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| Complete List of Authors: | Chi, Hui; Ministry Key Laboratory of oil and Gas Fine Chemical, College of Chemistry and Chemical Engineering Xinjiang Universit<br>Wang, Ji-de; Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education, Xinjiang University, ; Xinjiang University, College of Chemistry and Chemical Engineering<br>Cao, Li-Qin; Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education, Xinjiang University, |
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# Synthesis of cross-linked copolymers of (3-(2-pyridyl) acrylic acid)-copper (II) complex in supercritical carbon dioxide for catalytic oxidation of benzyl alcohol

Hui. Chi,[a] Liqin. Cao,*[a] Jide. Wang[a]

The copper (II) complex of poly [(3-(2-pyridyl) acrylic acid)-co-acrylic acid] {P(Pya-co-AA)} were prepared by precipitation polymerization in supercritical carbon dioxide.The complexes were synthesized through a simple and efficient method of using N, N'-methylenebisacrylamide (BIS) as a cross-linker, and $scCO_2$ as reaction solvent. The obtained products were characterized by Fourier transform infrared spectroscopy (FTIR), UV-Visible Spectroscopy, X-ray diffraction and X-ray photoelectron spctra (XPS) analysis. The results indicate that the metal ion is coordinated via the nitrogen and oxygen of Pya successfully. In the method, the properties of complexes were controlled by operating parameters such as the pressure of $scCO_2$, the ratio of copper, cross-linker concentration in $scCO_2$. The catalytic activity of the polymer-metal complexes was evaluated for the oxidation of benzyl alcohol with hydrogen peroxide. The results revealed the complexes were exhibit high catalytic efficiency and reused repeatedly in high yield**.**

## 1 Introduction

During the past few decades the design and synthesis of polymeric metal complex has become one of the most an attempt to give an organic polymer inorganic functions. The formation of C(aryl)-N and C(aryl)-O bonds using metal-mediated processes can modify some properties of these materials due to the interesting applications in development of new materials, catalytic activity, biological applications, electrical conductivity and adsorption capability.[1-5]In this way it is possible to obtain materials with different properties to those of the pure components at a lower cost and without the need to synthesize a new polymeric material.[6]3-(2-pyridyl) acrylic acid) (Pya) acted an important functional monomer has attracted considerable interests, because it contains both the carbonyl oxygen and nitrogen of pyridine ring, which imparts some desirable properties, such as a multidentate organic ligand with various coordination modes and strong coordination ability. These properties led to various types of application processes for Pya. Meanwhile, traditional methods for performing the catalytic conversion of primary and secondary alcohols generally require the use of toxic and expensive inorganic oxidants such as chromium (VI), and generate large quantities of waste.[7] The porous nature of some polymer metal complex and/or the presence of possibly catalytically active transition-metal centers are seen as the basis of size- and shape-selective catalytic applications of such materials.[8] Used polymer-Cu (II) complexes catalysts for oxidation of alcohols to the corresponding carboxylic acids efficiently in the presence of $H_2O_2$ has been described.[9] Moreover, the heterogeneous catalytic oxidation of alcohols by using polymer-Cu (II) catalysts presented the best catalytic activity (86% of phenol conversion) compared with commercial catalysts.[10] The dinuclear iron complexes were also found to be suitable catalysts for the oxidation of alcohols to the corresponding carbonyl compounds in acetone as solvent in yield of 53%.[11]

However, the synthetic methods of polymer-metal complexes require traditional volatile organic solvents, irradiation and initiator of heavy-metal salts,[12-14] and they may cause environment problems. Utilizing supercritical carbon dioxide ($scCO_2$) as reaction medium in synthesis procedure of polymer complex is a route to solve the problem because of their unusual properties such as nontoxic, nonflammable, chemical inert, inexpensive, and easily separated products from solvents.[15] $CO_2$ has an accessible critical condition (31.1 °C and 7.38 MPa), $scCO_2$ has low viscosity and high diffusion rate in the critical region and its solubility power is easily tunable via manipulation of both temperature and/or pressure without altering the composition of the medium.[16] Moreover, a unique advantage of $scCO_2$ as a transform medium is its ability to adjust solvent quality.$CO_2$ is used as the porogen in heterogeneous polymerization, where the resulting porous beads form the basis for ion exchange resins and polymer-metal complexes.[17, 18] In this method, monomeric metal complex and initiator dissolved in $scCO_2$ followed by thermal polymerization at high temperature, resulting in polymer complex. Thus we can control the complex with different compositions, surface area and morphologies by operating parameters.

Previously, we reported the precipitation polymerization of poly (4-vinylpyridine)-copper (II) complex.[19] In this paper, we extend this

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*Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uyghur Autonomous Region, Xinjiang University, Urumqi 830046, P. R. China. Email: caoliqin1975@hotmail.com; Fax: +86 991 8582807; Tel: +86 991 8581018*

research to bifunctional ligand and the effect on the coordination polymers. Reported herein are the synthesis and characterization of P(Pya-co-AA)-Cu(II). As a heterogeneous polymerization form in $scCO_2$, the dry green powder was obtained. The resultant products were characterized using standard nitrogen adsorption analysis, Fourier transform infrared (FTIR), X-ray diffraction (XRD) analysis, XPS analysis and UV-Vis analysis. The effect of operating conditions on compositions, surface area and morphologies was also discussed. In addition, the catalytic activity of the products was evaluated based on the oxidation reactions of benzyl alcohol.

## 2 Experimental

### 2.1 Materials and methods

The monomer, 3-(2-pyridyl) acrylic acid (Pya) purchased from jkchemical (97%) and acrylic acid (AA) purchased from Tianjin Chemical Reagent Plant. 2,2-Azobis (isobutyronitrile) (AIBN) was supplied by Shanghai Chemical Agent Fourth Factory, and was recrystallized twice from methanol. $CO_2$ with a purity of 99.9% was supplied by Wurumqi Gas Factory. Copper sulfate, N,N-methylenebisacrylamide (BIS), and other reagents were of analytical reagent grade and supplied by Tianjin Chemical Reagent Co. Ltd. (Tianjin, China).Reactions were carried out in a 100 mL stainless steel reactor (model FYX-0.1; Dalian Tong Chan High-pressure Reactors Manufacturing Co., Ltd., China) equipped with sapphire windows. Phase behavior during reaction was also observed in the reactor. The pressure in the reactor was measured in the range of 0–30 MPa, using a pressure gauge. The temperature of the reactor was controlled by a thermostat water bath (DF-101S; Jintan Medical Instruments Factory, China). A magnetic stirrer was used to mix the reaction system. For safety reasons, mirrors were be used to view through the high-pressure windows instead of directly viewing through the windows.

### 2.2 Synthesis of Cu (II) complexes of P(Pya-co-AA)

Synthesis of cross-linked P(Pya-co-AA)-Cu(II) complex were carried out in high-pressure apparatus described above. In the reaction procedure, three basic steps were performed to synthesize the P(Pya-co-AA). First, a suitable amount of copper sulfate, Pya and AA were used as the coordination ion and the functional monomer, respectively, and were placed into the autoclave. The mixture was then adequately stirred for 30 min. Second, the autoclave was charged with desired amount of the initiator, crosslinker and an appropriate amount of ethanol. The reactor was first immersed in an ice bath and then purged with a flow of $CO_2$ to remove air for 2 min, then filled with liquid $CO_2$. After the pressure reached the desired value, the autoclave was placed into thermostat water bath at 35.0°C, which was controlled by a temperature controller with an accuracy of ± 0.1 °C. The monomeric metal complex, the initiator and the cross-linker were dissolved in $scCO_2$. Third, after stirring about 30min, the autoclave was then gradually heated up to the desired working temperature to achieve an accurate pressure at a specified time. During the reaction process, the reaction system was mixed using a magnetic stirrer at an appropriate speed. At the end of the reaction, the system was cooled to room temperature, and $CO_2$ was slowly released. The physical form and the overall appearance of the polymer were noted, and the products were treated with $scCO_2$ by a high-pressure Soxhlet extractor to remove the unreacted monomeric metal complex, the cross-linker, and initiator residues. Green powder was collected and dried using a vacuum at 60 °C for 8 h.

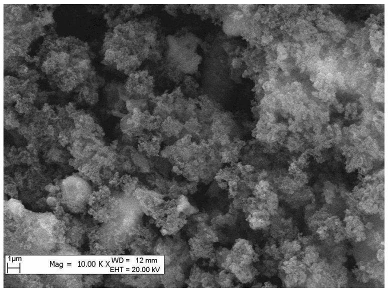
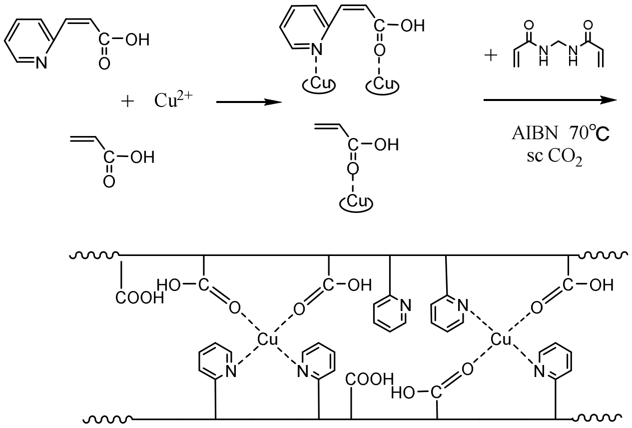


Fig. 1 Scanning electron microscope microphotograph of P(Pya-co-AA)-Cu (II) complex. Conditions: $^a$0.718 g of $CuSO_4$, 0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol, 20 MPa, 70 °C, 12 h.

Fig. 1 shows the SEM of P(Pya-co-AA)-Cu (II) complex synthesized at 20 MPa. The polymer complex is formed on the wall of the autoclave and the dry, fluffy, and green powder is obtained. The morphology of polymer is an aggregate of primary particles, which are about 0.5-0.2 μm in diameter. The product yield was calculated according to the mass of the final products and added monomer and copper sulfate, which is defined in Eq. (1):

$$\text{Yeild} = \frac{M_{\text{P(Pya-co-AA)-Cu(II)}}}{M_{\text{monomer}} + M_{\text{copper ion}} + M_{\text{BIS}}} \times 100\% \qquad (1)$$

Where M is the weight of the reagent (g), and MP(Pya-co-AA)-Cu (II) the total obtained product mass after washing. The yield was determined gravimetrically. Scheme 1 shows an illustration of the synthesis of the P(Pya-co-AA)-Cu (II) complex in $scCO_2$ and the possible structure of the complex.



**Scheme 1** Schematic illustration of the synthesis of the P(Pya-co-AA)-Cu (II) in $scCO_2$ and the possible structure of the complex.

### 2.3 Sample characterization

FTIR (Vertex 70) was used to characterize P(Pya-co-AA)and P(Pya-co-AA)-Cu (II) complex. The morphologies of the various samples were observed using a LEO1430VP scanning electromicroscope (LEO, Germany). TGA (Netzsch, Germany, STA-449 °C was conducted by heating the sample from 25 °C to 800 °C in nitrogen atmosphere to observe the pyrolytic behaviour of the cross-linked copolymer and polymer complex. The heating rate was maintained at 10 °C min$^{-1}$. X-ray photoelectron spctra (XPS) were measured by Kratos Amicus with X-ray.

Wide angle X-ray diffraction (XRD, Bruker D8 X, Germany) was used to characterize P(Pya-co-AA)and P(Pya-co-AA)-Cu (II) complex . The work condition of XRD was a Cu-Kα radiation via a rotating anode at 40 kV and 50 mA. The data were collected in the step of 5 ° min$^{-1}$ and range of scattering angles (2 θ) from 5 °C to 80 °C. The structure of samples in the supernatant was analyzed with a UV spectrophotometer (UV-2450 Shimadzu).

The Brunauer-Emmett-Teller (BET) surface areas of the complexes were measured by standard nitrogen gas adsorption analysis by using a commercial instrument (JW-BK, JingWeiGaoBo Co., Ltd., Beijing). About 0.2 g of the sample was pretreated prior to the BET surface area measurement. The sample was placed in sealed quartz tune and degassed at 105 °C for 2 h. Physical or chemical changes cannot occur in these conditions. After pretreatment, the quartz tube was set in the instrument, and the measurements were then performed.

The loading level of Cu (II) in the complexes was examined using Atomic absorption spectrophotometry (Analyst 300 spectrometer, PerkinElmer, Inc.). A certain mount of complex was placed in a muffle furnace at 700 °C, 2 h. Then the polymer was decomposed and removed completely, and Cu (II) was converted into the CuO powder. The powder was dissolved in the 5% sulfuric acid solution and the concentration of copper (II) was analyzed by atomic adsorption spectrophotometry. Thus the loading of Cu (II) is defined in Eq. (2):

$$\mathrm{Cu(II)} = \frac{C_{\mathrm{Cu(II)}} \times V_{\mathrm{Cu(II)}}}{M_{\mathrm{P(Pya\text{-}co\text{-}AA)\text{-}Cu(II)}}} \times 100\% \qquad (2)$$

where C Cu (II) was obtained concentration by atomic adsorption spectrophotometry (g mL$^{-1}$), V Cu (II) the volume of combustion product after dilution (mL) and M P(Pya-co-AA)-Cu (II) is the weight of the P(Pya-co-AA)-Cu (II) complex (g).

## 3 Discussion

### 3.1 FTIR spectra results of complex

Ring mode vibrations of the ligands are affected by coordination to Cu (II), corresponding to shift in energy for bands in the 1800–1000 cm$^{-1}$ region of IR spectra. The infrared spectra of P(Pya-co-AA)and P(Pya-co-AA)-Cu (II) complex are shown in Fig. 2. The shifting of υ(C=O) stretching vibration band from 1720 to 1740 cm$^{-1}$can be ascribed to presence of covalent bond between copper and the carbonyl oxygen of Pya. The characteristic band of pyridine group, observed as strong absorption band at 1595 cm$^{-1}$and 1220 cm$^{-1}$ in P(Pya-co-AA), also shift to 1610 cm$^{-1}$ and at 1232 cm$^{-1}$, respectively, in P(Pya-co-AA)-Cu (II) complex. These bands shift to higher frequency suggest the carbonyl oxygen and nitrogen of pyridine ring as coordination site in the Cu (II) complexes of P(Pya-co-AA).

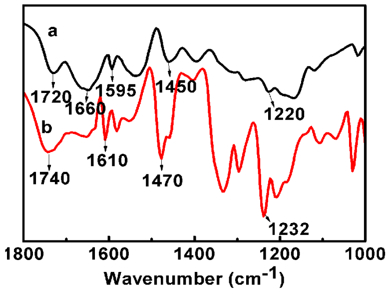


**Fig. 2** The FTIR spectra of (a) P(Pya-co-AA)a, and (b) P(Pya-co-AA)-Cu(II) complex b .Reaction conditions: a 0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol, 20 MPa, 70 °C, 12 h; b 0.718 g of CuSO$_4$, 0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol, 20 MPa, 70 °C, 12 h.

### 3.2 XRD analysis

The diffraction spectra of P(Pya-co-AA) exhibits of one major peaks at 2θ=20.4 °, while P(Pya-co-AA)-Cu (II) complex consisted of one major peak at 2θ=20.7 °. In Fig. 3, it was observed the XRD patterns of P(Pya-co-AA)-Cu (II) complex and P(Pya-co-AA) are very similar, no Cu peaks are observed in the diffractograms of the Cu (II) complexes of P(Pya-co-AA), meaning that the Cu particles are not composed of single crystallites. However, it displays high crystallinity after the monomer interacted with the copper ion. The behavior due to an amorphous structure of polymer-metal complex between Cu (II) and the polymer chains, which takes place in the polymeric network.[20]

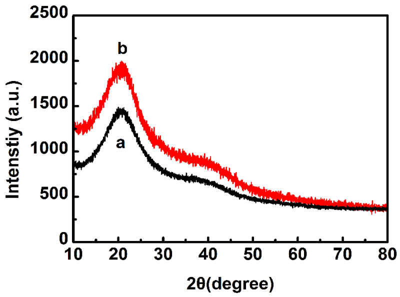


**Fig. 3** The XRD patterns of the parent (a) P(Pya-co-AA)$^{a}$, and (b) P(Pya-co-AA)-Cu (II) complex $^{b}$ .Reaction conditions: $^{a}$0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol, 20 MPa, 70 °C, 12 h; $^{b}$0.718 g of CuSO$_4$, 0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol, 20 MPa, 70 °C, 12 h.

### 3.3 UV analysis

Ultraviolet–visible spectra of aqueous solutions after isolation of P(Pya-co-AA)and P(Pya-co-AA)-Cu (II) complex are shown in Fig. 4, where the ratio denotes moles of polymer monomeric units/formula weight of copper sulfate. The spectrum for the P(Pya-co-AA)-Cu (II) show a broad band at 214 nm and 240nm, characteristic of the carbonyl oxygen and pyridine ring respectively. Comparing the absorption spectrum of P(Pya-co-AA)-Cu (II) complex and that of P(Pya-co-AA), we can see a red shift of electronic transitions, and the absorbance intensity is proportional to the concentration of Cu (II) ions, indicating that coordination of poly-Pya, which was ascribed to Cu-O coordination and Cu-N coordination in the polymer-metal complex, influences its corresponding absorption.

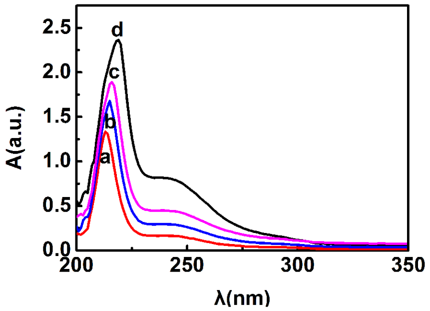


**Fig. 4** UV-Visible spectra of aqueous solutions of P(Pya-co-AA)-Cu (II) complexes at ratios: (a) 8/1; (b) 6/1; (c) 4/1; and (d) 2/1mol/mol.

### 3.4 Thermogravimetric analysis

The TGA curves of cross-linked P(Pya-co-AA)-Cu (II) complex are shown in Fig. 5. The P(Pya-co-AA)-Cu (II) complex separated into two segments, namely, at 183 °C and 415 °C, which is different from that of polymer. It is probably that complex formation between the polymer ligand and Cu (II) ion contribute to the change in degradation temperature. The changes in electronic density can weaken the chemical bonds in the pyridine ring and in the polymeric backbone chain, which results in a decrease in thermal stability.

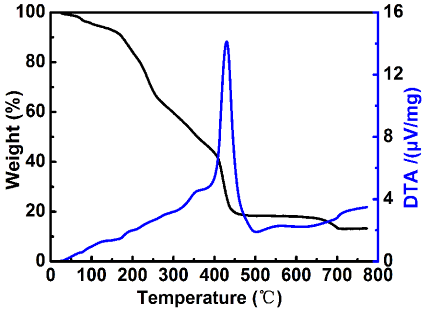


**Fig. 5** TGA and DTA curves of P(Pya-co-AA)-Cu (II) complex .Reaction conditions: 0.718 g of $CuSO_4$, 0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol, 20 MPa, 70 °C, 12 h.

### 3.5 XPS analysis

The change in the surface condition of P(Pya-co-AA)and P(Pya-co-AA)-Cu (II) complex was observed by XPS. As is shown in Fig. 6, the XPS measurements were performed for the energy regions of full scan, Cu 2p, O 1s, N 1s energy regions. Fig .6a displays the XPS spectra of Cu $2p_{1/2}$ peak and a $Cu_{3/2}$ peak appearing at 952.7 eV and 935.6 eV for P(Pya-co-AA)-Cu (II) complex. The binding energies of these peaks slightly shifted in the direction of lower binding energy region by comparison with peak positions of Cu 2p peaks of copper sulfate.[21] This is attributed to an electronic density reduction of copper ion because of the complex formation between the Cu (II) and the polymer ligand. Oppositely, Fig. 6b shows the O1s spectrum shows two O 1s peaks corresponding to double bonded oxygen and to the -OH group. The XPS spectra of O1s peak appears at 532.58 with another peak at 531.53 eV for P(Pya-co-AA)and that at 533.18 eV with another peak at 531.58 for P(Pya-co-AA)-Cu (II) complex . The changes observed in these peaks of P(Pya-co-AA)-Cu (II) complex are proposed to be involved in the oxygen bonding to the copper. Fig. 6c exhibits the XPS spectra of N1s peak appearing at 399.35 eV for P(Pya-co-AA)and that at 399.58 eV for P(Pya-co-AA)-Cu (II) complex. The chemical shifts of N1s are more than 0.2 eV, corresponding to the coordination of pyridine uint of P(Pya-co-AA) to Cu (II). Thus, we propose that copper ion is complexed by coordination with acidic (-COOH) and basic (-N) functional groups of pyridine.[22]

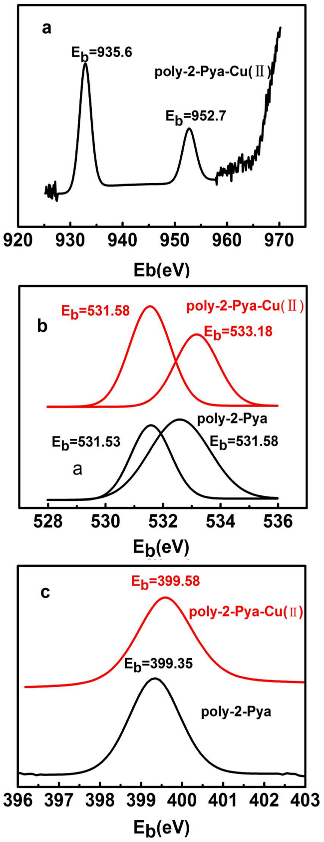


**Fig. 6** X-ray photoelectron spectra of P(Pya-co-AA)and P(Pya-co-AA)-Cu (II) complex in the energy regions of (a) Cu 2p, (b) O 1s, (c) N 1s.

### 3.6 Effect of operating parameters on the composition of the complex

As is already known, $scCO_2$ have high diffusing ability, which enables them to enter spaces rapidly; moreover, it can also dissolve small organic molecules, and its solvent strength increases with pressure. One aim of this work was to synthesize P(Pya-co-AA)-Cu (II) complex with controlled composition. This can be done by changing the parameters of the process to control the content of monomeric metal complex in the complex. Additionally, as reaction medium, the density of $CO_2$ has a strong effect on the morphology and structure of polymers. Thus, we can adjust the amount of monomeric metal complex the morphology of the complex by altering the pressure, the ratio of copper ion in $scCO_2$, and the cross-linker concentration. The effects of these parameters on the composition of P(Pya-co-AA)-Cu (II) complexes have been discussed above.

The effect of $CO_2$ pressure during the absorbing process on the composition of the composites was also studied in the pressure range of 15.0 MPa to 25.0 MPa. The results were summarized in Table 1. A distinctly trend was found, the average surface area and pore volume of samples are increased under condition of increased pressure, however, the yield are reduced when they reach a certain level. As the pressure increases, more $CO_2$ molecules enter the polymer network, the venting of these molecules left more pores. The increase in $scCO_2$ density increased the number of nuclei generated in the reaction system and reduced the particle diameter. However, at a higher pressure, the solubility of monomeric metal complex may be decreased, which due to the yields of polymer complex are decreased.

Table 2 shows the effect of the ratio (8:1-2:1) of copper ion respect to the monomer at constant feed compositions. The mount of loading of Cu (II) increases with the concentration of copper ion in the monomeric metal complex. When the proportion was increased to 2:1, the loading of Cu (II) reached 5.96%. This is easy to understand because larger concentration of copper ion is favourable to the intermolecular coordination of the macromolecular chains of Pya with Cu (II) taking place, when the mount of Pya monomer consisting of pyridine ring-N and C=O covalently bonded to Cu (II) is enough.

As shown in the table 3, precipitation polymerizations were performed at five different initial cross-linkers to monomer ratios (0%, 10%, 20%, 30%, and 40% (w/w)). A higher yield of products was obtained in the presence of an appropriate cross-linker ratio (20%), and the polymer-complex yield slightly decreased when the cross-linker ratio was further increased to 40%. This result indicates that a high cross-linker ratio is necessary to synthesize a P(Pya-co-AA)-Cu (II) complex. The main reason is that a high cross-linker ratio is favourable to its formation a suitable polymer network which could not only increase the surface area of polymer complex, but also improve the yield product through changing the solubility of the monomeric metal complex in the $scCO_2$. Therefore, when cross-linker ratio reached 40%, more monomeric metal complex are distributed in the $CO_2$-rich phase, resulting in a higher yield and loading of Cu (II).

**Table 1.** Effect of pressure on surface area and yield of the cross-linked P(Pya-co-AA)-Cu (II) complex [a].

| Entry | Cross-linker concentratio | Surface area ($m^2/g$) | Loading of Cu(II) | Yield (%) | Morphology |
|---|---|---|---|---|---|
| 10 | 0% | - | - | 70.5 | Wet |
| 11 | 10% | 14.9 | 2.8 | 79.6 | Yellow and white |
| 12 | 20% | 30.1 | 2.93 | 95.3 | Green powder |
| 13 | 30% | 43.5 | 3.62 | 86.5 | Green powder |
| 14 | 40% | 52.2 | 4.16 | 90.2 | Yellow and white |

[a] Reaction condition:0.718 g of $CuSO_4$, 0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol, 70 °C, 12 h.

**Table 2**. Effect of the ratio of copper ion on loading of Cu (II) and yield of the cross-linked P(Pya-co-AA)-Cu (II) complex [a]

| Entry | Ratio of copper ion | Loading of Cu (II) (%) | Yield (%) | Morphology |
|---|---|---|---|---|
| 6 | 1/2 | 5.96 | 85.1 | Blue and green |
| 7 | 1/4 | 2.93 | 95.3 | Green powder |
| 8 | 1/6 | 2.11 | 86.2 | Green powder |
| 9 | 1/8 | 1.23 | 84.9 | Light green powder |

[a] Reaction condition:0.718 g of $CuSO_4$, 0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol, 70 °C, 12 h.

**Table 3.** Effect of cross-linker concentration on surface area, loading of Cu (II) and yield of the cross-linked P(Pya-co-AA)-Cu (II) complex [a].

| Entry | Pressure (MPa) | Surface area ($m^2 g^{-1}$) | Yield (%) | Morphology |
|---|---|---|---|---|
| 1 | 15 | 17.2 | 86.1 | Yellow and white |
| 2 | 17 | 29.2 | 91.5 | Green powder |
| 3 | 20 | 30.1 | 95.3 | Green powder |
| 4 | 22 | 51.6 | 89.8 | Green powder |
| 5 | 25 | 68.4 | 77.2 | Yellow and white |

[a] Reaction condition:0.718 g of $CuSO_4$, 0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol, 70 °C, 12 h.

### 3.7 Catalytic activity

The oxidation of benzyl alcohol catalyzed by the complexes occurs readily to form the corresponding benzaldehyde as major products. The reactions were conducted at 80 °C. Control experiments without catalyst under the same reaction conditions showed no oxidation. In Fig. 7 a, benzyl alcohol concentration is changed slightly without any catalyst; in Fig.7 b, benzyl alcohol concentrations decrease with increasing time using P(Pya-co-AA)-Cu (II) complex as catalyst. It is probably that the high activity of polymer-Cu (II)-based catalysts is attributed to the formation of a more stable active species based on hard and soft acid and base principles.[23] The Cu complex of P(Pya-co-AA)-Cu (II) has been found to exhibit high catalytic efficiency in comparison with those Cu-pyridine system reported by Ilaria Gamba.[24] This high reaction activity might be due to the distinctive future of large surface of the copolymer complex after crosslinked in that all of the catalytically active sites were sufficiently located on the surface.

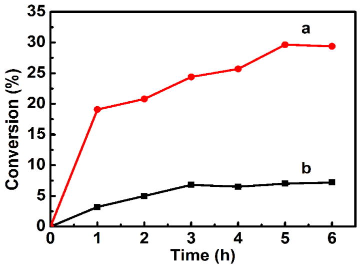


**Fig. 7** Change in benzyl alcohol concentration with reaction time: (a) without any catalyst (b) 50 mg of P(Pya-co-AA)-Cu (II) complex. Experimental parameters: [

benzyl alcohol]=3 mL, [$H_2O_2$]= 4 mL, [acetone]=10mL,T= 80 °C. The composite prepared at 20.0MPa with 0.718 g of $CuSO_4$, 0.895 g of Pya, 0.865 g of AA, 0.352 g of BIS, 0.176 g AIBN, 2 mL of alcohol in the fluid phase for 70 °C,12 h., 20 MPa, 70 °C, 12 h.

### 3.7.1 Effect of oxidation condition

The oxidation of benzyl alcohol was studied in more detail to optimize the reaction variables such as solvent, alcohol/oxidant molar ratio and length of reaction time. We checked first the activity of P(Pya-co-AA)-Cu (II) complex in different solvents ($C_2H_5OH$, $CH_3CN$, and acetone) with $H_2O_2$ as the oxidant (Supporting information Table. 4). The best conversions have been observed in acetone. The effect of varying the alcohol/oxidant molar ratio was studied with P(Pya-co-AA)-Cu (II) complex in acetone during the oxidation of benzyl alcohol. Addition of another aliquot of $H_2O_2$ increased the amount of benzaldehyde, showing that more than stoichiometric amount of $H_2O_2$ is utilized in the reaction. This result is consistent with those reported by the previous researchers.[25, 26] Table 4 shows that the best yield was obtained with the 75 mmol of $H_2O_2$. In that case the maximum conversion of phenol is 35.1%, 85.5% of benzaldehyde and 8.4% of benzoic acid was formed. When hydrogen peroxide was added to a solution of P(Pya-co-AA)-Cu (II) complex and benzyl alcohol over 30 min and the mixture was stirred for 5 h oxidation occurred and benzaldehyde was formed in 29.6% yield. A trace amount of benzoic acid was also obtained. Stirring the mixture for 5 h more products could be obtained.

**Table 4.** Oxidation of benzyl alcohol

| Solvent | $H_2O_2$ (mmol) | T (h) | C (%) | Production distribution (%) | |
|---|---|---|---|---|---|
| | | | | Benzaldehyde | Benzoic acid |
| $C_2H_5OH$ | 35 | 5 | 5.5 | 82.4 | 15.6 |
| $CH_3CN$ | 35 | 5 | 23.5 | 90.2 | 6.5 |
| acetone | 35 | 5 | 29.6 | 89.4 | 2.6 |
| acetone | 55 | 5 | 32.0 | 86.5 | 6.0 |
| acetone | 75 | 5 | 35.1 | 85.5 | 8.4 |
| acetone | 35 | 1 | 19.1 | 95.0 | 1.3 |
| acetone | 35 | 3 | 24.4 | 91.1 | 2.3 |

Reaction condition: benzyl alcohol 35mmol, $H_2O_2$ 35mmol, solvent 10mL, 80 °C, 50 mg of P(Pya-co-AA)-Cu(II) complex prepared at 20.0MPa with 0.718 g of $CuSO_4$, 0.895 g of Pya, 0.865 g of AA, 0.176 g AIBN, 2 mL of alcohol in the fluid phase for 12 h, 70 °C.

### 3.7.2 Effect of operating parameters condition on catalytic activity of the polymer complex

These complexes synthesized under different operating conditions were also examined as catalyst for the oxidation of benzyl alcohol under the same reaction conditions. As shown in Fig. 8, Fig. 9and Fig. 10, it easily observed that the reaction of the conversion increases with the increasing surface area and loading of Cu (II), both of which can be controlled by changing the parameters of the synthesis process. The main reason is that the large surface area and loading of Cu (II) are still key factors in the polymer catalyst reaction.

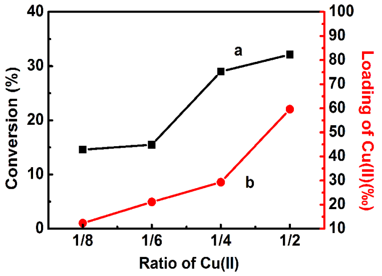


**Fig. 8** The effect of pressure on (a) the conversion of the oxidation of benzyl alcohol and (b) surface area. Experimental parameters: [ benzyl alcohol]=3 mL, [$H_2O_2$]= 4 mL, [acetone]=10 mL,T= 80 °C.

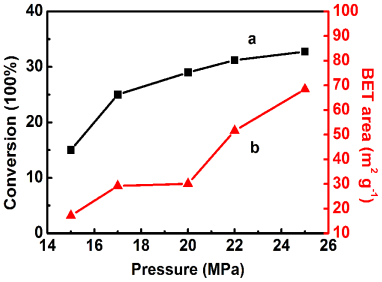


**Fig.9** The effect of ratio of Cu (II) on (a) the conversion of the oxidation of benzyl alcohol and (b) loading of Cu (II). Experimental parameters: [ benzyl alcohol]=3 mL, [$H_2O_2$]= 4 mL, [acetone]=10mL,T= 80 °C.

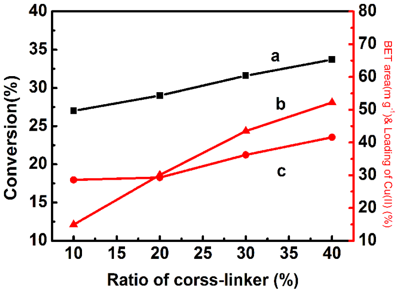


**Fig.10** The effect of ratio of cross-linker on (a) the conversion of the oxidation of benzyl alcohol (b) surface area and (c) loading of Cu (II). Experimental parameters: [ benzyl alcohol]=3 mL, [$H_2O_2$]= 4 mL, [acetone]=10mL,T= 80 °C.

### 3.7.3 Reusability of complex for catalyst oxidation of benzyl alcohol

For the industrial application of the oxidation of benzyl alcohol, the lifetime of the polymer-Cu (II) complex and its level of reusability are very important factors. In this experiment, the catalyst was reused 3 times in the reaction of oxidation of benzyl alcohol. It was obvious that the polymer-Cu (II) complex still showed consistent catalytic activity after being reused so many times, as shown in Table 5. Although the catalytic activity slightly decreases at the 4th recycled run, activity of the complex was still remaining above 25%. In addition, the filtrate resulting from the reaction mixture had no catalytic activity under identical conditions. We concluded that there was no leaching of the catalytically active species from the beads during the reaction. This result may be ascribed to the insoluble polymer complex heterogeneously catalyzed the reaction. The mechanism requires further investigation.

**Table 5**. Reusability of P(Pya-co-AA)-Cu (II) complex on catalysis for benzyl alcohol

| Recycle time | Conversion (%) | Selectivity of Benzaldehyde(%) | Selectivity of Benzoic acid(%) |
|---|---|---|---|
| 1 | 29.6 | 89.4 | 2.6 |
| 2 | 26.2 | 86.5 | 5.2 |
| 3 | 26.5 | 86.3 | 4.9 |
| 4 | 20.2 | 88.9 | 3.2 |

Reaction condition: benzyl alcohol 35mmol, $H_2O_2$ 35mmol, solvent 10mL, 80 °C, 50 mg of poly-Pya-Cu(II) complex prepared at 20.0MPa with 0.718 g of $CuSO_4$, 0.895 g of Pya, 0.865 g of AA, 0.176 g AIBN, 2 mL of alcohol in the fluid phase for 12h, 70 °C.

## 4 Conclusions

Cross-linked copolymers of poly (3-(2-pyridyl) acrylic acid)-copper (II) were prepared through precipitation polymerization in $scCO_2$. Under the optimized conditions, the products are green and insoluble powder. When the ratio of copper (II) ion and the cross-linker concentration related with monomer are 4/1 and 20%, at 70 °C, 20 MPa with a yield of 95.3%, the average surface area is 30.1 $m^2 g^{-1}$, the loading of Cu (II) is 2.93%.The complex was found to be useful catalysts for the oxidation of alcohols using $H_2O_2$ in acetone as solvent, the conversion rate of benzyl alcohol and the selectivity of benzylaldehyde reach 29.6% and 89.4% respectively, under the temperature of 80 °C for 5 h. The catalytic activity of the products was also effected by operating parameters such as the pressure of $scCO_2$, the ratio of copper, cross-linker concentration with different the average surface area and the loading of Cu (II) , the conversion rate of benzyl alcohol ranged from 14.6% to 33.7% under the same oxidation conditions. At the same time, catalytic activity does not change after using three times.

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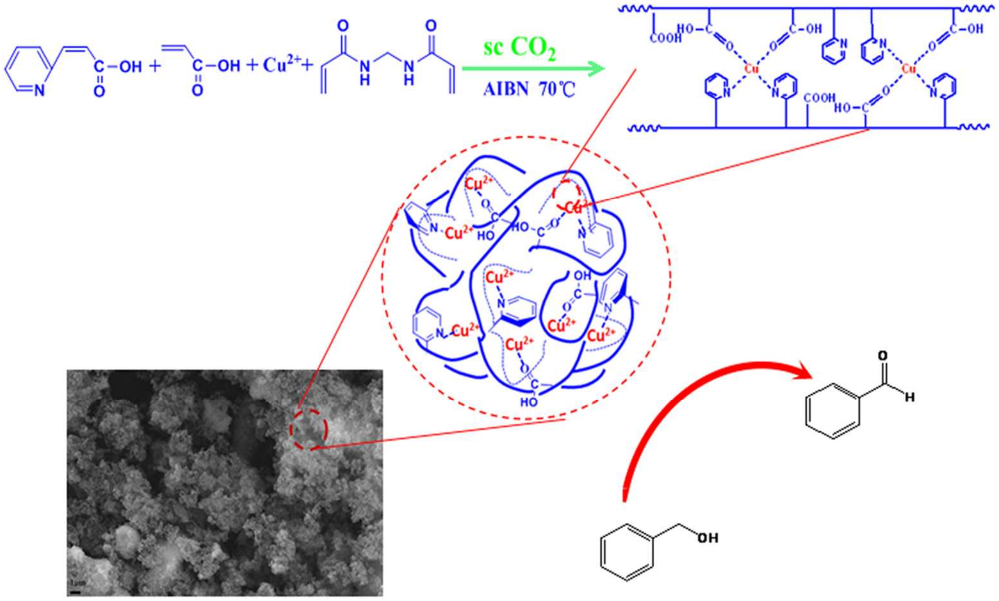

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