



Polymeric resins as nano-catalysts: A brief review

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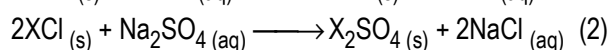
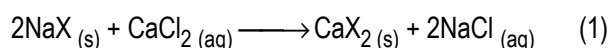
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Ion exchange resins (IERs) or polymers are cross linked, high molecular weight, water insoluble, polyelectrolytes. They have specific features like cross-linking, ion exchange capacity, particle size, swelling, porosity and acid base strength. Generally, resins have suitably substituted acidic groups like sulfonic and carboxylic groups attached for cation exchangers, and alkaline groups like quaternary ammonium group for anion exchangers. The materials i.e. nanoparticles are immobilized or loaded on the surface of IER are commonly known as nanocomposites. These metal supported resins as nano-catalyst have useful applications in catalysis reactions (i.e. reduction, oxidation, hydroformylation reaction, hydrodehalogenation reaction, cross-coupling reaction and catalytic transfer hydrogenation etc.). In this review, the synthetic processes and basic chemical principles of IERs involving ion exchange processes, and nanocatalytic applications of metal supported IERs have been discussed.

Keywords: Ion exchange resin, cation and anion exchange resin, metal nanoparticles, nano-catalyst, catalytic transfer hydrogenation.

Introduction

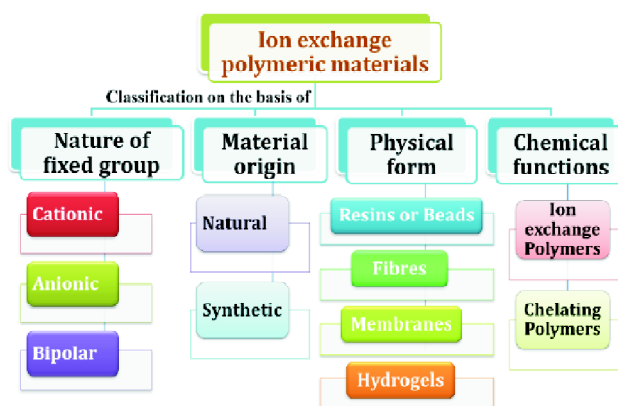
The word ion exchange (IE) usually refers to the exchange of ions of like sign stuck between liquid solutions in contact with vastly insoluble solid supported bodies^{1,2}. The ion exchanger itself is required to contain its own ions, and exchange it widely to be of experimental value. Both artificial and clay minerals like natural substances have the properties to exchanging the ions. However, for analytical purposes mainly synthesized organic ion exchangers are preferred¹. IERs are water insoluble polymers of high molecular weight that contain either acidic functional groups for exchanging cation or basic functional groups for exchanging anion within aqueous solution surrounding them^{1,3,4}. The physical properties of IERs, which decide their capability to suitably act as exchangers are the degree of cross-linking, particle size, porosity, purity, acid base strength and stability^{1,3,5-7}. Therefore, IERs are widely used in different separation, purification and determination processes^{3,4,7}. A typical cation and anion exchange is,



where, X represents a structural unit of the ion exchange, s

and aq indicate that the electrolyte is in solid phase and aqueous solution respectively.

The IE polymeric materials or IERs are classified on the basis of their nature of fixed ionic group, material origin, physical form and chemical functions⁹ (Scheme 1). A useful resin must fulfil the following requirements: it must contain a sufficient number of accessible IE groups¹; it must be sufficiently cross-linked to have only a negligible solubility and chemi-



Scheme 1. Classification of IERs, on the basis of their ionic groups, origin, physical form and chemical functions.

cally stable^{3-6,8-10}; it must be sufficiently hydrophilic in nature to permit diffusion of ions through the constitution at a fixed rate⁶ and also the swollen IERs must be denser than water¹.

In the present review, different advancement in the applications of IERs in the nano catalytic work i.e. for the reduction and oxidation of specific compounds, hydroformylation reaction, hydrodehalogenation reaction, catalytic transfer hydrogenation etc. have been discussed. The main objective of this review is the further developments in the catalytic applications of metal supported IERs, in the field of chemical science.

Physical properties and development of IERs

The cross linked polymers are available in both solid and liquid/gel state. Solid state cross-linked polymers consist of a random mixture of amorphous and crystalline substances¹. It is expected that the shorter and less-branched polymer chains can organize themselves into ordered layers more simply as compared to the long chains. The skeleton of these materials, which is also known as matrix comprises of an irregular macromolecular 3-D network of hydrocarbon chains. It is seen that a number of synthetic polymers continue to be in this state even in well above room temperature. Molecules containing either -N-H or -O-H functional groups tend to form strong secondary bonds. This phenomenon is the reason behind the relatively high boiling point of water, and also for the fact that its liquid form is denser than the solid form (ice). IE membranes are close to ideal electrolytes and provide excellent mechanical properties. But their ionic conductivity is relatively poor, i.e. in the order of 10^{-8} S/cm at room temperature (MW = 0.9×10^6 g/mol)¹². A gel as cross-linked system is basically a semi-solid that exhibits properties that range from soft and weak to hard and tough. By weight, gels are usually liquid, yet they behave like solids due to a 3-D cross-linked network within the liquid. Solid and liquid state IE is based on stoichiometric process, the reason may be the dissolved species that is taken up by a solid or liquid form¹³.

Most typical IERs are based on cross linked polystyrene^{14,15}. IERs are commonly available in the form of tiny (0.5–1.0 mm radius) microbeads^{3,4}. Generally, the yellowish or whitish IERs are fabricated from an organic polymer substrate^{1,3,4,9}. The resins are prepared as spherical beads 1.0 to 2.0 mm in diameter^{3,4,10}. Under the microscope, these appear as solid but the structure is quite open on a molecu-

lar scale. The beads are typically porous, which helps to provide a large surface area on and inside them. The process is called ion exchange when 'trapping' of ions take place with a simultaneous release of other ions.^{4,10,14}. Table 1 shows the available physical state and ionic form of some cross linked IERs.

Table 1. Physical and ionic form of some IERs

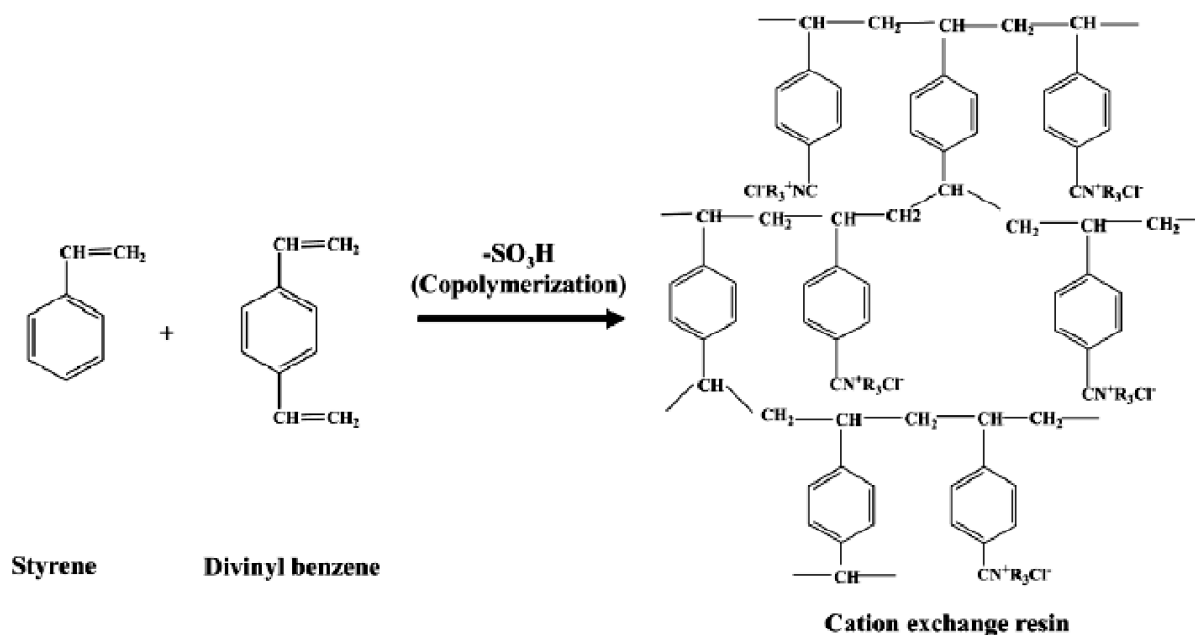
Sl. no.	Name of resin	Ionic form	Physical state
1.	Amberlite IRP69	Sodium	Fine powder
2.	Amberlite IR-120 H	Hydrogen	Gel form
3.	Duolite AP143	Chloride	Fine powder
4.	Amberlite XAD-4	Non-ionic	Solid beads
5.	DOWEX MARATHON A	Chloride	Solid
6.	Amberlite IRP88	Potassium	Powder
7.	Amberlite IRP64	Hydrogen	Powder

The observable facts of IE were first identified and described in 1850s as occurring unsurprisingly in aluminosilicate minerals, such as clays, aerolites, and ultramarines¹⁶⁻¹⁸. Largely, however, of these natural ion exchangers such as zeolites and clays get decomposed irreversibly in acid solutions and have intense IE capacity. Therefore, in the hydrometallurgy field it resulted to the limited applications. The phenol-formaldehyde resin was first synthesized by Adams and Holmes in 1934 and they showed its use as a substitute for zeolites. In 1939, the synthesis and production of IER under the original Adams and Holmes patent began investigation⁵. The IE became a feasible processing choice with the introduction of synthetic polymeric IE materials in 1944¹⁹ which was first used in hydrometallurgy for the recovery of uranium from ores in the year 1960²⁰. Many attempts have been made to engineer IER with superior properties.

Mechanism of formation of cation and anion exchange resins (CER and AER)

CER:

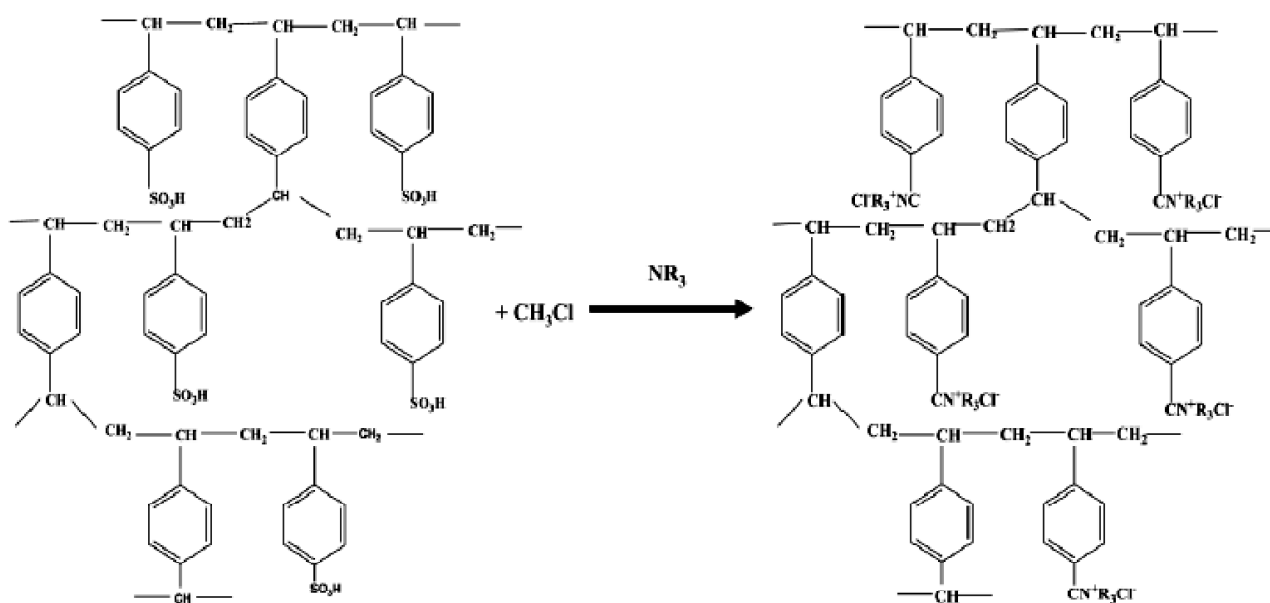
The negatively charged functional groups in CER containing covalent bonds exchange positively charged ions. Scheme 2 shows a typical CER synthesized by the copolymerization of styrene and divinyl benzene containing sulfonic acid groups (-SO₃H) introduced into most of the benzene rings of the styrene-divinylbenzene polymer, and the final product formed is known as 'CER'^{1,3-5,15}. Some examples of polystyrene type ion exchangers are given in Table 2.



Scheme 2. Polystyrene resin formation.

Table 2. Examples of polystyrene type ion exchangers

Resin name	Class	Functional group
Dowex 50	Cation exchanger (strong)	
IRC 150	Cation exchanger (weak)	
Dowex 1	Anion exchanger (strong)	
Dowex 2	Anion exchanger (strong)	
Dowex 3	Anion exchanger (weak)	
IR 45	Anion exchanger (weak)	



Scheme 3. An AER formation.

AER:

AER containing positively charged functional groups that have the capability to exchange negatively charged ions are prepared by chloromethylating the benzene rings of styrene-divinylbenzene copolymer to attach CH_3Cl groups and then reacted with tertiary amines (Scheme 3) [e.g. $(\text{C}_2\text{H}_5)_3\text{N}$, $(\text{CH}_3)_3\text{N}$]^{1,3,4,10,14}.

The characterization of typical AER (i.e. Amberlite XAD-4) and CER (i.e. Dowex 50) through Infrared (IR) spectroscopy has been shown in Fig. 1 (A) and (B).

Working mechanism of IERs:

The main functions regarding the IE process is because of its functional groups present in the exchangeable sites, those are enduringly fixed within the resin matrix. The ions of resin matrix eagerly binds with the counter ions, which may participate in the exchange process. These counter ions are exchange with the similar charged ions present in the solution. Until the equilibrium state is reached the process continues. Hence, it can be stated that exchange process depends on the binding affinity of new ions present in the solution with the functional group available in the resin matrix (Fig. 2). Praharaj *et al.*²¹ reported that the type of interaction present between new counter ion and functional group

is the electrostatic attraction. On an average, greater an ion size and/or valency have greater affinity with opposite charged ion.

For example, in the typical process of water softening, a polymer, i.e. CER consists of sulphonate (SO_3^-) functional group fixed in the resin matrix and sodium cation (Na^+) as counter ion. The cations bind with fixed anions through electrostatic force of attraction, resulting in a neutral charged resin matrix. During the exchanging phenomena, when the functional group of resin matrix is in contact with the stream of hardness ions ($\text{Mg}^{2+}/\text{Ca}^{2+}$), it has greater affinity for hardness ions other than bond cations (Na^+). So that the Na^+ is displaced and its place is occupied by hardness ions.

IE influencing parameters

The IE process of cross linked polymer depends upon following factors, which may affect direct or indirect way. All these factors are ideal for most practical situations.

(a) *Size of the exchanging ions:* Larger the size of exchanging ions, slower will be the release and diffusion rates.

(b) *Cross linkage of resin structure:* Cross linking structure can affect the swelling and porosity of resins.

(c) *Particle size:* The particle size of bead form of resin only affects the exchanging rate of ionic species.

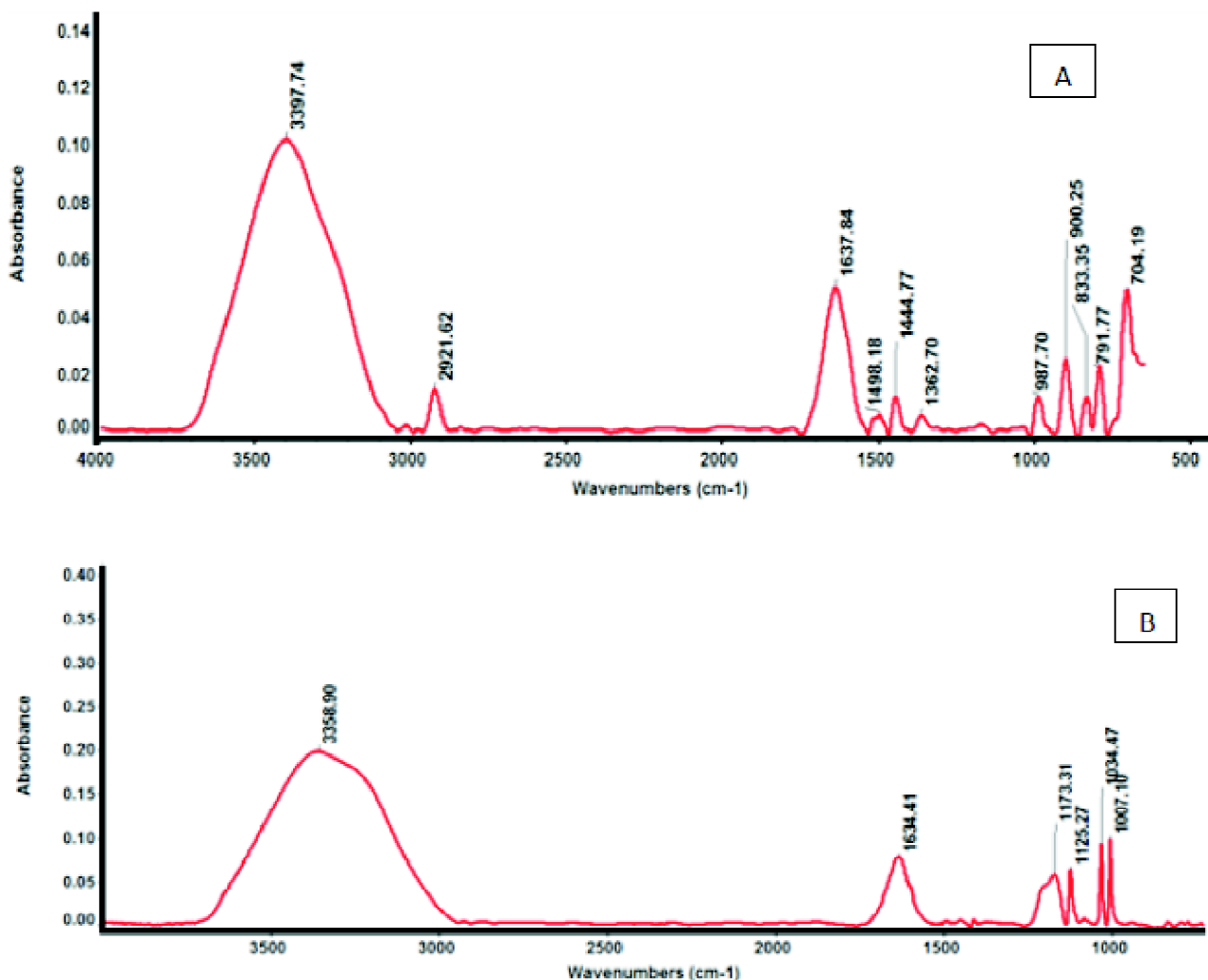


Fig. 1. FTIR spectra of a typical anion and cation exchange resin: (A) Amberlite XAD-4 and (B) Dowex 50.

(d) *Nature of counter ions:* The counter ions (like H^+) with low affinity for resin matrix (functional group ions) can easily be replaced with other selective ions, resulting in higher exchanging capacity.

(e) *Resin form:* The high loading capacity of resins contains H^+ ions and possesses lower pH value than Na^+ , 22.

(f) *Affinities of various ions:* The radius of hydrated ions shows their relative affinities for the resin. As the ion radius is smaller with greater charge, the relative affinities depend upon charge present on resins such as: ion with single charge < ion with 2 charges < ion with 3 charges < ion with multi

charges^{3,9}.

Few chemical companies and their available resins are as shown in Table 3^{1,3,4,9}.

Polymeric nano-catalyst

The wide-ranging use of IERs has increased the necessity for development of methods for accurate and rapid characterization of their chemical properties. Although numerous methods have been suggested which are designed for a particular resin or IE system, only a few information's have been published concerning the applicability of these catalytic methods to the variety of IERs now commercially avail-

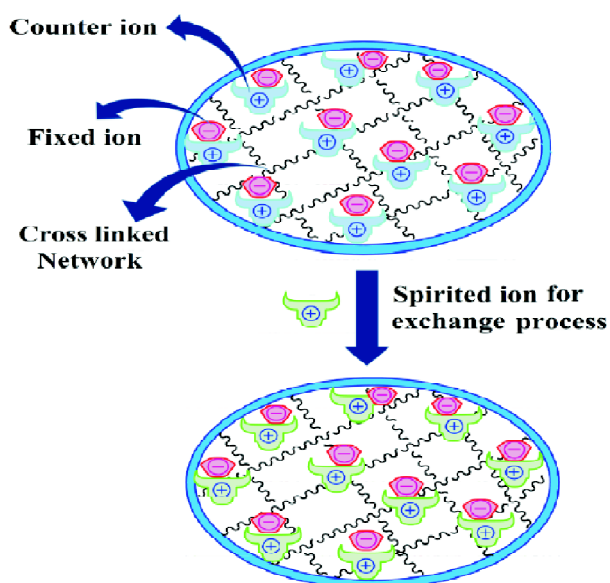


Fig. 2. Mechanism of typical IE process.

able²⁴. The usefulness of IERs is insoluble property of the resin stage. Their insolubility renders them environmentally compatible. After the contact with the ion-containing solution, filtration is done to separate the resin beads. Other than catalytic application IERs are widely used in different separation, purification and decontamination processes like water purification, wastewater treatment, water softening, hydrometallurgy, sensors, biomolecular separations, chromatography etc.^{23–25}.

As a catalyst, resin works most powerfully. Various researches have been done in the field of catalysis by IERs^{26–28}. Newman reported the first example of a reaction catalyzed by a metal CER in 1953²⁹. Some of examples are: in the

catalytic dehydration of fructose to 5-HMF (5-Hydroxymethylfurfural), in acetone/DMSO mixture a strong acid cation-exchange resins are used as a catalyst³⁰. Similarly the heterogeneous catalyst IERs was used in biodiesel fuel production process from oils with high content of free fatty acid³¹. As well as the catalytic performance of IERs for biomass transformation and gas phase hydrogenation processes are also has been reported^{32,33}. A type of IERs, i.e. nafion with fluorocarbon backbone is a strong metal-complex catalyst³⁴. The nafion polymer is strongly electron withdrawing and hence, its sulfonic acid sites are quite strong. For these reasons nafion is used as an acid catalyst³⁵. For the hydration of alkynes nafion used as a catalyst³⁶.

Resins are also used as a nano-catalyst. When a resin interacts with novel nanoparticles it forms a resin supported nano-cluster. Praharaj *et al.*²², Yang and Xuecheng³⁷ reported that, resin bound nanoparticles matrix as a nano-catalyst can be used for faster reduction of 4-nitrophenol (Fig. 3). An efficient catalytic effect of macroreticular basic resin supported

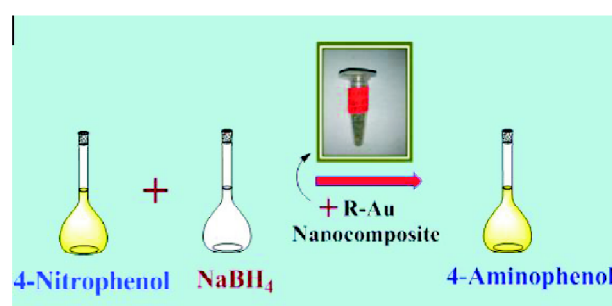


Fig. 3. Reduction of 4-nitrophenol to 4-aminophenol catalysed by R-Au nanocomposite.

Table 3. Chemical companies and their available resins

Permutit Co. Ltd., London	Rohm & Haas Co., USA	Dow Chemical Co., USA	Cemical Process Co., USA	Ion Exchange India Pvt. Ltd.	Resin type
Zeo-Karb 225*	Amberlite IR-120*	Dowex 50*	Duolite C-20	Indion 224	Sulphonated polystyrene resin
De-Acidite FF*	Amberlite IR-400*	Dowex 1*	Duolite A-42	Indion 254	Strong base anion exchanger
De-Acidite E	Amberlite IR-410*	Dowex 2*	Duolite A-1 to A-7	Indion NSSR	Weak base anion exchanger
Zeo-Karb 226*	Amberlite IR-4B	Nalcite HCR* and WBR*	Duolite CS-101	Indion 860	Carboxylic resin
	Amberlite IRC-50*	–		Indion 234	

*The resins are in bead form.

Pd and Pd-Ag nanoparticles on production of hydrogen using formic acid decomposition was reported by Mori³⁸. Klasovsky *et al.*³⁹ have reported the deposition nanoclusters of unusual β -PtO₂ having diameter (d) = (1.9±0.5) nm on polyaniline results in a catalyst that exhibits phenomenally low light-off temperatures in carbon monoxide oxidation and that too in the presence of other environmental pollutants. The obtained results show that the intensive contact between an electron-conducting polymer support and the grown-up nanoparticles provide IE between redox centers, thereby enhancing the catalytic activity dramatically³⁹. Melamine formaldehyde resin (MFR) is one of the most useful thermo-setting materials⁴⁰. The ability of MFR to host several cations has been established⁴¹. Rad *et al.*⁴² established that doped nano-sized Cu₂O on melamine formaldehyde resin (nano-Cu₂O) is a highly efficient heterogeneous catalyst for Huisgen 1,3-dipolar cycloaddition between different terminal alkynes and *b*-azido alcohols resulting in ¹H-1,2,3-triazole derivatives at room temperature.

Similarly, other catalytic applications of IERs supported metal catalyst are as follow:

Hydroformylation reaction

The "Monsanto" process is one of the most essential instances of carbonylation reaction. But in the homogeneous system, the solubility of the catalysts and the precipitation ultimately leads to the loss of the costly rhodium metal. Consequently, on the polymeric IERs surface, rhodium immobilization leads to the betterment of the catalyst and it is recoverable without any difficulty⁴³. Similarly, heterogenization of soluble hydroformylation, the catalyst led to the simple departure of the product and precious metal than the trivial homogeneous catalyst. The hydroformylation of 1-hexene was effectively carried out by derivatization of Amberlite IRA-93 (AER) via anion exchange followed by immobilization of the rhodium metal. The catalyst was reported to be extremely stable, highly selective and very reactive even after its five cycles⁴⁴.

Catalytic transfer hydrogenation (CTH)

The reduction is one of the important methods in organic synthesis and there are numerous other methods of reduction that have been applied in the laboratory and industries. The reduction of organic compounds can be characterized

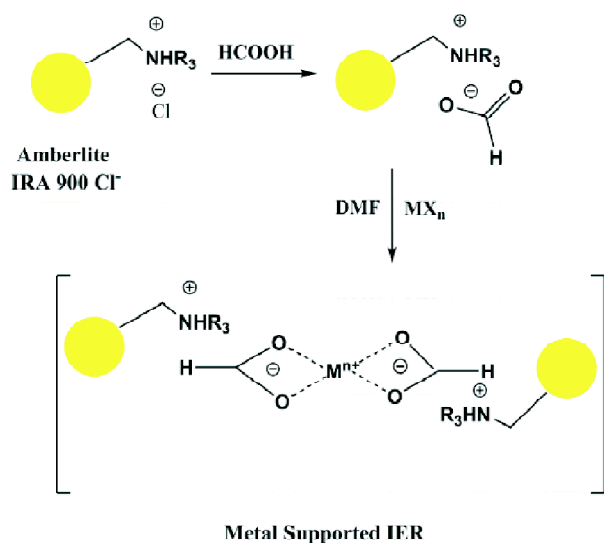
as the addition of hydrogen to the unsaturated groups. The reduction of ketones to alcohols and the addition of hydrogen across single bonds lead to cleavage of functional groups⁴⁵. Transfer hydrogenation refers to the addition of hydrogen to a molecule from a source other than gaseous H₂. The addition of hydrogen may be metal-hydrogen sources, metal-free hydrogen sources. The most common sources of metal-free hydrogen are hydrazine, trialkylsilane, formic acid, cyclohexene, ammonium formate and diimide⁴⁶⁻⁴⁹.

CTH is one of the easiest methods for the transformation of unsaturated compounds to saturated compounds by using the safest hydrogen source. A number of diverse catalytic systems have been used for the catalytic hydrogen transfer reactions. Since palladium is considered to be the better valued metal under standardized conditions, numerous works have been done previously with palladium. In the homogeneous and heterogeneous medium, recently many metals are used as CTH processes⁵⁰⁻⁵². Some solid-supported catalytic hydrogenation processes have been illustrated here. Asymmetric transfer hydrogenation of acetophenone was effectively done with poly ethylene glycol (PEG) supported ruthenium precatalyst and HCOONa in neat water. The reaction rate was found to be good with excellent yields, in addition, enantioselectivities were also been achieved. The immobilized catalyst system was recycled easily more than 10 times with zero loss in enantioselectivity⁵³.

Kirschning and the team found the polymer assisted solution-phase synthesis in the flow-through mode (PASS flow) technique for the first time. By using continuous-flow reactors^{54,55} through monolithic glass/polymer composite containing palladium nanoparticles have been employed in the transfer hydrogenation reaction. This flow-through mode condensed the reduction of alkenes, alkynes, nitro-substituted aromatic compounds and benzyl ethers and in addition, the catalytic activity in Suzuki, Sonogashira and Heck cross-coupling reactions was also weathered in the existence of the catalyst⁵⁶.

The CTH of carbonyl compounds by the ruthenium-polymer catalyst and chemo-selective transfer hydrogenation of aryl aldehydes with the assistance of Ru-based resin supported formate was done efficiently by Basu *et al.*⁵⁷. Effective and selective reduction of aromatic aldehydes and 1,2-

diketones were also done and it was noticed that the aryl ketones did not react. The synthesis of these catalysts is illustrated in Scheme 4. Formerly, Basu and the research group has synthesized palladium nanoparticles supported on polymeric IER formate [ARF-Pd(0)]. Amberlite resin IRA-900 Cl⁻ form was firstly converted to amberlite resin formate (ARF) by charging 10% (v/v) formic acid over it for a long period of time followed by binding palladium with organic



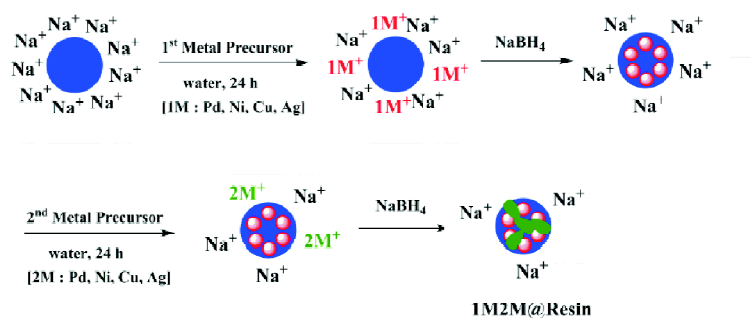
Scheme 4. IER supported metal catalyst preparation.

macroporous polyionic resins. The catalytic activity of this catalyst for alkene, 1,2-diketones and imine reduction were found satisfactory under mild reaction conditions. In addition, the nitroarenes were also reduced by this Pd-supported nanocomposite^{58,59}. It is worth mentioning that organic polymer-supported palladium nanoparticles were used as a heterogeneous catalyst for the nitro reductions. Pd nanoparticles

immobilized resins were designated as “VersaCat Pd”. Polystyrene-based IER with a Pd nanoparticles immobilized on its surface was developed for the catalytic reduction of nitrobenzene in the presence of molecular hydrogen (H₂). It is noteworthy that the catalyst is superior to Pd/C (10%), and was found to be recyclable up to six consecutive runs with significant conversions. Transmission electron microscopy (TEM) images clearly show that Pd nanoparticles are constantly distributed with a size of 50–200 nm on the polymeric matrices and also that there were no remarkable changes observed after the first catalytic run. Nevertheless, considerable rupture of the polymeric surface occurred after six runs, as seen from the scanning electron microscopy (SEM) studies⁶⁰. Kirschning and team reported that the nano amorphous alloy Ni-B supported on the polymer surface showed catalytic transfer hydrogenation of aromatic nitro compounds in the presence of hydrazine hydrate as a source of hydrogenation⁶¹. Domingos *et al.*⁶² developed two variant bimetallic nanoparticles combining one of three different metals (M = Cu, Ag and Ni) with Pd (M-Pd@R and Pd-M@R) on the surface of amberlite resin. Firstly, they immobilized the metal ions (Pd, Ag, Ni and Cu) on the amberlite resin surface by IE procedure followed by the reduction of the metals with NaBH₄ which furnishes monometallic catalyst. After purifying the monometallic catalyst, it was used as the support for the deposition of the second metal as shown in Scheme 5. The high reactivity of the catalyst in reduction was attributed due to the synergistic effect of palladium with a second metal in the bimetallic catalysts⁶².

Hydrodehalogenation reaction

Halogenated aromatics (including polyhalogenated biphenyls, polychlorinated dibenzo-*p*-dioxins (PCDDs),



Scheme 5. A typical bimetallic nanoparticles formation steps.

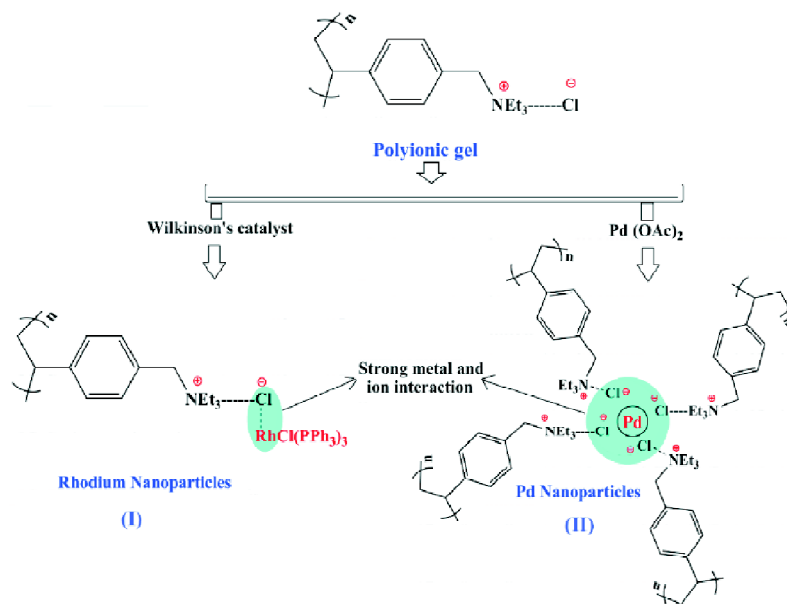
dibenzofurans (PCDFs), etc.) are often highly lethal to the human and animals and so are considered to pose a serious danger to environmental pollution^{63,64}. Numerous hydrodehalogenation methods have been developed using an array of monometal-based systems, principally based on Pd, Fe and Ni catalysts^{65–68}. For hydrodehalogenation reactions, the main focus has been imposed on IERs supported metal catalysts. Polymeric resins have been widely used to remove the halogens from polyhaloaromatics. A methodology of palladium resin composite and its application in catalytic hydrodechlorination of 4-chlorophenol has been developed by Zhang *et al.*⁶⁹. They found that Pd-polymeric resin composites can convert halogenated compounds to less toxic chemicals *in situ* and also lessen the challenges allied with resin regeneration. In this work, three neutral resins (i.e. MN200, MN100, and XAD₄) and two AERs (i.e. IRA910 and IRA96) were taken as Pd supports. The dechlorination was found to be faster at acidic pHs for the neutral resins while for the anionic resins it was observed to be faster at basic pHs. For build up phenol, catalytic activity resulted after a loss of 8 cycles⁶⁸. Pd/Fe bimetallic nanoparticles were synthesized by immobilization of Pd and Fe on to the macroporous AER, D201 through simultaneous reduction of their chloride-complex precursors by NaBH₄. The reactivity of the resultant composite for monochlorobenzene (MCB) dechlorination was studied in terms of Pd loadings, solution pH, kinetics and cyclic runs. It was concluded that all the MCB was ultimately dechlorinated to benzene. Fast and inclusive dechlorination of MCB by Pd/Fe-D201 was observed within 5 catalytic cycles and no Pd leaching was found to be observed during the iron corrosion process⁷⁰. It was seen that aggregation was the usual cause of the reduction in the reactivity of nanoscale zerovalent iron (nZVI). Ni *et al.*⁷¹ developed bimetallic nickel-iron nanoparticles immobilized on the strong acid polystyrene cation exchange resins in order to minimize the aggregation and environmental leakage risks of nZVI and to also to improve their reactivity. The reaction rate of resin-bound nZVI was found to be about 55% higher than that of dispersed nZVI. It is worth mentioning that the co-existence of Ni and Fe considerably improved the debromination rate of polybrominated diphenyl ethers due to the surface coverage of catalytic metal on the reductive

metal and the catalyst can be recovered by magnetic separation after carrying out the reactions⁷¹. The hydrodehalogenation of multiple haloaromatics was carried out in the presence of the meta-metal oxide supported with amberlite resin formate and it was observed that the coexistence of crystalline nanoparticles (Pd and Fe₂O₃) of average range ~4–5 nm in the resin matrix. In this case, NaBH₄ was employed as the reducing agent in the aqueous medium. It is clear that this reaction protocol is pretty simple and can be implemented as an industrial purpose. The catalyst was found to be quite stable to air and other solvents. It can be reused up to five catalytic runs and was recovered after by simple filtration^{43,72}.

Cross-coupling reaction

Thiot *et al.*⁷³ demonstrated that polystyrene-based polyionic gel beads constitute a highly polar micro-environment that is appropriate for resourceful metal scavenging, stabilization of metal nanoparticles as well as for subsequent heterogeneous catalyst preparation. The palladium immobilization was carried out with polyionic gel and Pd(OAc)₂ at 30°C and in a similar manner, the rhodium-soaked catalyst was prepared using polyionic gel and Wilkinson's catalyst. The catalytic activity in the Suzuki coupling reaction was effectively carried out in the presence of Pd-NPs and the hot filtration test accompanied by a three-phase test to check the heterogeneity of the reaction. The structures of polyionic-gel stabilized Pd and Rh NPs are depicted in Scheme 6^{73,74}.

The C-C cross-coupling reactions were capably done by polymer-supported metal catalysts. Amberlite resin format supported with palladium(0) has been prepared, i.e. ARF-Pd which illustrated excellent catalytic activity in Mizoroki-Heck, Suzuki-Miyaura as well as Sonogashira coupling reactions with a wide range of substrates. Recycle experiments were also carried out by using Suzuki-Miyaura couplings between 1,4-dibromobenzene and phenylboronic acid as a model reaction, after which, the catalyst (ARF-Pd) was washed with methylene chloride, water and finally dried under vacuum for further use. The catalyst was quantitatively recovered by simple filtration (without leaching) followed by recycling for five consecutive runs. This was verified by the X-ray photoelectron spectroscopy (XPS) study of the fresh and recycled catalysts⁷⁵.



Scheme 6. Mechanism for formation of polyionic gel based (I) Rh nanoparticles (in presence of Wilkinson's catalyst) and (II) Pd nanoparticles (in presence of Pd(OAc)₂).

Kinetic and mechanistic support for determination and renovation of catalyst

The kinetic study of the catalytic activities of metal supported IERs gives us a clear notification about their formation and function. The kinetic study of resin immobilized metal nanocomposite catalyst revealed that the geometric factor, opening up catalyst sites through the ensemble effect, is the main reason for the differentiated catalytic activity. Among most of the researches explain the kinetics behind these catalytic works. The catalytic reductions are studied mainly in corresponding to pseudo-first order rate constants (k). The activation energy can be calculated from the set of kinetic data and by using the Arrhenius equation. In cases of heterogeneous/micro heterogeneous catalysis, the rate of reaction generally increases linearly with the amount of the catalyst. To experimentally determine the effect of the amount of catalyst on the reaction rate the amount of catalyst was varied while other parameters were kept constant. It was found that, with an increasing amount of catalyst, the rate of reaction also increases. The resin supported metal catalysts are very effective for catalytic reduction. At the end of the reaction, the resin catalyst particles remained active which can be separated from the product. After the purification step, the particles could be recycled a number of times (4–5 time) for the reduction or oxidation reaction (Fig. 4)^{22,37,43,76}.

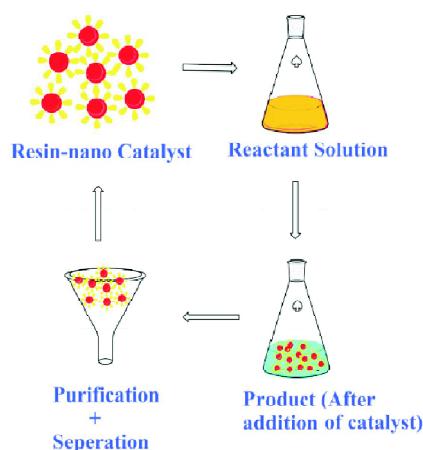


Fig. 4. Schematic presentation for catalysis process and regeneration step of nano-resin composite beads.

As described above that the metal nanoparticles and cross linked resins spectra may clearly identify and characterized by using different instrumental approach. This mechanistic concept can be used to predict for the characterization of metal supported resin nano-catalyst and its catalysis process. The advanced Surface Enhanced Fourier transform infra red (SE-FTIR) spectroscopy can be employed for the characterization and identification of the catalytic processes. The spectra reveal the composition of liquids, solids and

gases. FTIR microscopy is a very well established technique which serves as an immensely important tool in the micro destructive analysis of small samples. Also, the latest introduction of imaging as well as mapping equipments facilitates collection of a huge number of data thereby providing a distribution map for the compounds identified. It is a versatile tool with a gamut of applications in numerous fields, including quality verification of materials; identification of compounds such as compounded plastics, blends, fillers, paints, rubbers, coatings, resins and adhesives; microanalysis of small sections of materials to identify contaminants; monitoring automotive or smokestack emissions; reformulation of polymers, rubbers and other materials through thermo gravimetric infra-red (TGA-IR) or gas chromatography infra-red (GC-IR) analysis; analysis of thin films and coatings; monitoring air quality, testing water quality and analyzing soil thereby addressing environmental and health concerns; rapid determination of the *trans* fat content of manufactured food products and many more. In FTIR spectroscopy all spectral scans gets in the region $4000\text{--}400\text{ cm}^{-1}$. For this, the use of mainly two FTIR accessories i.e. attenuated total reflectance (ATR) and diffuse reflectance (DRS). In which, solid/organic solvent samples (without participating sample preparation step) and all inorganic liquid samples are analyzed respectively. Further, calculation of the percentage of catalysis process can be calculated with the help of IR peak intensity and peak area.

Advantages and disadvantages of IERs

A number of facts indicate the reward in the use of IERs which include: very low running costs of IE processes, very little energy requirement, the regenerate chemicals of IERs are cheap and main plus point is, the resin beds can last for many years^{5,10,20,77}.

There are many restrictions, which may be taken into account with awareness, for the duration of design. They are as follows:

Organic contamination:

After the manufacture, new trade category IERs often contains organic residual that could result as a source of non-ionized organic contamination. As the slowly de-cross linkage (structure opening) of polymer, very old resin will shed organic fragments. This type of contamination may be used

for many purpose, the demineralised water from an ultra filtration membrane can be passed thoroughly when removal is needed^{77,78}.

Chlorine contamination:

The contamination of chlorine can damage the resins. Since the urban areas water contain traces of chlorine, means that urban water supply is an undesirable demineralised feed. Chlorine contamination can be removed by passing the feed through activated carbon⁷⁷.

Bacterial contamination:

For bacteria or other micro-organisms elimination resin beds do not be used as filters. For sterile water, normally we can treat the demineralised water by non chemical (i.e. heat, UV irradiation or fine filtration etc.). Disinfectants such as formaldehyde can be used for decontamination of resin beds^{77,78}.

Future prospective

The future perspectives of the same include following: Firstly, SE-FTIR approach for detection of catalysis process for several reductions and oxidation process based on metal supported resin nano-composites catalyst. Secondly, resin immobilized metal nano-composites may be used as adsorbent for different dyes removal from water sample and its detection through FTIR. In addition, it can also be used for the removal of dyes from different food samples.

Conclusion

The IER's are extensively used in most of the fields. In this review, the polymeric IERs have been highlighted as efficient and recoverable nano-catalyst as well as their importance in accelerating the process of catalysis. In the field of catalytic research, the use of IERs and its composite form is achieving much more importance and commercial success. It is used as chelating resin and as reducer resin for reducing one compound to another. The presence of metal catalyst on resin support can pick up the catalytic rate. The main applications are emphasis in the section of hydroformylation reaction, CTH, hydrodehalogenation reaction and cross coupling reaction. IERs are now commercially available in several products as adsorber, advanced composite catalyst and in the form of resinate. Moreover, several nano-catalytic concepts which are recently get desirable performance. It is accepted that the economical applications of these organic

polymeric resin as catalyst and catalytic support, can be divulged in coming years.

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