles has also been utilized for Suzuki coupling reaction in DMF/water solvent at 423 K temperature (Figure 16).[130] A base free route is suggested using a sodium salt of boronic species instead of organoboron compound (Figure 16). Karimi et al. have carried out the reaction with Pd-grafted mesoporous ionic-liquid framework organosilica in aqueous media in presence of K_2CO_3 at very mild conditions.[131] The reaction is very successful at room temperature with satisfactory yield. Not only Pd, Au metal anchored mesoporous support also has high efficiency and true heterogeneity for Suzuki homo coupling reactions at mild conditions which is not quite rare in literature.[132]

Another example of C-C cross coupling is **Heck or Mizoroki-Heck reaction** involving an interaction between unsaturated halide (or triflate) with an alkene in presence of base and palladium catalyst or palladium □hioetherific-tethered catalyst to form a substituted alkene via C-C bond formation. Allowing substitution on planar system the reaction is very much important in organic synthesis ranging from natural product to bioactive compound and the development of organic electronics.[133] Bases used in this reaction are generally triethylamine, potassium carbonate, sodium acetate, etc. The reaction occurs through the oxidation addition of halide with Pd(0) species to form Pd(II) halide intermediate, then formation of a π-complex with alkene, next some rearrangement and β-elimination to form a new palladium-alkene π-complex, finally reductive elimination to give final product with regeneration of catalyst.[133] The reaction in non-hazardous water-ethanol mixture using Pd loaded mesoporous polymer shows a high percentage of conversion in very short time,[125] whereas there is always a positive effort to use more green solvent like water for such reaction and a bit lower reaction temperature. Mondal et al. have successfully employed Pd-loaded triallylamine based mesoporous polymer catalyst for Heck coupling reaction.[133] The scheme in Figure 17 illustrates a simple route for the synthesis of this Pd-based mesoporous polymer and Heck coupling reaction over this catalyst. Another convenient and environment friendly method is the reaction in solvent-free condition as reported by Ma et al. They employed a highly reusable Pd supported on 1,1,3,3-tetramethylguanidinium (TMG) ionic liquid modified mesoporous SBA-15 catalyst for Heck coupling of different aryl halides with substituted olefins at 413 K temperature to produce C-C coupled arylated olefins and the yield was high enough with respect to reaction time and amount of the catalyst showing excellent activity for several reaction cycles without significant metal leaching.[134] On the contrary, Pd supported on $NiFe_2O_4$ catalyst, highly efficient for Mizoroki-Heck reactions of chloro, bromo and iodo substituted aryl halides with styrene in DMF solvent, has an advantage of separation magnetically from reaction mixture.[135]

Hiyama coupling, another palladium-catalyzed cross-coupling reaction used in organic natural products synthesis involves reaction of an organosilanes with organic halides chemistry to form carbon-carbon bond (C-C bond) in presence of an activating agent such as a fluoride ion or a base. The use of expensive fluoride source and hazardous organic solvents like DMF, DMSO etc. is recently modified by Modak et al. who suggested a suitable mechanistic pathway Hiyama coupling reaction without any fluoride source at moderate temperature over a newly developed Pd-grafted PMO.[124] They used NaOH to maintain the alkaline condition and water as solvent to make the process more environment-friendly. The heterogeneity of the Pd-catalyst was proved by different test like hot filtration test, three phase test, solid phase poisoning test which show minimum metal leaching with retention of catalytic activity. Recently, another interesting catalyst is Pd nanoparticles loaded SBA-15 material designed by deposition of Pd nanoparticles in the micropores of SBA-15, consisting hydrophobic trimethylsilyl (TMS) or triphenylsilyl (TPS) group functionalized mesopores.[136] In Figure 18, we have shown a scheme for synthesis of this novel catalyst. This nanocatalyst shows an excellent activity for the Hiyama cross-coupling between various aryl triethoxysilanes and aryl halides under relatively mild reaction conditions (373 K) to form different biphenyl derivatives.

Ullmann reaction named after scientist Frietz Ullmann, is a homo coupling reaction of aryl halides to form symmetric biaryl derivative in presence of Cu, Pd, Au catalysts (Figure 19). A number of reports have been published till date about Ullmann reaction in aqueous media to provide a green route for synthesis of biphenyls over heterogeneous catalysts. Ullmann reaction of iodobenzene to form biaryl with maximum ~80% yield and high selectivity in water as solvent was carried out over a novel Pd doped Ph and Al- functionalized MCM-41 catalyst.[137] Coupling of substituted chlorobenzene over heterogeneous palladium catalysts, supported on ordered mesoporous silica-carbon nanocomposites was carried out both at normal and elevated temperature showing product formation increasing with temperature.[138] The reaction is also catalyzed by a novel recyclable catalyst comprising Au nanoparticles embedded bifunctional phenyl containing periodic mesoporous organosilica (Au@PMO)[139] with unexpected high yield (above 90%) and negligible leaching of metal (Figure 19).

Stille reaction or **Migita-Kosugi-Stille** coupling, used extensively in organic synthesis is the reaction of an organotin or organo stannanes compound with a sp^2-hybridized organic halide catalyzed by palladium usually performed under inert atmosphere (Figure 19). The mechanism involves three basic steps like there coupling reactions, oxidative addition, transmetalation and reductive elimination. A highly efficient, reusable Pd mesoporous catalyst reported by Singh et al. was synthesized by grafting Pd anchored triazole ligand on the surface of functionalized benzene containing periodic mesoporous organosilica with uniform hexagonal arrangement prepared under basic conditions using CTAB surfactant.[140]

Beside these reactions, there are **Negishi coupling** involving C-C cross coupling of an organozinc compound with an organic halide over a nickel or palladium based homogeneous or heterogeneous catalyst[141] and **pinacol coupling** which is a acid catalyzed homo coupling of carbonyl compound to form a 1,2-diol.[142] Though the reactions over metal doped mesoporous supports are not reported till date, but research is going in full phase to design suitable mesoporous catalysts for carrying out these coupling under mild reaction conditions.

b. Reaction involving C-S coupling

In order to design new target molecules in synthetic organic, biological and pharmaceutical research via carbon-sulfur bond formation, C-S coupling reaction of aryl or substituted aryl halides with different sulfur containing reagents for e.g. thiol,[143] thiophenol,[144] thiourea,[145] etc. has drawn great attention of modern scientists. Replacing transition metals like Fe, Ni, Pd, Cu, Co mediated hazardous homogeneous catalysts; metal based heterogeneous supports are much more effective for C-S coupling reactions to form diaryl sulfides in various polar organic solvents and an inert atmosphere (Figure 20). Various metals, mixed metal oxide nanoparticles, metal complexes supported mesoporous catalysts are reported till date suggesting an easy, reusable, simple mechanistic pathway for this aryl-sulfur coupling reactions.[144]

Mesoporous Cu-Fe-hydrotalcite solid catalyst is a ligand free novel environmentally green catalyst for C-S coupling reactions using thiols with different aryl halides in DMF solvent and K_2CO_3 base. The homogeneous mixed phase of two oxides (CuO and Fe_2O_3), good BET surface area (123 m^2g^{-1}) and large pore diameter (~15 nm) are mainly attributed to the observed high conversion of products achieved within reaction time 4-10 h.[143] CuO well-dispersed on mesoporous silica prepared in a sol-gel route is a highly reusable heterogeneous support for S-arylation of aryl iodides with thiols in presence of Cs_2CO_3 base and DMSO solvent. $Cu(Oac)_2$ loaded on organic inorganic hybrid mesoporous silica functionalized with furfural group is also applied for aryl-sulfur coupling of thiophenol with aryl iodide in presence of K_2CO_3 base and DMF solvent.[144] The yield observed for different substituted diaryl sulfides was very satisfactory with proper reusable efficiency shown up to 5th cycle. A synthesis scheme of mesoporous Cu grafted furfural functionalized organic-inorganic hybrid silica is shown in Figure 21. A probable mechanism has also been suggested showing generation of Cu(0) active species from Cu(II) grafted organosilica in presence of base, followed by consecutive oxidation addition of aryl iodide and thiophenol to form another intermediate. As observed in catalytic cycle the intermediate formed releases aryl-sulfur coupled product with regeneration of active species via reductive elimination step (Figure 21).[144]

To avoid the toxicity and hazards of the polar solvents used in different C-S coupling reaction, we explored the reaction in completely green solvent water over NiO-ZrO_2 self-assembled mesoporous nanocrystals at relatively lower temperature (353 K).[145] 4-chlorothiophenol is used as sulfur source and different substituted aryl iodides to produce value added aryl-sulfur compounds with appreciable yield. NiO species present in the material mainly takes the active part for catalysis which is illustrated with a proposed mechanism in Figure 20. As an alternative to the volatile and toxic thiol or foul-smelling thiophenol sulfur source, which leads to enormous environmental and safety problems, thiourea is widely used now-a-days for large scale operation. Three component one-pot coupling of aryl halides, benzyl bromides and thiourea in aqueous media is another significant approach towards green organic synthesis.[146] A Cu-grafted mesoporous organo functionalized SBA-15 catalyst synthesized via simple post-grafting technique was employed for this one-pot thioetherifications carried out at 373 K temperature. A significant yield of aryl sulfides is resulted onto this heterogeneous, non-toxic Cu-mesoporous catalyst.[146]

There are also other coupling reactions like C-N, C-O, etc. which to the best of our knowledge are not observed to proceed over heterogeneous mesoporous materials till date.

c. Three component coupling reaction

There are some three component one-pot coupling reactions which are observed to be catalyzed by mesoporous catalysts in liquid phase heterogeneous media. These reactions of a variety of organic reagents to synthesize a new heterocyclic compounds are highly important in different fields for synthesis of natural products, fine chemicals, pharmaceutical components etc. One of such reactions is one-pot thioetherifications involving C-S coupling which is already mentioned in the previous section.[147]

Another highly significant three component coupling reaction **A^3 coupling** i.e. coupling of aldehyde, alkyne and amine, used extensively in the manufacturing of various nitrogen-containing heterocycles, natural products and biologically active compounds etc. to form propargylamine in a convenient approach. Though many metals viz. Au, Ag, Au, Cu, In, etc. based homogeneous catalysts showed efficiency for A^3coupling reactions,[148] due to the disadvantage of separation of those catalysts from reaction mixture, lack of recycling efficiency, metal leaching etc. metal immobilized heterogeneous supports are much more desirable for such reactions.[149] Ag nanoparticles supported mesoporous SBA-15 has been proved to be highly efficient for A^3 coupling reactions in glycol as 'green' solvent at 373 K temperature. The product conversion observed was believed to be highly dependent on Ag particle size and a high yield of propargylamines was obtained with *ca.* 8 nm optimized size Ag-loaded SBA-15.[150] A 2D-hexagonal periodic mesoporous organosilica containing imidazolium ionic liquid framework synthesized in acidic condition with P123 surfactant has been immobilized with 0.2 mol% of Au and a keen investigation was performed to study the catalytic ability of that Au loaded PMO heterogeneous support for A^3 coupling reaction under mild conditions.[151] In Figure 22 we have illustrated the synthesis of Au@ionic liquid PMO catalyst and its application in A^3 coupling reaction. Chloroform has been proved to be most appropriate solvent for the reaction at relatively lower temperature (333 K) with an average high yield of around 70-80% for the corresponding propargylamine derivatives.

Biginelli condensation is another three component one-pot reaction which creates 3,4-dihydropyrimidin-2(1H)-ones from aryl aldehyde, ethyl acetoacetate (EAA) and urea in presence of Brønsted or Lewis acid as catalyst. In 2010, Al-MCM-41 mesoporous catalyst was employed for this reaction in octane solvent to obtain various essential substituted dihydropyrimidinones with high yields and a high catalytic yield was obtained with a small loss of the activity after repeatedly using.[152] Later in 2012, superparamagnetic Fe_3O_4 nanoparticles impregnated on cysteine functionalized mesoporous SBA-15 has been designed and it has been proved to be a highly reusable and magnetically recoverable catalyst for one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones via the Biginelli reaction in pollution free ethanol solvent.[153] A method of synthesis of the Fe_3O_4@ cysteine functionalized SBA-15 material has been shown in Figure 23. An idea of one-pot reaction and the separation of catalyst with large bar magnet have also been illustrated in this Figure. The catalyst exhibited high yield of products using different substituted aldehydes within very short reaction time along with a suitable catalytic cycle suggested to be taking place over Lewis acidic Fe_3O_4 active sites of the catalyst. A more environment friendly approach was made by Pramanik et al. who synthesized a novel phosphonic acid functionalized 2D hexagonal mesoporous organosilica and applied this metal free catalyst for Biginelli condensation reaction under solvent-free conditions at 333 K.[154] Reaction pathway is very clean with very high yield of the products and recycling efficiency. The high Brønsted acidity of phosphonic group with huge surface area and large pore diameter of silica support can be attributed to the high activity of this heterogeneous organocatalyst.

Beside the above mentioned organic reactions taking place over mesoporous supports there are other reactions like Diels-Alder reactions, hydroformylation of olefins, aldehydes, polymerization reactions etc. are also found to be efficiently catalyzed by some metal supported or metal-free mesoporous materials under mild reaction conditions.[155-157] Further, hierarchical porosity can be introduced in the ordered porous silica composites by using anionic polystyrene spheres and triblock copolymers as templates[158] and resulting materials can be utilized as potential supports in heterogeneous catalysis for bulkier molecules where diffusion of reactant molecules could be facilitated.

5. FUTURE PERSPECTIVES AND CONCLUSIONS

To overview the potentials of mesoporous siliceous and non-siliceous materials in liquid phase heterogeneous catalysis, the present review offers a concise idea showing numerous examples of organic transformations with proper illustrations. Additionally an outline of the synthesis strategies of functionalized mesoporous materials presented here helps with suggestive information about how to design and prepare the mesoporous catalysts, tune their pore structure and specific surface area as well as impregnation with various active transition metal nanoparticles, complex or organic functional groups at the pore surface. Based on this one can prepare a number of new metal doped and organically functionalized mesoporous materials and explore their potentials in versatile catalytic transformations under liquid phase reaction conditions. Replacing conventional hazardous, toxic homogeneous catalysts, which create serious environmental problem and ecological imbalance, many reactions mediated by those metallocatalysts or metal-free heterogeneous organocatalysts in aqueous solvent or without solvent, at lower temperatures or without use of any toxic reagents. These green catalytic pathways are highly demanding for the development of industrial manufacturing processes. Thus, it is expected that in future, more and more applications of these green catalysts in each and every industrial fine chemical synthesis will create a pollution free world for the benefit of all human beings.

Acknowledgements

AB wishes to thank DST, New Delhi for providing funding through DST-SERB and DST-UKIERI research grants.

LIST OF ABBREVIATIONS

nm	Nanometer
3D	3 dimensional
CMC	Critical micelle concentration
$	Dollar sign
$VO(acac)_2$	Vanadyl(IV) acetylacetonate
Cp*	Cyclopentadienyl
Mpa	Megapascal
RT	Room temperature
HMS	Hexagonal mesoporous silica
EA	Ethyl acrylate
ECA	Ethyl cyanoacetate
EclA	Ethyl chloroacetate
EAA	Ethyl acetoacetate
TMG	1,1,3,3-tetramethylguanidinium
NP	Nanoparticle
BET	Brunauer-Emmett-Teller
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
AIBN	2,2′-azobis(isobutyronitrile)

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Legends for Figures

Figure 1	Surfactant assisted synthesis of mesoporous silica with 2D ordered hexagonal pore arrangement.
Figure 2	Steps of heterogeneous catalytic cycle over mesoporous solid.
Figure 3	Different oxidation products of cyclohexene, cyclohexanol and cyclohexanone with adipic acid as the final product.
Figure 4	A schematic representation of synthesis of mesoporous ceria-silica composites and its catalytic application for oxidation of primary alcohol (benzyl alcohol).
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Figure 19	Ullmann homo coupling reaction over Au incorporated PMO and Stille reaction over Pd@PMO.
Figure 20	A general scheme for C-S coupling reaction over mesoporous solid catalyst.

Figure 21	Synthesis scheme of mesoporous Cu grafted furfural functionalized organosilica and its role in mechanistic catalytic C-S cross coupling reaction cycle.
Figure 22	A synthesis scheme for mesoporous Au nanoparticles doped imidazole functionalized PMO and A^3 coupling reaction over this catalyst.
Figure 23	Magnetically recoverable Fe_3O_4@cysteine grafted mesoporous SBA-15 catalyst and its role in one-pot Biginelli condensation reaction.

Table 1. Possible types of mesoporous materials with examples.

Framework composition	Type of materials	Examples
Purely inorganic	Mesoporous silicas	MCM-41/MCM-48,[8] SBA-15[22] etc.
	Metal containing mesoporous silicas	Ti-MCM-41, Zn-silica etc.
	Mesoporous metal oxides and mixed metal oxides	TiO_2, AlO_2, ZrO_2, $ZnTiO_3$ etc.
	Mesoporous metallophosphates	Silicotitanium phosphate, Silicoalumino phosphate etc.
Organic-inorganic hybrid	Periodic mesoporous organosilicas (PMOs)	Various metal containing PMOs etc.
	Metal oxophenylphosphates	Iron phosphonate, chromium phosphonate etc.
Purely organic	Mesoporous carbons	CMK-3
	Mesoporous polymers	Triazine based polymer, porphyrine based polymer

Table 2. Different redox reactions in liquid phase over mesoporous materials.

Type of reactions	Catalysts	Reaction involved	Product Yield (%)	Ref.
Oxidation of hydrocarbon	Ti doped PMO	Epoxidation of styrene, trans-stilbene norbonene, etc.	65-80	45
	Cu-complex doped MCM-41	Epoxidation of cyclohexene, cyclooctene, styrene, etc.	92-99	46
	Cu(II)-complex grafted SBA-16	Partial oxidation of cyclohexene	21-77	47
	UO_2^{2+}-MCM-41	Allylic oxidation of α-pinene, β-pinene etc.	80-88	48
	Fe- & Ti-SBA-1	Partial oxidation of styrene	59-70	49
	Au loaded mesoporous silica	Oxidation of cyclohexane	10-34	50
	Core-shell Fenton catalyst	Oxidation of cyclohexanone	69	52
	Cr-mesoporous polyaniline	Oxidation of alkane, alkene	70-98	53
	Porous co-ordination polymer	Conversion of β-isophorone to ketoisophorone	85	54
	Pd@N doped nanoporous carbon	Selective aerobic oxidation of indane, ethyl benzene	14-30	55
	Boron- and Fluorine loaded mesoporous carbon nitride	Selective oxidation of cyclohexane to cyclohexanone	2-8	56
	g-C_3N_4 polymer	Oxidation of strained hydrocarbons	26-100	57,58
Oxidation of alcohols	Au-ceria or iron oxide-HMS	Oxidation of 1-octanol	10-79	59
	Mesoporous CeO_2-silica	Oxidation of benzyl alcohol	51	37
	Mesoporous Cr_2O_3 -PMA composite	Oxidation of 1-phenylethanol	85-87	60
	Iron oxide on mesoporous carbon (FeO_x/H-CMK-3)	Oxidation of benzyl alcohol to benzaldehyde	72	61
	Pd@Silica core-shell nanosphere	Solvent-free aerobic oxidation of long chain primary alcohols	10-61	62
Oxidation of	Cr-mesoporous polymer	Partial oxidation of different	7-97	63

sulfides		aromatic and aliphatic sulfides		
	WO_3 NP-MCM-48	Oxidation of different sulfides	100	64
	Mn and Cu oxo complexe-MCM-41	Oxidation of methyl phenyl sulphide	65-100	65
	Mesoporous g-C_3N_4 polymer	Selective oxidation of sulphides	39-98	66
Ammoximation	Ti-grafted ethane bridged porous inorganic-organic hybrid silica	Oxidation of cyclohexanone, cyclodecanone	42-90	71
Oxidation of amines	Mesoporous cobalt oxide-silica composite	Oxidation of aniline and its derivatives	26-100	67
	Ti, Zr-doped mesoporous silica	Oxidation of aniline	100	68
	Mn, Cu, Co& Zn-NH_2-grafted organic-inorganic hybrid silica	Oxidation of amine	90-100	69
Hydroxylation of aromatics	Fe incorporated mesoporous silica	Hydroxylation of phenol	20-50	72
	Ferrocene loaded nanocomposite of mesoporous polymer and silica	Conversion of phenol to form dihydroxybenzene	25-30	73
	VO(acac)$_2$ incorporated PMO	Selective conversion of benzene to phenol	12-38	74
	$FeCl_3$/g-C_3N_4	Conversion of benzene to phenol	38	75
	Mesoporous Zn doped aluminophosphate	Selective hydroxylation of benzene to phenol	99	76
Hydrogenation & other reductions	Chiral Ir and Ru complexes-loaded mesoporous silica	Asymmetric hydrogenation of aryl substituted ketones and quinolones	80-99	78,79
	PtPd/AuPd/AuPt -embedded TiO_2/Al_2O_3/SiO_2/ZrO_2	Selective conversion of nitrobenzene to aniline	65-87	80
	Mesostructure NiO-Al_2O_3	Reduction of nitrobenzene and its derivatives	36-57	81
	Ru-mesoporous polystyrene	Hydrogenation of D-glucose	40-43	82
	Pd nanoparticles-loaded mesoporous carbon	Selective hydrogenation of phenol to cyclohexanone	23-80	83

Table 3. Different liquid phase acid-base reactions mediated by mesoporous materials.

Type of reactions	**Catalysts**	**Reaction involved**	**Product yield (%)**	**Ref.**
Friedel-Crafts reaction	Mesoporous perovskite $ZnTiO_3$	Reaction of *p*-xylene, toluene, benzene with benzyl chloride	90-93	19
	Mesoporous iron phosphate	Benzylation of benzene, toluene, *p*-xylene	100	88
	Silicotungstic acid-loaded mesoporous alumina	Benzoylation of anisole with *p*-toluoyl chloride	80-100	89
	Mesoporous sulphated Nb oxide	Reaction of toluene and anisole with benzyl alcohol	100	90
	Mesoporous Mo-doped carbon sphere	Alkylation of toluene using benzyl alcohol	100	91
	Mesoporous GaSBA-1	Benzylation of various aromatics using benzyl chloride	95-100	92
	Cu(II) complex-bis(oxazoline) loaded mesoporous silica	Asymmetric benzoylation of 1,2-diphenyl-1,2-ethanediol	29-40	93
	Sulphated Zr-MCM-41 and Zr-MCM-48	Reaction of phenol with tert-butyl alcohol	18-91	94
Esterification	Mesoporous $ZnTiO_3$	Reaction of palmitic, lauric, oleic acid with methanol	73-92	19
	Mesoporous zirconium oxophosphate	Esterification of long chain fatty acid with alcohol and vice versa	46-91	85
	Tungstophosphoric acid-loaded MCM-48	Esterification of palmitic, lauric, stearic, isostearic, myristic acids with different alcohols	48-97	97
Trans-esterification	Sulphonated porous zinc phosphonate	Transesterification of long chain fatty acids with methanol	35-81	84
	Zn-doped mesoporous silica	Transesterification of ECA, EClA, EAA, EA etc.	25-94	20
	Amine-grafted OMS	Transesterification of glyceryl tributyrate with methanol	75-95	98
	$H_3PW_{12}O_{40}/Ta_2O_5$ porouscomposite	Reaction of palmitic, oleic, linoleic acid with methanol	20-68	99

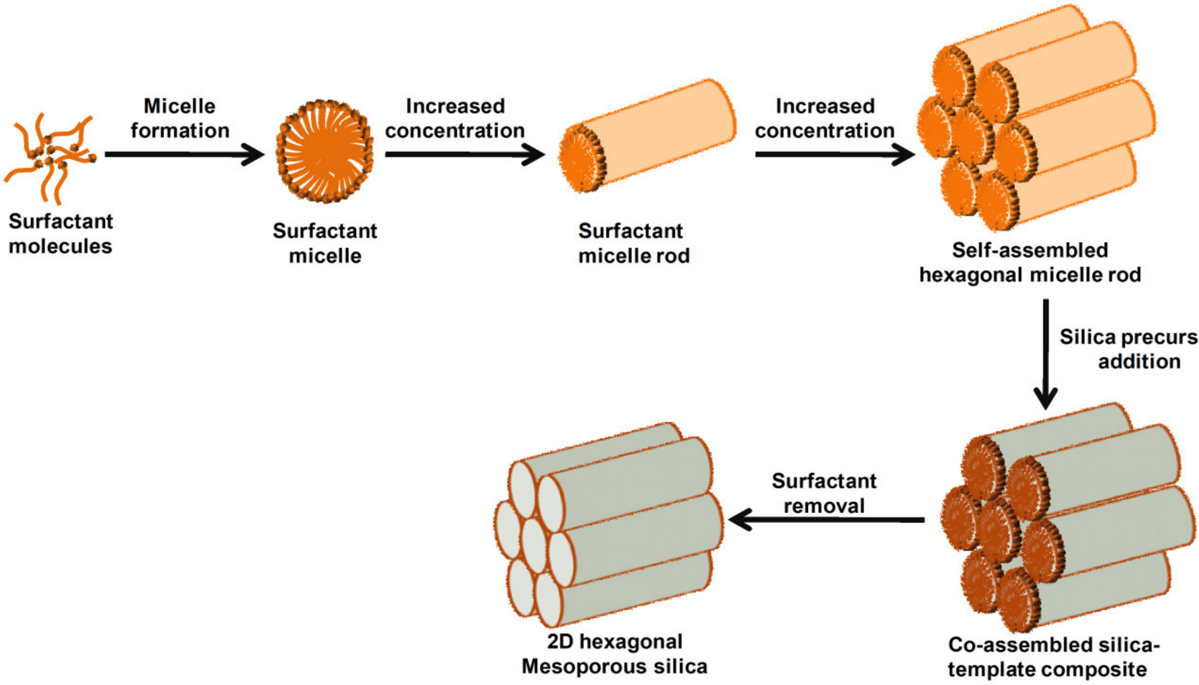
	MgO-grafted mesoporous silica	Vegetable oil with ethanol	72-96	100
Acetalization reactions	Mesoporous silica	Acetalization of cyclohexanone with methanol	87-89	103
	Mesoporous sulphatedzirconia	Reaction of cyclohexanone with methanol, ethylene glycol	72-98	101
	Ni-Zr supported mesoporous carbon	Reaction of acetone and glycerol	68-100	104
	Mesoporous SO_3H-loadedorganosilica	Reaction of heptanal with 1-butanol	39-97	105
Aldol condensation	Mg-Zr supported mesoporous carbon	Cross-aldol reaction of furfural and acetone	98	107
	Mesoporous γ-Al_2O_3	Homo aldol reaction of cyclohexanone	60-80	108
	Mg-Al mixed oxide loadedHMS	Condensation of benzaldehyde and heptanal	100	109
	(S)-proline loaded MCM-41	Reaction of *p*-nitrobenzaldehyde &2,2-dimethyl-1,3-dioxan-5-one	20-96	110
Knoevenagel condensation	Mesoporous $Ce_xZr_{1-x}O_2$	Condensation of benzaldehyde and malononitrile	72-90	111
	Mesoporous Ni-Al mixed oxide	Reaction of benzaldehyde and malononitrile	99	112
	Mesoporous amine grafted zirconia	Condensation of benzaldehyde with diethyl malonate	80-98	113
	Guanidine base loaded SBA-15	Condensation of cyclohexanone with benzyl cyanide	30-65	114
	Urea embedded porous polymer	Condensation of benzaldehyde with ECA, EAA,etc.	21-99	115
Baeyer-Villiger oxidation	Mesoporous Mg-Al mixed oxide	BV oxidation of cyclohexanone, cyclooctanone, methyl isopropyl ketone, ethyl methyl ketone	62-89	117
	Metalloprophyrin-bridged PMO	Selective conversion of cyclohexanone to ε-caprolactone	10-100	118
	Mesoporous Zr-phosphate	Conversion of cyclic ketones like adamantanone to lactones	96	119
Beckmann rearrangement	Al doped MCM-41	Cyclohexanone oxime	46-50	121
	SO_3H-grafted SBA-15	Cyclohexanone oxime to ε-caprolactam	14-52	122

Table 4. Various organic coupling reactions carried out under liquid phase conditions over mesoporous catalysts

Type of reactions	Reaction name	Reaction involved	Catalysts used	Product Yield (%)	Ref.
C-C coupling reaction	Sonogashira coupling	Reaction of iodobenzene & phenylacetylene	PdNP loaded mesoporous starch	90-99	126
		Substituted aryl halides with phenylacetylene	Pd-grafted triazine functionalized mesoporous polymer	60-90	125
		Reaction of substituted aryl halides & phenylacetylene without Cu co-catalyst	Pd-loaded periodic mesoporous silica	72-90	124
		Reaction of substituted benzoyl chloride and phenyl acetylene	Mesoporous tin silicates	76-97	127
	Suzuki or coupling	Reaction of substituted aryl halide with sodium salt of phenyltrihydroxyborate,	Pd-incorporated triazine functionalized mesoporous polymer	60-95	125
		Reaction of substituted aryl halides with substituted phenylboronic acids	Pd(II) complex anchored 2D-HMS	63-99	128
		Reaction of different aryl halides with phenyl boronic acids	Pd@imidazolium-functionalized SBA-15	87-99	129
		Substituted aryl halides with substituted phenyl boronic acids	PdNP@ mesoporous carbon	>99	130
		Coupling of substituted aryl halides with different substituted phenyl boronic acids	Pd grafted mesoporous ionic-liquid framework organosilica	55-99	131
		Coupling of substituted aryl halides with different substituted phenyl boronic acids	Au Schiff-base complex anchored mesoporous support	84-95	132
	Heck reaction	Coupling of substituted aryl halides with acrylic acid or styrene	Pd loaded mesoporous polymer	50-95	125
		Coupling of substituted aryl iodides with styrene	Pd@ mesoporous triallylamine polymer	88-95	133
		Reaction of substituted aryl iodides with substituted olefins	Pd supported TMG ionic liquid modified SBA-15	60-94	134
		Reaction of substituted aryl halides (Cl, Br, I) with styrene	Pd supported $NiFe_2O_4$	72-97	135
	Hiyama	Cross couplings of various	Pd loaded	65-95	124

	coupling	substituted aryl halides with alkyl and aryl trimethoxysilane	phloroglucinoldiimine modified PMO		
		Substituted aryl halides with different trimethoxysilane	Pd NP loaded SBA-15	70-95	136
	Ullmann reaction	Reaction of iodobenzene to form biaryl	Pd doped Ph-functionalized MCM-41	70-88	137
		Homo coupling of chlorobenzene in water	Pd@ mesoporous silica-carbon nanocomposites	100	138
		Reaction of various aryl iodides	AuNP@phenylene containing PMO	80-95	139
	Stille reaction	Organotin compound with a sp^2-hybridized organic halide	Pd loaded triazole& benzene grafted PMO	60-80	140
	Negishi coupling	Cross coupling of an organozinc compound with an organic halide	-	-	141
C-S coupling reaction	-	Reaction of 4-chlorothiophenol & substituted aryl iodides	Mesoporous NiO-ZrO$_2$ nanocrystals	39-89	145
		Reaction of thiols with different aryl halides	Mesoporous Cu-Fe-hydrotalcite	50-90	143
		S-arylation of aryl iodides with thiols	CuO well-dispersed on mesoporous silica	66-97	147
		Reaction of substituted aryl iodide with thiophenol	Cu(OAc)$_2$ loaded mesoporous furfural functionalized silica	75-88	144
		Coupling of aryl halides, benzyl bromides with thiourea	Cu-grafted imine functionalized SBA-15	80-88	146
Three component coupling	Biginelli condensation	One pot reactionof aryl aldehyde, EAA and urea	Al-MCM-41	68-89	152
		Reaction of substituted aryl aldehyde, EAA and urea	Fe$_3$O$_4$ nanoparticles @ cysteine loaded SBA-15	78-85	153
		One pot reactionof aryl aldehyde, EAA and urea	Phosphonic acid functionalized 2D HMS	83-92	154
	A^3 coupling	Coupling of aldehyde, alkyne and amine in glycol	AgNP doped mesoporous SBA-15	40-95	150
		Three component reaction of aldehyde, alkyne and amine	Oxidized Cu NP supported on titania	50-88	149
		Coupling of substituted aryl aldehyde, substituted phenylacetylene with different amine bases	Au@ionic liquid framework PMO heterogeneous support	75-88	151

Figure 1 (Paland Bhaumik)



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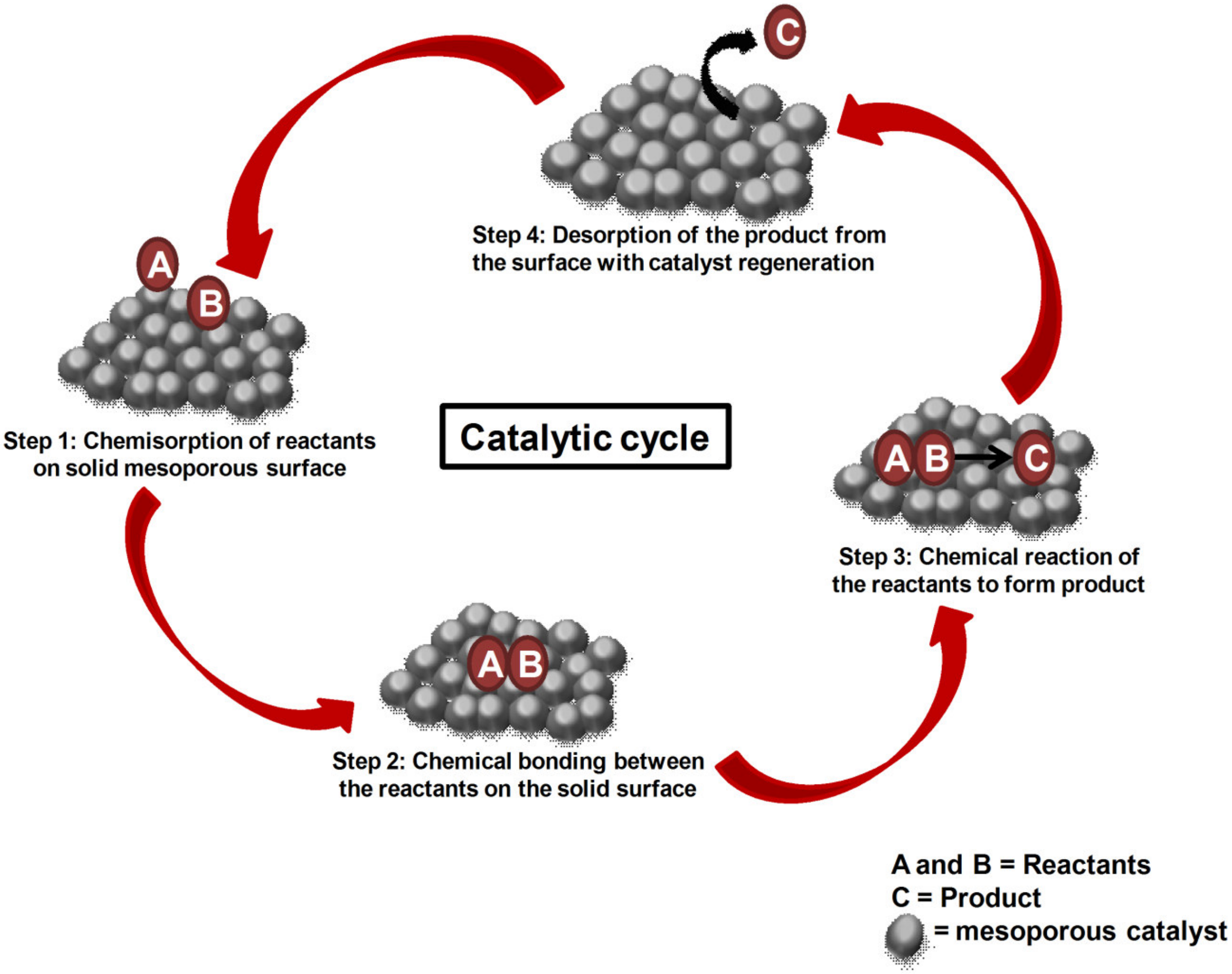

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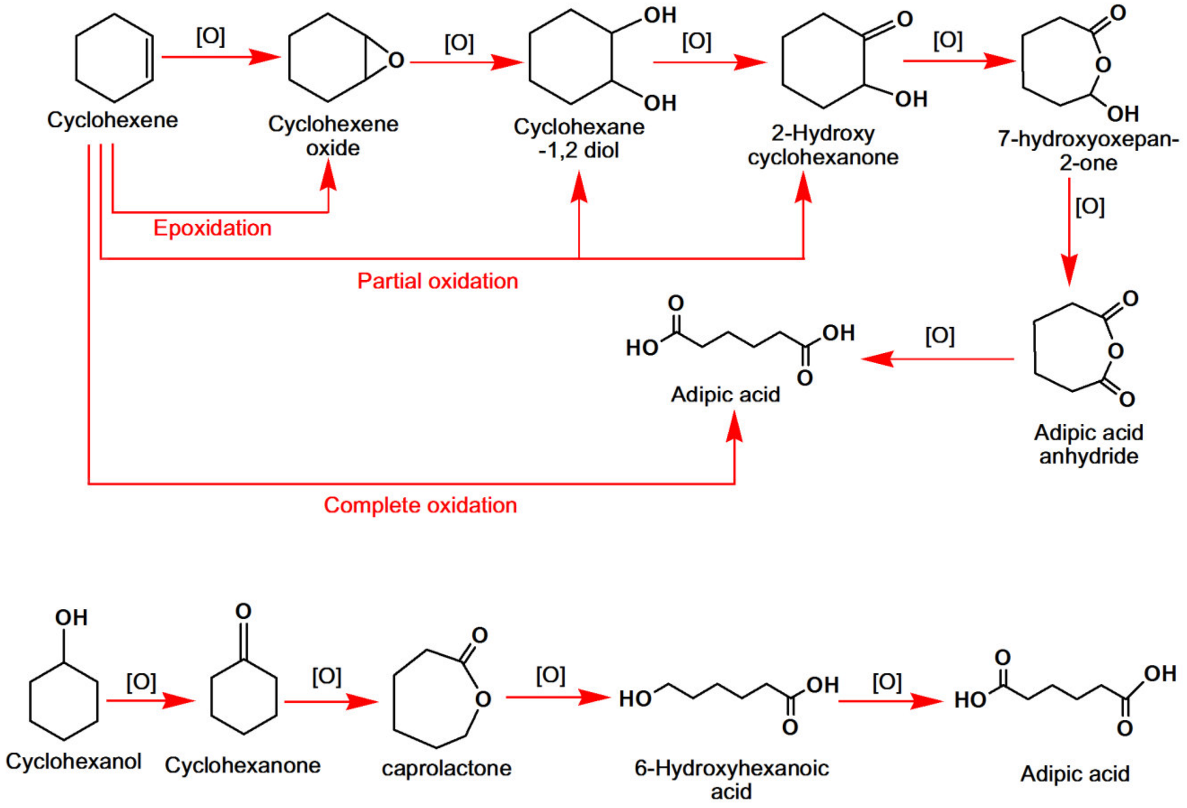

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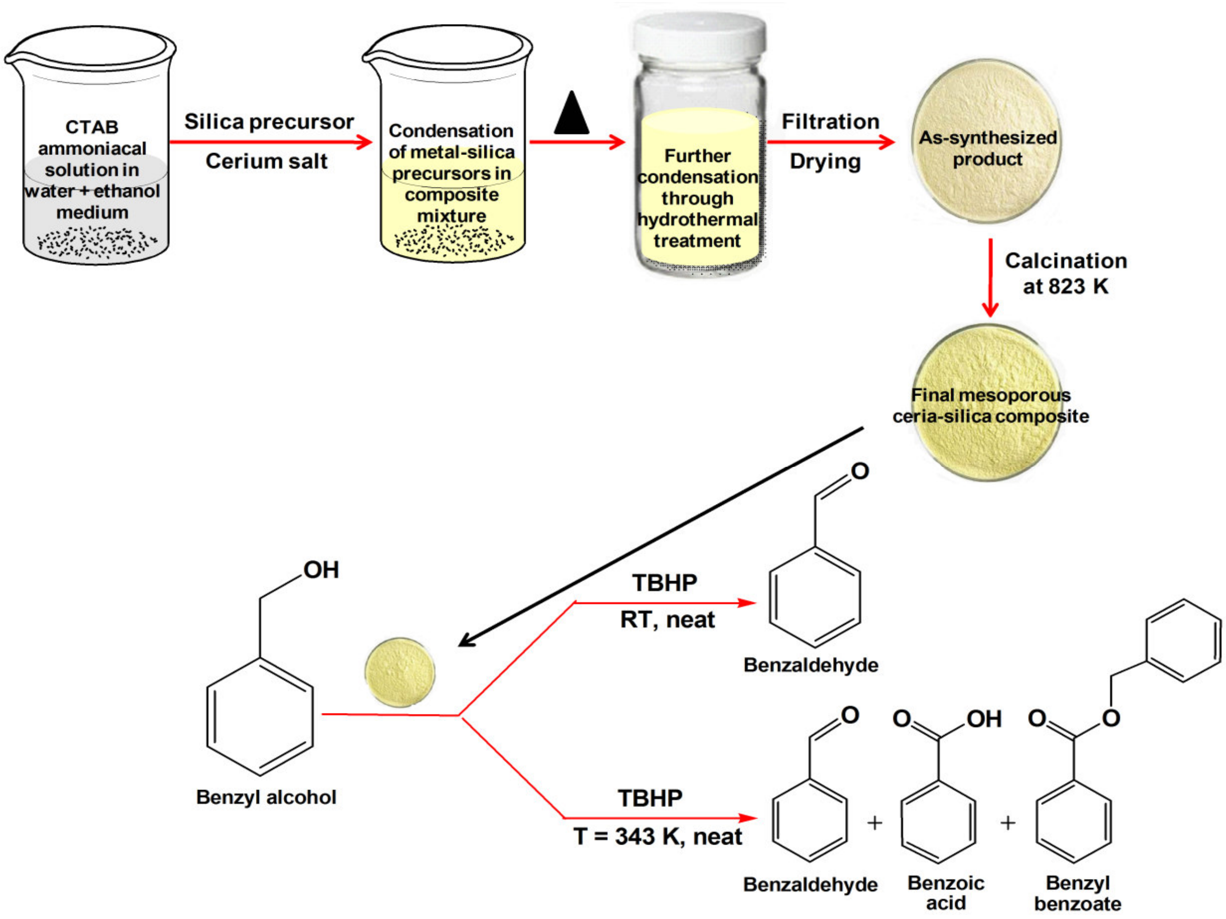

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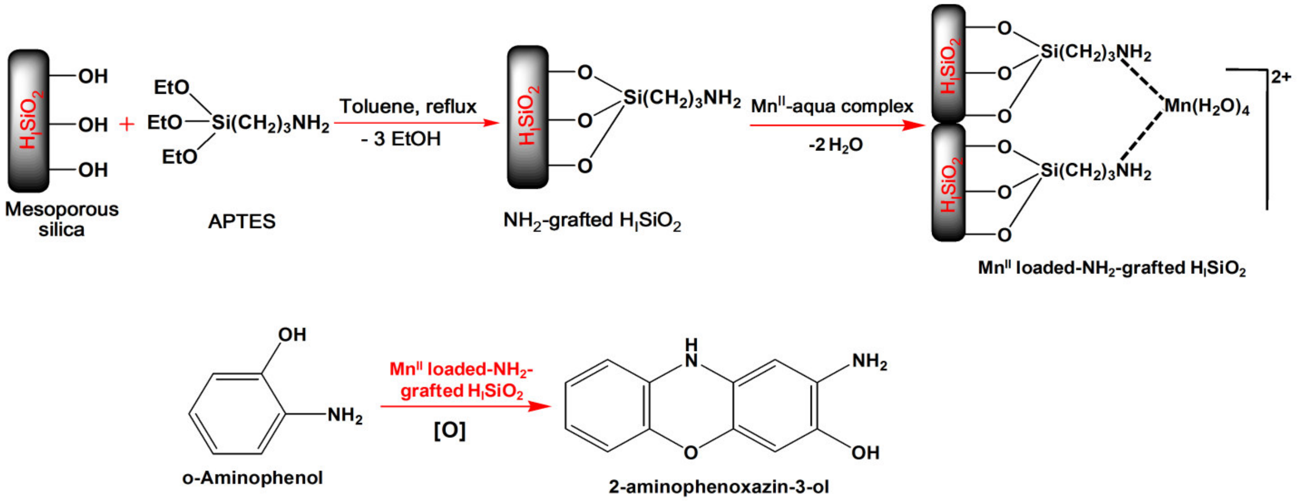

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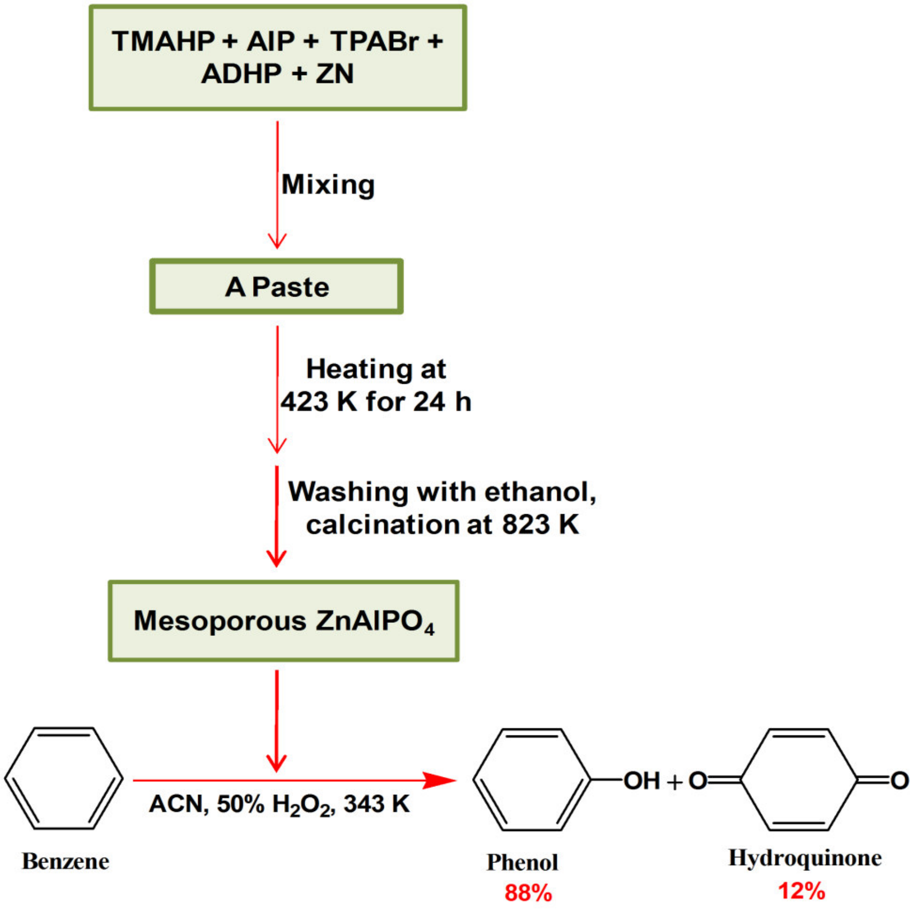
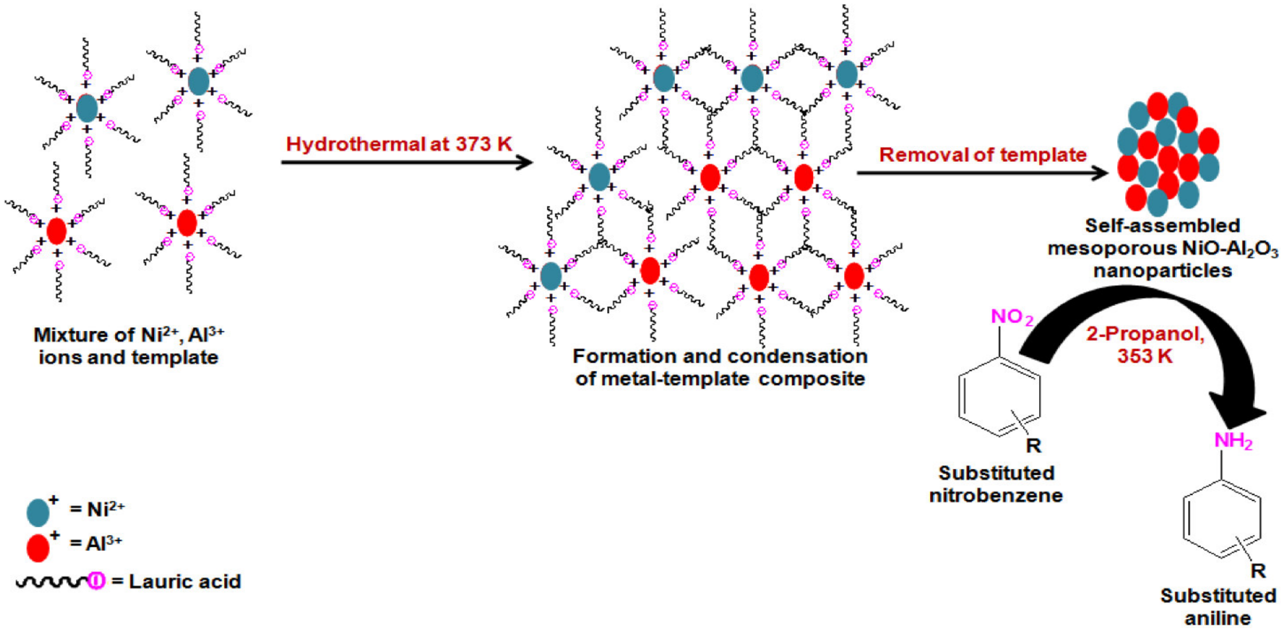


TMAHP = Tetramethyl ammonium hydroxide pentahydrate
AIP = Aluminum isopropoxide
TPABr = Tetrapropyl ammonium bromide
ADHP = Ammonium dihydrophosphate
ZN = Zinc nitrate
ACN = Acetonitrile

Figure 7 (Pal and Bhaumik)



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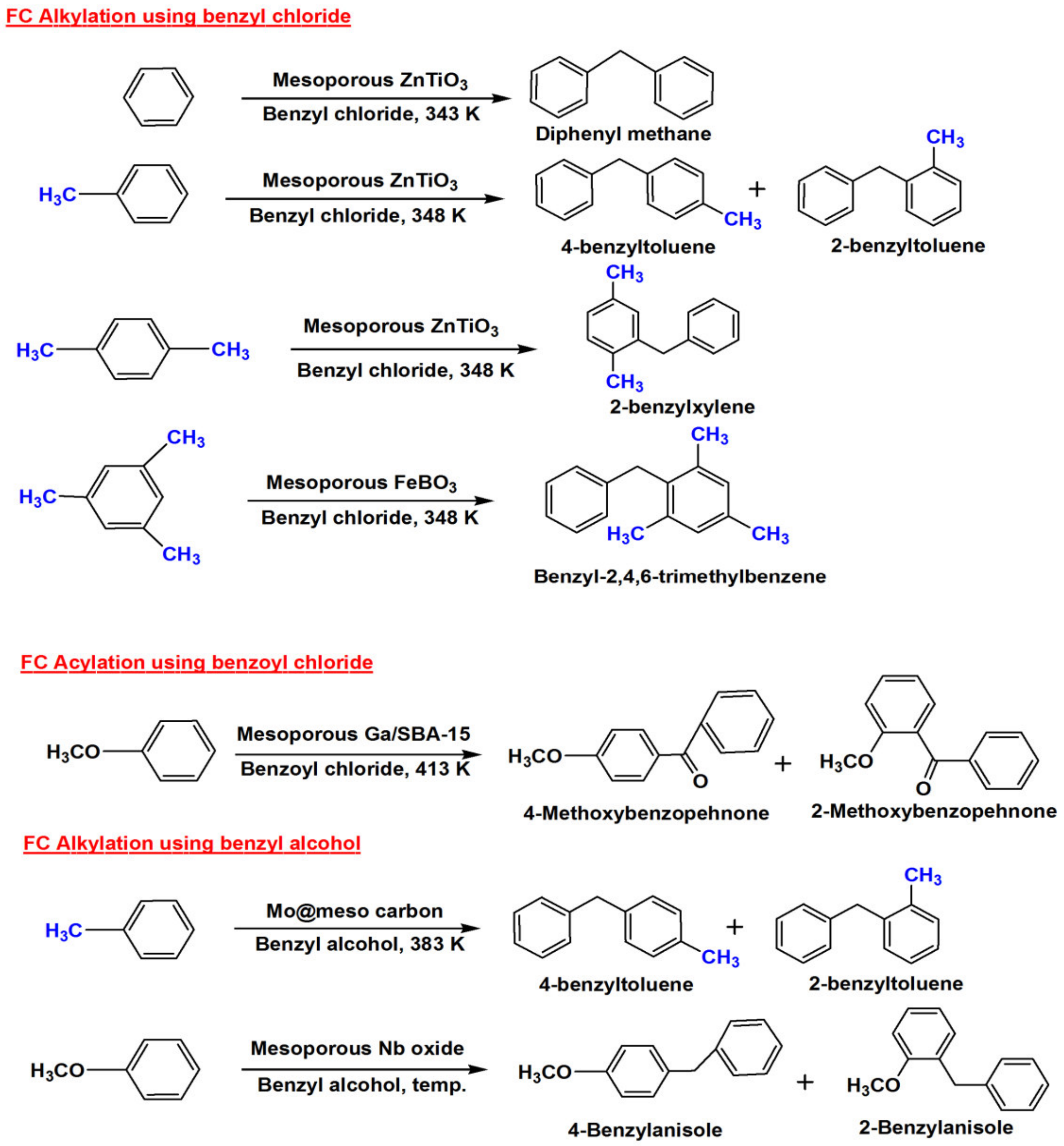

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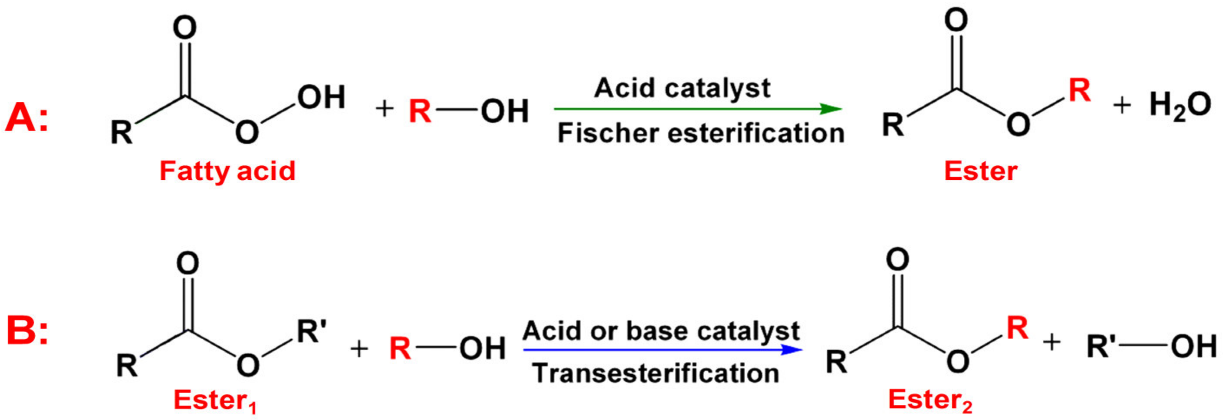

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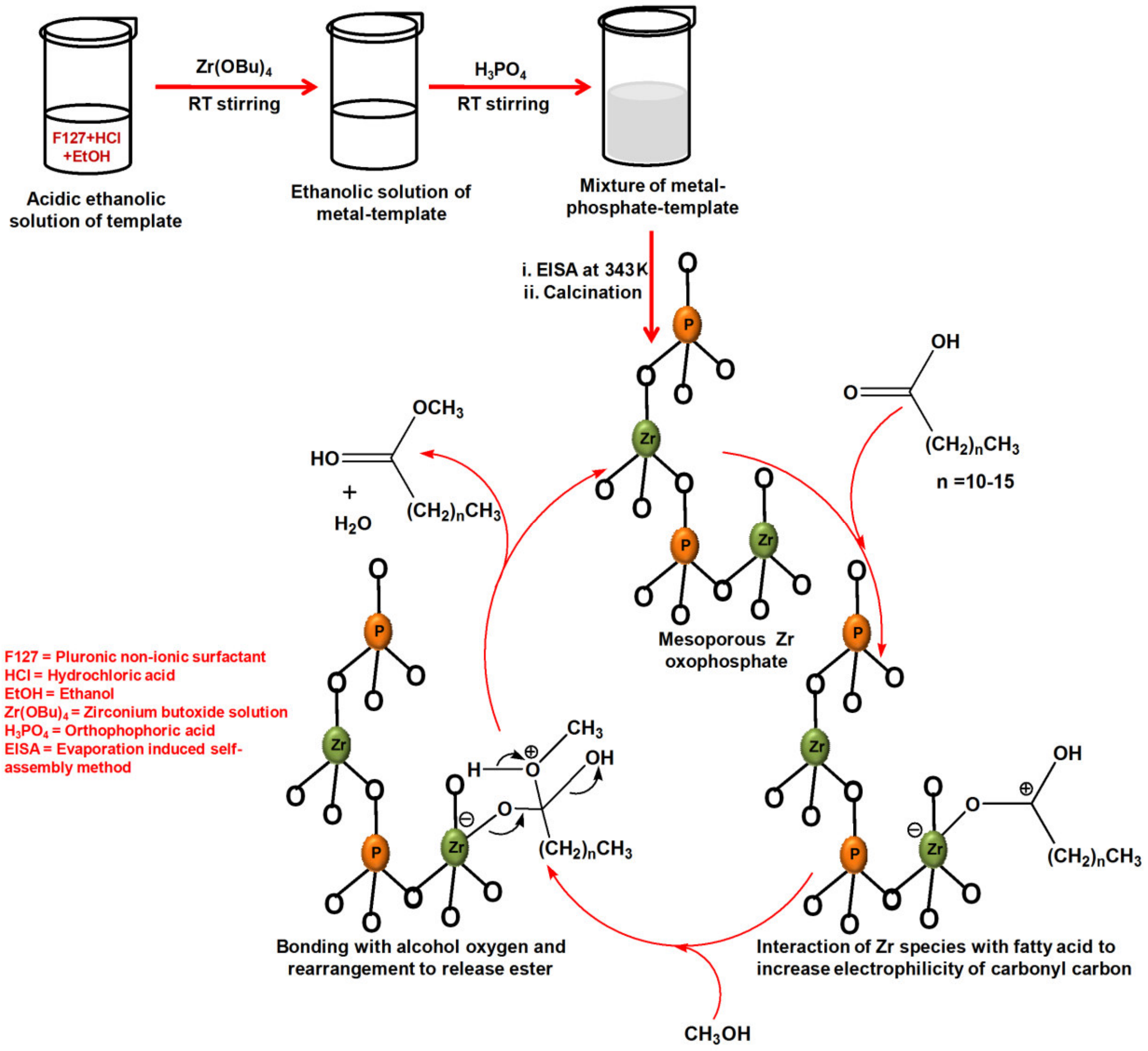

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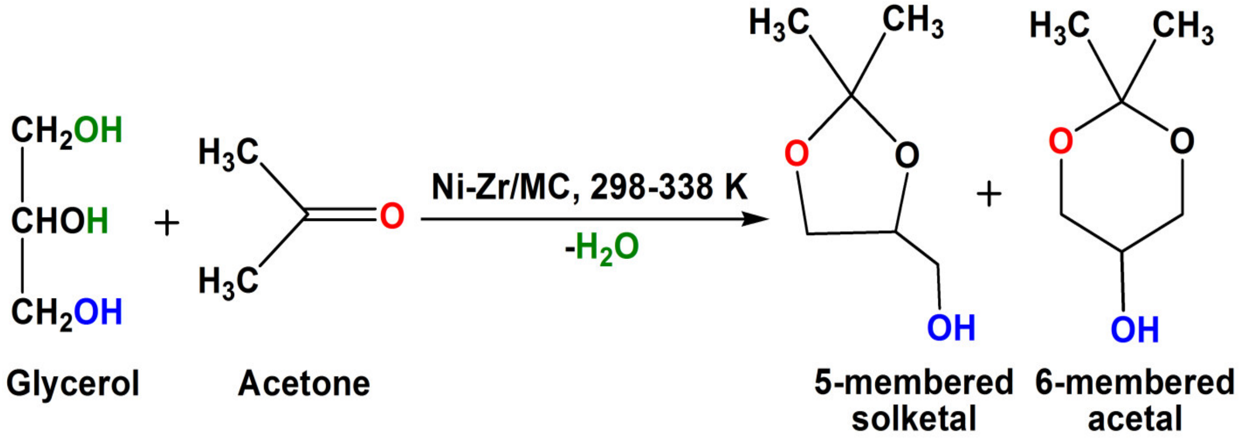

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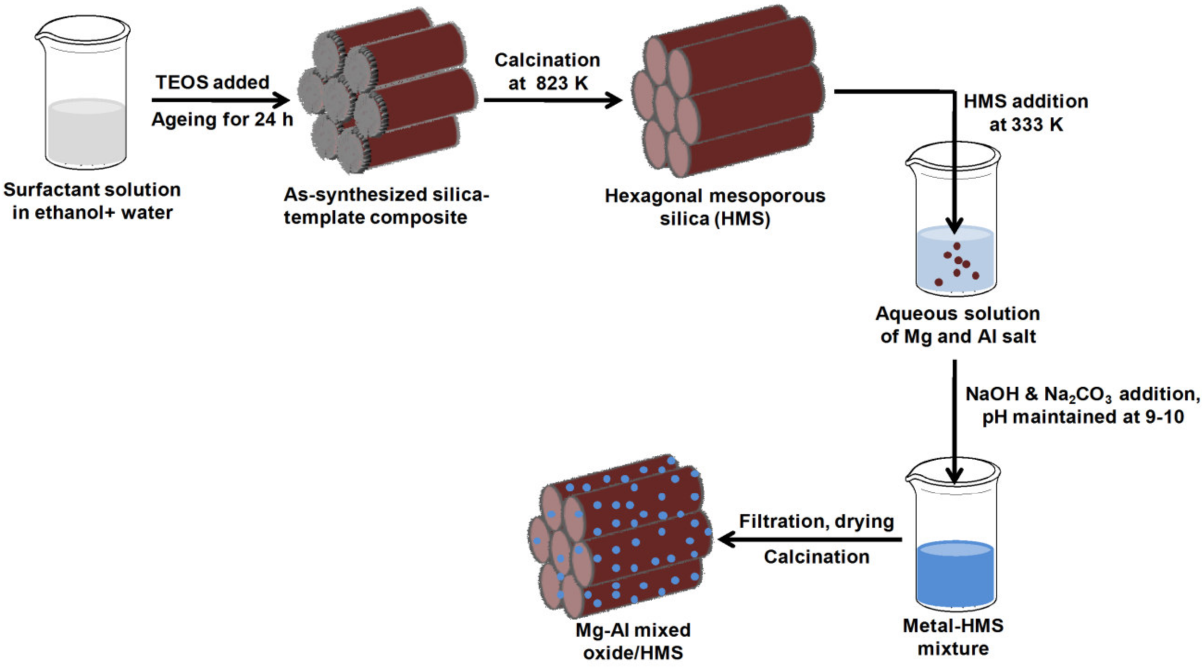

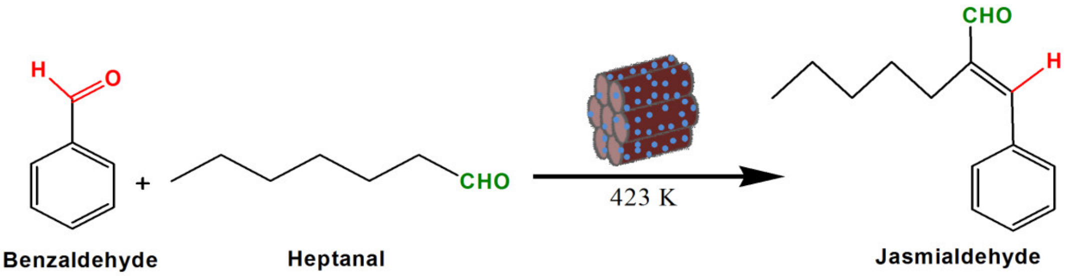

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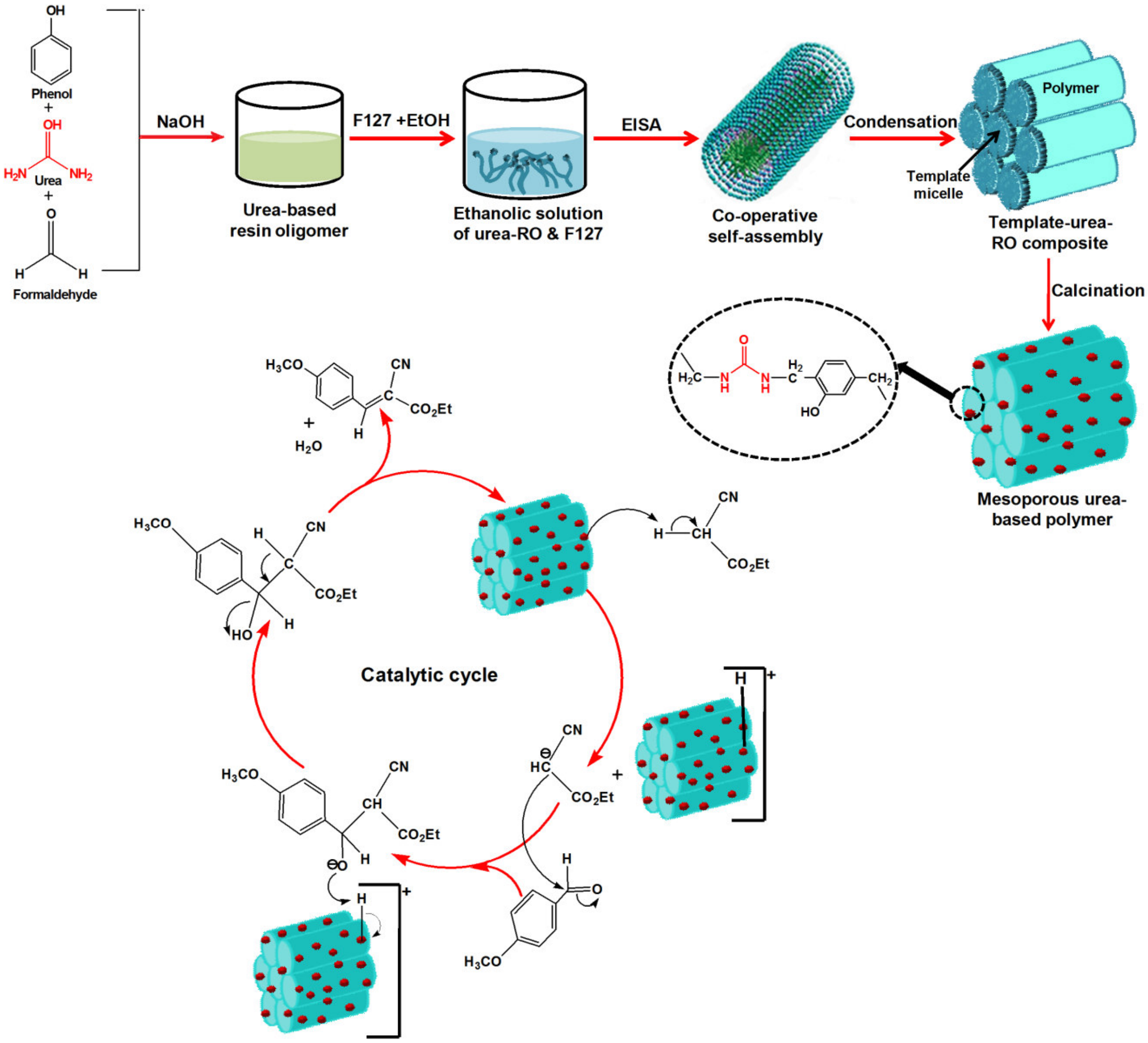

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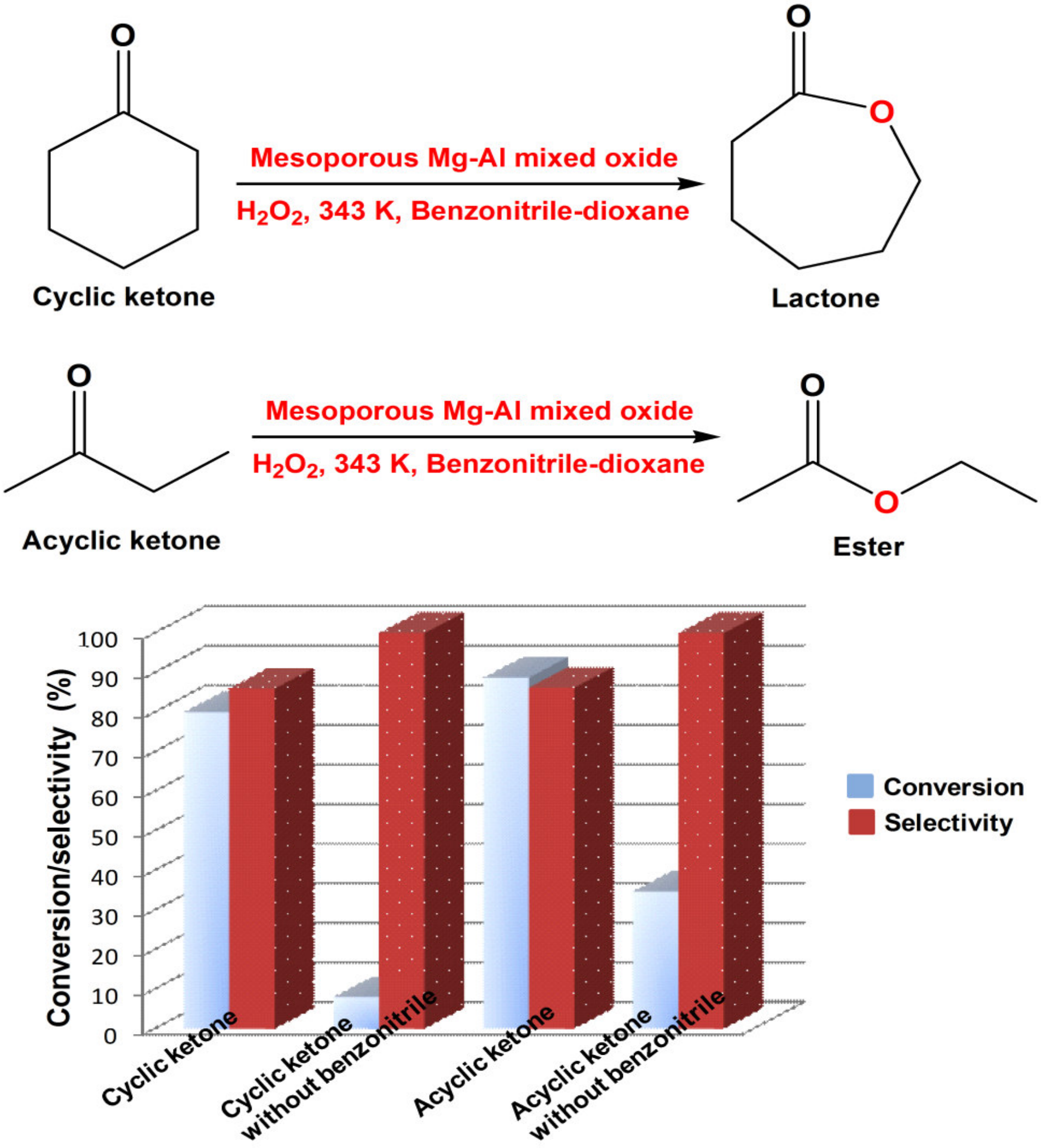

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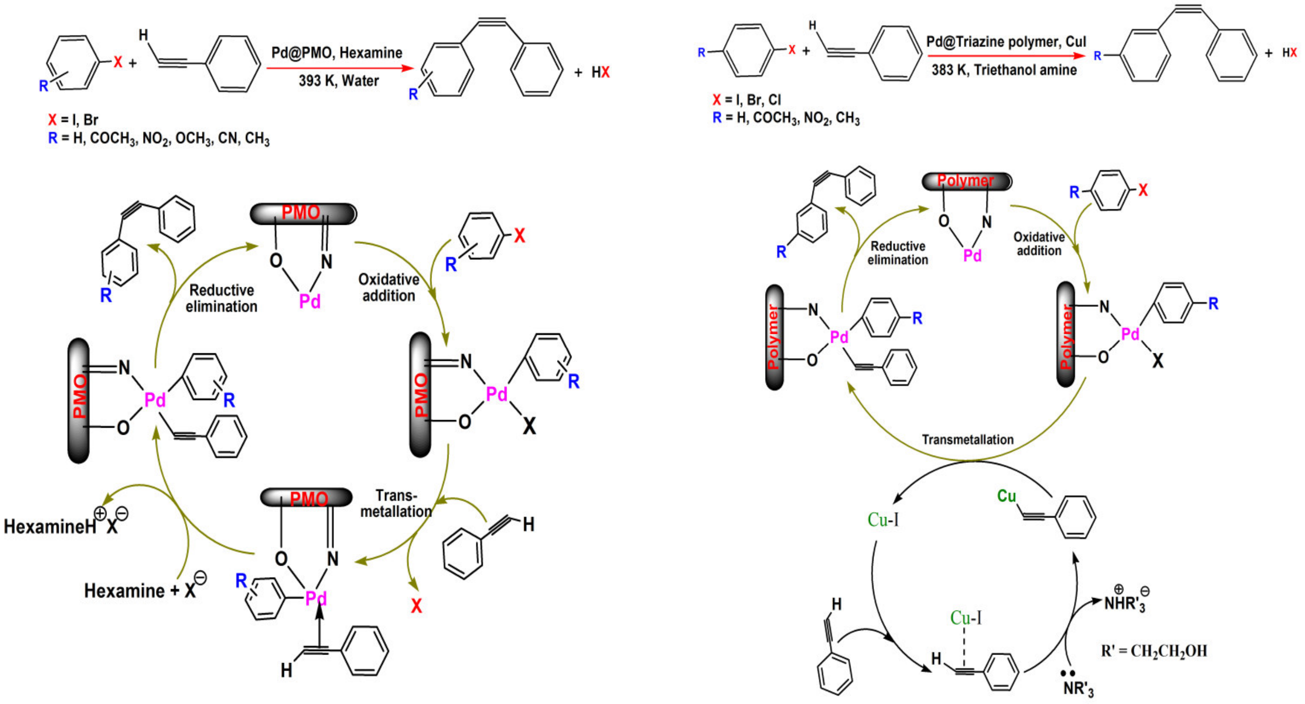


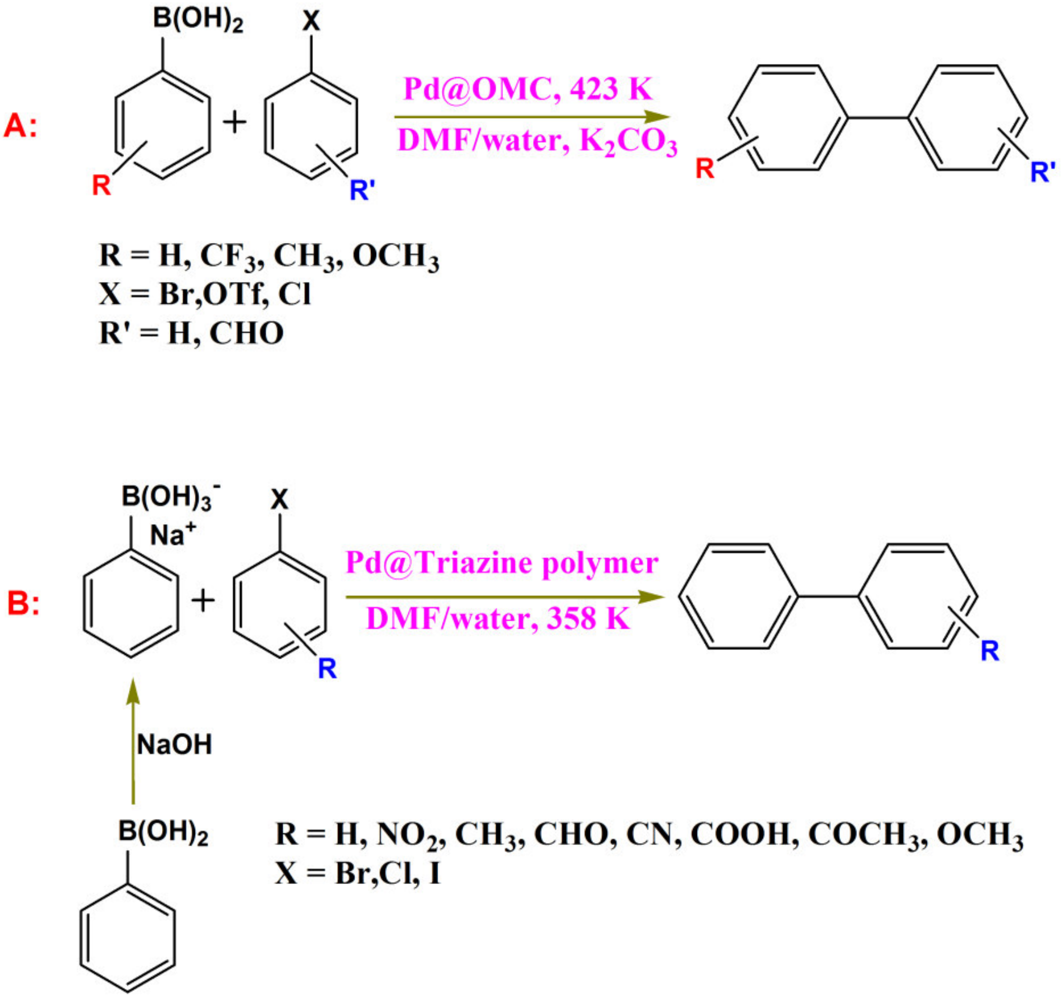
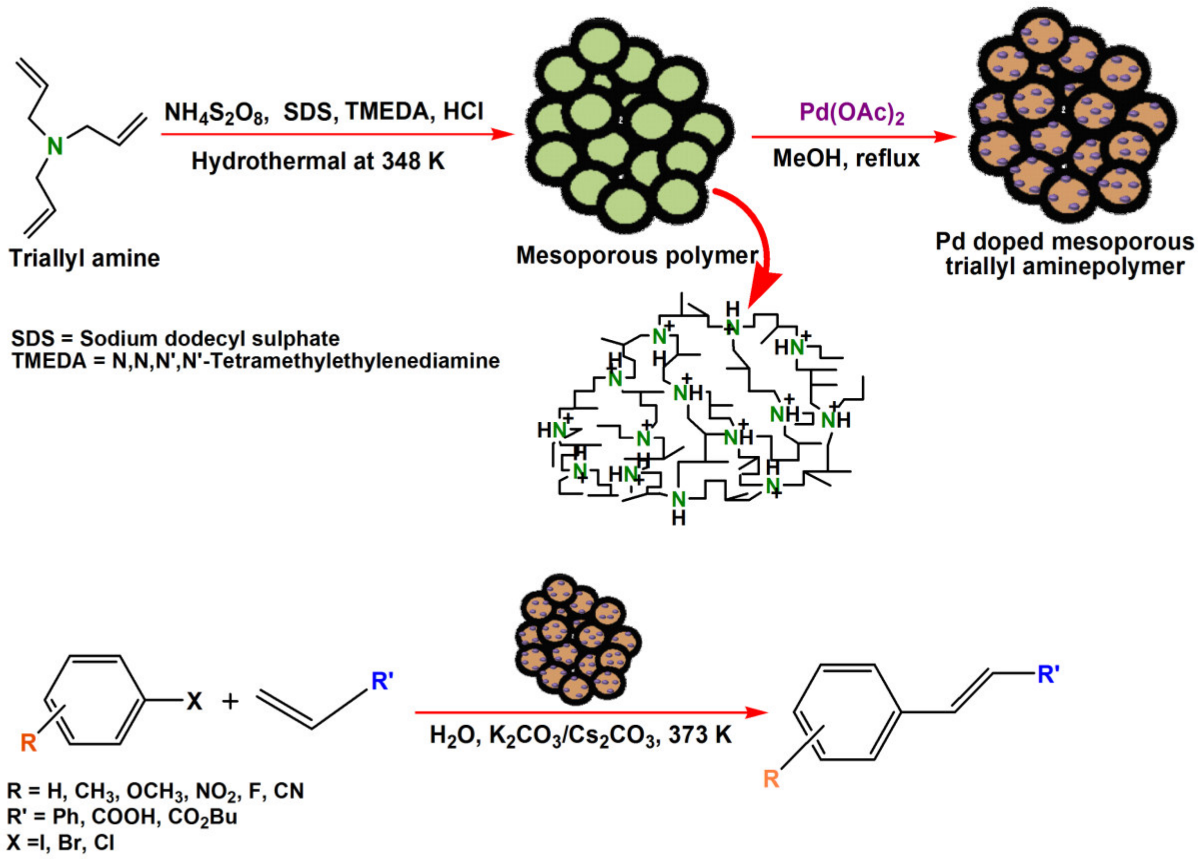


Figure 16 (Pal and Bhaumik)

Figure 17 (Pal and Bhaumik)



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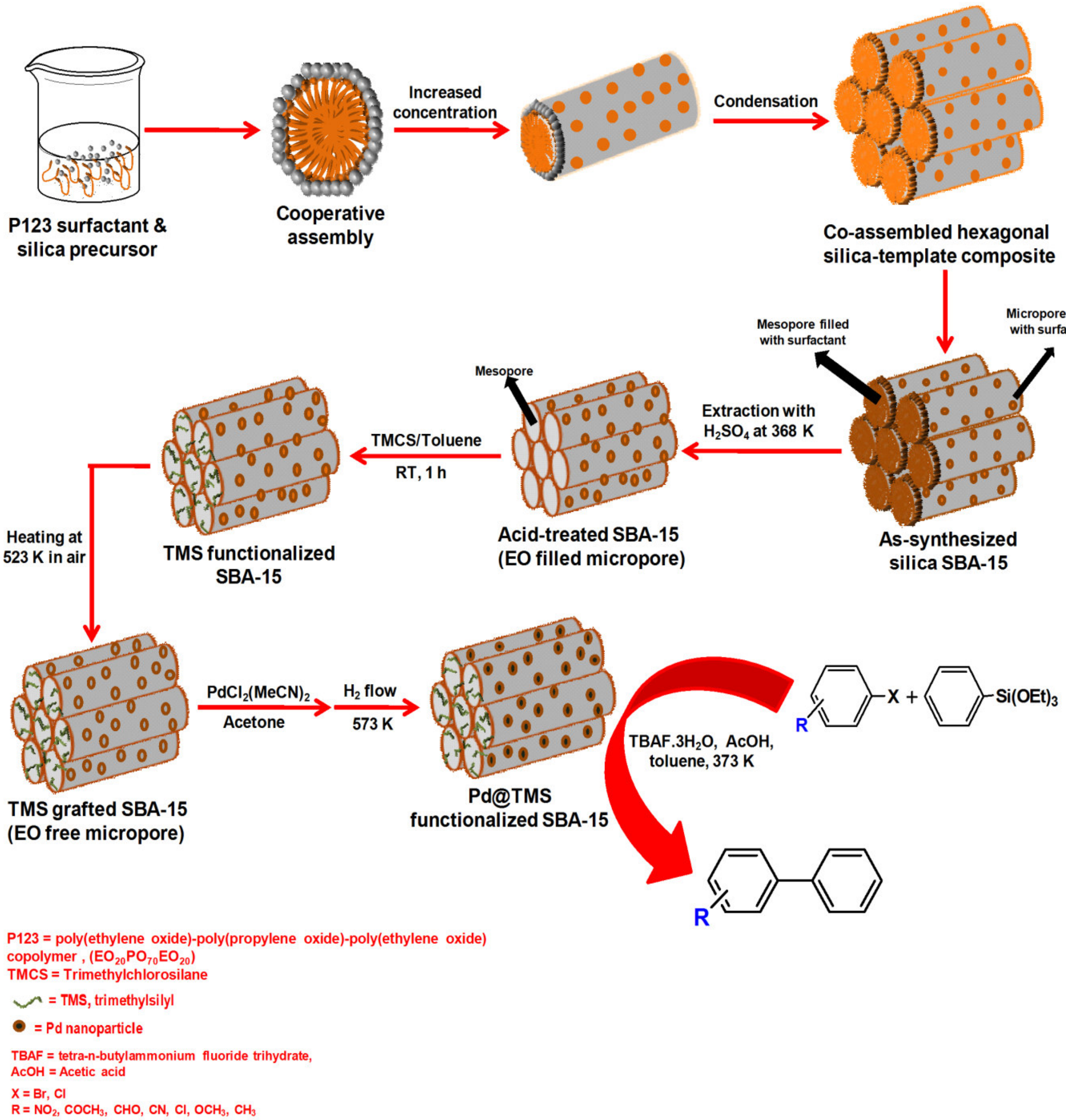

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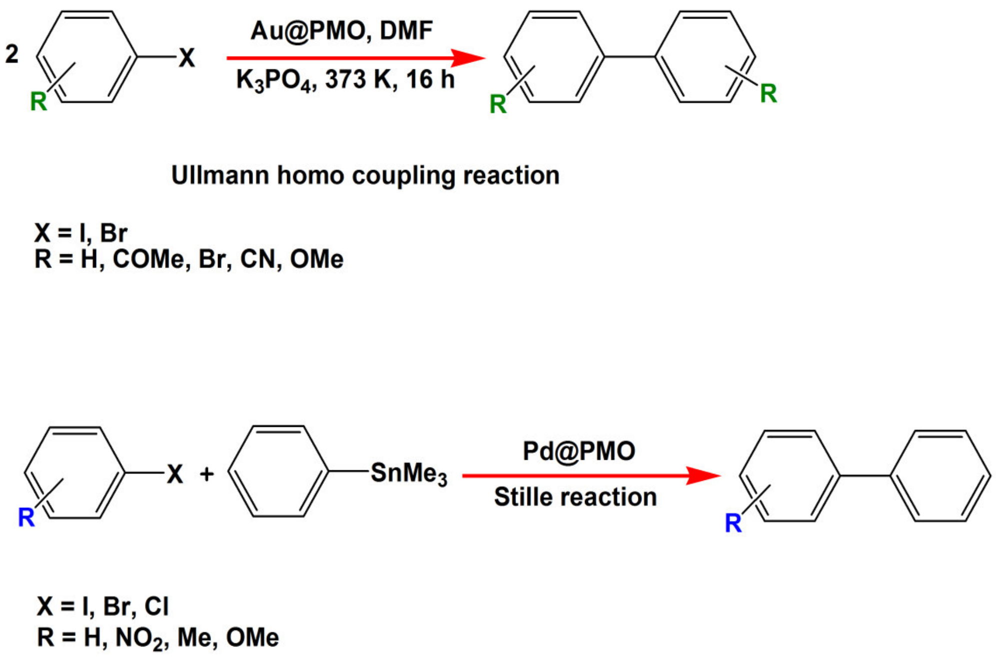
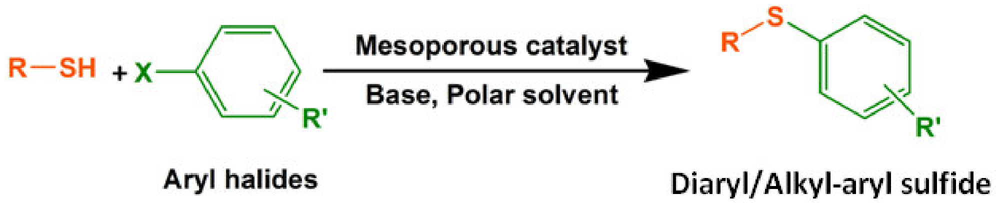


Figure 20 (Pal and Bhaumik)



R = Substituted aryl or alkyl
R' = H, OCH_3, CH_3, NO_2, F, CO_2Et etc.
X = I, Br, Cl

Figure 21 (Pal and Bhaumik)

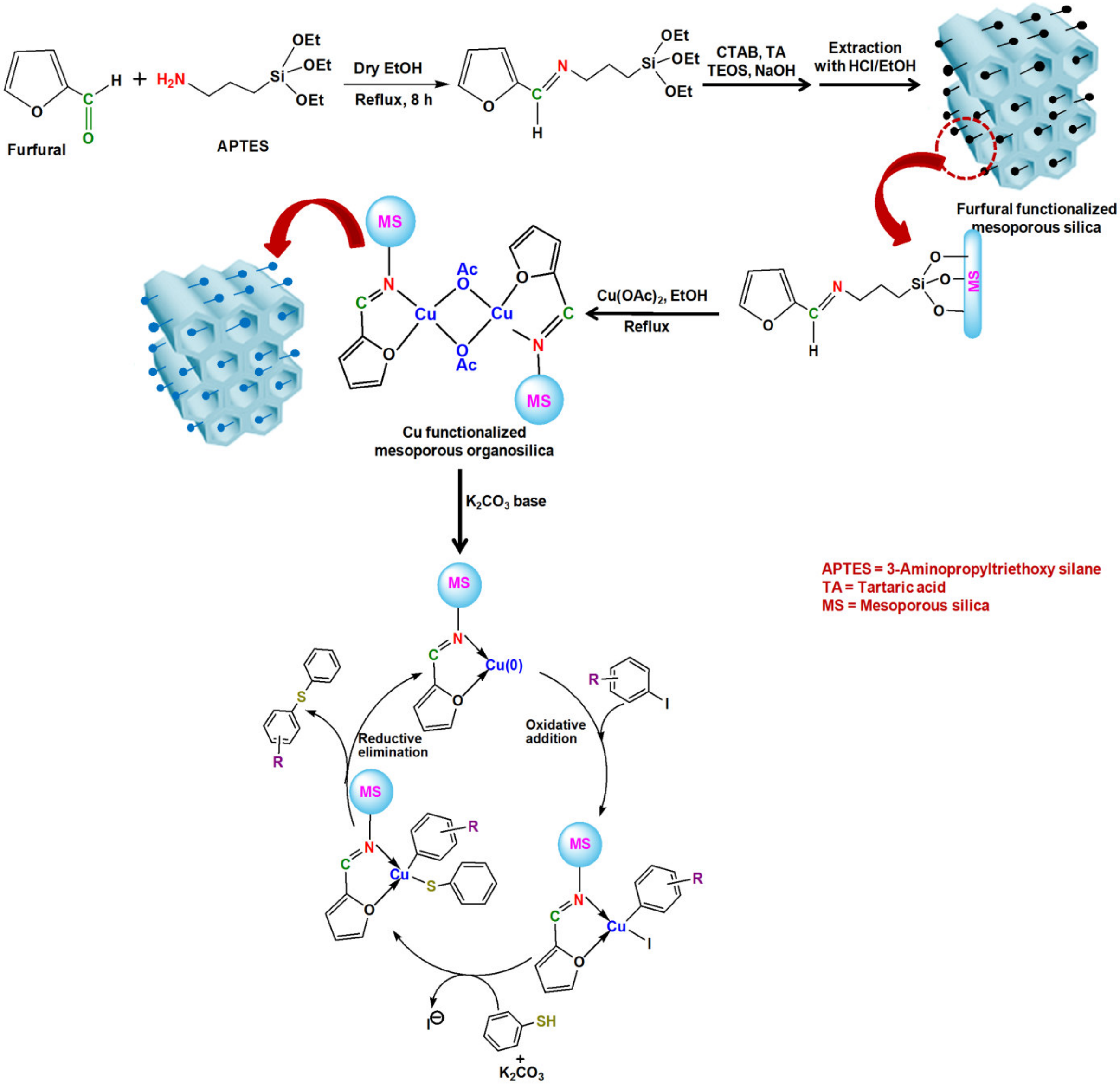


Figure 22 (Pal and Bhaumik)

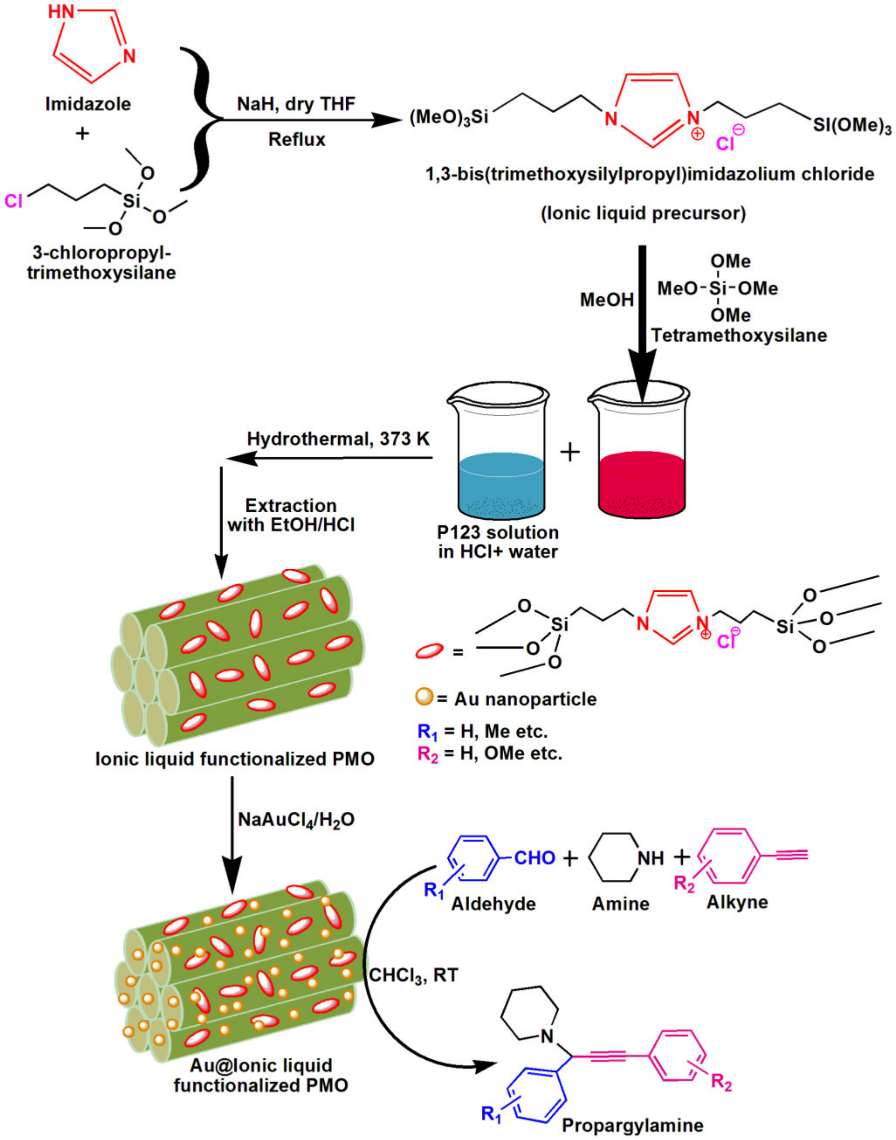


Figure 23 (Pal and Bhaumik)