



Acetalization of carbonyl compounds catalyzed by polymer-bound metal complexes

Shun-Jun Ji^{a,*}, Lin Wu^{a,b}

^a College of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, China

^b Department of Chemistry, Yancheng Teachers' College, Yancheng 224002, China

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Abstract

A series of chelating resin containing N, O, S atoms were synthesized by incorporating ethanolamine, 2-mercaptoethylamine (MEA), iminodiacetic acid (IDA), 8-quinolinol and anthranilic acid into chloromethylated polystyrene-divinyl benzene (CPS), and then they were treated with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ aqueous solution to form the metal complex on the surface. Conversion of functional groups of the CPS resin was confirmed by IR spectra and elemental analysis. IR and ESR were used to investigate the coordination behavior of these resins. The metal content of these metal complexes was estimated by atomic absorption spectroscopy. The thermal stability of them was seen by TGA. By catalyzing the acetalization of carbonyl compounds they were found to be effective and could be reused with no substantial loss of activity for up to 10 cycles. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Acetalization; Carbonyl compounds; Polymer-bound metal complex

1. Introduction

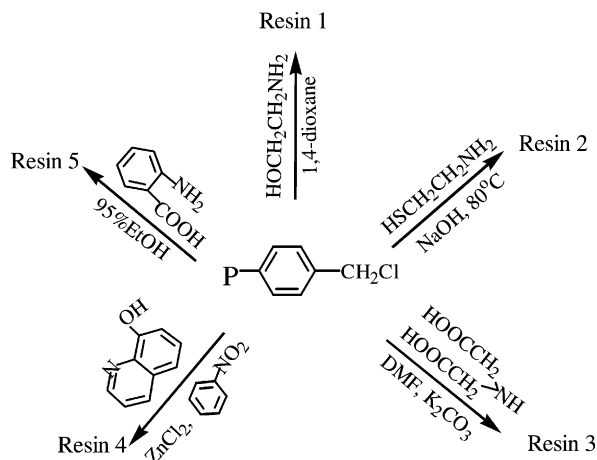
Immobilization of homogeneous transition metal catalysts to organic polymer gives heterogeneous catalyst, the heterogeneous catalyst has advantages in many ways over conventional homogeneous systems, one of them is the easy separation from the product mixture at the end of a reaction, as well as allowing for more purification of the product mixture, this means that the supported complex can be reused in subsequent reactions [1,2]. Application of polymer-supported metal complexes in organic transformations has been receiving extraordinary attention in recent years [3–6]. Several reactions of synthetic

importance such as epoxidation of olefins [7–11], oxidation [12–14], hydrogenation [15,16], etc. have been satisfactorily catalyzed by polymer-supported metal complexes under mild conditions. Acetalization is commonly utilized as a protecting method for carbonyl groups because dimethyl acetals and 1,3-dioxolane are stable under neutral and basic conditions [17–19]. Acetals also are used for solvents or intermediates in organic reactions [20,21]. They are generally prepared by reaction of carbonyls and alcohols or diols in the presence of concentrated sulfuric acid [22], TsOH, BF_3 -etherate, or FeCl_3 , etc. [23].¹ These homogeneous catalysts often suffer from shortcomings such as troublesome isolation

* Corresponding author. Tel.: +86-512-65112372;
fax: +86-512-65112371.
E-mail address: shunjun@suda.edu.cn (S.-J. Ji).

¹ Typical examples of homogeneous 1,3-dioxolane formation. For TsOH see [23a–c]; for BF_3 -etherate see [23d]; and for FeCl_3 see [23e].

of products and the production of large volumes of salt wastes during neutralization of the acids. From the standpoint of environmental demand for chemical procedure, much attention has been paid to the development of heterogeneous catalyst for the acetal transformations. During the past few years, metal complexes supported by cation exchange resin [24], solid acid and montmorillonite, etc. were used to catalyze the acetalization. In a recent report, Kawabata et al. [25] reported titanium cation-exchanged montmorillonite for this purpose. Up to now, there have been no reports of acetalization catalyzed by chelating resin-bound metal complexes, herein we wish to report a catalytic acetalization method using a few chelating resin-bound metal complexes catalyst.



Scheme 1. Synthesis of chelating resin.

2. Experimental

2.1. Reagents and equipment

Chloromethylated polystyrene-divinyl (CPS) benzene of 7.5% cross-linked (chlorine content 18%) was purchased from Nankai university factory. 2-Mercaptoethylamine (MEA) hydrochloride and iminodiacetic acid (IDA) were bought from ACROS. Benzaldehyde, cyclopentanone, *n*-butyraldehyde and ethanolamine were chemical grade reagents, they were distilled before use. Other reagents were all analytical purity. Elemental analysis was carried out on Italy 1106 elemental analyzer. Infrared spectra was recorded in Magna-550 with KBr matrix. The metal content of polymer-bound metal complexes was obtained from HITACHI atomic absorption spectroscopy, thermal analysis was recorded on Perkin-Elmer TGA7, ESR spectra of the resin-complexes in solid state at room temperature was recorded on JES-FE3AX spectrometer (JEOL, Japan). Refractive index of product was determined by ShenGuang MC autorefractometer (Shanghai, China).

2.2. Synthesis of the polymer-bound metal catalyst

2.2.1. Functionalization of chloromethylated polystyrene-divinyl benzene

Chloromethylated polystyrene-divinyl benzene were functionalized with various organic compounds to give chelating resins as shown in Scheme 1.

The procedures were as follows.

Resin 1: A solution of 11.1 g ethanolamine and 75 ml 1,4-dioxane was stirred at room temperature for a few minutes, then to it 36 g CPS beads were added. The mixture was stirred and heated at 80 °C for 6 h, then filtered, washed with 95% EtOH thoroughly, and dried. Elemental analysis: N: 4.36%, C: 66.88%, H: 7.48%.

Resin 2: Thirty-six grams of CPS beads and 10 g MEA hydrochloride were added to 70 ml DMF containing 10 g 5% NaOH, this mixture was heated at 80 °C for 24 h with stirring, upon completion, the mixture was filtered off and washed with 95% EtOH and water thoroughly, and dried. Elemental analysis: N: 4.28%, C: 63.74%, H: 6.84%.

Resin 3: Iminodiacetic acid 6 g was dissolved in a mixture of aqueous sodium carbonate (5%) and DMF (60 ml), CPS beads then were added, the resultant mixture was heated with stirring at 80 °C for 24 h. After the reaction, the mixture was filtered and washed with water to give bright white resin 3. Elemental analysis: N: 0.68%, C: 71.92%, H: 6.33%.

Resin 4: Resin 4 was prepared according to literature [26]. Chloromethylated beads (36 g) was suspended in nitrobenzene (100 ml) and treated with 8-hydroxyquinoline (26.4 g) with stirring in the presence of anhydrous zinc chloride (25 g) at 110 °C for 11 h. The yellow greenish reaction mixture was filtered and washed successively with 10% HCl, H₂O, dilute NaOH solution and H₂O until the washings

became neutral, then dried. Elemental analysis: N: 1.70%, C: 80.00%, H: 6.40%.

Resin 5: It was prepared according to document [16]. Elemental analysis: N: 1.64%, C: 73.50%, H: 6.31%.

2.2.2. Preparation of resin-bound metal complexes

An amount of dried resin above (1 g) was added to a Erlenmeyer flask containing 20 ml metal ion in pure water (0.02 mol/l), the pH of the solution was adjusted to the required value with dilute acetic acid and sodium acetate, the mixture was stirred for 24 h at about 50 °C, then filtered and washed with water thoroughly. The residual metal ion content in solution was measured by atomic adsorption spectroscopy. The metal ion immobilized was calculated from the discrepancy in the amount of initially charged metal ions and that of metal ions remaining in the supernatant after the immobilization [27], the metal content was 0.241 mmol/g (resin 1-Fe(III)), 0.215 mmol/g (resin 1-Cu(II)), 0.102 mmol/g (resin 1-Co(II)), 0.081 mmol/g (resin 1-Ni(II)), 0.156 mmol/g (resin 2-Fe(III)), 0.138 mmol/g (resin 3-Fe(III)), 0.2125 mmol/g (resin 4-Fe(III)). The wet resin and resin-bound metal complexes were dried with infrared lamp and subjected to IR, ESR and TGA analysis.

2.2.3. A typical procedure for acetalization of carbonyl compounds

In a typical experiment, carbonyl compounds (0.1 mol) was dissolved in 30 ml cyclohexane and to it 0.15 mol of ethane-1,2-diol was added followed by an amount of polymer-bound metal complex catalyst. The system was refluxed for a certain time with stirring (Scheme 2), the reaction was monitored by TLC (silica gel, petrol ether:ethyl acetate was 4:1) and GC. Here, we used a set of oil–water separated apparatus to remove the azeotropic water in order to improve the yield of the product. On completion, the resin-metal complex catalyst was filtered off and washed with cyclohexane, then the filtrate was incor-

porated and distilled under reduced pressure to get the isolated product, the refractive index was determined if necessary.

3. Results and discussion

3.1. Characterization of the catalyst

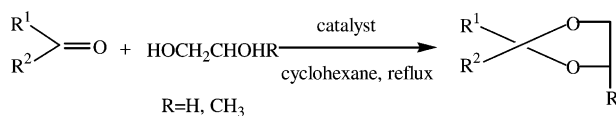
The functionality of these resins was determined by the nitrogen content and they are 3.11 mmol/g (resin 1), 3.06 mmol/g (resin 2), 0.49 mmol/g (resin 3), 1.21 mmol/g (resin 4) and 1.17 mmol/g (resin 5), respectively. The IR spectra of these chelating resin and resin-metal complexes was measured with KBr pellets. Results showed that the chloromethyl groups in CPS have strong absorbances around 1264 and 672 cm^{-1} , after functionalization, the absorbance at 1264 cm^{-1} decreased or disappeared, meanwhile new absorbance emerged, this indicates that chloromethyl group could react with some organic compounds, but not completely, this might be due to steric hindrance.

ESR and TGA of the resin-complexes were also carried out. For example, ESR of resin 1-Cu(II) has a single peak (3394G, $g = 2.0469$), while $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ has three g values ($g_x = 2.0445$, $g_y = 2.1905$, $g_z = 2.0423$), because the change of peak position and g values are relative to the character of bond [28], so we can deduce that new bond in resin 1-Cu(II) formed. TGA analysis of resin 1-Fe(III) indicates that its degradation starts about 200 °C, a weight loss of about 5% below this temperature may be due to moisture content. Hence, it was ensured that this catalyst may be used in catalytic studies below 200 °C.

3.2. Catalytic acetalization of carbonyl compounds

3.2.1. Acetalization of cyclohexanone and ethane-1,2-diol

We used resin 1-Fe(III) complex (Fe: 0.241 mmol/g) to catalyze the acetalization of cyclohexanone and



Scheme 2.

Table 1
Acetalization of cyclohexanone and ethane-1,2-diol catalyzed by resin 1-Fe(III)^a

Entry	Mole ratio	Time (h)	Amount of catalyst (g)	Temperature (°C)	Yield (%) ^b
1	1:1.0	4.5	2.0	85–100	80
2	1:1.3	4.5	2.0	84–93	91
3	1:1.5	4.5	2.0	88–98	93
4	1:1.7	4.5	2.0	88–93	90
5	1:2.0	4.5	2.0	86–97	90
6	1:1.5	1.0	2.0	81–95	77
7	1:1.5	3.0	2.0	84–100	78
8	1:1.5	4.0	2.0	84–97	83
9	1:1.5	6.0	2.0	84–97	92
10	1:1.5	4.5	0.5	91–96	87
11	1:1.5	4.5	1.0	84–98	90
12	1:1.5	4.5	1.5	88–92	90
13	1:1.5	4.5	3.0	88–96	90
14	1:1.5	4.5	2.2	87–97	91 ^c

^a Reactions were run in 30 ml of cyclohexane containing 0.1 mol substrate.

^b Isolated yield. These reactions were monitored by TLC and GC.

^c 10 cycles.

ethane-1,2-diol using cyclohexane as solvent, the influence of different amount of catalyst, different mole ratio of reactants, different reaction time on the yield of product was investigated (Table 1). Results shown in Table 1 indicate that when the mole ratio of cyclohexanone and ethane-1,2-diol is 1:1.5, amount of catalyst is 2.0 g, reaction time is 4.5 h, the reaction condition was optimum and the yield of corresponding product is up to 93% (entry 3). In addition, this catalyst could be reused up to 10 cycles without substantial loss of activity (entry 14).

When the Fe(III) complex of other resin catalyst and other metal complex of resin 1 were used, the results

are summarized in Tables 2 and 3. From the results, it was found that not only these resin-Fe(III) complexes could catalyze this reaction, but Cu(II), Co(II), Ni(II) complex of resin 1 could catalyze this reaction. It can also be deduced from these results that when the content of Fe(III) of different resin is equal, resin 1-Fe(III) can effectively catalyze this reaction with high yield of 93%, the Fe(III) complex of other resin with lower yields probably owing to the absorbance of them to the product. From Table 3, it can be concluded that when the amount of different metal of resin 1 is equal, the catalytic activity of them is Fe(III) > Cu(II) > Co(II) > Ni(II), the reason for this may be the same as above.

Table 2
Acetalization of cyclohexanone and ethane-1,2-diol catalyzed by other resin-Fe(III)^a

Entry	Catalyst	Temperature (°C)	Yield (%) ^b
1	Resin 1-Fe(III)	88–98	93
2	Resin 2-Fe(III)	91–101	77
3	Resin 3-Fe(III)	87–96	85
4	Resin 4-Fe(III)	90–101	75
5	Resin 5-Fe(III)	89–98	60 ^c

^a Reactions were run at above temperature for 4.5 h in 30 ml of cyclohexane mole ratio of carbonyl compounds, diol and catalyst was 1:1.5:0.0048.

^b Isolated yield. These reactions were monitored by TLC and GC.

^c Conversion rate was 100% and side product was detected.

Table 3
Acetalization of cyclohexanone and ethane-1,2-diol catalyzed by other resin 1-metal^a

Entry	Catalyst	Temperature (°C)	Yield (%) ^b
1	Resin 1-Fe(III)	88–98	93
2	Resin 1-Cu(II)	87–97	88
3	Resin 1-Co(II)	87–99	77
4	Resin 1-Ni(II)	87–98	71

^a Reactions were run at above temperature for 4.5 h in 30 ml of cyclohexane mole ratio of carbonyl compounds, diol and catalyst was 1:1.5:0.0048.

^b Isolated yield. These reactions were monitored by TLC and GC.

Table 4

Acetalization of other carbonyl compounds and ethane-1,2-diol catalyzed by resin 1-Fe(III)^a

Entry	Substrate	Temperature (°C)	Boiling point (°C) ^d	Yield (%) ^b
1	Cyclohexanone	88–98	174–180	93
2	Cyclohexanone	84–96	166–170	79 ^c
3	Cyclopentanone	83–96	150–152	72
4	Benzaldehyde	84–91	226–230 (101 °C, 1333.2 Pa)	74
5	Acetophenone	86–92	mp: 56–57 (lit: 57–58 °C) [29]	3 ^e
6	<i>n</i> -Butyraldehyde	72–90	130–134	40 ^e
7	1-Tetralone	83–95		No reaction

^a Reaction conditions: catalyst (Fe, 0.241 mmol/g), 2.0 g; substrate, 0.1 mol; solvent, 30 ml cyclohexane; 4.5 h.^b Isolated yield.^c React with propane-1,2-diol.^d 760 mmHg.^e The yield was calculated according to the initial substrate, conversion rate was 10% (entry 5) and 74% (entry 6), respectively.

3.2.2. Acetalization of other carbonyl compounds and diols

Resin 1-Fe(III) complex was utilized to catalyze acetalization of other carbonyl compounds and diols (Table 4), results showed that this catalyst could also catalyze acetalization of aromatic and aliphatic carbonyl compounds, but the yield of most of their product was lower compared to the acetal of cyclohexanone and ethane-1,2-diol.

4. Conclusion

In this paper, we have presented preparation of polymer-bound metal Fe(III), Cu(II), Co(II), Ni(II) complex with simple synthetic manipulations from CPS. A systematic characterization of them and catalytic activity for acetalization were performed. The efficiency of catalyst for acetalization has been established and easy recoverability with simple separation, and this will benefit the development of green chemistry.

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