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Modified crosslinked polyacrylamide anchored Schiff base–cobalt complex: A novel nano-sized heterogeneous catalyst for selective oxidation of olefins and alkyl halides with hydrogen peroxide in aqueous media

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ABSTRACT

A new nano-sized polymer-supported Schiff base–cobalt complex catalyst based on crosslinked polyacrylamide was synthesized and characterized. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of the catalyst show nanosize fiber-like image of the polymeric catalyst. The catalyst activity was studied in the oxidation of various olefins including non-activated terminal olefin in water with hydrogen peroxide as an oxygen source. The catalyst showed high degree of selectivity. The effects of reaction parameters such as solvent, oxidant, temperature, molar ratio of catalyst and catalyst structure on the oxidation of styrene were investigated. The oxidation of benzyl halides to their corresponding carbonyl compounds in the presence of this heterogeneous catalyst was studied as well. The catalyst can be recycled several times without significant loss in its activity.

1. Introduction

Schiff bases represent one of the most widely utilized classes of ligands in metal coordination chemistry [1,2]. They are easily synthesized and form complexes with almost all metal ions. Over the past few years, there have been many reports in the literature on their applications in homogenous and heterogeneous catalysis. These complexes show high catalytic activity in various reactions such as polymerization reactions, oxidation, decomposition of hydrogen peroxide, carbonylation reaction, Heck reaction, Diels–Alder reaction, and Lewis acid assisted organic transformations [3].

In order to develop environmentally benign methods, there is currently a rapid growth in the use of supported transition metal catalysts such as polymer-supported systems [4]. Polymers modify the reactivity of metal complexes by changing the electronic and steric properties of the coordinating ligands. In addition, heterogenization of active metal complexes on polymeric supports offers the practical benefits such as ease in handling and separation, recovery, recycling, non-toxic characteristics, and amenability for continuous processing. The incompatibility of conventional polystyrene-supported species with solvents and substrates has led to the design of synthetic polymeric supports that are compatible with both aqueous and organic phases. Some examples of these supports are polyacrylamide, poly(vinylpyrrolidone), and poly(ethylene glycol) [5–7]. These supported systems have different polarity, solvation, and reactivity compared to polystyrene-supported species.

Oxidation is among the most important reactions in the chemical industry which is usually catalyzed by transition metal complexes [8]. In this field, olefin oxidations that degrade large compounds or introduce oxygen functionality into molecules are the most synthetically useful oxidation reactions. Many synthetic methodologies are widely reported in the literature for oxidizing double bonds such as ozonolysis [9], oxidation with $KMnO_4$ [10], OsO_4 [11] or RuO_4 [12] and combination of oxidant and a transition metal catalyst [13]. The most well-known methodology is the combination of oxidant and a transition metal catalyst due to the transition metal ability in activating oxidants. In this regard, many different transition metal complexes of Ti (IV), Mo (VI), Mn (III), Cr (VI), Co (II), Cu (II), Fe (III), etc. have been introduced as catalysts [14–20]. Among these, cobalt complexes are useful catalysts in oxidizing olefins, as cobalt (II) appears to be a good oxygen transfer agent [21]. Reversible redox cycle between Co^{II}–Co^{III} oxidation states causes oxygen atom transfer to the double bonds by cobalt complexes. A variety of oxygen sources such as NaOCl, PhIO, O_2, ammonium periodate, alkyl hydroperoxides and H_2O_2 are used as oxidants in the catalyzed oxidation processes. H_2O_2 is an attractive oxidant in catalytic oxidation of organic compounds and widely used in industry due to its inexpensiveness, cleanliness, easy handling, and availability. In addition, it produces water as its only by-product in the oxidation reaction [22].

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One of the main problems in industry is related to the use of organic solvents in the processes. The manufacture, transport, stock, handling and disposal of solvents are aspects that demand great care and expense. Therefore, water is considered as an alternative solvent to expensive, flammable and toxic organic solvents. Evident show that organic reactions carried out in aqueous media may offer advantages over those occurring in organic solvents [23]. For example conducting the reactions in aqueous media is usually more selective, and separating of organic compounds from the aqueous phase is easily achieved. Therefore, the use of water in organic reactions is a useful alternative to organic solvents and is a step in developing green technology.

In continuation of our study on using modified polyacrylamide support [5], herein, we report the synthesis and characterization of a new heterogeneous Schiff base–cobalt complex derived from a modified crosslinked polyacrylamide support, capable of catalyzing oxidation of olefins and alkyl halides in the presence of H_2O_2 as oxidant in aqueous media. This catalytic system allows efficient oxidation to be carried out with a high degree of selectivity.

2. Experimental

2.1. Materials and techniques

All chemicals were of commercial reagent grade and obtained from Merck or Fluka companies. Acrylamide (Fluka) was recrystallized from chloroform. Alkenes were passed through a column containing active alumina to remove peroxidic impurities. Other reagents and solvents were used without further purification. Hydrogen peroxide (30%) was stored at 5 °C and titrated with potassium permanganate (0.1 N) to check its concentration. All products were characterized with FT-IR, ^{1}H and ^{13}C NMR spectroscopy; FT-IR was performed using a Shimadzu FTIR-8300 spectrophotometer and NMR was performed on a Bruker Avance DPX instrument (250 MHz). All yields refer to the isolated products. Progress of reactions was followed by TLC on silica-gel Polygram SIL/UV 254 plates or by GC on a Shimadzu model GC 10-A instrument. The Co analysis and leaching test were carried out by inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro). CHN analysis was carried out on thermo finningan FIASHEA 1112 instrument. X-ray diffraction data obtained with XRD, D8, Advance, Bruker, axs. Scanning electron micrographs were obtained by SEM, XL-30 FEG SEM, Philips, at 20 kV. All samples are sputter-coated with gold prior to SEM observation. Transmission electron microscopy (TEM) analyses were performed on a Philips model CM 10 instrument. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was performed on Cary 5 instrument by photometric mode with 300 nm/min scan rate. The surface area of the catalyst was measured using the Braunuer–Emmet–Teller (BET) method on Chem BET-3000, Quantachrome instrument and N_2 as adsorbent.

2.2. Preparation of the catalyst

2.2.1. Preparation of 5% NNMBA-crosslinked polyacrylamide

N,*N*′-Methylene-bis-acrylamide (NNMBA) (1.14 g, 7.4 mmol) and acrylamide (10 g, 0.14 mol) were dissolved in ethanol (250 mL). $K_2S_2O_8$ (62 mg, 0.23 mmol) was added to this solution and stirred. The polymer began to precipitate within 30–40 min. The suspension was stirred at 70–75 °C for additional 5 h. The polymer formed was collected by filtration, washed several times with water, ethanol, and methanol and dried at 60 °C under reduced pressure.

2.2.2. Preparation of crosslinked poly(acrylohydrazide)

Crosslinked polyacrylamide (1 g) was added in small portions to an excess of well-stirred hydrazine hydrate (10 mL). The mixture was refluxed at 100–110 °C for 9 h. It was then poured slowly into a large volume of EtOH (250 mL). The resin was filtered off and washed with NaCl solution until the filtrate was free from hydrazine. The gel was washed with distilled water and methanol and subsequently dried at 60 °C under reduced pressure. The amine content was determined by alkalimetric method. HCl (10 mL, 0.182 M) that was standardized against potassium hydrogen phthalate (KHP) (0.1 M) was added to poly(acrylohydrazide) (0.1 g) and was stirred at room temperature for 12 h. The mixture was then filtered and washed with distilled water (5 mL × 2). The filtrate was titrated with freshly prepared NaOH (0.196 M). The average amount of NaOH used in three times titration was 5.3 mL, and the capacity of the polymer was calculated to be 7.8 mmol of amino group per gram of the polymer.

2.2.3. Preparation of crosslinked poly(acrylohydrazide-imino-salicylaldehyde)

Croslinked poly(acrylohydrazide) (1 g, 7.8 mmol NH_2) was added to salicylaldehyde (1.9 g, 15.6 mmol) in ethanol (35 mL). The reaction mixture was stirred at 60 °C for 18 h. The resultant yellow product was filtered, washed with water, ethanol and acetone and dried under reduced pressure. The imine content was evaluated from CHN analysis. Poly (acrylohydrazide); %C = 46.8, %N = 26, %H = 7.2, %O = 20 and poly(acrylohydrazide-imino-salicylaldehyde); %C = 59.7, %N = 15.4, %H = 6.1, %O = 18.9. Average imine content was calculated from percent of imine functionalization using elemental data given. It was found to be 3.1 mmol/g.

2.2.4. Preparation of the polymer supported cobalt complex

Crosslinked poly(acrylohydrazide-imino-salicylaldehyde) (1 g) was treated with a solution of $Co(OAc)_2{\cdot}4H_2O$ (1.4 g) in methanol (35 mL) at 60 °C for 18 h. Upon complexation, the mixture was filtered and washed thoroughly with distilled water, methanol and acetone. It was then conditioned for a total of 9 h (1× 3 h each refluxing in acetone, ethanol and acetonitrile). The resultant brown powder was dried under vacuum overnight. The metal content of the catalyst found by ICP, was 1.8 mmol/g.

2.3. Catalytic oxidation of olefins with cobalt complex

The catalyst (11 mg, 0.02 mmol) was suspended in water (5 mL), and olefin (1 mmol), H_2O_2 30% (0.3 mL, 5 mmol) and dodecane as internal standard were added to this suspension. The mixture was heated at 75 °C with constant stirring. Small amounts of the reaction mixture were frequently removed from the reaction vessel and were analyzed by gas chromatography. The conversion was calculated based on the initial amount of the substrate, and the selectivity was calculated based on total amounts of products. Upon reaction completion, the polymeric catalyst was removed by filtration and the corresponding product was obtained via extraction with EtOAc and purified on a silica-gel plate. Assignments of products were performed by comparison of their ^{1}H NMR, ^{13}C NMR, and physical data with those of the authentic samples.

2.4. Catalytic oxidation of benzyl halides with cobalt complex

In a typical experiment, the catalyst (11 mg, 0.02 mmol), benzyl halide (1 mmol) and H_2O_2 30% (0.3 mL, 5 mmol) were mixed in H_2O (5 mL) and heated at 75 °C with constant stirring. The reaction progress was followed by TLC. After completion of the reaction the above procedure was followed. IR spectroscopy confirmed the chemical structure of the products.

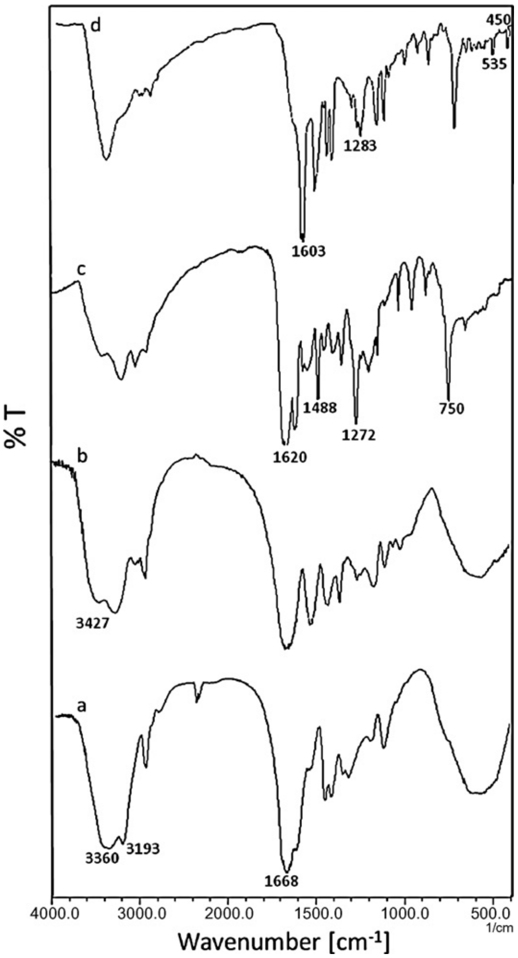


Fig. 1. FT-IR spectra of (a) crosslinked polyacrylamide, (b) crosslinked poly(acrylohydrazide), (c) crosslinked poly(acrylohydrazide-imino-salicylaldehyde) and (d) polymer supported cobalt complex.

2.5. General procedure for recycling of the catalyst

After the oxidation reaction, the suspension was cooled to room temperature and filtered off. The used polymer was washed with water, ethanol and acetone and dried under vacuum. It was then reused in the next reaction cycle with a new portion of reagents.

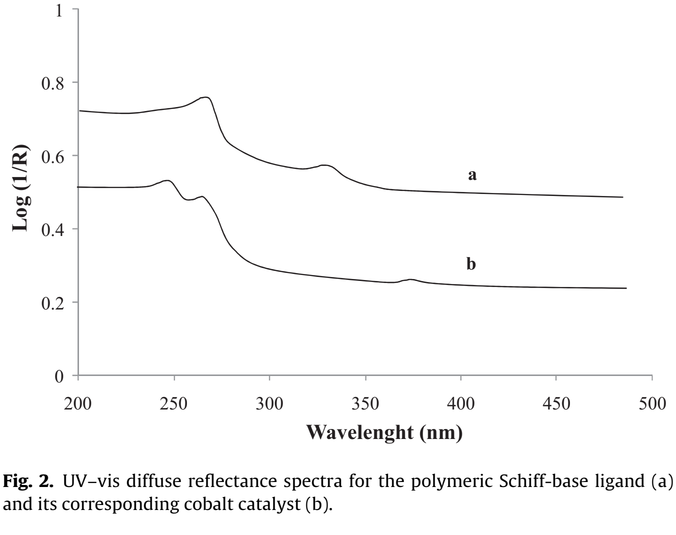


Fig. 2. UV–vis diffuse reflectance spectra for the polymeric Schiff-base ligand (a) and its corresponding cobalt catalyst (b).

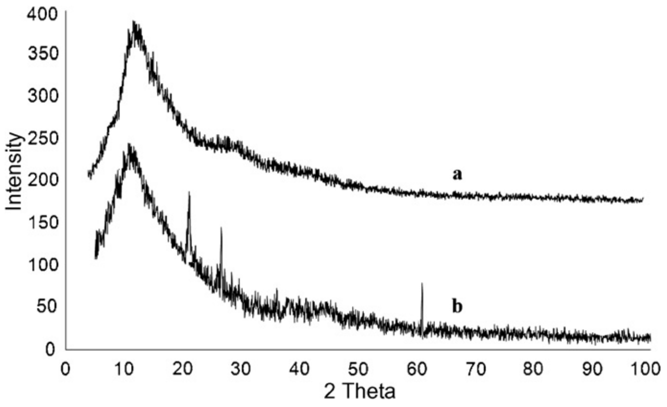


Fig. 3. Powder X-ray diffraction patterns of (a) crosslinked polyacrylamide-anchored Schiff base and (b) corresponding cobalt complex.

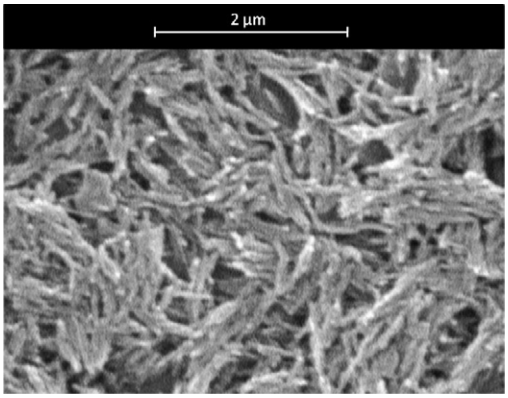


Fig. 4. SEM image of crosslinked polyacrylamide-anchored Schiff base–cobalt complex.

Table 1
Electronic transitions of polymeric Schiff-base ligand and its corresponding cobalt (II) complex.

Metal ion	Electronic transition	Ligand (λ_{max}) (nm)	Complex (λ_{max}) (nm)
Co (II)	$\pi \rightarrow \pi^*$	265	240
	$n \rightarrow \pi^*$	328	261
	C → T	–	380
	d → d	–	–

2.6. Catalyst characterization

IR spectrum of the polymer showed the characteristic absorption of amide (N–H) group at 3193 and 3360 cm^{-1}, and carbonyl

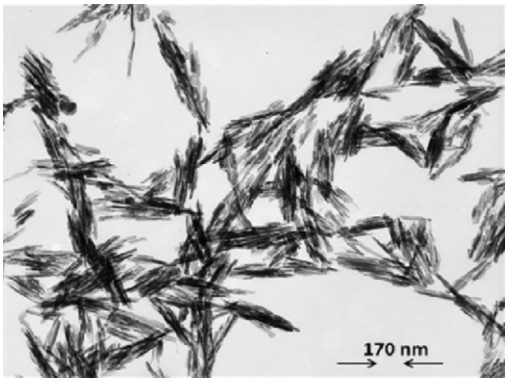
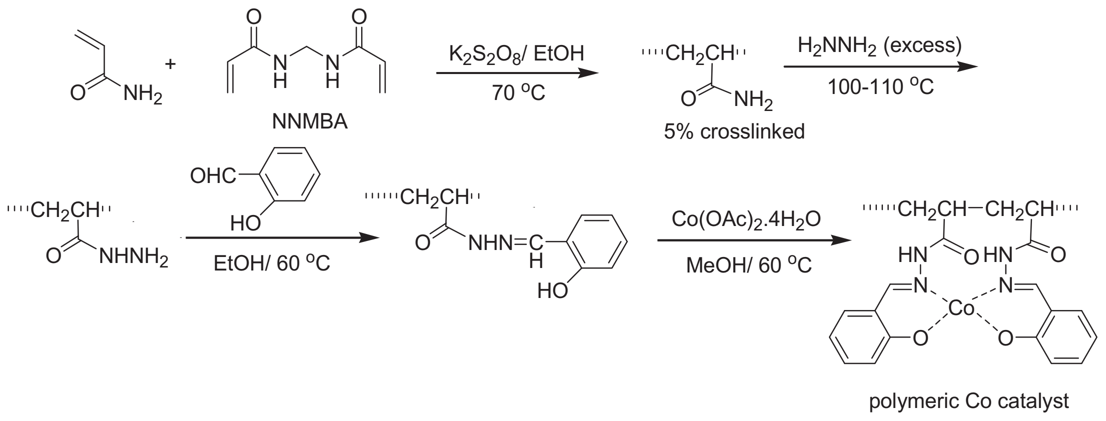
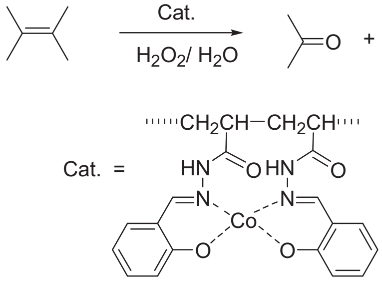


Fig. 5. TEM image of crosslinked polyacrylamide-anchored Schiff base–cobalt complex.



Scheme 1. Synthetic strategy for the preparation of modified polyacrylamide loaded cobalt catalyst.

group (C=O) at 1668 cm^{-1}. Poly(acrylohydrazide) was obtained by transamidation reaction of crosslinked polyacrylamide with excess of hydrazine hydrate. The resultant polymer had a high content of amino group per gram of the polymer which was determined by alkalimetric method and was found to be 7.8 mmol/g of the resin. IR spectrum of the poly(acrylohydrazide) showed the characteristic absorption of amino (N–H) group at 3427 cm^{-1}. Crosslinked poly(acrylohydrazide-imino-salicylaldehyde) was prepared by the reaction of poly(acrylohydrazide) with salicylaldehyde in ethanol. IR spectrum of the polymer showed peaks at 1620 cm^{-1}, corresponding to the formation of imine group (CH=N) and at 750 and 1488 cm^{-1} due to the bending of ortho substitution out of phase (OOP) and C=C stretching of aromatic ring, respectively. The imine content was evaluated from CHN analysis and was found to be 3.1 mmol/g. Treating the solution of $Co(OAc)_2·4H_2O$ with the Schiff-base ligand lead to the formation of polyacrylamide supported cobalt complex. In order to make the process completely heterogeneous, the catalyst was conditioned by washing thoroughly with solvents to remove any loose Co species. The metal content of the catalyst found by ICP was 1.8 mmol/g of the resin. IR spectra of the polymer before and after cobalt loading showed a shift in frequency from 1620 to 1603 cm^{-1} for υ(C=N) and from 1272 to 1283 cm^{-1} for υ(C–O). In addition, IR spectrum of the complex showed two new absorption bands at 450 and 535 cm^{-1}, which were attributed to the formation of M–N and M–O, respectively. These variations confirmed the coordination of cobalt ion with the azomethine nitrogen and phenolic oxygen of the polymeric Schiff-base ligand. FT-IR spectra of all polymers are presented in Fig. 1.



Scheme 2. Oxidation of olefins using polymeric cobalt catalyst.

Table 2
Effect of different solvents and oxidants on the oxidation of styrene using polyacrylamide-supported cobalt complex.[a]

Entry	Solvent	Oxidant	Conversion (%)[b]	% Selectivity to benzaldehyde[c]
1	CH_3CN	H_2O_2	66	55
2	EtOH	H_2O_2	40	70
3	CH_2Cl_2[d]	H_2O_2	No reaction	–
4	CH_3COCH_3[d]	H_2O_2	30	50
5	EtOAc	H_2O_2	35	62
6	H_2O	H_2O_2	100	89
7	H_2O	$NaIO_4$	100	91
8	H_2O	Bu_4NIO_4	100	90
9	H_2O	H_2O_2/urea (UHP)	60	75
10	H_2O	*Tert*-BuOOH	88[e]	40
11	H_2O	–	Trace	–
12[f]	H_2O	H_2O_2	30	70

[a] Reaction conditions: styrene (1 mmol), oxidant (5 mmol), cat. (2 mol%), solvent (5 mL) at 75 °C for 6 h.
[b] Conversion based on starting material = [1 − (concentration of substrate left after reaction/initial concentration of substrate) × 100.
[c] % Selectivity of benzaldehyde = (concentration of benzaldehyde/total concentration of all oxidation products) × 100.
[d] At reflux temperature.
[e] Crude mixture of oxidation products (benzaldehyde, styrene oxide, phenylacetaldehyde, acetophenone and benzoic acid).
[f] Without catalyst for 24 h.

Table 3
Effect of molar ratio of catalyst to substrate on the oxidation of styrene.[a]

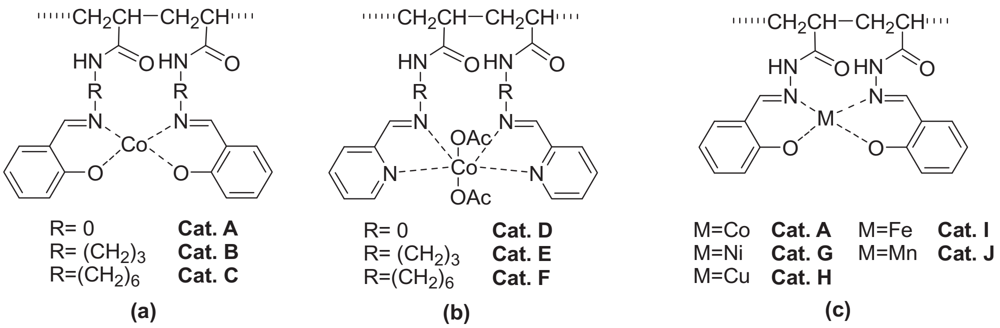
Entry	Mol% cat.	Conversion[b]	% Selectivity to benzaldehyde	TON[c]
1	0.2	45	100	225
2	0.5	53	100	106
3	1	75	96	75
4	2	100	89	50
5	4	100	68	25

[a] Reaction condition: styrene (1 mmol), H_2O_2 (30%) (5 mmol), cat. (0.2–4 mol%) in H_2O (5 mL) at 75 °C for 6 h.
[b] Conversion based on starting material.
[c] mmol of converted substrate/mmol cobalt in the catalyst.

Table 4
Oxidation of styrene with H_2O_2 in water catalyzed by different polyacrylamide-supported metal complex.[a]

Entry	Catalyst	Metal content (mequiv./g)	Conversion (%)[b]	% Selectivity to benzaldehyde	TON[c]
1	A	1.8	100	89	50
2	B	1.29	68	75	34
3	C	1.6	35	82	17.5
4	D	1.4	62	75	31
5	E	1.1	38	82	19
6	F	0.96	30	70	15
7	G	1.5	15	60	7.5
8	H	2	90	85	45
9	I	1.8	72	72	36
10	J	0.56	35	60	17.5

[a] Reaction condition: styrene (1 mmol), H_2O_2 (30%) (5 mmol), cat. (2 mol%) in H_2O (5 mL) at 75 °C for 6 h.
[b] Conversion based on starting material.
[c] mmol of converted substrate/mmol cobalt in the catalyst.



Scheme 3. Different types of Schiff-base metal complexes.

Further evidences for metal ion complexation were obtained from electronic spectra of Schiff-base ligand and its corresponding metal complex (Table 1). The complexation of cobalt (II) ions with Schiff-base ligand shows a shift in $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions from 265 to 240 nm and 328 to 261 nm which provided evidence for the coordination of cobalt (II) ions through nitrogen atom of azomethine group. The appearance of a new band at 380 nm for metal complex is attributed to charge transfer process ($L \rightarrow M$) from ligand to cobalt (II) ions. No $d \rightarrow d$ transition has been observed neither for ligand nor for complex. UV–vis diffuse reflectance spectra for the polymeric Schiff-base ligand and its corresponding cobalt catalyst is presented in Fig. 2.

XRD pattern of the heterogeneous catalyst is shown in Fig. 3. The strongest peak of the XRD pattern corresponds to the planes of amorphous polymer matrix, while other peaks reveal a single phase of the supported cobalt particles. In addition to XRD, scanning electron microscopy (SEM) was used to study the morphology of the supported catalyst (Fig. 4). SEM showed a nanometer up to micrometer fiber-like images for the polymeric catalyst. Transmission electron microscopy (TEM) image of the catalyst showed that the fiber lengths mostly range from 50 to 250 nm in size (Fig. 5). The BET surface area of the polymeric Schiff-base ligand was 4.3 m^2/g, which significantly increased to 25.3 m^2/g for its corresponding cobalt catalyst. It is probably due to the fiber-like images of the catalyst. Although the BET surface area of the catalyst was rather small, considerable activity was observed in the oxidation of olefins.

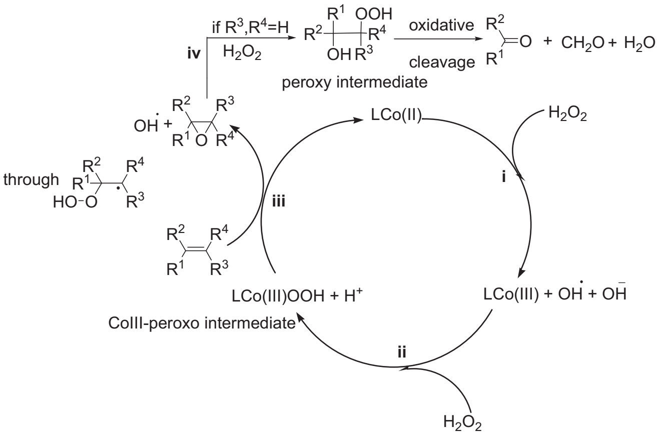
3. Results and discussion

3.1. Preparation of the catalyst

The design of the Co catalyst is shown in Scheme 1. Polyacrylamide crosslinked with *N,N′*-methylene-bis-acrylamide (NNMBA) (5%) was prepared by free radical solution polymerization of acrylamide monomer in ethanol using $K_2S_2O_8$ as an initiator. The polar nature of the crosslinking agent makes it compatible with the polymer backbone as well as the reaction medium. We found that polymers with less than 5% NNMBA was sticky and not physically proper to be used in further reactions.

3.2. Catalytic oxidation with polymeric cobalt complex catalyst

The catalytic activity of the polymer-supported cobalt complex was investigated in the oxidation of different alkenes (Scheme 2). The oxidation of styrene was initially studied as a model reaction. In the process of oxidation the choice of solvent and oxygen donor is crucial, so these parameters were optimized and the results are summarized in Table 2. Among water, acetonitrile, ethanol, dichloromethane, acetone and ethyl acetate, water was chosen as the reaction medium. The excellent catalytic activity in water was attributed to the polarity of solvent and its ability in maxi-



Scheme 4. Proposed oxidation mechanism.

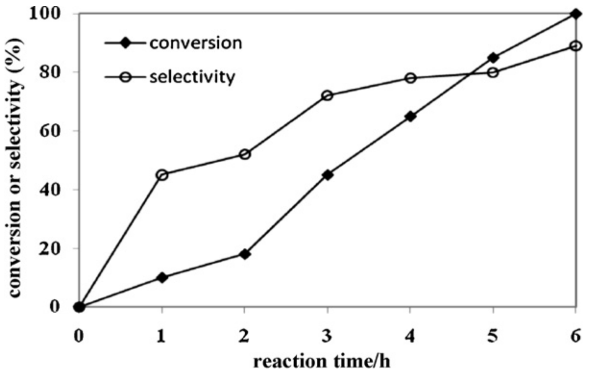


Fig. 6. Effect of reaction time on conversion and selectivity of styrene oxidation over the polymeric Co catalyst at 75 °C using H_2O_2 as an oxidant.

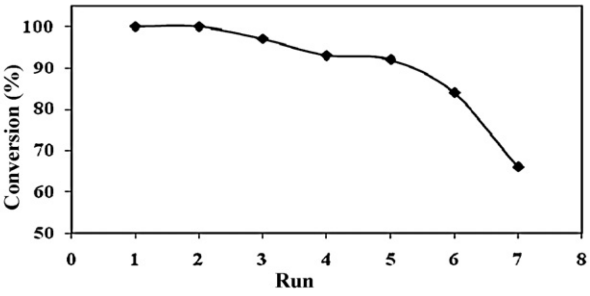
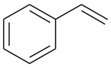
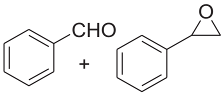
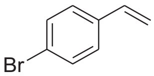
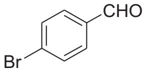
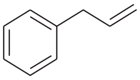
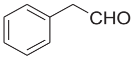
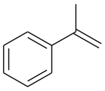
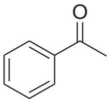
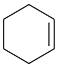
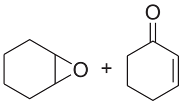
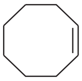
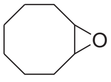
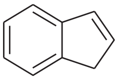
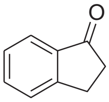
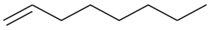
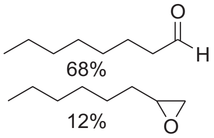


Fig. 7. Effect of successive cycles on catalytic activity of the supported catalyst for the oxidation of styrene. Reaction condition: styrene (1 mmol), H_2O_2 (30%) (5 mmol), 2 mol% catalyst in H_2O (5 mL) at 75 °C for 6 h.

Table 5
Oxidation of olefins with H_2O_2 in the presence of polyacrylamide-supported cobalt complex in water.[a]

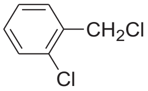
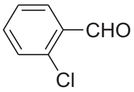
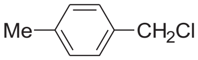
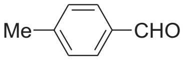
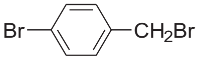
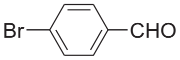
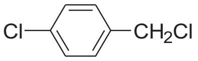
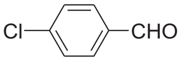
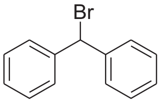
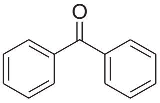
Entry	Olefin	Product (% selectivity)	Conversion (%)	TON[c]	H_2O_2 efficiency (%)[d]
1		 89% + 11%	100	50	40
2		 100%	85	42.5	36
3		 100%	88	44	37
4		 100%	100	50	40
5[b]		 71% 29%	80	40	26
6[b]		 100%	75	37.5	25
7[b]		 100%	65	32.5	22
8[b]		 68% 12%	37	18.5	14

[a] The molar ratio for cat.: substrate: H_2O_2 are 1:50:250. The reactions were performed in H_2O (5 mL) at 75 °C for 6 h.
[b] The reaction proceed for additional 6 h.
[c] mmol of converted substrate/mmol cobalt in the catalyst.
[d] H_2O_2 efficiency (%) = products (mol)/consumed H_2O_2 (mol) × 100.

mum swelling of the polymeric catalyst. Various oxidants such as $NaIO_4$, Bu_4NIO_4, urea–H_2O_2 (UHP), *t*-BuOOH and H_2O_2 were examined in the oxidation of styrene in water. H_2O_2, $NaIO_4$, Bu_4NIO_4 and *t*-BuOOH gave excellent conversion of styrene. However, *t*-BuOOH gave a crude mixture of oxidation products and $NaIO_4$ and Bu_4NIO_4 are expensive and unsafe reagents. As a result, hydrogen peroxide was chosen as the oxygen source. It is inexpensive, readily available, has a high content of active oxygen and generates only water as a by-product. Blank experiment under the same conditions showed that without oxidant the reaction does not take place (Table 2, entry 11) and without the catalyst very poor conversion was observed (Table 2, entry 12). Percent of selectivity to benzaldehyde is also shown in Table 2. Higher selectivity to benzaldehyde is observed in water with different oxidants. Even in the absence of catalyst selectivity toward benzaldehyde is high. Aqueous media probably facilitates the ring opening of epoxide leading to the oxidative cleavage and formation of carbonyl compound. The optimum H_2O_2/substrate molar ratio in our system is 5/1. When lower ratio of H_2O_2 was used, the amounts of oxidation products decreased. This may be due to the thermal decomposition of hydrogen peroxide. About 1.5 equiv. of the H_2O_2 was decomposed during this period. On the other hand, higher ratio of H_2O_2 causes overoxidation to benzoic acid. We also studied the effect of temperature on the oxidation of styrene with H_2O_2 in water. It was observed that only small amount of the oxidation product was detected at room temperature (50% conversion of styrene after 24 h), while by increasing temperature up to 75 °C the conversion was increased considerably. Finally, the catalyst loading was varied from 0.2 to 4 mol% in the model reaction (Table 3). It is clear that with increasing the amount of the catalyst, the conversion increased, but the selectivity and TONs (turnover number) decreased. For example, by increasing the catalyst loading from 0.2 to 4 mol%, the conversion of styrene reached to 100% but selectivity to benzaldehyde formation decreased to 68%. Thus 2 mol% of the catalyst was chosen as an optimum value for acceptable conversion of substrate and good selectivity.

In order to get an insight into the effect of the ligand structure on the process, a series of catalysts with different Schiff-base lig-

Table 6
Oxidation of benzyl halides with H_2O_2 in the presence of polyacrylamide-supported cobalt complex in water.[a]

Entry	Substrate	Product	Time (h)	Isolated yield (%)
1			6	87
2			6	85
3			4	90
4			6	75
5			9	82

[a] The molar ratio for cat.: substrate: H_2O_2 are 1:50:250. The reactions were performed in H_2O (5 mL) at 75 °C.

ands and different spacer arms were synthesized (Scheme 3, a and b). The metal contents of the catalysts were determined by ICP as shown in Table 4. Salicylaldehyde ligands showed higher yields and efficiency than pyridine carbaldehyde ligands (entries 1–6). Furthermore, by increasing the length of spacer arms, efficiency of catalyst in oxidation of styrene decreased (entries 1–3 and 4–6). Catalysts with six carbon spacer arm (C and F) were nearly inactive. In order to show the superiority of the cobalt catalyst, Schiff-base complexes with different metal ions: Fe, Co, Cu, Ni and Mn were synthesized (Scheme 3, c) and the ability of these metal catalysts in the oxidation of styrene with H_2O_2 was investigated. The most active catalyst, among these catalysts, was cobalt complex due to its higher yield in the oxidation of styrene with hydrogen peroxide. This catalyst (A) has the highest TON value which confirmed its highest catalytic activity between different types of catalyst. The obtained results are summarized in Table 4. Benzaldeyde is the main product in almost all cases nevertheless of the structure of the catalyst and metal ion. It confirmed the role of reaction condition for oxidative cleavage and formation of carbonyl compounds.

In addition, effect of reaction time on styrene oxidation over the Co catalyst at 75 °C using H_2O_2 as an oxidant was investigated. The styrene conversion and selectivity toward benzaldehyde reached 100% and 89%, respectively (Fig. 6). Based on the conversion curve, it is necessary to have an induction period of about 2 h at the beginning of the reaction. Based on the selectivity curve, a remarkable increase of the selectivity toward benzaldehyde was obtained in the last 3 h (Fig. 6).

To determine the general scope of reaction, oxidation of various olefins including linear, cyclic and phenyl-substituted olefins were performed under the same reaction condition used for styrene. The results with respect to conversion and product selectivity are represented in Table 5. The reactivity of the olefins toward oxidation depends on the particular structure of the substrate. In addition, the type of substrate influences the product distribution. Reports in the literature show that different cobalt complexes, in the presence of oxidant, catalyze olefin oxidation to form different products. For example, styrene can produce benzaldehyde, styrene oxide, phenylacetaldehyde, acetophenone, 1-phenyl-ethane-1,2-diol, and benzoic acid [16,21b,24,25]. Our catalytic system allows efficient oxidation with high degree of selectivity. Phenyl-substituted olefins undergo oxidative cleavage and efficiently produce aldehydes and ketones selectively (entries 1–4). Oxidative cleavage occurs, possibly by forming epoxide first followed by the nucleophilic attack of hydrogen peroxide to epoxide and then decomposition of the peroxy intermediate. The formation of benzaldehyde and styrene epoxide from styrene also suggests that styrene epoxide may be the intermediate product for the formation of benzaldehyde. In the case of cyclic olefins, there is competition between oxidation of the allylic position and oxidation of double bond. This is dependent on the type of substrate.

Table 7
A comparison of the presented catalyst with some previously reported heterogeneous cobalt catalysts for oxidation of styrene or cyclohexene.

No.	Catalyst	Conditions	Yield (% Selectivity)	Ref.
1[a]	Polymer supported $CoLCl_2$[c]	MeCN/rt/4h/Ph-I = O/2 mol% cat.	70 (100%[d])	[21a]
2[a]	Polymer supported $CoLCl_2$[c]	MeCN/rt/4 h/H_2O_2/3 mol% cat.	73 (100%[d])	[21a]
3[b]	Isomorphously substituted cobalt VSB-5	Acetone/70 °C/6 h/H_2O_2/0.15 g cat.	57 (70%[e])	[21b]
4[b]	Co HAP-γ-Fe_2O_3	MeCN/60 °C/8 h/H_2O_2/25 mg cat.	57.3 (100%[e])	[21c]
5[b]	Co(cylam)-functionalized SBA-15	MeCN/40 °C/12 h/H_2O_2/4 mol% cat.	30 (12%[f])	[26]
6[b]	Co(cylam)-functionalized SBA-15	MeCN/40 °C/12 h/*t*-BuOOH/4 mol% cat.	40 (60%[f])	26
7[b]	Co(Salen)-POM	MeCN/60 °C/6 h/H_2O_2/2 mol% cat.	85 (82%[e])	[28]
8[a]	Colbalt porphyrin immobilized on montmorillonite	MeCN/r.t/24 h/1 atm. O_2/isobutyraldehyde/20 mg cat.	75.7 (65.9[d])	[29]
9[b]	Co(Salen)-polyacrylamide	H_2O/75 °C/6 h/H_2O_2/2 mol% cat.	85 (89%[e])	–

[a] Cyclohexene used as substrate.
[b] Styrene used as substrate.
[c] L = 2-(alkylthio)-3-phenyl-5-(pyridine-2-ylmethylene)-3,5-dihydro-4H-imidazole-4-one.
[d] Selectivity for cyclohexene epoxide.
[e] Selectivity for benzaldehyde.
[f] Selectivity for styrene oxide.

Oxidation of cyclohexene was accompanied by allylic oxidation, and 2-cyclohexene-1-one and cyclohexene-oxide were produced in the reaction mixture with 29% and 71% selectivity respectively (entry 5). Cyclooctene was efficiently converted to the corresponding epoxide with no other products (entry 6). Different product distribution in cyclohexene and cyclooctene is mainly due to the difference in activity of the double bond which is attributed to the different ring size of substrates. The allylic hydrogen of cyclohexene is abstracted because the removal of hydrogen allows formation of stable intermediate. This intermediate indebted its stability to the maximum overlap of the n and π molecular orbitals. On contrary, conformational constraint of the ring system of the cyclooctene restricts maximum overlap for the allylic radical [26]. Oxidation of indene gave indone as the only product (entry 7). Although, the catalyst is able to transform non-activated terminal olefins to the oxygenated products, but it is not active for oxidation of these linear alkenes. Oxidation of 1-octene gave 37% conversion with 68% selectivity to 1-octanal and 12% selectivity to 1-octene oxide (entry 8).

The efficiency of hydrogen peroxide utilization was determined by $KMnO_4$ titration method at the end of each reaction. As shown in Table 5, the H_2O_2 efficiency was obtained from 14% to 40% based on different substrates. The low conversion of the substrate made that the H_2O_2 efficiency was lower. Furthermore, the longer reaction times (entries 5–8) would increase decomposition of hydrogen peroxide and decrease H_2O_2 efficiency.

The mechanism for the oxidation of double bonds by H_2O_2 catalyzed over cobalt catalyst is similar to one reported in the literature [26,27] and consists of (i) one-electron oxidation of cobalt (II) to Co (III) by hydrogen peroxide, (ii) activation of the oxidant at the metal center and formation of Co^{III}-peroxo intermediate, (iii) the concerted transfer of oxygen to the C═C double bond and epoxide formation, and (iv) nucleophilic attack of oxidants following by decomposition of the peroxy intermediate in the case that oxidative cleavage occurs. The reversible redox cycle between Co^{II}–Co^{III} oxidation states which involved the formation of peroxo species and oxygen atom transfer was the key factor in these cycles (Scheme 4).

Oxidation of benzyl halides to the carbonyl compounds was also studied. Primary and secondary benzyl chlorides and bromides yielded their corresponding aldehydes and ketones with H_2O_2 in the presence of the supported catalyst. The results are tabulated in Table 6.

The recyclability of supported catalysts is one of the most important benefits and makes them useful for commercial applications. Thus, the recovery and recyclability of supported catalyst was investigated using styrene as a model substrate. The catalyst was recyclable and was used in oxidation of styrene at least six times. However, there is a progressive loss of activity accompanied by diminished yield (Fig. 7). The IR spectrum of the recycled polymer was the same as the original polymer. The amount of cobalt leached out of the solution was also determined by ICP analysis and it was about 2.5%.

A comparison of our catalyst with some previous heterogeneous cobalt catalysts reported in the literature for oxidation of olefins is shown in Table 7. It shows that the most common reaction medium for oxidation reactions was organic solvents. Thus, the present method offers considerable advantages in terms of green aqueous media, short reaction times, high yields and high degree of selectivity in addition to inherent advantages of heterogeneous catalyst.

4. Conclusion

In conclusion, a new polyacrylamide-supported cobalt complex was synthesized and characterized. Electron microscopy of the catalyst showed fiber-like image of the polymeric catalyst in nanometer range. The catalyst efficiently oxidized olefins to the corresponding oxygenated products in the presence of H_2O_2 as a sole oxidant in aqueous media. In addition, various benzyl halides yielded their corresponding aldehydes and ketones without further oxidation to carboxylic acids. The catalyst was used for several times without considerable loss in its efficiency.

Acknowledgment

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