Review Article

Solid-Phase Organic Synthesis and Catalysis: Some Recent Strategies Using Alumina, Silica, and Polyionic Resins

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Solid-phase organic synthesis (SPOS) and catalysis have gained impetus after the seminal discovery of Merrifield's solid-phase peptide synthesis and also because of wide applicability in combinatorial and high throughput chemistry. A large number of organic, inorganic, or organic-inorganic hybrid materials have been employed as polymeric solid supports to promote or catalyze various organic reactions. This review article provides a concise account on our approaches involving the use of (i) alumina or silica, either having doped with metal salts or directly, and (ii) polyionic resins to either promote various organic reactions or to immobilize reagents/metal catalysts for subsequent use in hydrogenation and cross-coupling reactions. The reaction parameters, scopes, and limitations, particularly in the context of green chemistry, have been highlighted with pertinent approaches by other groups.

1. Introduction

The concept of solid-phase organic synthesis (SPOS) dates back mid-1940s, and the solid-phase peptide synthesis in 1960s developed by Merrifield has been a pioneering work [1]. Over the last two decades, there has been a surge generating tremendous interest in expanding this field of solid-phase synthesis [2–10]. There is a clear emphasis in synthetic chemistry towards developing environmentally friendly and sustainable routes to a myriad of materials. The emphasis is most apparent in the growth of green chemistry [11–14]. According to Paul Anastas—one of the founders of the concepts of green chemistry, "*Catalysis is a foundational stone of Green Chemistry*" [11, 12]. One important aspect of clean technology is the usage of environmentally friendly surface catalysts, typically a solid catalyst that can be easily recovered when the reaction is complete [15]. Polymer supports play a critical role in combinatorial chemistry, and consequently, solid-phase organic synthesis continues to grow in importance [16–23]. One of the major advantages of this technique that has attracted attention of the chemists is the clean isolation of the products by simple filtration. As a result, this technique has become a valuable tool in combinatorial chemistry and high throughput chemistry, an integral part

of drug discovery and research [24–26]. The solid-phase organic synthesis of small organic molecules depends largely on the adaptation of solution reactions to solid phase [27]. Alternative synthetic routes that avoid need of any toxic solvents and reduce the number of steps with high atom economy and energy efficiency are some of the key features of green chemistry. On the other hand, good dispersion of the active reagent sites, involving high selectivity, easier work-up, and improved efficiency are attractive features for solid-phase technology.

Both inorganic and organic polymers have been employed to mediate or promote organic reactions [28–30]. As regards use of inorganic oxides, silica and modified silica, alumina, zeolites, clays, and so forth have found wide applications in promoting various organic reactions in solution phase or in solvent-free conditions [31–38]. On the other hand, organic polymers such as polystyrene (PS) or that partially crosslinked with divinylbenzene (DVB) have remained the major choice besides uses of some other dendrimers [39–50]. The choice of solid phase, polymers with suitable linkers, the nature of binding with the substrate/reagent (covalent or noncovalent), stability, and recyclability have remained some of the salient points for successful and efficient solid-phase synthetic protocol.

Pd-catalyzed
C–C couplings

Quinoxaline
synthesis

N- or S-
alkylations

KF-alumina

Inorganic oxides
and/or doped
inorganic oxide

S-acylation

Silica or
Fe(III)-silica

Selective
benzimidazole
synthesis
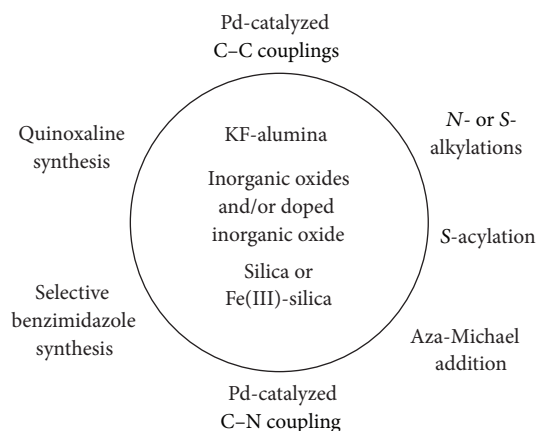
Aza-Michael
addition

Pd-catalyzed
C–N coupling

FIGURE 1

Towards developing new organic reactions and catalysis, our group has primarily employed two categories of polymers: (i) inorganic oxides either directly or having doped with some other inorganic salts, and (ii) polyionic resins to immobilize reagents/metal nanoparticles (NPs) as the solid-phase catalysts or heterogeneous nanocatalysts. This review article will primarily focus on our efforts vis-à-vis mentioning notable and relevant achievements from other research groups. The subject has been organized according to nature of the target molecules to synthesize, nature of reaction, and also the type of solid supports employed in various reactions.

Figure 1 illustrates examples of our efforts towards the synthesis of C–C and C–X (heteroatom) bond-forming reactions and synthesis of libraries of small heterocyclic molecules of biological importance having promoted or catalyzed on commercially available silica gel, alumina or doped with iron(III) salt or potassium fluoride, respectively.

2. KF/Alumina Mediated/Catalyzed Organic Reactions

Commercially available alumina (Al_2O_3) is known to catalyze or promote a variety of organic transformations [2, 51]. However, alumina doped with potassium fluoride (KF/alumina) has been extensively used as solid basic surface in vast range of organic transformation [52], since it was introduced by Ando et al. [53–56]. Alumina doped with KF can ionize C-acids up to pKa ~35 [57]. Although the actual basic site developed on the surface on alumina is dependent of temperature and partially debatable, the ^{19}F magic angle NMR and IR spectroscopic measurements have shown that the fluoride anion species in KF/alumina is more electron rich than fluoride anion in pure solid. The conditions of loading of KF seem to be critical to its functioning and displaying varying properties.

2.1. Buchwald-Hartwig C–N Cross-Coupling Reaction. The first reaction was studied on the surface of KF/alumina is the Buchwald-Hartwig C–N cross-coupling reactions between aryl halides and an amine. Initial independent reports by

Buchwald and Hartwig clearly noticed that the success of such coupling is tricky to the use of the base, and sodium or potassium *tert*-butoxide was found to be best for such C–N cross-coupling reactions [58–61]. Secondly, initial conditions were not successful for heteroaryl substrates, possibly because of formation of stable palladium complex that does not further participate in the catalytic cycle. Buchwald however circumvented this problem by using chelating ligands so as to avoid formation of substrate-based palladium complexes [62].
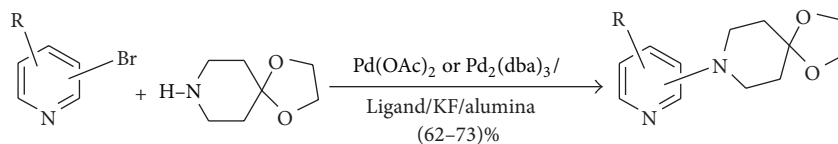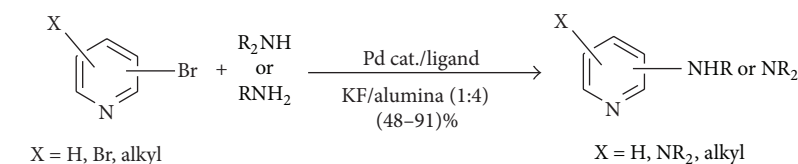
Palladium-catalyzed C–N hetero cross-coupling reactions between bromopyridines and amines (both primary and secondary) can be efficiently performed on a KF/alumina (basic) surface (Scheme 1), thus negating the use of strong bases such as sodium *tert*-butoxide. The reaction conditions have been optimized with reference to catalytic systems, solvents, and the surface. A variety of phosphines both as mono- and bisphosphine ligands are found to be equally active [63].

To broaden the scope of this C–N hetero cross-coupling, the reaction protocol has been extended to haloaromatics. The reactions are not only found to be applicable to bromoarenes but also offer high selectivity in cross-coupling of polyhaloaromatics. Indeed, there has been high selectivity between mono- or polyaminations (*bis-*, *tris-*, or *tetra-*) depending on the proportion of KF and alumina [64]. Higher proportion of KF and slight higher temperature can lead to polyamination, while lower amount of KF in KF/alumina generally affords only monoaminated product (Scheme 2).
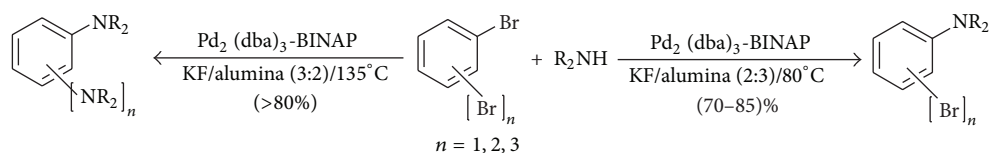
Notable features of the use of KF doped with alumina (KF/alumina) are (i) the use of NaOBu^t can be avoided; (ii) conditions are not ligand-specific; (iii) solvent-free reactions generally give better yields; (iv) applicable to both bromoarenes and *N*-heteroaryl bromides; (v) varying proportions of KF per gram of alumina offer selectivity; and (vi) recycling of the solid surface is possible.

2.2. Double Michael Addition. The Michael addition reaction, an important C–C bond-forming reaction, is known to produce adducts, which have found wide synthetic applications [65–68]. Several acidic and basic catalysts are used to affect this conjugate addition reaction. Side reactions, frequently encountered in the presence of a base catalyst, are secondary condensations, polymerizations, and double additions. However, the reactions in which two C–C bonds are selectively formed by intermolecular and consecutive double Michael reactions in one-pot are very rare. It was observed that KF/alumina can promote consecutive Michael additions of the nucleophile derived from acetophenone to electron deficient alkenes. Thus, an efficient and highly selective one-pot procedure for the double Michael reactions was developed leading to the formation of pimelate ester derivatives [69]. This is the first example of selective double Michael additions of aromatic and aliphatic methyl ketones to electron-deficient alkenes mediated over KF/alumina (Scheme 3).
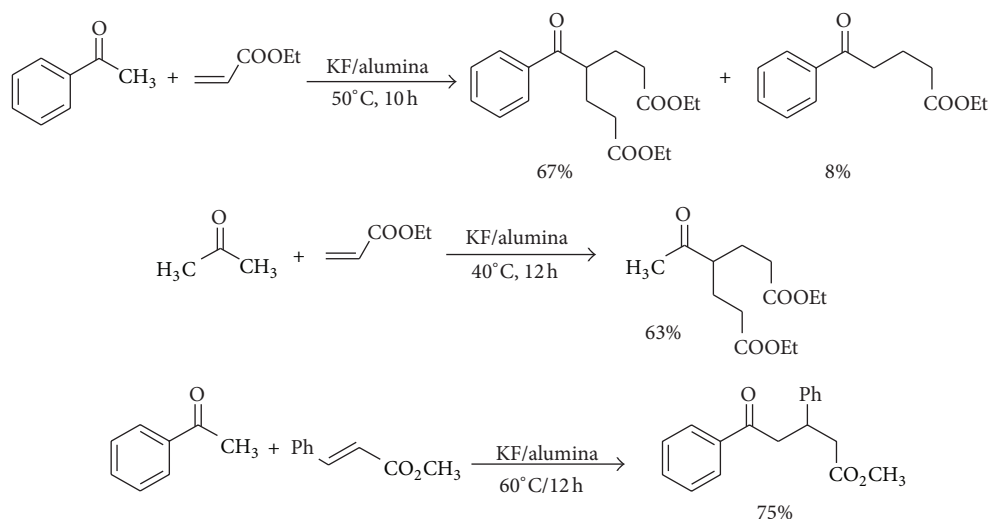
Both aliphatic and aromatic ketones underwent bis-addition with similar efficiencies and afforded the desired products. Mixture of acetone and ethyl acrylate yielded the
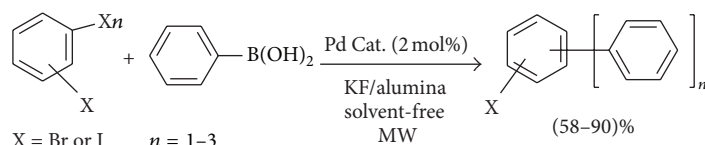
Scheme 1

Scheme 2

Scheme 3

corresponding bis-adduct, diethyl 3-acetyl-heptanedioate, in 63% yield, keeping the other methyl group intact. While testing similar reactions using methyl crotonate or methyl cinnamate as the Michael acceptors, the reaction ended up selectively with the formation of monoadducts only even after prolonged reaction time and elevated temperatures. The possible reason of reluctance to undergo double additions may be attributed to the steric inhibition at the β-carbon of the conjugated olefins. This was further corroborated with the result that the double Michael adduct was indeed formed in 72% yield with methyl methacrylate.

2.3. Suzuki Coupling Reaction. Biaryls and higher homologues are an important class of conjugated polyaromatic compounds, originating from benzene as unique building blocks. Polyaryls have found wide range of applications

as liquid crystals, laser-dyes, and conducting polymers. In addition, biaryls and higher homologues are often present as subunits in numerous biologically active natural products, pharmaceuticals and agrochemicals [70–80]. An efficient palladium-catalyzed cross-coupling of polyhaloaromatics with arylboronic acids on KF/alumina was developed under microwave-assisted condition (Scheme 4) [81]. The results have expanded the scope of the Suzuki reaction on a solvent-free inorganic surface leading to the synthesis of a large variety of polyaromatics. The reaction is fast, operationally simple, and allows rapid access to a variety of polyaromatic hydrocarbons.
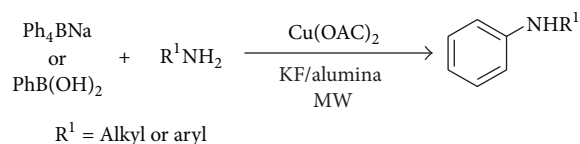
2.4. N-Arylation of Amines. An experimentally simple microwave-assisted solvent-free *N*-arylation of primary amines with sodium tetraphenylborate or arylboronic acids,

Scheme 4

promoted by inexpensive cupric acetate, on the surface of KF/alumina has been developed (Scheme 5) [82]. The reaction is selective for mono-*N*-arylation, and a variety of functional groups are tolerated in the process establishing the versatility of KF/alumina.

Primary amines were monoarylated successfully using either sodium tetraphenylborate or arylboronic acids. Aromatic amines bearing either electron-donating or electron-withdrawing groups gave the corresponding unsymmetrical diarylamines in good to excellent yields. Aliphatic primary amines and benzylamine also produced *N*-arylated products in 70–75% yields. Halo-substitutions, either on the aryl amine or the arylboronic acid, remained unaffected under the reaction conditions.

2.5. Synthesis of Quinoxalines.

Functionalized quinoxalines represent a privileged class of *N*-containing heterocycles and exhibit a wide range of biological activities including antiviral, antibacterial, anthelmintic, anti-inflammatory, kinase inhibitory, and anticancer activities [83–89]. A facile and expeditious solid-phase synthesis of libraries of quinoxalines promoted on KF/alumina surface via tandem oxidation-condensation or condensation reactions has been developed (Scheme 6) [90]. The reaction protocol is operationally simple and mild. Moreover, solvent-free reaction condition makes the reaction procedure eco-friendly and economically viable. The methodology has been established as a direct and expeditious process of preparation of functionalized quinoxalines from different substrates like α-hydroxy ketones, α-bromoketones, or α-dicarbonyl compounds, using a heterogeneous basic surface of KF/alumina.
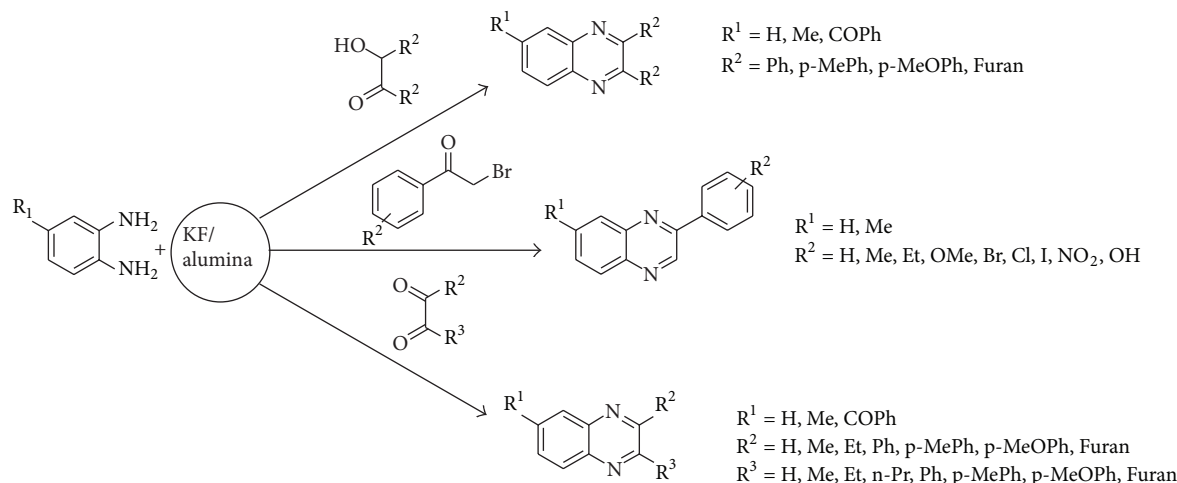
3. Reactions Promoted by Silica Gel

Silica gel is nontoxic, nonflammable, nonreactive, and stable with ordinary usage. In chemistry, silica gel is used in chromatography as a stationary phase [91]. Owing to its highly developed surface (5–800 $m^2\,g^{-1}$) and high porosity, it is used as sorbent for dehydration of gases and fluid, as a catalyst support for various reactions. Chemical reactions catalyzed or promoted by silica gel usually proceed under mild conditions and with high chemo-, regio-, and stereoselectivity and are operationally simple. In the quest of developing solid surface mediated organic reactions, a few reactions are described using silica gel as a potential surface.

3.1. Hetero-Michael Conjugate Additions.

β-Amino ester and its derivatives are attractive targets for chemical synthesis of products with a wide range of biological activities and
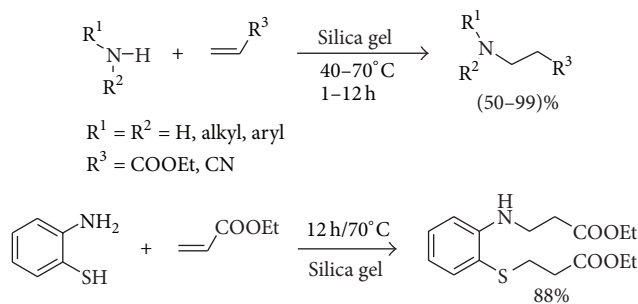

Scheme 5

pharmacological properties [92–94]. β-Amino esters are useful intermediates in certain attractive syntheses of β-lactam antibiotics [95–97]. Optically active β-amino esters and derivatives often find applications as chiral auxiliaries in asymmetric synthesis [98]. A solvent-free protocol for the synthesis of β-amino esters and nitriles has been developed via conjugate addition of amines to electron-deficient alkenes promoted on silica gel. The silica surface may be recovered and recycled. Both aliphatic and aromatic primary or secondary amines worked efficiently to yield the desired adducts in good to excellent yields (Scheme 7) [99]. The method has been found to be mostly successful when the silica gel of the type used for thin layer chromatography is used. Bulky hindered secondary amines such as diisopropylamine and dicyclohexylamine that were previously reported to be unproductive could efficiently undergo aza-Michael additions to produce corresponding β-amino esters [100]. It was interesting to see that *o*-amino thiol bearing both heteroatoms (N and S) could afford the *bis*-adduct, which indicates that thiols are also reactive under similar conditions (Scheme 7).

In general, the reactions proceed smoothly under solvent-free conditions except in the eventual purification by column chromatography. Few reactions have been scaled up to 10 mmol of the amines, and the desired products are isolated without any significant change of yield. The applicability of this "green" methodology to a diverse variety of amines including aromatic and sterically hindered amines remains to be the attractive feature and can be utilized by synthetic and industrial chemists.

3.2. Selective N-Alkylation of Amines.

Further application of silica gel has been observed in selective *N*-alkylation of amines. Traditionally, amines are alkylated in solution phase using inorganic acids as the catalysts and alkyl halides or dimethyl sulphate as the alkylating agents [101–111], besides methanol [112] and dimethyl carbonate [113]. However, yields or product-selectivity (mono- or bis-alkylations) are, with few exceptions, low and depend on the nature of the catalysts and reaction conditions. Though direct nucleophilic attack of amines to alkyl halides using a strong base is the most straightforward procedure; over alkylation, use of strong

Scheme 6

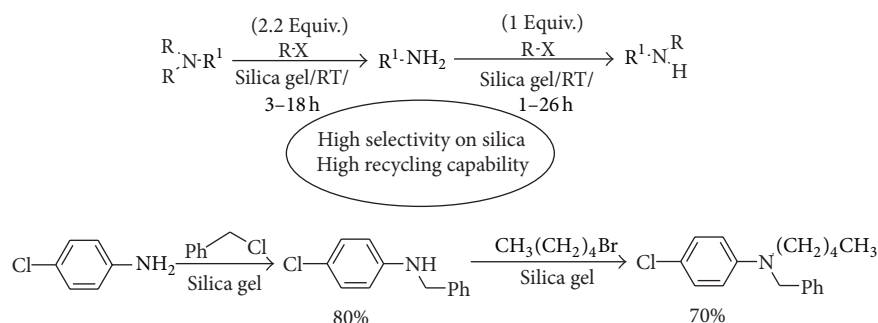R^1 = R^2 = H, alkyl, aryl
R^3 = COOEt, CN

Scheme 7

Table 1: Reaction of thiophenol with acetyl chloride on various inorganic solid supports.

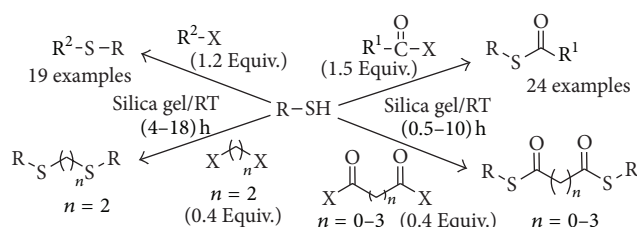| Solid support[a]	Time (min.)	% Acetylation[b]
Silica	120	92
Neutral alumina	120	64
Bentonite	30	56
Mol. Sieves, 4 Å	120	20
Talc	60	39
Neat	120	Nil

[a]Solid supports used 200 mg mmol^{-1}; [b]yield by HPLC analysis along with another product (disulfide) and unreacted thiophenol.

base and other harsh conditions greatly limit providing a practical, generalized, and selective procedure. In continuation to explore organic reactions using solid surfaces, a highly selective procedure for mono- and bis-alkylations has been developed via N-alkylation of amines with alkyl halides in solid phase using silica at room temperature (Scheme 8) [114]. The procedure is simple and extremely useful for the control of the mono-, bis-, or overalkylations by varying the reaction conditions and molar proportions of amines and alkyl halides. The selectivity for mono- or bis-alkylations greatly depends on temperature, time of the reaction, proportion of the reactants, and also partly on the type of silica gel. Inactivated alkyl halides reacted with anilines to produce preferably the monoalkylated anilines in major quantities, even after using excess alkyl halide and continuing the reaction for prolonged time. The method was applied successfully to aliphatic bis-amine such as ethylene diamine and reaction with benzyl chloride or allyl bromide afforded the desired tetra-alkylated product in 73–79% yields. Selectivity of mono- and bis-alkylations under different conditions has been further broadened to synthesize unsymmetrical trialkyl/aryl amines (Scheme 8). The silica gel, after purification and activation, can be reused for ten consecutive runs (tested) without any substantial reduction in the yield as is observed from the recycling experiment.

3.3. S-Acylation and Alkylation of Thiols. Acylation and alkylation of thiols are essential transformations in organic synthesis and often used for protection of thiols and are also known in several biological phenomena [115–119]. S-Acylation is the posttranslational attachment of fatty acids to cysteine residues [120]. S-Acylated peptides have many potential uses for elucidating the biophysical, structural, and other properties of numerous S-acylated proteins of mammalian cells [121, 122]. On the other hand, thioethers are useful class of organic compounds and find versatile applications as key reagents in organic synthesis, bioorganic, heterocyclic, and medicinal chemistry. The promising solvent-free and highly selective N-alkylation promoted by silica gel has prompted to investigate S-alkylation and S-acylation reactions. Initial studies revealed that the reaction between thiophenol and acetyl chloride could be achieved at room temperature when stirred with silica gel under solvent-free conditions producing S-phenyl ethanethioate in 93% yield. Neither acetic anhydride nor acetic acid was found to be effective for a similar conversion. Silica gel was also found to be a much better choice for promoting the S-acetylation reaction, while neutral alumina yielded the thioester in 64% yield, and bentonite or molecular sieves afforded considerable amounts of disulfide (Table 1).

Scheme 8

$$R_2N\text{-}R^1 \xrightarrow[\text{Silica gel/RT/}]{\substack{(2.2 \text{ Equiv.}) \\ R\text{-}X \\ 3\text{-}18\,h}} R^1\text{-}NH_2 \xrightarrow[\text{Silica gel/RT/}]{\substack{(1 \text{ Equiv.}) \\ R\text{-}X \\ 1\text{-}26\,h}} R^1\text{-}N\overset{R}{\underset{H}{}}$$

High selectivity on silica
High recycling capability

$$Cl\text{-}C_6H_4\text{-}NH_2 \xrightarrow[\text{Silica gel}]{Ph\text{-}CH_2Cl} Cl\text{-}C_6H_4\text{-}NH\text{-}Ph \; (80\%) \xrightarrow[\text{Silica gel}]{CH_3(CH_2)_4Br} Cl\text{-}C_6H_4\text{-}N(CH_2)_4CH_3,Ph \; (70\%)$$

Scheme 8

Scheme 9

$$R^2\text{-}S\text{-}R \; (19 \text{ examples}) \xleftarrow[\substack{\text{Silica gel/RT} \\ (4\text{-}18)\,h}]{\substack{R^2\text{-}X \\ (1.2 \text{ Equiv.})}} R\text{-}SH \xrightarrow[\substack{\text{Silica gel/RT} \\ (0.5\text{-}10)\,h}]{\substack{R^1\text{-}C(O)\text{-}X \\ (1.5 \text{ Equiv.})}} R\text{-}S\text{-}C(O)R^1 \; (24 \text{ examples})$$

$$R\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}R, \; n=2 \xleftarrow{X\text{-}(CH_2)_n\text{-}X, \; n=2 \; (0.4 \text{ Equiv.})}$$

$$X\text{-}CO\text{-}(CH_2)_n\text{-}CO\text{-}X, \; n=0\text{-}3 \; (0.4 \text{ Equiv.}) \rightarrow R\text{-}S\text{-}CO\text{-}(CH_2)_n\text{-}CO\text{-}S\text{-}R, \; n=0\text{-}3$$

Scheme 9

Further attempts have been made to obtain general and efficient conditions for the *S*-acylation and *S*-alkylation reactions of several aromatic and aliphatic thiols with different acid chlorides and activated alkyl halides, respectively, in the presence of silica gel (Scheme 9). A smooth conversion was observed in each case, affording the desired products in good to excellent yields. Moreover, it was found that the recovered silica can be reused for seven consecutive runs, without any appreciable loss of activity [123].

3.4. Selective Synthesis of 1,2-Disubstituted Benzimidazoles. Functionalized benzimidazoles represent an important class of *N*-containing heterocyclic compounds and have received considerable attention in recent times because of their vast applications as antiulcer, antihypertensive, antiviral, antifungal, anticancer, and antihistamines among others and also act as ligands for complexation with transition metals which are used for modeling biological systems [124–127]. Several synthetic strategies have been developed for the preparation of functionalized benzimidazoles [128–140].

Synthetic methods for 1,2-disubstituted benzimidazoles **3** often are associated with cooccurrence of several side reactions and by-products as shown in Scheme 10.

An efficient, simple protocol has been developed for highly selective synthesis of 1,2-disubstituted benzimidazole **3**, catalyzed by iron(III) sulfate supported on silica at ambient temperature under solvent-free conditions (Scheme 11) [141]. Silica-supported iron catalysts have been prepared and used in affecting various organic reactions [142–148]. Aldehydes bearing different functional groups as well as heteroaryl aldehydes reacted smoothly with *o*-PDs leading to the formation of corresponding 1,2-disubstituted benzimidazoles with complete selectivity and in good to excellent yields. No
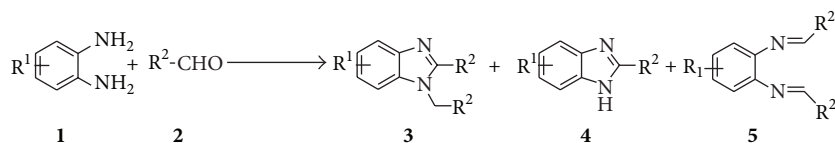
electronic or steric impact was found to be prominent in the selective formation of **3**.

Although the exact mechanism is not clear, the Lewis acid-mediated mechanism is expected to play (Figure 2). Adsorption of iron(III) sulfate on the surface of silica is believed to make polynuclear iron(III) hydroxyl complexes **4** [149]. Silica being a water absorbent could facilitate formation of the bis-Schiff base **5**, which has been reported and indeed was isolated when the reaction was stopped after 20 min. The Schiff base **5** may undergo cyclization followed by 1,3-hydride shift induced by electrophilic catalyst [150], resulting in the formation of the 1,2-disubstituted benzimidazole **3**. An indirect evidence in favour of 1,3-hydride shift of the Schiff base **5**, isolated from *o*-phenylenediamine and salicylaldehyde (**6**), showed reluctance to undergo cyclization at room temperature. This is possibly because of intramolecular H–bonding with *o*–OH group [151], making the nitrogen less nucleophilic, and thus required higher temperature for the cyclization (Scheme 12). The existence of intramolecular hydrogen bonding in the Schiff base (**6**) was also demonstrated by ^{1}H–NMR studies at varying concentrations of the Schiff base (**6**) [141].
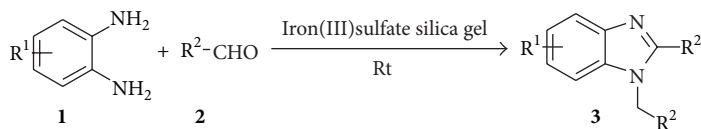
4. Reactions on Organic Polymer Support

The polymeric supports used by Merrifield for his early work in solid-phase peptide synthesis were based on 2% divinylbenzene (DVB) cross-linked polystyrenes (PS). PS has been found to be one of the most accepted polymeric material used in various synthesis because it is inexpensive, readily available, mechanically robust, chemically inert, and smoothly functionalizable [152, 153]. Crosslinking imparts mechanical stability, improved diffusion and swelling properties to the resin. Various percentages and types of crosslinking agents have been incorporated into the PS resins, the most common being DVB, but other examples include ethylene glycol dimethylacrylate (EGDMA) and tetraethylene glycol diacrylate (TEGDA) to give different solvation properties [154, 155]. A schematic representation of polymerization of styrene with functionalized monomers is shown in Figure 3.

TentaGel [156] and ArgoGel [157] (Figure 4) are two commercially available examples, where the incorporation of the PEG chains dramatically increases resin compatibility with polar solvents.
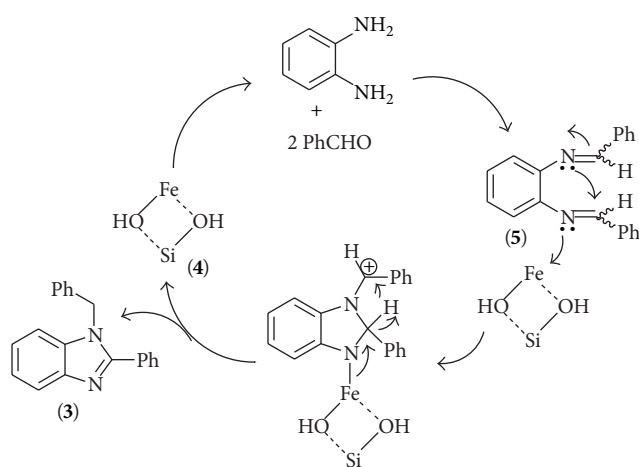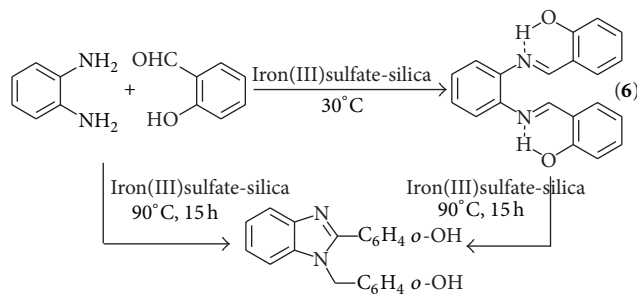
Scheme 10

Scheme 11

Figure 2

Scheme 12

Generally, reagents and catalysts are immobilized onto polymer surface involving (i) covalent binding, (ii) entrapment, where a preformed catalyst is enveloped within a polymer network, and (iii) ion-pairing, where cations or anions are bound to complementary resin sites [158]. Immobilization of reagents and catalysts can also be done by microencapsulation [159], where the polymers are physically enveloped by thin films of reagents or catalysts, and perhaps stabilized by the interaction between π electrons of benzene rings of the polystyrene used as a polymer backbone and vacant orbital of reagents or catalysts [160].

4.1. Catalytic Transfer Hydrogenation (CTH) Using Supported Formate.
Catalytic transfer hydrogenation (CTH) with the aid of a stable hydrogen donor is a useful alternative method to catalytic hydrogenation using molecular hydrogen (H_2) [161–166]. In transfer hydrogenation, several organic molecules such as hydrocarbons, primary and secondary alcohols, and formic acid and its salts have been employed as the hydrogen source [167–173]. The use of reagents such as hydrazine is less frequent. The use of a hydrogen donor has some advantages over the use of molecular hydrogen, since it avoids the risks and the constraints associated with hydrogen gas as well as the necessity for using pressure vessels and other equipment.

4.1.1. Palladium-Catalyzed Transfer Hydrogenation (CTH) of Alkenes and Imines.
In connection with our interest in palladium-catalyzed transfer hydrogenation (CTH) of alkenes and imines using potassium formate [82], we wanted to develop a stable hydrogen donor anchored to a solid surface to be used in CTH (Figure 5). In search of suitable polymeric supports, ion-exchange resins were used. It was observed that Amberlite IRA-420 anion (chloride form) exchange resins, commercially available and inexpensive polyionic resin, could exchange the anion with formate anion ($HCOO^-$) easily and quantitatively. The resulting Amberlite Resin Formate (anion), designated as ARF, could be utilized as a solid-phase version of the H-donor in Pd-catalyzed CTH. The ARF was air stable, can be stored for several weeks, and also can be recovered from a reaction and reused. Several alkenes and imine were thus hydrogenated using the ARF and catalytic amount of palladium acetate under mild conditions (Scheme 13) [174].

The reduction of the C–C double bond proceeded smoothly at 70–75°C requiring only gentle agitation; work-up was then achieved by simple filtration, extraction with diethyl ether and followed by evaporation of the solvent. Both the cyano and ester groups remained unaffected under the reaction conditions. The reduction of a dicyanoalkylidene derivative was found to occur with similar efficiency. The method is operationally simple and applicable to a variety of unsaturated organic compounds. The use of a palladium catalyst exhibits some substrate selectivity, and the transfer
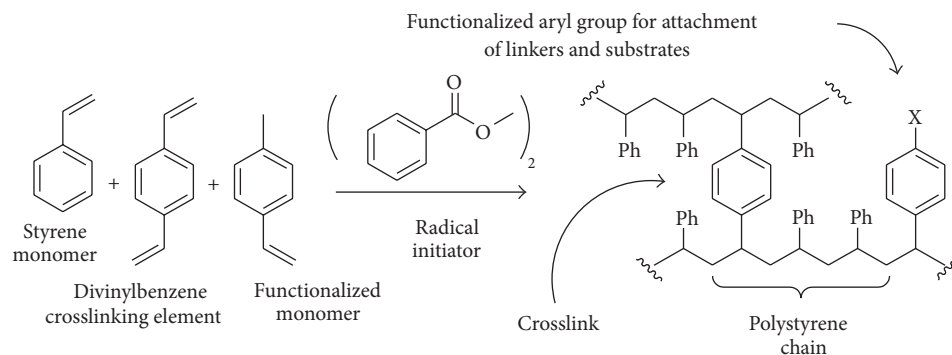
Functionalized aryl group for attachment
of linkers and substrates

Styrene
monomer

Divinylbenzene
crosslinking element

Functionalized
monomer

Radical
initiator

Crosslink

Polystyrene
chain

Figure 3

TentaGel

$n = 70$ X = OH or NH_2
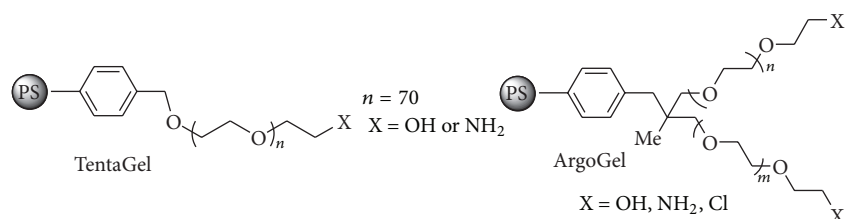
ArgoGel

Me

X = OH, NH_2, Cl

Figure 4

hydrogenation appears to proceed at a slower rate in comparison to that of potassium formate.

4.1.2. Palladium-Catalyzed Transfer Hydrogenation (CTH) of Nitroarenes. With the success of reducing C–C and C–N bonds using the solid-supported formate as suitable H-donor [174], further attempts have been made in the reduction of nitroarenes to anilines, which is a synthetically important transformation both in the laboratory and in industry. Formic acids and their salts are frequently employed as H-donor in CTH reactions, and nitroarenes can be reduced to anilines using ammonium formate and Pd-C or Raney nickel [175–177]. However, reductive elimination of halogen substituents on the aromatic nucleus and formation of *N*-formyl derivatives instead of arylamines are the major drawbacks of using ammonium formate/Pd-C. On the other hand, combination of $NaBH_4$ with Cu(II), Co(II), or Rh(III) halides has been used for reduction of the nitro group, which is inert to $NaBH_4$ itself [178, 179]. Metal hydrides are, however, water-sensitive as well as expensive chemicals. The reduction of nitro group was carried out using 2 mol% $Pd(OAc)_2$ and (aminomethyl) polystyrene with formate anion (ARF) in a minimum quantity of DMF at 100–120°C for 6–14 h (Scheme 14) [180].

4.1.3. Ruthenium-Catalyzed Transfer Hydrogenation (CTH) of Carbonyl Groups. Reduction of carbonyl functionality by transition metal-catalyzed transfer hydrogenation (CTH) with the aid of a suitable H-donor is a valuable synthetic tool. Generally, reduction of aryl ketones is performed under CTH using isopropyl alcohol as the H-donor [181–186]. In order to check the efficiency of Amberlite Resin Formate (ARF), reduction of aryl ketones was studied using the combination of catalytic amount of Ru(III) salts and

the polyionic resin formate. The results constitute an efficient method for chemoselective transfer hydrogenation of aryl aldehydes with the aid of resin-supported formate in the presence of catalytic (2.5 mol%) amount of commercially available $RuCl_3\cdot3H_2O$ in DMF or DMA solution, as outlined in Scheme 15 [187].

On the basis of comparison with a well-defined Ru(II) complex [Dichloro(p-cymene)ruthenium(II)] dimer; (2 mol %) under similar conditions, it is presumed that the Ru(III) salt might undergo in situ reduction to Ru(II), which then catalyzes the hydrogenation of the aldehydes. Aryl and heteroaryl aldehydes, substituted with various electron withdrawing and donating groups and the presence of *o*-substituents, do not seem to influence the rate of the reduction as revealed by the similarity of the results, and all compounds afford corresponding alcohols in high yields. Several other potential reducible groups like halogens, nitro, and so forth are not affected under the reaction conditions. Aliphatic aldehydes are also reduced to corresponding alcohols efficiently. Interestingly, aryl ketones are not reduced under similar conditions. The selectivity between aryl aldehyde and aryl ketone might offer a distinct advantage when both the functional groups are present. Thus, an experiment was conducted taking a mixture of an aryl aldehyde and an aryl ketone (1 mmol each) at 85°C to finally afford the reduced alcohol from the aryl aldehyde, but the aryl ketone remained unchanged and recovered almost quantitatively. Whereas aryl ketones are not reduced under the conditions, reduction of benzil to benzoin proceeds smoothly in good to excellent yields. Distinct advantages of cleaner reaction and easy isolation of the product are notable features when comparing the application of heterogeneous ARF and a simple formate salt (herein potassium formate) in homogeneous phase.
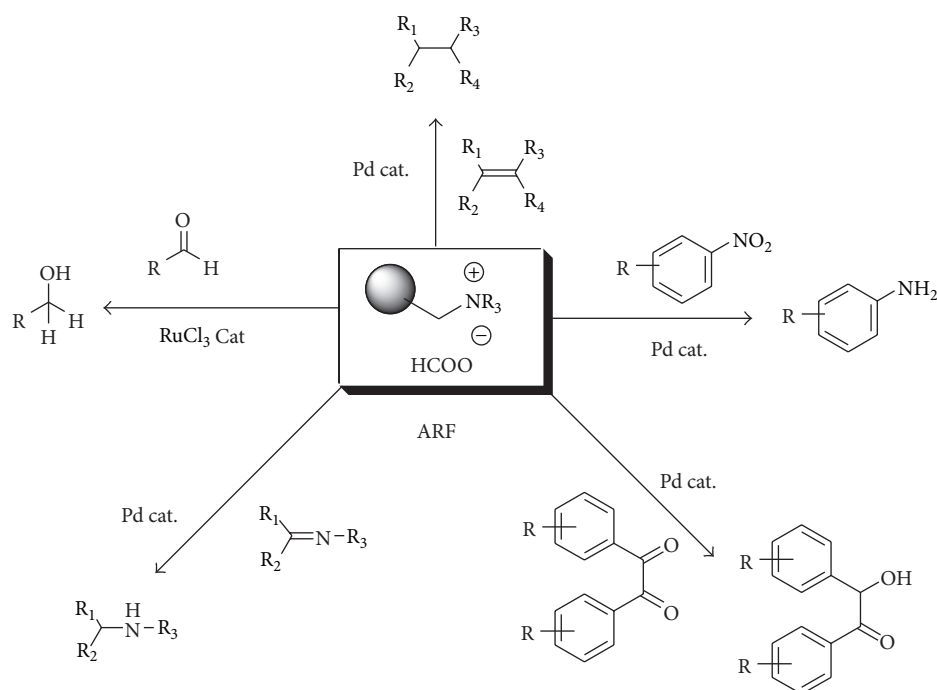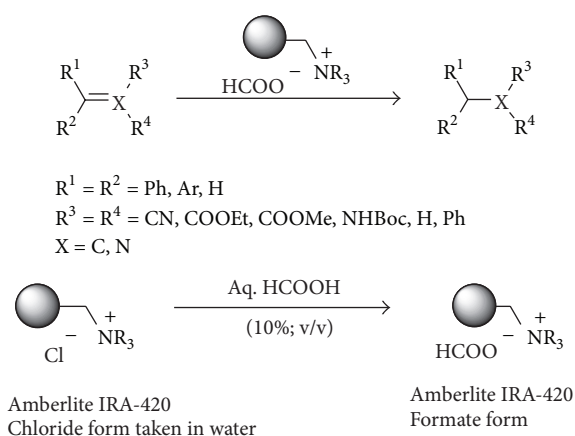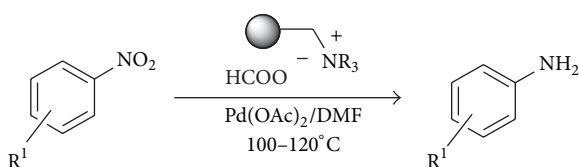
Figure 5

$R^1 = R^2$ = Ph, Ar, H
$R^3 = R^4$ = CN, COOEt, COOMe, NHBoc, H, Ph
X = C, N

Amberlite IRA-420
Chloride form taken in water

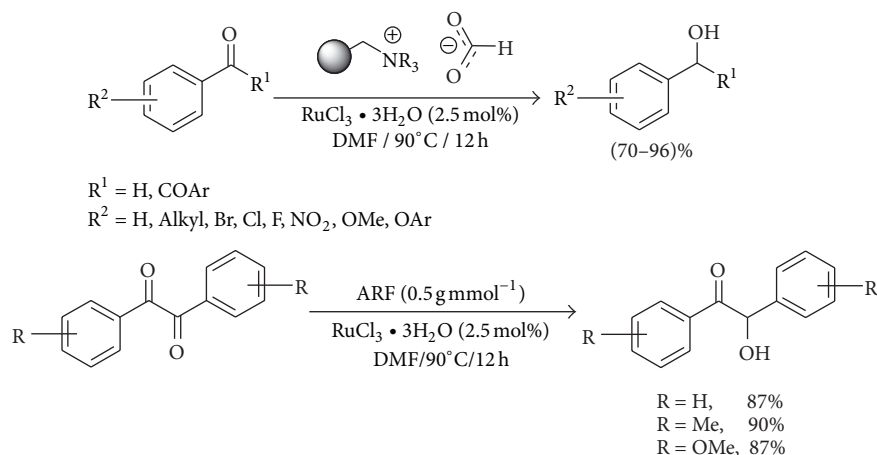Amberlite IRA-420
Formate form

Scheme 13

Scheme 14

The reaction conditions appear to be mild and base-free and give high yields of the corresponding alcohols and free of any by-product.

4.1.4. Catalytic Transfer Hydrogenation (CTH) Using Coimmobilized Catalyst/Reagent. It is well established that Pd promotes direct oxidation of formic acid to carbon dioxide
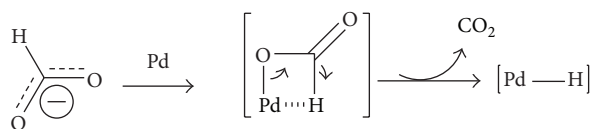
[173]. The combination of formic acid and palladium acetate is known to undergo anionic ligand exchange to form a palladium diformate complex, eventually producing Pd(0) through decarboxylation and loss of molecular hydrogen. The high degree of chemoselectivity in palladium-catalyzed transfer hydrogenation using HCOOH or its salts has been explained on the basis that the hydrogen is delivered directly from a palladium formate species, which has much stronger hydridic nature as compared to that of a palladium hydride species (Scheme 16).

In CTH, either a source of palladium is required for each operation or it may be supported by a polymer framework and reused several times. It is reasoned that the palladium catalyst might be anchored to the ARF so that it could be used and recycled (Scheme 17). It is observed that palladium can be immobilized onto the polyionic resins surface and used efficiently in the CTH of a variety of functional groups. Thus, a new solid-phase entity (ARF-Pd) has been developed coimmobilizing both the catalyst and the reagent and expected to be potentially useful in CTH of different functional groups.
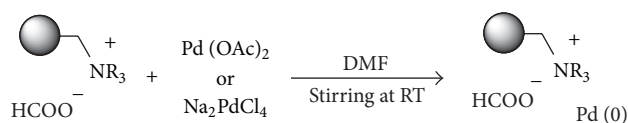
The efficiency and stability of this newly developed ARF-Pd was first examined in the reduction of electron-deficient alkenes conjugated with ketones, nitriles, and carboxylate esters (Scheme 18) [188]. Further applications of this new heterogeneous reductive system are tested with 1,2-dicarbonyl compounds. When benzil or substituted benzil is used as the substrate, the reduction of one of the carbonyl groups with ARF-Pd in DMF at 110°C has been completed within 10–12 h to furnish the corresponding α-hydroxyketone (benzoin) in a 77–88% yield. Aromatic nitro compounds are also reduced using the coimmobilized palladium in DMF. This new technique is highly chemoselective in the reduction

SCHEME 15

SCHEME 16

SCHEME 17

of alkenes, imines, and nitro groups, thus establishing an efficient, environmentally benign, economically friendly, and sustainable process.

4.2. C–C Cross-Coupling Reactions. Transition metal-catalyzed cross-coupling reactions constitute the central part of contemporary organic synthesis [189–192]. In particular, the palladium-catalyzed carbon-carbon bond-forming processes represent the foremost in the arena of organic process development. The Heck, Suzuki-Miyaura, Sonogashira reactions (Scheme 19) are excellent tools for carbon-carbon coupling reactions between aryl halides or triflates and suitable partners [193].

The coupling of terminal alkynes with an aryl or vinyl halide performed with a palladium catalyst, a copper cocatalyst and an amine base, is termed as the Sonogashira coupling reaction [194–206]. Typically, the reaction requires anhydrous and anaerobic conditions, but the newer procedures which have been developed show that the restrictions are not so important.

Over the last decade, commendable research has been done to achieve significant developments and to establish practical methodologies [207–210]. Widespread uses of palladium-catalyzed coupling reactions are found in modern organic synthesis, becau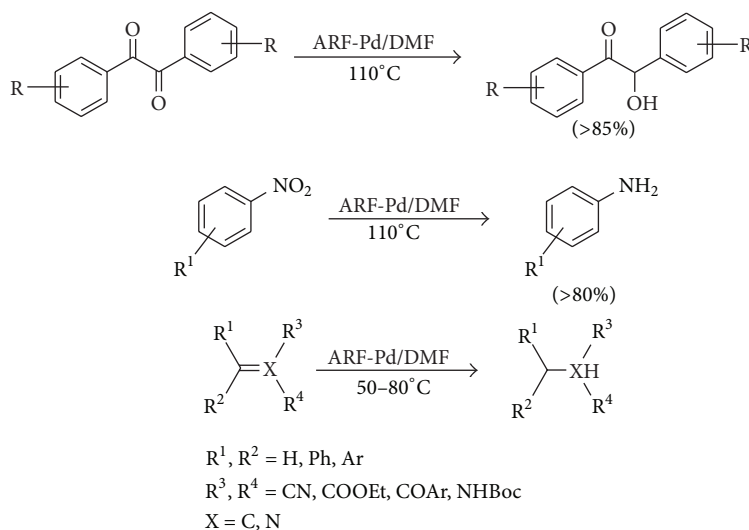se the resulting coupled products often find good applications in the preparation of materials, pharmaceuticals, and other bioactive compounds [211–218]. As a part of recognition of these extremely useful reactions, Nobel prize was awarded to Heck, Suzuki, and Negishi [219]. Many efforts have been reported to immobilize Pd, using a support, encapsulating in a polymer or dendrimer or immobilization by ligand/polymer, but the problem of leaching and recyclability still exists [220–236].

4.2.1. Use of ARF-Pd in C–C Cross-Coupling Reactions. Excellent activity, high selectivity, and reusability of the ARF-Pd as potential reductive system have prompted to explore it as a viable heterogeneous Pd catalyst in various C–C coupling reactions (Scheme 20) [237]. One of the key questions on which the researchers have focused is "how can minimization of catalyst cost and catalyst contamination of the product be best achieved?" It may be noted that the investigation of the heterogeneous ARF-Pd has addressed a great extent to this question.
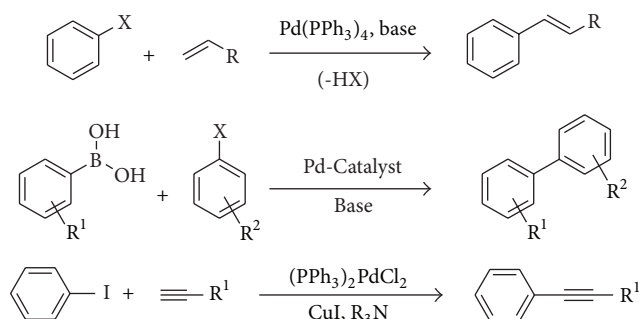
The catalytic activity of ARF-Pdwas first examined in the Heck coupling reactions and then for the Suzuki and Sonogashira reactions, as outlined in Scheme 20.

Indeed the Heck coupling between 3-chloroiodobenzene and ethyl cinnamate in the presence of the heterogeneous catalyst ARF-Pd, the cross-coupled product, *trans*-ethyl-3-chlorocinnamate, has been isolated in 86% yield. Exclusive *trans*-selectivity is achieved, as is assigned on the basis of the coupling constant (J = 15.9 Hz). Although several iodoarenes undergo Heck coupling with an alkene, interestingly, the bromoarenes remain unchanged which is typically seen for other halogens like chloro or fluoro groups attached with the aromatic moiety. The *ortho*-substituent did not cause any steric inhibition, as usually experienced in other coupling reaction, which may be attributed to high activity of the catalyst.

The Suzuki-Miyaura reaction (Scheme 20) has been carried out using 4-bromo-2-methyl anisole, phenyl boronic acid, Na_2CO_3 in the presence of ARF-Pd. Heating the mixture at $110°C$ for 5 h under N_2 followed by removal of ARF-Pd by simple filtration and chromatographic purification of

SCHEME 18

SCHEME 19

the residual mixture furnished the desired unsymmetrical biphenyl in 82% yield. Both *bis-* and *tris-*coupled aryl benzenes have also been prepared in good to excellent yields when reactions are performed using di- and tribromoarenes, respectively, showing notable activity of the heterogeneous palladium catalysts (ARF-Pd). It may be noted that *ortho-* dibromobenzene affords a mixture of mono- and biscoupled products in the presence of $Pd(OAc)_2$ as the source of palladium.
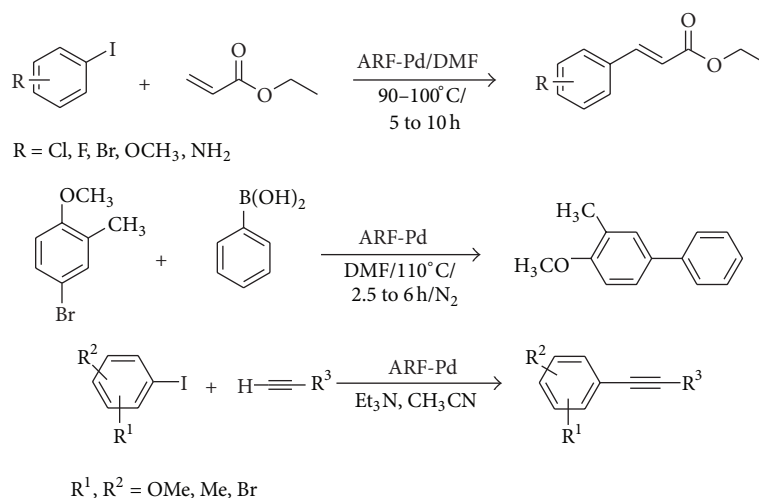
The Sonogashira coupling reaction normally requires 1–10 mol% $Pd(PPh_3)_2Cl_2$ (or $Pd(PPh_3)_4$) and copper(I) iodide as the catalytic system. Using the ARF-Pd, the reaction of 3-iodoanisole and 1-ethynyl-4-methylbenzene carried out in the presence of Et_3N as the base in acetonitrile solvent at 80°C for 6 h afforded the desired cross-coupled product in excellent yield (Scheme 20). Similar coupling reactions with other iodoarenes and acetylenes are also found to be successful [237].

In all cases, products are isolated in pure form simply by filtering off the resin-bound palladium catalyst followed by chromatographic purification of the concentrated residue. Recycling experiments are tested by taking Suzuki-Miyaura coupling between 1,4-dibromobenzene and phenylboronic acid. The results have revealed that the catalyst is remarkably
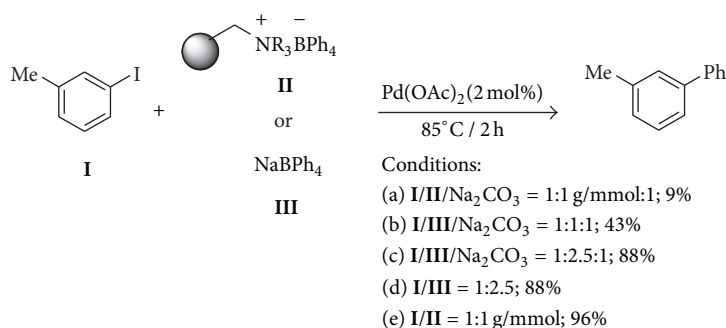
active even in the fifth run. Consecutive five runs were tested to evaluate the activity of ARF-Pd. The palladium content throughout the recycling runs remained at a steady state with marginal increase of Pd distribution on the resin surface, which might be due to repeated agitation of the beads during the reactions and exposing more surface area with palladium content.

4.2.2. Suzuki Coupling Using Solid-Phase Immobilized Organoboron Species.
The concept of a resin-capture-release technique generating the polymer-bound reactive species has been established as a potential method for several organic transformations [238–240]. A variety of techniques are reported in the literature to immobilize different components of Suzuki cross-coupling reaction [241–253]. Polymer-bound boronic acids though reported as early as 1976 [254], Frenette and Friesen [255] investigated their utility in Suzuki coupling reaction in 1994.

Further application of polyionic resin bound reagents and/or catalysts has been established when an ion-exchange resin-supported organoborate species is derived as a heterogeneous phenylating agent [256]. Thus, Amberlite ion-exchange resins (chloride form) are exchanged with tetraphenylborate anion (Ph_4B^-) by continuous rinsing with an aqueous solution of $NaBPh_4$ until the washings gave negative response to chloride anion (monitored with $AgNO_3$ solution followed by addition of aqueous ammonia). The polyionic resins with the tetraphenylborate counter anion (Ph_4B^-) have been used directly for the Suzuki coupling reaction. Initial studies on coupling with 3-iodotoluene in the presence of palladium catalyst [$Pd(OAc)_2$; 2 mol% and Na_2CO_3; 1 equiv.] afford the unsymmetrical biphenyl in 90% yield (Scheme 21, condition (a)). Similar coupling of 3-iodotoluene and $NaBPh_4$ in the presence of Na_2CO_3 afforded only 43% yield of the coupled product (Scheme 21, condition (b)). However, on increasing the quantity of $NaBPh_4$, the resulting coupled product could be isolated in 88% yield
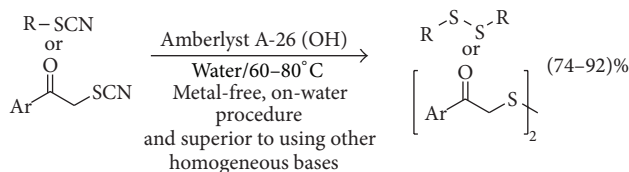
SCHEME 20

SCHEME 21

(Scheme 21, condition (c)). An interesting observation is that the yield of the coupled product is not influenced by the absence of base (Scheme 21, conditions (d) and (e)). Such base-free conditions for SM reactions could offer significant practical advantages and have not previously been reported with the organoborate ion bound with solid-phase polymeric frameworks.

4.2.3. Organic Disulfide (S–S Linkage) Synthesis. Organic disulfides (bearing S–S linkage) are useful compounds of widespread occurrence possessing unique and diverse chemistry in the synthetic, biochemical, and agrochemical areas [257–259]. Disulfide-linked aggregates ubiquitously occur in proteins and many other bioactive molecules. Disulfide bonds play an important role in the folding and stability of some proteins [260, 261]. Industrially, disulfides find vast applications as vulcanizing agents for rubbers and elastomers, contributing them considerable tensile strength [262, 263]. Apart from various solution-phase approaches for the synthesis of disulfide from thiols and other precursors, there are few reports on the synthesis of disulfides promoted by polymeric resin hydroxides. In a recent report, Sengupta and Basu have shown that Amberlyst A-26(OH) can efficiently promote smooth conversion of disulfides from alkyl and acyl

methyl thiocyanates in good to excellent yields (Scheme 22). They have also demonstrated that the use of polyionic resin hydroxide has resulted in much better results over other homogeneous bases like NaOH, NH_3, K_2CO_3 [264].

5. Conclusion

Thus, a series of reactions has been developed exhibiting the potential of using both inorganic and organic polymeric frameworks as the solid phase. The present review has shown that alumina, silica surface alone or having doped with various inorganic salts could be utilized in carrying out different organic reactions under solvent-free conditions producing molecules of biological and industrial importance. Similarly, polyionic resins have been shown to immobilize reagents and/or catalysts and employ in transfer hydrogenation of alkenes, imines, and nitroarenes and in different C–C cross-coupling reaction. Mild reaction conditions, easy work-up procedure, selective synthesis of the target molecules, and recycling capability of the supported reagent or catalyst are some of the advantages of adopting solid-phase organic reactions. Further development of newer solid phases, immobilization procedures resulting in regular dispersion and finally their new applications are expected in the years to come.

SCHEME 22

Acknowledgments

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