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REVIEW

Porous and chelated nanostructured multifunctional materials: recoverable and reusable sorbents for extraction of metal ions and catalysts for diverse organic reactions

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Abstract This review article gives an insight into recent developments in chelating agents modified nanostructures in metal extraction and catalysis. The ability of functionalization by anchoring specific functional groups on the surface of nanostructures makes it possible to synthesize different types of desired chelated nanostructures for their use as catalysts and metal ion scavengers. Keeping these aspects in outlook this review emphasizes mainly on the synthesis of chelating agent functionalized nanostructures and their applications in the field of metal ion extraction and catalysis. The review article provides comprehensive information about the work that has been done in the past 5 years in the field of metal ion extraction and catalysis using chelating agent modified nanoparticles.

Keywords Porous · Chelated · Nanoparticles · Catalysts · Sorbents · Metal ions · Reusable

Introduction

Environmental pollution and hence affected human health due to release of metal ions in the environment, particularly as industrial waste, poses a serious problem. The removal and recovery of these metal ions is, therefore, a significant concern [1]. The key to extract these metal ions in an economically viable manner lies in the use of highly efficient, cost-effective and environmentally acceptable techniques. A broad range of physiochemical separation processes such as precipitation, sorption, membrane processes, electrolytic recovery, solid-phase extraction (SPE) and liquid–liquid extraction are available for this purpose [2–5]. Among these techniques, SPE is fast, generates less waste, regenerates the solid phase and does not require toxic solvents. Therefore, SPE has emerged as a powerful tool for separation/enrichment of metal ions using modified sorbents [6]. Further, chelation plays an important role in enhancing their adsorption capacity and easy separation. Chelated sorbents are more efficient and can be recovered and reused for many cycles [7–9].

In recent years, nanotechnology has emerged as one of the most key technologies in the field of metal extraction, catalysis, pharmacy, biotechnology, electronics, etc. [10–12]. The fabrication of nanostructured chelated sorbents, particularly for metal ion extraction, is emerging as an important field of analytical chemistry due to their unique properties [13]. Nanostructured sorbents show high surface reactivity with their large surface areas so that their surfaces can be easily modified by various chelating agents [14]. Chelating agent modified nanoparticles, being highly selective can easily bind to metal ions with strong chemical activities, thus providing high sorption capacity, high enrichment factors for separation and recovery of various metal ions. For this purpose, accurate selection of appropriate support and chelating agent is required for full recovery of metal ions with high enrichment factor [15].

In addition to the application of nanostructured materials for extraction of metal ions, the use of these materials to catalyse diverse organic reactions has received much attention in recent times [16–24]. It is well known that activity of catalysts depend on size, dimensions and morphologies and, therefore, the porous and nanostructured materials are expected to exhibit enhanced catalytic efficiency and reusability [25–27]. These porous and chelated nanostructured multifunctional materials, along with their

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metal extraction and catalytic properties, have also shown biological activities such as antibody purification from human plasma, removing oxidative stress, etc. [28–32]. But, in the present review, we have focused on the synthesis and application of porous and chelated nanostructured multifunctional materials for extraction of metal ions and as catalysts for diverse organic reactions.

Porous and chelated nanostructured materials for extraction of metal ions

The extraction of metal ion plays a significant role in soil, air and water remediation. Nanoparticles provide high surface area and are, therefore, suitable for this purpose. The extraction of metal ions, as explained earlier, can be done easily and efficiently by SPE.

SPE technique requires a support material to prepare an efficient sorbent. Based on the chemical nature, these can be divided as inorganic sorbents including modified metal/metal oxide nanoparticles, organic sorbents (generally carbon nanotubes) and organic–inorganic based sorbents (Table 1) [33–35]. In general, nanostructured sorbent systems are fabricated by functionalization of ligands over sorbent coated nanoparticles followed by metal immobilization (Fig. 1; Table 2).

Inorganic-based sorbents

The use of surfactant-coated mineral oxides (generally alumina and silica) as sorbent materials has received much attention for extraction of various metal ions. These sorbent materials provide high surface areas. The modification of sorbent helps in their selectivity and increased activity. The most commonly used methods of modification are physisorption and chemisorption. However, chemical methods provide high stability and reusability.

Alumina nanoparticles

Afkhami et al. modified alumina nanoparticles with 2,4-dinitrophenylhydrazine (DNPH) by prior treatment with sodium dodecyl sulphate (SDS) for increasing its adsorption capacity. They found that SDS-coated alumina formed hemi-micelles which trapped DNPH molecules homogeneously, thus changing colour of alumina from white to orange. The immobilization of DNPH on SDS-coated alumina nanoparticles favoured uptake of metal ions by complex formation, thus extracting metal ions like Pb(II), Cr(III), Cd(II) efficiently [2]. Ezoddina et al. coated nano-sized alumina with sodium dodecyl sulphate-1-(2-pyridylazo)-2-naphthol (SDS-PAN) by formation of hemi-micelles. They observed that at lower pH, positively charged nano-γ-alumina surfaces sorbed negatively charged SDS efficiently. These modified alumina nanoparticles were used for preconcentration of Cd and Pb samples [15].

Baezzat et al. modified SDS-coated alumina nanoparticles with 3-mercapto-D-valine. They found that coating alumina nanoparticles with SDS provided greater efficiency for metal ion recovery. The presence of free lone pairs on nitrogens of the ligand coordinated with metal ions, thus causing their extraction. This method provided higher recoveries of zinc, iron and copper ions [36].

Magnetic nanoparticles

The use of magnetic nanoparticles has provided better kinetics for adsorption of metal ions. Zhai et al. modified

Table 1 Various chelated nanostructured inorganic sorbent-support systems for extraction of metal ions

S. no.	Support material	Ligand	Selective for following metal ion	References
1.	Alumina nanoparticles	2,4-Dinitrophenylhydrazine	Pb(II), Cd(II), Cr(III), Co(II), Ni(II) and Mn(II)	[2]
2.	Alumina nanoparticles	Sodium dodecyl sulphate-1-(2-pyridylazo)-2-naphthol	Cd(II) and Pb(II)	[15]
3.	Alumina nanoparticles	Sodium dodecyl sulphate, 3-mercapto-D-valine	Zn(II), Fe(II) and Cu(II)	[36]
4.	Silica coated-magnetic nanoparticles	2,6-Diaminopyridine	Cu (II) and Zn(II)	[37]
5.	Magnetic nanoparticles	(3-Aminopropyl)-triethoxysilane (APTES) and glutaraldehyde (GA)	Cu(II)	[39]
6.	Magnetic nanoparticles	Dithizone	Cr(III), Cu(II), Pb(II), Hg(II) and Zn(II)	[40]
7.	Gold nanoparticles loaded in activated carbon	Bis-(4-methoxy salicylaldehyde)-1,2-phenylenediamine	Co(II), Cu(II), Ni(II), Fe(II), Pb(II) and Zn(II)	[1]
8.	Mesoporous silica nanoparticles	*N*,*N*(octane-1,8-diylidene)di(2-hydroxy-3, 5-dimethyl-aniline)	Pd(II)	[42]
9.	Halloysite nanotubes	Murexide	Pd(II)	[3]

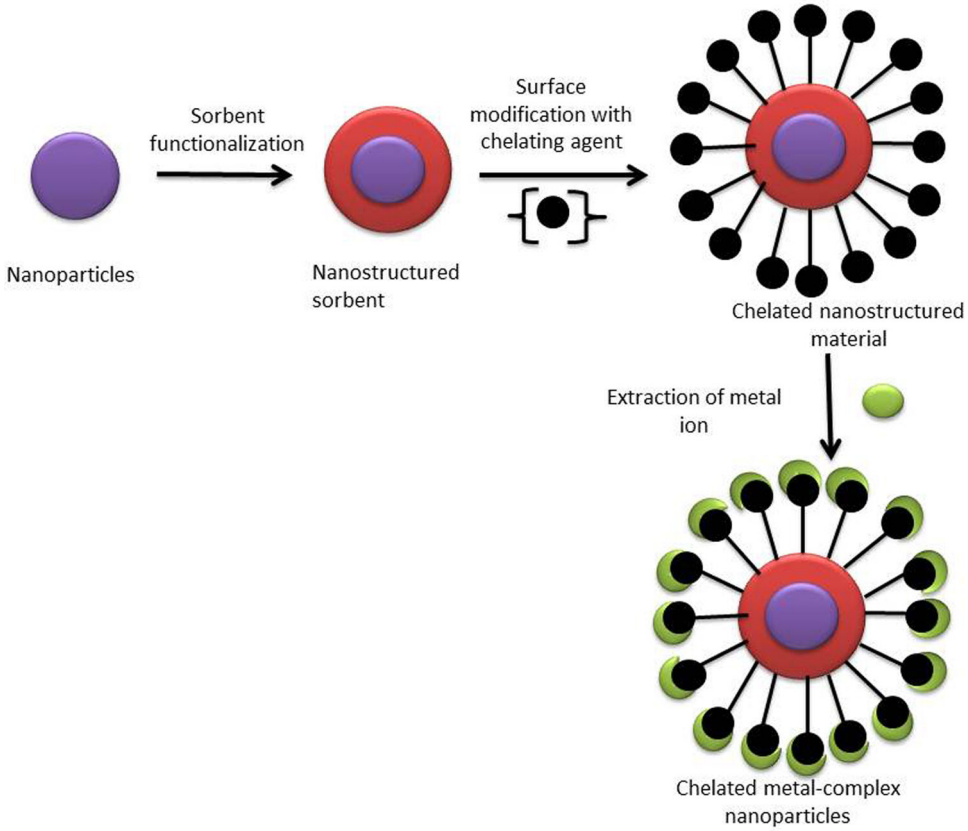


Fig. 1 Sequence of events in the preparation of chelated nanostructured materials

Table 2 Various chelated nanostructured organic sorbent-support systems for extraction of metal ions

S. no.	Support material	Ligand	Selective for following metal ion	References
1.	Multiwalled carbon nanotubes	2-(2-Hydroxy-5-nitrophenyl)-4,5-diphenyl imidazole	Co(II), Cu(II), Ni(II), Fe(II), Pb(II) and Zn(II)	[6]
2.	Multiwalled carbon nanotubes	(*E*)-*N*1-(4-nitro-benzylidene)-*N*2-(2-((*E*)-4-nitrobenzylideneamino)ethyl) ethane-1,2-diamine	Cu(II), Zn(II), Pb(II) and Cd(II)	[45]

silica-coated Fe_3O_4 nanoparticles with 2,6-diaminopyridine. The stereochemical interactions of two amino and one pyridine ring with target ion resulted in selective coordination for Cu(II) and Zn(II). Since the adsorption capacity of these two ions is comparable, the magnetic nanoparticles were of great use because of high selectivity and magnetically separable property [37]. Huang and Hu synthesized silica-coated magnetic nanoparticles (SCMNPs) and modified them with γ-mercaptopropyltrimethoxysilane (γ-MPTMS) for extraction of trace amounts of Cd, Cu, Hg and Pb. For the recovery of metal, magnetic nanoparticles were separated easily using an external magnetic field. This method provided high enrichment factors and rapid adsorption of metals under study [38].

Ozmen et al. used a quick and easy metal separation process by preparing (3-aminopropyl)-triethoxysilane (APTES) and glutaraldehyde (GA) and modified them with Fe_3O_4 magnetic nanoparticles. These nanoparticles were then used for effective removal of Cu(II)from wastewater in acidic pH range (4.0–5.3). This separation process was completed in around 15 min and thus proved to be efficient for this purpose [39].

Hu et al. modified the surface of magnetic Fe_3O_4 nanoparticles with dithizone, mercaptopropyltrimethoxysilane and bismuthiol-II. These modified magnetic nanoparticles proved to be efficient for the fast preconcentration and determination of trace amount of Cr(III), Cu(II), Pb(II), Hg(II) and Zn(II) in environmental and biological samples [38, 40, 41].

Organic monolayer-coated metal nanoparticles have proved to be good sorbents due to chemical stability and selectivity. Karimipour et al. synthesized gold nanoparticles loaded in activated carbon (Au-NP-AC) and modified it by bis-(4-methoxy salicylaldehyde)-1,2-phenylenediamine (BMSAPD). This sorbent was used for enrichment and preconcentration of trace amounts of Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} ions via complexation by BMSAPD ligand. They retained metal ions by elution with HNO_3 [1].

Silica nanoparticles

Awual et al. prepared a nano-conjugate adsorbent (NCA) by anchoring an organic ligand *N*,*N*(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethyl-aniline) (DHDM) onto mesoporous silica by direct immobilization approach. DHDM has strong electrostatic interactions with hydroxyl-containing mesoporous surface. This sorbent exhibited distinct colour based on charge transfer on sorption of Pd(II) in both solid and liquid states. Pd(II) adsorption was found to increase sharply on increasing contact time and concentration of ligand [42].

Halloysite nanotubes

Besides mineral oxides, halloysite (2-layered alumino silicate clay mineral) nanotubes have also been used for the purpose of metal extraction. Since halloysite nanotubes (HNTs) have reactive hydroxyl groups on the surface, their modification with some organic compound tends to increase the sorption selectivity of metal ions. Li et al. synthesized and used murexide functionalized HNTs for selective extraction of Pd(II). Acidic environment was provided for protonation of binding sites of chelating agent, thus favouring selective adsorption of Pd(II). Pd(II) was retained on the column at pH 1.0 and quantitatively eluted by 2.5 mL of 0.01 mol L^{-1} HCl–3 % thiourea solution at a flow rate of 2.0 mL min^{-1} [3].

Organic-based sorbents

Multiwalled carbon nanotubes (MWCNTs) have high tensile strengths and great thermal and chemical stability. Due to high surface area and large micropore volume, these are good adsorbents for metal ion extraction [43, 44].

Ghaedi et al. modified MWCNTs with 2-(2-hydroxy-5-nitrophenyl)-4,5-diphenyl imidazole for enrichment of trace amounts of various ions. To obtain highly efficient metal ions, optimization of the influence of variables including pH, amount of ligand and solid phase, type and condition of eluent and common coexisting ions was done. The metal ions (Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}) were then desorbed using nitric acid [6].

Soylakab et al. modified MWCNTs with (*E*)-*N*1-(4-nitrobenzylidene)-*N*2-(2-((*E*)-4-nitrobenzylideneamino)ethyl) ethane-1,2-diamine (NBNBAEED). Due to the existence of donating nitrogen atom as well as –NH group in NBNBAEED, both the stability and selectivity of its Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} ion complex over other metal ions increased, thus providing fast adsorption and high metal recovery [45].

Porous and chelated nanostructured materials as reusable catalysts for diverse organic reactions

The photocatalytic reactions occur mainly on surface of a catalyst. Since nanostructures provide a large surface-to-volume ratio, they show high photocatalytic activity [46]. Since metal nanoparticles can easily aggregate in catalytic reactions and hence can decrease the available surface area, metal nanoparticles are modified with various sorbents. The chelated nanostructured materials have been used for catalysing various organic reactions as explained below.

Reduction reactions

Both metal and metal oxides modified with suitable chelating agents have been used as catalysts in reduction reactions. Du and He immobilized gold nanoparticles into previously fabricated amino-functionalized silica nanoparticles with centre-radially hierarchical mesopores (Au–NH_2–HMSNs) and used them as catalyst in catalytic reduction of 2-nitroaniline (Fig. 2). The centre-radially hierarchical mesopores enhanced diffusion of guest molecules, thus providing excellent catalytic activity and stability [47].

Jiang et al. prepared nano-Ni core mesoporous-silica shell (NCMSS) particles using EDTA as the chelating agent (Ni@SiO_2/EDTA) and used them as a catalyst for reduction of 4-nitrophenol to 4-aminophenol in the presence of excess amount of $NaBH_4$ (Fig. 3). The reaction was found to show pseudo-first order kinetics with respect to 4-nitrophenol. Since only a small amount of catalyst provides great results, NCMSSs have a great potential in catalytic fields in future [26].

Sharma et al. immobilized copper(II) acetylacetone complex over amino functionalized silica@magnetite

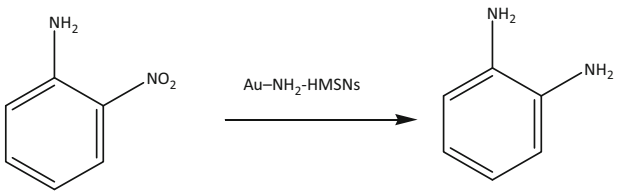


Fig. 2 Reduction of 2-nitroaniline using Au–NH_2–HMSNs

nanoparticles (Cu–acac@Am–Si–Fe_3O_4) for catalytic reduction of nitro group using $NaBH_4$ as source of hydrogen (Fig. 4). They also studied the kinetics for reduction reaction of *o*-nitroaniline to benzenediamine. Since nano-catalytic system can be easily recovered using magnets, they can be reused for multiple cycles [48].

Negroa et al. prepared three Fe–N non-noble electrocatalysts using networked graphitic structures as support. They found that catalysts with higher cobalt and iron content showed maximum oxygen reduction reaction (ORR) activity. This electrocatalyst showed promising applications in low-temperature fuel cells [49].

Veerakumara et al. synthesized gold nanoparticles (AuNPs) using highly branched polyethylenimine (PEI) and acylated PEI as the chelating agents. These modified gold nanoparticles were found to be excellent catalyst for selective reduction of nitro compounds in presence of sodium borohydride (Fig. 5). This catalyst was found to be stable for a long time without any provided support [50].

Oh et al. synthesized nitrogen-modified carbon nanofibres by pyrolysis of cobalt, polypyrrole (PPy) using ethylenediamine (ED) as the chelating agent for obtaining stable oxygen reduction catalysts. They found that combined use of PPy and ED increased activity and stability of catalyst by increasing total nitrogen contents [51].

Photocatalytic degradation reactions

Yang et al. synthesized YMn_2O_5 nanoparticles using different chelating agents. They found that YMn_2O_5 nanoparticles prepared using citric acid exhibited slightly high photocatalytic activity than the sample prepared using EDTA as the chelating agent. These nanoparticles showed excellent photocatalytic activity for oxidative decomposition of methyl red under UV and visible light irradiation [27].

Zhanga et al. synthesized $Bi_2Fe_4O_9$ nanoparticles using different chelating agents and observed their photocatalytic activity. The use of EDTA favoured the synthesis of relatively small particle sized $Bi_2Fe_4O_9$ nanoparticles. These nanoparticles were found to exhibit excellent photocatalytic degradation of methyl red [46].

Makarova et al. modified surface of nanocrystalline titanium dioxide with specific chelating agents for

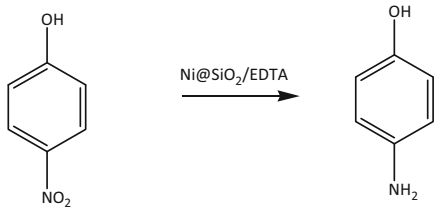


Fig. 3 Reduction of 4-nitrophenol using Ni@SiO_2/EDTA

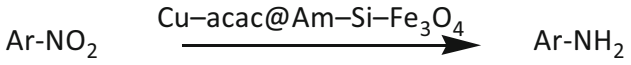


Fig. 4 Reduction of nitro group using Cu–acac@Am–Si–Fe_3O_4

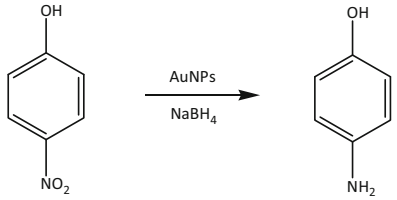


Fig. 5 Selective reduction of nitro compounds using AuNPs/PEI

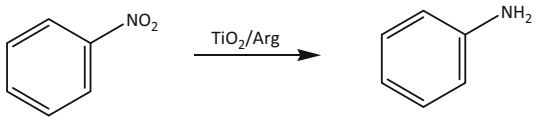


Fig. 6 Reduction of nitrobenzene using TiO_2/Arg

photochemical reduction of nitrobenzene. The modification was done using arginine, lauryl sulphate and salicylic acid (Fig. 6). It was found that arginine-modified TiO_2 (TiO_2/Arg) was more stable and showed better photocatalytic decomposition as compared to other chelating agents [52].

Wang et al. synthesized $BaTiO_3$ nanoparticles using acetylacetone and citric acid as chelating agents. These nanoparticles were tested for their photocatalytic activities for removal of humic acid from water. The tetragonal phase $BaTiO_3$ nanoparticles were found to be excellent photocatalysts for decomposition of organic pollutants [53].

Habibi and Mokhtari fabricated novel sulphur-modified niobium (V) oxide nanoparticles by a modified sol–gel method. A very stable sol-containing niobium (V) chloride and oxalic acid were used with isopropanol as chelating agent and thiourea as sulphur source. Unlike unmodified niobium (V) nanoparticles, the doped ones induced charge transfer across the niobium pentoxide interface. These nanoparticles can be suitably used as semiconductor photocatalysts and for visible light sensitization [54]. Sun et al. synthesized nano-sized $BiVO_4$ by a hydrothermal process in the presence of EDTA as chelating agent. With reduction of hydrothermal temperature and increase in concentration of EDTA, the size of $BiVO_4$ nanoparticles decreases. This sample showed a high photocatalytic activity for degradation of phenol solution [55].

Saien and Mesgari prepared nitrogen-doped TiO_2 nanoparticles using hematoporphyrin as the support material. These nanocomposites exhibited highly efficient visible-light photocatalytic activity for degradation of methyl

orange. These nanocomposites can be reused again without any loss in its activity [56].

Hydrogenation/dehydrogenation reactions

Tianbin et al. synthesized Zr-based metal organic frameworks (Zr/MOF) that contained both mesopores and micropores by the reaction of 1,4-benzenedicarboxylic acid (H_2BDC) and $ZrOCl_2{\cdot}8H_2O$ using citric acid as the chelating agent and cetyltrimethylammonium bromide (CTAB) as surfactant. The Ru@Zr/MOF (ruthenium nanoparticles embedded on Zr-based MOF) catalyst was prepared in supercritical CO_2–methanol solution. This resulted in Ru nanoparticles with small size that were uniformly supported in the Zr–MOF unlike in the case of immobilization where particles were of larger size. This catalyst showed significant catalytic activity in hydrogenation of benzene and its derivatives (Fig. 7) [57].

Qureshi et al. prepared Pd nanoparticles supported on porous silica nanospheres KCC-1. The silica-supported Pd nanocatalysts were prepared by modification of the supports with 3-aminopropyltrimethoxysiliane (3-APTES). 3-APTES acted as binding agent for $PdCl_2$ with the aim of obtaining well-spaced and uniformly dispersed Pd atoms on the silica surface. These proved to be efficient, chemoselective catalysts for hydrogenation of alkenes and α,β-unsaturated carbonyl compounds (Fig. 8). A comparison between Pd nanoparticles supported on KCC-1 and those prepared on traditional mesoporous silica materials under similar conditions was done. It was found that the nanoparticles on KCC-1 showed excellent catalytic activity and particle dispersion. This catalyst can be reused many times without any significant loss in its catalytic activity [58].

Oxidation reactions

Sharma and Sharma immobilized palladium complex on silica nanospheres functionalized with 3-aminopropyltriethoxysilane (SiO_2@APTES@Pd-FFR). This nano-catalyst was found to be highly selective for oxidative amination of aldehydes (Fig. 9). The high activity of this nanocatalyst provided ease in time and cost along with high yield and enhanced dispersion. Since this catalyst provided high turnover frequencies and can be easily reused without loss in its

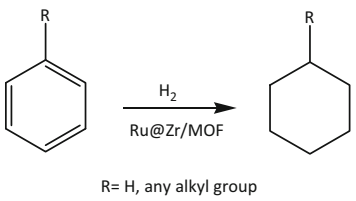


Fig. 7 Hydrogenation of benzene by Ru@Zr/MOF

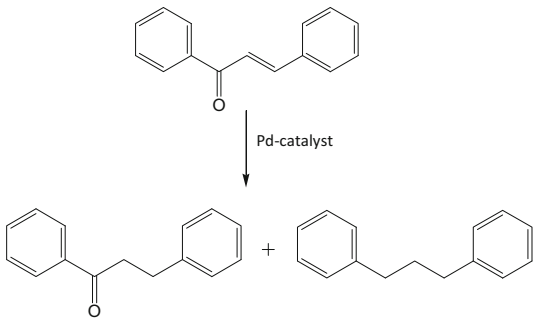


Fig. 8 Hydrogenation of alkenes and α,β-unsaturated carbonyl compounds

Fig. 9 Oxidative amination of aldehydes using SiO_2@APTES@Pd-FFR

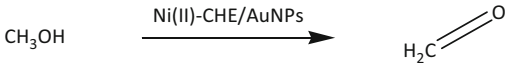


Fig. 10 Electrocatalytic oxidation of methanol by Ni(II)–CHE/AuNPs

activity, the catalyst proved to be useful for industrial and environmental applications [59].

Gholivand and Azadbakht prepared nano-structured Ni(II)–chelidamic acid-modified gold nanoparticles (Ni(II)/CHE/AuNPs) by electrodeposition of Ni(II)/CHE complex on the surface of the AuNP–Au electrode in alkaline solution. This catalyst was tested for electrocatalytic oxidation (Fig. 10) and determination of methanol. This electrode proved to be an excellent catalyst for oxidation of methanol [60].

Kumar et al. prepared nano-spinel $CuAl_2O_4$ and investigated the effect of ethylenediamine addition. This catalyst was found to have high surface area, low activation energy and high porosity. Due to more number of active sites at low temperature, it is highly active for selective oxidation of benzyl alcohol to benzaldehyde (Fig. 11). This explained that addition of ethylenediamine during preparation process enhanced the catalytic activity of copper aluminate [61].

Also, Cruz et al. also used self-prepared copper(II) complexes supported on hybrid mesoporous SBA-15 functionalized with imidazole ionic liquid and an amino chelate ligand, as efficient catalyst for selective oxidation of benzyl alcohol to benzaldehyde in aqueous phase [62].

Pandey et al. prepared stable CuO nanoparticles immobilized on resin in presence of cyclodextrin as an

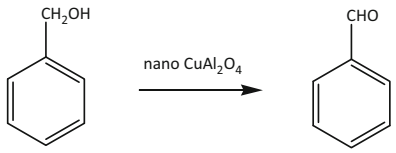


Fig. 11 Selective oxidation of benzyl alcohol using nano-$CuAl_2O_4$ spinel

organic support material. These nanoparticles were found to be effective catalyst for liquid phase oxidation of alcohols to aldehydes. The catalytic activity was found to be better than the earlier used Cu(0) nanocomposites [63].

Coupling reactions

Dutta and Sarkar immobilized palladium nanoparticles on chemically modified silica gel which were stabilized by encapsulation through PEG tentacles. These nanoparticles were prepared by reaction of modified silica gel with potassium tetrachloropalladate(II) in presence of an acyl metal salt of a Fischer carbene complex. This nanocatalyst proved to be an efficient heterogeneous catalyst for Suzuki, Stille and Sonogashira cross-coupling reactions (Fig. 12) [64].

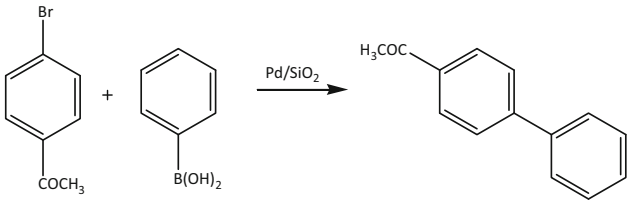


Fig. 12 Coupling reaction of 4-bromoacetophenone with phenylboronic acid using Pd@SiO_2/PEG

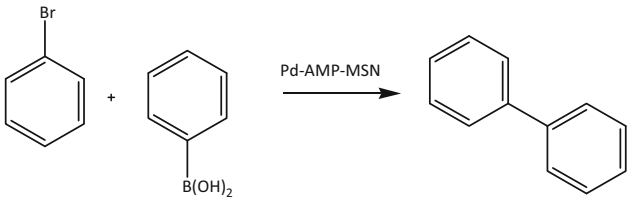


Fig. 13 Suzuki–Miyaura cross-coupling reaction of aryl halides with phenylboronic acids using Pd–AMP–MSN

He et al. synthesized a novel palladium(II) organometallic catalyst by coordinating Pd(II) ions with PPh_2-functionalized mesoporous silica nanospheres. Unlike the ones previously prepared by traditional methods, this catalyst exhibited higher activity and selectivity for water-medium C–C coupling reactions and could be used repeatedly for various cycles [65]. Mondal et al. prepared palladium(II) 2-aminopyridine complex in situ by co-condensation reaction of tetraethylorthosilicate (TEOS) with ((chloromethyl)phenylethyl)trimethoxysilane (CMPE-TMS) using CTAB as the structure directing agent and supported it on mesoporous silica nanospheres (Pd–AMP–MSN). It was shown to have high catalytic activity for Suzuki–Miyaura cross-coupling reactions of aryl iodides, aryl bromides and also aryl chlorides with phenylboronic acids in water medium with high yields (Fig. 13) [66].

Isfahani et al. immobilized palladium nanoparticles on nanosilica triazine dendritic polymer (Pd–nSTDP). These were found to be efficient catalysts for Sonogashira cross coupling of aryl halides with aromatic and aliphatic terminal alkynes where water was used as solvent (Fig. 14). This catalytic system can also be used for preparation of V- and star-shaped molecules and the catalyst can be recovered and reused [67].

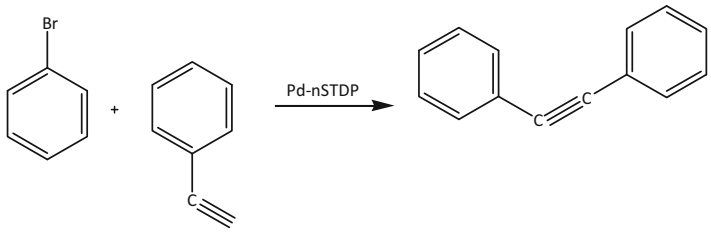
Vaghei et al. synthesized novel SBA-15/AO/Pd(II) nanocatalyst by grafting of amidoxime on SBA-15 and deposition of palladium chlorides. This catalyst, under mild conditions, was found to have high catalytic activity for the Suzuki–Miyaura cross-coupling reaction of aryl halides with phenylboronic acid (Fig. 15) [68].

Naghipour and Fakhri prepared Pd-based nanocatalyst supported on magnetite nanoparticles using chitosan-Schiff base as the chelating agent. This catalyst (Pd/Fe_3O_4@-chitosan-Schiff base) in mild experimental conditions was found to be highly efficient for Suzuki–Miyaura and Heck–Mizoroki C–C coupling reactions. Also, since the catalyst is supported on magnetite nanoparticles, it can be easily recovered magnetically [69].

Miscellaneous reactions

Nyalosaso et al. prepared aluminium-derived silica monodisperse nanospheres (Al–MSS-22) by a one-step synthesis–functionalization method and its surface

Fig. 14 Sonogashira cross coupling of aryl halides with terminal alkynes using Pd–nSTDP as catalyst



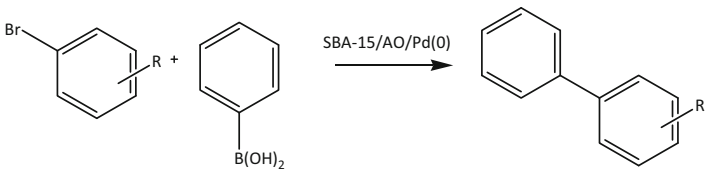


Fig. 15 Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acid using SBA-15/AO/Pd(II)

properties were studied. It was found that this aluminosilicate nanocatalyst showed catalytic activity in various esterification reactions of ethanoic acid with selected alcohols and polyols (Fig. 16) [70].

Tang et al. immobilized salicylaldimine transition metal complexes on mesoporous silica nanoparticles (Sal–MSN). These nanoparticles, because of high surface area of support, provide high concentration of catalytically active sites. These nanocatalysts were found to be efficient catalysts for epoxidation of styrene [71].

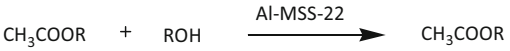


Fig. 16 Esterification of ethanoic acid with alcohols/polyols using Al–MSS-22 as catalyst

Li et al. used aqueous phosphine–Rh complexes immobilized on non-porous fumed-silica nanoparticles ($(HRh(CO)(TPPTS)_3@SiO_2)$) for their catalytic activity in higher olefin hydroformylation. They showed that the structure and hydration of support material are the two important factors in hydroformylation reaction. It was found that addition of basic alkali metal salts in the system favoured hydroformylation of 1-hexene [72].

Chen et al. synthesized dialkylaminopyridine-functionalized mesoporous silica nanospheres (DMAP–MSN). This nanocatalyst showed high turnover frequency for Baylis–Hillman, acylation and silylation reactions and could also serve as efficient catalyst for various other nucleophilic reactions (Fig. 17) [73].

Peng et al. synthesized acid–base bi-functionalized mesoporous silica nanoparticles. These nanoparticles were

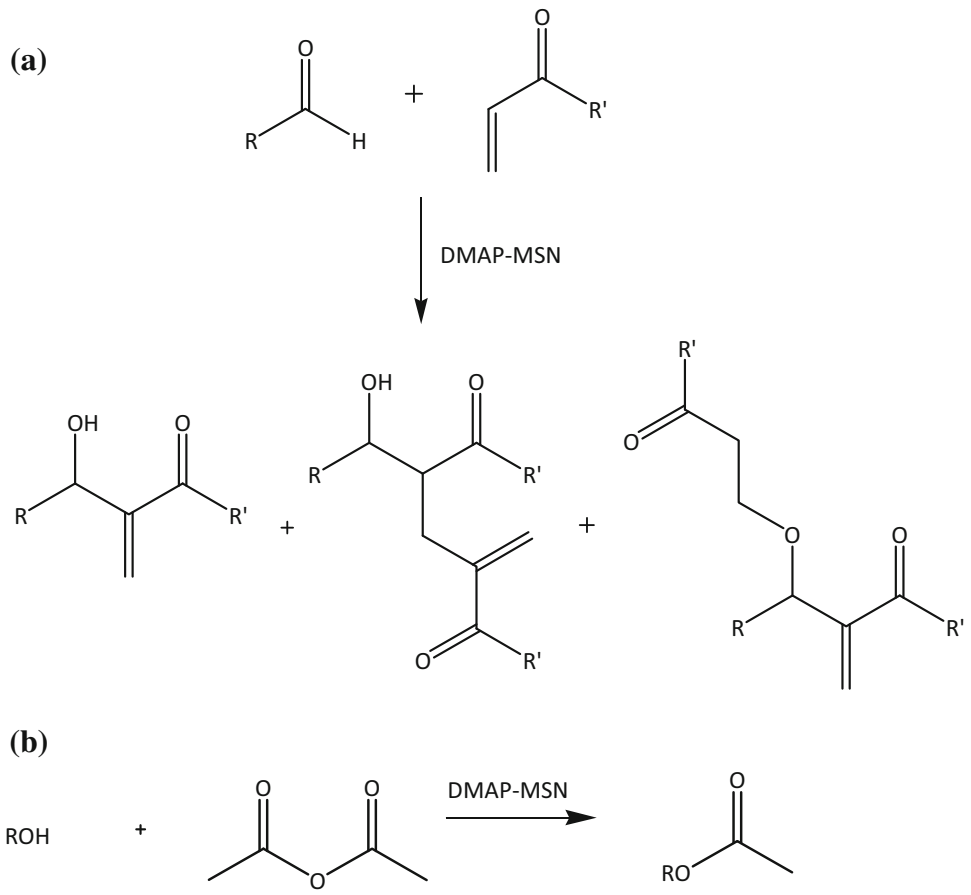


Fig. 17 **a** Baylis–Hillman reaction using DMAP–MSN catalyst. **b** Acylation reaction using DMAP–MSN catalyst

studied for catalytic activity for one-pot conversion of 5-hydroxymethylfurfural (HMF) in an ionic liquid by using cellulose, cellobiose, glucose and fructose as starting materials. It was found that these nanoparticles showed high catalytic activity towards cellulose-to-HMF conversion (Fig. 18) [74].

Tang et al. immobilized salicylaldimine cobalt complexes on mesoporous silica nanoparticles (Co–MSN/

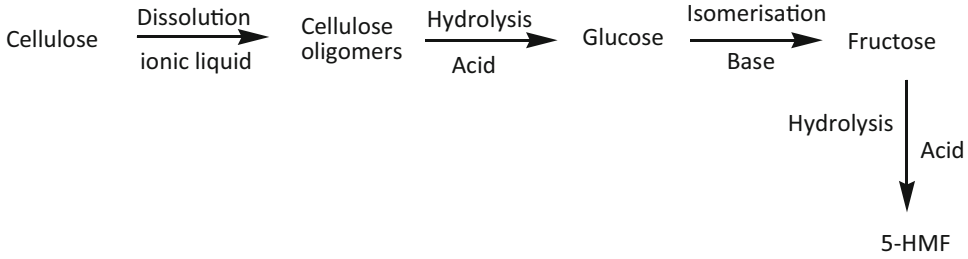


Fig. 18 Scheme for conversion of cellulose to 5-HMF

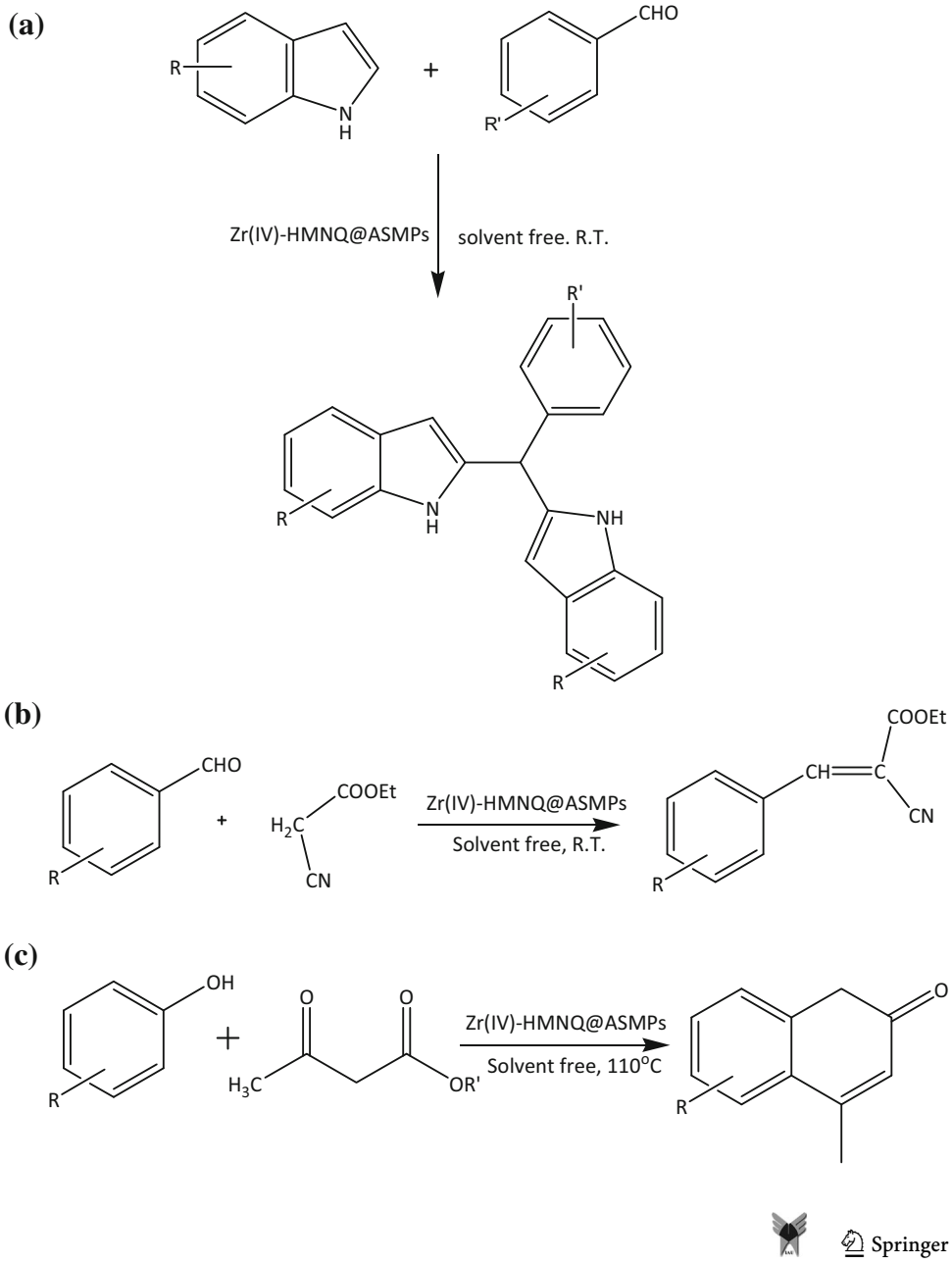


Fig. 19 **a** Friedel–Crafts reaction using Zr(IV)–HMNQ@ASMPs catalyst. **b** Knoevenagel condensation reaction using Zr(IV)–HMNQ@ASMPs catalyst. **c** Pechmann condensation reaction using Zr(IV)–HMNQ@ASMPs catalyst

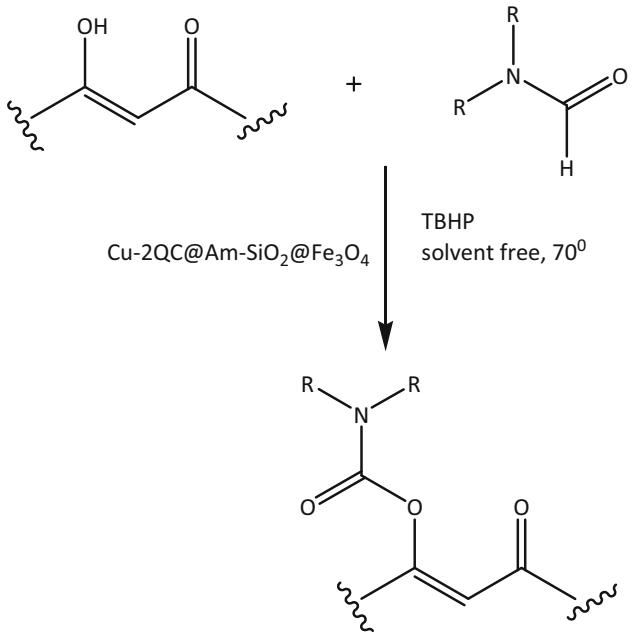


Fig. 20 Synthesis of carbamates via C–H activation of formamides using Cu–2QC@Am–SiO_2@Fe_3O_4 catalyst

MAO). These nanocatalysts showed higher activity than existing homogeneous analogue and proved to be highly efficient for catalytic polymerization of 1,3-butadiene [75].

Sharma et al. synthesized zirconium (IV)-modified@amine functionalized silica nanocomposites by grafting of 3-hydroxy-2-methyl-1,4-napthoquinone covalently (Zr(IV)–HMNQ@ASMPs). These catalysts were found to be efficient for Friedel–Crafts, Knoevenagel and Pechmann condensation reactions (Fig. 19). The catalyst provided high selectivity and could be reused for a number of cycles [76].

Sharmaet al. immobilized quinolone-2-carboxyaldehyde on amine functionalized silica-coated magnetite nanoparticles. This was followed by metallation with copper acetate (Cu–2QC@Am–SiO_2@Fe_3O_4). This catalyst showed efficient activity for synthesis of carbamates via C–H activation of formamides (Fig. 20). The catalyst was easily recovered and could be reused for multiple cycles [77].

Conclusions

Nanostructured modified chelating agents prepared by functionalization method have been discussed in view of applications in the metal extraction and catalysis. With their controllable morphology, particle size and incorporation of active sites at the surface through synthesis–functionalization procedure, desired properties of nanostructured chelating agents can be easily achieved. Such advanced functionalized

Table 3 Various nanostructured chelating sorbents as nanocatalysts for diverse organic reactions

S. no.	Nanocatalyst	Organic reaction	References
1.	Au–NH_2–HMSNs	Reduction of 2-nitroaniline	[47]
2.	Ni@SiO_2/EDTA	Reduction of 4-aminophenol	[26]
3.	Cu–acac@Am–Si–Fe_3O_4	Reduction of aromatic nitro groups	[48]
4.	Fe–N non-noble electrocatalysts	Oxygen reduction reaction	[49]
5.	AuNPs/PEI	Reduction of nitro compounds in presence of $NaBH_4$	[50]
6.	N-modified carbon nanofibres/ED	Oxygen reduction reaction	[51]
7.	$Bi_2Fe_4O_9$/EDTA	Photocatalytic degradation of methyl red	[46]
8.	$BaTiO_3$/acac or CA	Photocatalytic removal of humic acid from water	[53]
9.	YMn_2O_5/CA	Oxidative decomposition of methyl red	[27]
10.	Nb_2O_5@S/ isopropanol	Semiconductor photocatalyst	[54]
11.	$BiVO_4$/EDTA	Photocatalytic degradation of phenol solution	[55]
12.	N-doped TiO_2/ hematoporphyrin	Photocatalytic degradation of methyl orange	[56]
13.	Ru@Zr/MOF	Hydrogenation of benzene and its derivatives	[57]
14.	Pd@SiO_2/3-APTES	Hydrogenation of alkenes and α,β-unsaturated carbonyl compounds	[58]
15.	SiO_2@APTES@Pd-FFR	Oxidative amination of aldehydes	[59]
16.	Ni(II)–CHE/AuNPs	Oxidation of methanol	[60]
17.	Nano-$CuAl_2O_4$ spinel	Selective oxidation of benzyl alcohol to benzaldehyde	[61]
18.	Cu@SBA-15/amino alcohol chelate ligand	Selective oxidation of benzyl alcohol to benzaldehyde	[62]
19.	CuO@cyclodextrin	Alcohol oxidation	[63]
20.	Pd@SiO_2/PEG	Suzuki, Stille and Sonogashira cross-coupling reactions	[64]
21.	Pd@SiO_2/PPh_2	Water-medium C–C coupling reactions	[65]
22.	Pd–AMP–MSN	Suzuki–Miyaura coupling reactions of aryl halides with phenylboronic acids	[66]
23.	Pd–nSTDP	Sonogashira coupling of aryl halides with aromatic and aliphatic terminal alkynes	[67]
24.	SBA-15/AO/Pd(0)	Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acid	[68]

Table 3 continued

S. no.	Nanocatalyst	Organic reaction	References
25.	Pd/Fe_3O_4@chitosan-Schiff base	Suzuki–Miyaura and Heck–Mizoroki C–C coupling reactions	[69]
26.	Al–MSS-22	Esterification of ethanoic acid with alcohols/polyols	[70]
27.	Sal–MSN	Epoxidation of styrene	[71]
28.	Acid–base bi-functionalized mesoporous silica nanoparticles	One-pot conversion of cellulose to 5-hydroxymethylfurfural	[74]
29.	Co–MSN/MAO	Polymerization of 1,3-butadiene	[75]
30.	Zr(IV)–HMNQ@ASMPs	Friedel–Crafts, Knoevenagel and Pechmann condensation reactions	[76]
31.	Cu–2QC@Am–SiO_2@Fe_3O_4	Synthesis of carbamates via C–H activation of formamides	[77]

materials possess remarkable properties, making them potentially useful in applications requiring surface reactivity of the solid substrates in the liquid phase. The importance of chelating agents is well known but their incorporation in nanotechnologies can increase their usability manifolds. The results discussed hereby are of referential importance to the design and synthesis of other multifunctional nanostructured materials (Table 3).

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