CHEMICAL ENGINEERING TRANSACTIONS

VOL. 62, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Fei Song, Haibo Wang, Fang He

ISBN 978-88-95608- 60-0; **ISSN** 2283-9216

DOI: 10.3303/CET1762023

Application of the Nitrogenous Polymeric Metal Complex in Organic Synthesis

Tingting Ru

Jilin Jianzhu University, Jilin 130118, China
rutingting@jliae.edu.cn

To research chemical formation of the nitrogenous polymeric metal complex, this paper studies the catalysis of the polymeric metal complex in chemical reaction via the organic combination reaction. In this paper, a series of N-functionalized nitrogenous polystyrene ligands are prepared by making chloromethylate polystyrene resin (CPS) reacting with ethanol amine, 2-mercapto ethylamine (MEA), 8-hydroxyquinoline, anthranilic acid and imidogen oxalic acid (IDA) respectively, and crosslinked polyacrylamide is obtained by adopting solution polymerization and reversed phase suspension polymerization methods. Moreover, the polymeric metal complex is obtained by making nitrogenous polymer acting on the water solutions of FeCl3, 6H2O, CuCl2, 2H2O, CoCl2, 6H2O, NiCl2 and 6H2O at certain pH and temperature, the characteristics of nitrogenous polymeric ligand and nitrogenous polymeric metal complex are presented by adopting elemental analysis, Fourier transform infrared, atomic absorption, thermogravimetric analysis (TGA) and electron spin resonance (ESR) etc., and catalytic performance of the nitrogenous polymeric metal complex on acetal (ketone) reaction and alcohol oxidation is inspected. The results indicate that polymeric metal complex can be really formed by making functionalized polystyrene acting on transition metal salt in certain conditions, and various N-functionalized nitrogenous polystyrene ligands have selectivity to the adsorption of metal ions.

1. Introduction

Polymeric metal complex catalyst is an important field in functionalized polymer research, and it is a new substance formed by virtue of the interaction between polymeric ligand and metal element. Metal complex can be used as catalyst both inorganic synthesis and chemical industry (Lindoy et al., 2013, Oehninger et al., 2013). For a long time, the homogeneous-phase metal complex catalysts used in industry are easy to loss during the use, they have certain corrosivity on equipment (Matsuoka et al., 2015), and some of them even may pollute the environment, so how to overcome the disadvantages is a problem needing to be solved urgently. Since from the 1960s, as enlightened by the enzyme catalyzing various chemical reactions in the biological body (Guo et al., 2013), the people synthesize many polymeric metal complex catalysts with higher activity, better selectivity and more favourable stability artificially (Saha et al., 2014, Shirazi and Akhbari, 2016), and they obtain the heterogeneous polymeric metal complex catalysts by immobilizing or linking the homogeneous metal complex to polymeric carriers, thus the heterogeneous polymeric metal complex catalysts can possess advantages and avoid disadvantages of the two.

For the specific polymeric effect (Alonso-Moreno et al., 2014), polymeric metal complex catalyst can overcome the disadvantages of being sensitive to air and water, being easy to lose activity and having separation and recovery difficulties after reaction of the homogeneous complex catalyst (Lu et al., 2014). Along with promotion of the environmental protection awareness of the human being, research in this field becomes the topic concerned by many scholars (Emmett and Willis, 2015).

In this paper, it firstly discusses catalysis of the various N-functionalized nitrogenous polystyrene metal complexes to the acetal (ketone) reaction, and the favourable catalytic activity is proved.

Please cite this article as: Tingting Ru, 2017, Application of the nitrogenous polymeric metal complex in organic synthesis, Chemical Engineering Transactions, 62, 133-138 DOI:10.3303/CET1762023

2. Experimental Part

2.1 Main reagents

Main reagents, reagent purities and manufacturers of this experiment are listed in Table 1. For concrete information, please refer to the table below:

Table 1: Experimental reagents

Drugs	Purity	Manufacturer
Chloromethyl polystyrene	Crosslinking degree 7.5%; Cl%: 18%	Nankai University school factory
Cyclohexanone	AR	Shanghai chemical reagent purchase and supply station
Benzaldehyde	AR	Shanghai chemical reagent company
p-nitrobenzaldehyde	AR	ACROS organics

2.2 Instruments and equipment

Instruments and equipment: common glass ground instrument, sand core funnel, circulating water vacuum pump, oil pump, water tank, voltage regulating transformer, magnetic stirrer, motor stirrer, infrared drying lamp, ultraviolet lamp, chromatographic column, dryer, PHB-3 0.1 portable acidity meter, elemental analyzer, infrared spectrometer, gas chromatograph, nuclear magnetic resonance spectrometer, atomic absorption spectrometer, and electron paramagnetic resonance spectrometer.

2.3 Experimental characterization

(1) Infrared spectroscopy: MagNa-550 infrared spectrometer is used in detecting (KBr) polymeric ligand and the metal complex.
(2) Thermal analysis: Perkin-Elmer TGA7 thermal gravimetric analyzer is used in the test in nitrogen atmosphere.
(3) EPR: JES-FE3AX electron paramagnetic resonance spectrometer of the Japan JEOL Company is used in testing metal coordination condition of the polymeric metal complex in indoor temperature.
(4) Photoelectron spectroscopy: ESY ESC VG ESC LB MKII meter is used in testing, vacuum degree in the analysis room is 2.5 x 10-6 Pa, and excitation source is Mg ka ray.
(5) Elemental analysis: Italian 110E elemental analyzer is used in testing the nitrogen content in nitrogenous polymeric ligand and then determining the Cl conversion rate in CPS.
(6) Ion load measurement: take 1g nitrogenous polymeric resin, put it in beaker, soak it in 20ml 0.02mol/l metal ion solution fully for a certain time, filter it with sand core funnel, and wash the polymeric compound with deionized water till to that metal ion concentration of the liquid after leaching is less than 1 x 10-6g/l; combine the washing filter liquor, detect metal ion concentration (Hg/ml) in filter liquor with HITACH180-80 atomic absorption spectrophotometer, and obtain ion adsorption (mmol/g).
(7) Thin-layer chromatography (TLC) and gas chromatography (GC) are used in detecting reaction degree.
(8) Shen Guang MC automatic refractometer of Shanghai Physical Optical Instrument Factory is used in testing refractive index of the product.

2.4 Experimental steps

(1) Preparation of the functionalized polystyrene metal complex: take 1g N-functionalized nitrogenous polystyrene resin, put it in the 20ml beaker with 0.02 mol/l metal ion solution, adjust pH value of the solution with diluted HAc or NaAc according to need, soak it in certain temperature for a certain time, filter it, wash it fully with water, and dry it. Residual metal ion content in solution can be tested according to atomic absorption, and the metal ion content loaded by resin is the difference between original metal ion content and the residual metal ion content in solution.
(2) Catalytic acetal (ketone) reaction: add 0.1 mol aldehyde or ketone, 0.15mol dihydric alcohol or 0.3mol monohydric alcohol, 30ml cyclohexane (solution) and a certain amount of polymeric metal catalyst in 50ml three-necked flask, realize backflow and water diversion, cool it slightly after finishing reaction, separate the water layer, realize fractionation or reduced pressure distillation of the organic layer, collect the fraction in a certain range, and measure infrared spectroscopy and refractive index. TLC (silica gel, with petroleum ether PE: ethyl acetate AC as 4:1) and GC are used in reaction for monitoring the reaction.
(3) Catalytic oxidation reaction: add 0.02mol benzyl alcohol, 5.36g 30% H_2O_2 water solution, 10ml chloroform and a certain amount of polymeric metal catalyst in 50ml three-necked flask successively, give reaction for a certain time in 40-45°C, filter it, wash with chloroform fully, add a little water in mixture, realize delamination, dry it with Na_2SO_4, concentrate it, and conduct TLC separation (with PE: AC as 4:1).

(4) Catalytic acetal (ketone) reaction: add 0.1 mol cyclohexanone, 0.15mol ethylene glycol, 30ml cyclohexane (solution) and a certain amount of PAM metal catalyst in 50ml three-necked flask, realize backflow and water diversion, cool it slightly after finishing reaction, separate the water layer, dry the organic layer with anhydrous Na2SO4, dry the solution with rotary evaporator, and separate or analyze contents of the various components in the mixture with TLC (silica gel, with PE: AC as 4:1) or GC.

3. Results and Discussion

3.1 Preparation and characterization of the functionalized polystyrene metal complex

It prepares a series of nitrogenous, oxygenous or sulphureous functionalized polystyrene ligands (refer to Figure 1), functionalized polystyrene metal complexes (refer to Figure 2) and CPS+nitrogenous micromolecular→N-functionalized nitrogenous polystyrene ligand by making chloromethylate polystyrene resin (rNS) reacting with ethanol amine, 2-mercapto ethylamine (MEA), 8-hydroxyquinoline, anthranilic acid and imidogen oxalic acid (IDA) respectively. Characterization is given according to IR and elemental analysis, and the results are summarized in the Table 2 and Table 3 below.

It is discovered from the experiment that: this catalyst can catalyze the oxidation reaction of benzyl alcohol to some extent, while the reaction conversion rate is lower, reaction time is longer, there are more by-products, and progress of the reaction cannot be promoted by adding phase transfer catalyst. We shall further explore conditions of this reaction in the future works.

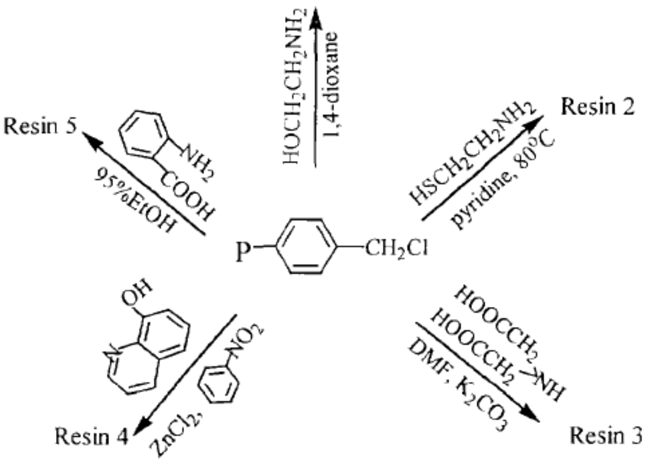


Figure 1: Synthesis of chelating resin

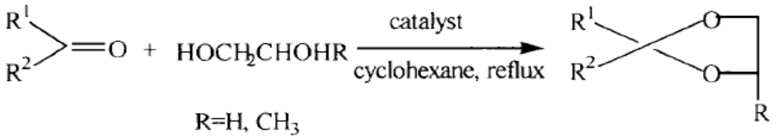


Figure 2 Polystyrene metal complexes

Table 2: IR absorbance peak and elemental analysis of functionalized resin

			EA(%)	
Entry	IR (cm^{-1})	C	H	N
CPS	1264(-CH2-),672(C-Cl)	-	-	0
Resin 1	3406(O-H)	66.88	7.48	4.36
Resin 2	3445(N-H)	63.74	6.84	4.28
Resin 3	3422(O-H),1724(-CO-)	71.92	6.33	0.68
Resin 4	3370(O-H)	80.00	6.40	1.70
Resin 5	3367(N-H),1685(-CO-)	73.50	6.31	1.64

Table 3: Oxidation of benzvl alcohol catalyzed by Resinl-Fe (III) [a]

Entry	Catalyst(g)	Time(h)	Conversion (%)	Yield (%)
1	Resin 1-Fe(III)	48	36.1	34.0
2	Resin 2-Fe(III)	24	0	0[b]
3	Resin 3-Fe(III)	48	28.7	19.0
4	No catalyst	48	0	0

[a]Conditions: mole ratio of alcohol and hydrogeon peroxide is 1:2; catalyst, 1g; solvent, 10m1 CHCl3, temperature: 40-45°C

[b]Phase transfer catalyst (cetyl trimethyl ammonium chloride) added.

3.2 Infrared characterization of metal complex and the metal nanoparticles

Figure 3 is infrared spectrums of polyvinyl pyridine (A), polyvinyl pyridine metal (Ag+) complex (B) and polyvinyl pyridine metal (Ago) nanoparticle (C) decorated on silicon wafer. When metal ion is introduced in polyvinyl pyridine, metal ion shall have complexing action with nitrogen, which should be presented as offset of the absorption peak at 1605cm-1 towards high wave number in the infrared spectrogram, and other peaks should show smaller changes. Thus, we mainly give comparison to change of the characteristic absorption peaks of polymer during wave numbers 1400cm-1-1700cm-1.

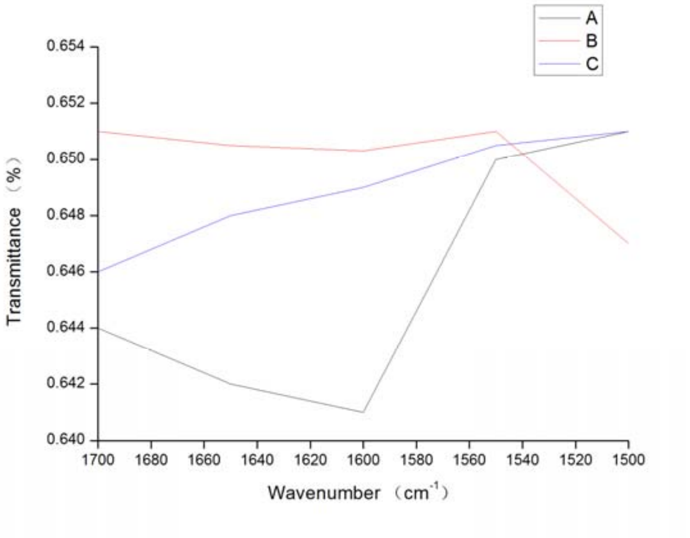


Figure 3: FT-IR spectra of PVP(A), PVP-Ag+(B) and PVP-Ago(C) on the silicon water

Figure 4 is the binding energy spectrogram of X-ray photoelectron spectroscopy nitrogen of polyvinyl pyridine decorated silicon wafer. We can see from the energy spectrogram data that peak area of the nitrogen on sample surface is more than twice as large as that of the nitrogen in initiator, while the nitrogen content reduces according to calculation, for the surface carbon content far surpasses the carbon content in initiator after that the initiator on surface of silicon wafer causes polymerization of the monomer vinyl pyridine, which results in relatively reduction of the content of surface nitrogen.

Figures 5(A)-(B) are X-ray photoelectron spectroscopy spectrograms of Cu2+2p and Cu(0) 2p obtained after restoring polyvinyl pyridine metal complex. Figure 5(A) is energy spectrogram of Cu2+2p, which is a typical energy spectrogram of bivalent copper ion, there are four binding energy peaks appeared in the figure, and two of them are vibration-excitation peaks which occur in the low kinetic energy end of the main photoelectron peak. Figure 5 (B) is energy spectrogram of Cu(0) obtained after restoring metal complex, and the main peak of Cu(0)2p at 932.0 eV is lower than the binding energy of Cu2+ for 2.0 eV, which is caused by reduction of the electronic binding energy obtained after restoring Cu2+, also the vibration-excitation peak does not occur basically at the place of high binding energy, which proves that we have restored metal complex and obtained metal hybrid material.

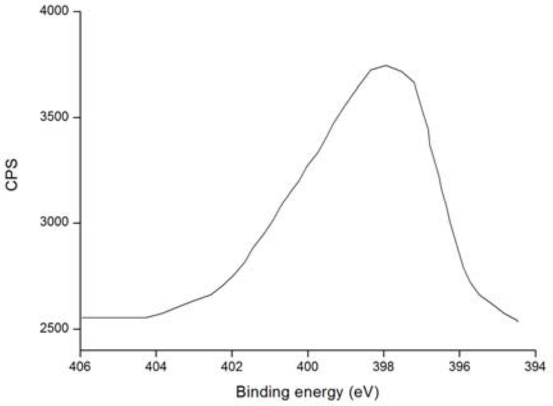
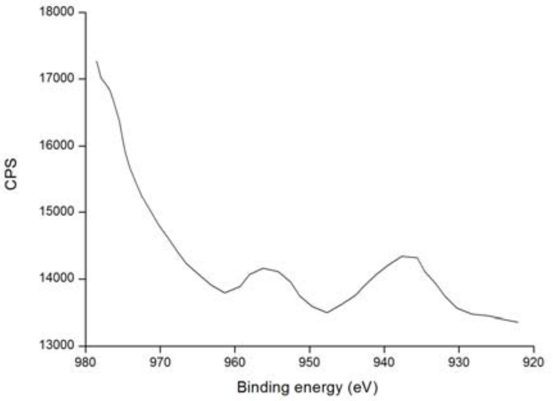
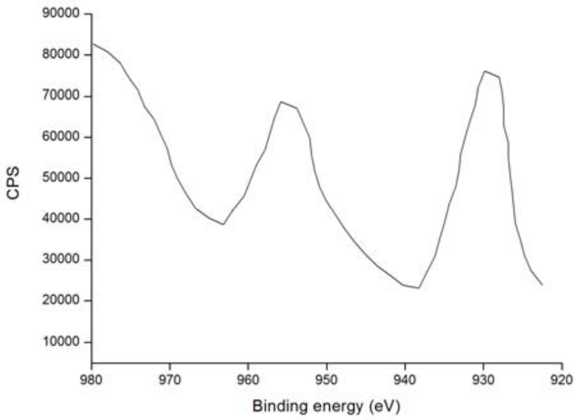


Figure 4: The XPS spectra of N of PVP brush on silicon wafer.



(A) PVP metal complex on silicon wafer



(B) PVP metal nanoparticles on silicon wafer

Figure 5: The Cu 2p spectra of PVP metal complex and nanoparticles on silicon water

4. Conclusions

The five prepared N-functionalized nitrogenous polystyrene ligands can form polymeric metal complexes by acting on metal ions. Each N-functionalized nitrogenous polystyrene ligand possesses selectivity as to adsorption of different metal ion, and adsorption capacity has relation with such factors as adsorption time, temperature, medium and solution pH. By giving research on catalysis of the various N-functionalized nitrogenous polystyrene metal complexes on acetal (ketone) reaction, it proves that this catalyst possesses favourable catalytic activity, can be reused, has wide application prospect in industrial and environmental protection especially for the active propulsion to the development of green chemical industry, and overcomes the problem of insufficiency of the corresponding homogeneous metal salt catalyst. The N-functionalized nitrogenous polystyrene metal complex synthesized has certain catalytic action on the oxidation of benzyl alcohol, while the catalytic activity is not high, and there are more by-products.

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