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Efficient allylic oxidation of cyclohexene with oxygen catalyzed by chloromethylated polystyrene supported tridentate Schiff-base complexes

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ABSTRACT

Four novel chloromethylated polystyrene supported tridentate Schiff-base metal complexes (PS–DA–M, M = Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+}, respectively) were prepared by chloromethylated polystyrene and tridentate Schiff-base ligands, which were synthesized by 2,4-dihydroxyacetophotone with 2-aminopyridine. The complexes were characterized by the methods of ICP, FT-IR, XPS and TG/DTA. The catalytic activity of the complexes in the oxidation of cyclohexene with molecular oxygen was determined. The results showed that oxidation reaction was occurred in the allylic carbon atoms. The products are cyclohexene oxide, 2-cyclohexene-1-ol, 2-cyclohexene-1-one and 2-cyclohexene-1-hydroperoxide. Although all of four complexes showed good catalytic activity, PS–DA–Cu exhibited the best. The conversion of cyclohexene can be reached to 51.9% under the temperature of 343 K when using 2 mg of PS–DA–Cu to catalytic oxidation of 2 ml of cyclohexene. The influences of reaction temperature, the amount of catalyst, the reaction time were investigated, and the mechanism of cyclohexene oxidation was also discussed.

1. Introduction

Transition metal complexes as catalysts for the oxidation of cyclohexene have attracted a deal of attention in recent years, mainly for the oxidation products of cyclohexene and the derivatives present the highly reactive carbonyl groups in the cycloaddition reactions [1–3]. Of the variety of ligands employed so far, the noteworthy examples include porphyrin derivatives, macrocyclic, phthalocyanine, and Schiff-base [1,2,4–12]. Among these substrates, Schiff-base transition metal complexes are the attractive oxidation catalysts. It can be prepared simply and cheaply for industrial applications. However, homogenous catalyst is difficult to be separated from reaction system, and thus influence the recycle. To overcome these disadvantagements, Schiff-base complexes were immobilized with zeolite [11], modified silica [13], chitosan [14], and chloromethylated polystyrene [15–18].

In addition, during the process of catalytic reaction, these catalysts need a mono-oxygen source such as H, PhIO, NaClO, to carry out oxygen transferring to the olefin. However, these oxidants were not environmental friendly. With much attention has been directed toward the development of environmental, molecular oxygen as a cheap, environmentally clean and convenient oxidant is suitable [5,7,10,19–24]. Meanwhile, it was observed that the oxidation efficiency of molecular oxygen is poor. So the great demand for these oxidation products and the high-energy intensity of the present process warrant a replacement with a more effective catalytic process [25–28].

In this work, chloromethylated polystyrene supported tridentate Schiff-base metal complexes (PS–DA–M, M = Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+}, respectively) were prepared by chloromethylated polystyrene and tridentate Schiff-base ligand, which was synthesized by 2,4-dihydroxyacetophotone with 2-aminopyridine. It was found that cyclohexene could be effectively catalyzed by these complexes under mild conditions using oxygen without reductant. The allylic hydroperoxide was obtained as an important product, which was suggested as an efficient allylic oxidation pathway.

2. Experimental

2.1. Materials and instruments

Chloromethylated polystyrene (PS) contains 4.5 mmol of Cl/g and of 10% cross-linked di-vinybenzene. Cyclohexene was of chemical purity. Other chemicals used were of analytical purity. ICP measurements were carried out using a Perkin-Elmer ICP/6500. FT-IR spectra were recorded on a Digilab Merlin FTS 3000 FT-IR spectrophotometer in KBr pellets. The reaction products of oxidation were determined by a HP 6890/5973 GC/MS instrument and analyzed by a Shimadzu GC-16A gas chromatograph

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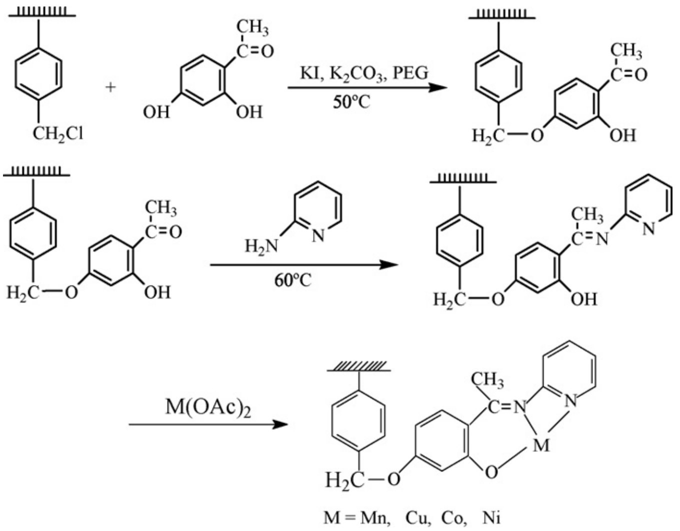

Scheme 1. The synthesis routine of PS–DA–M.

(GL-16A gas chromatograph with a 5 m × 3 mm OV-17 column, 80–200 °C (10 °C/min), Inj. 220 °C, Det. 220 °C). The thermal data were recorded on a Perkin-Elmer TG-DTA 6300 instrument at a heating rate of 15 °C/min.

2.2. *Synthesis of chloromethylated polystyrene supported tridentate Schiff-base metal complexes (PS–DA–M)*

The method of preparation of 2,4-dihydroxyacetophotone was the same as mentioned in Ref. [29]. The yield of 2,4-dihydroxyacetophotone is 65% and m.p. is 417.4 K.

Chloromethylated polystyrene (5.0 g, equivalent to 22.5 mmol of Cl) was added into 50 ml of acetone. Then acetone solution (30 ml) of 2,4-dihydroxyacetophotone (3.42 g, 22.5 mmol) was added to the above suspension followed by anhydrous K_2CO_3 (2.0 g), KI (0.2 g) and PEG (0.05 g), respectively. The reaction mixture was stirred and refluxed for 48 h under a nitrogen atmosphere. After cooling, an orange polymer precipitated out, which was filtered and washed with water and anhydrous ethanol, respectively. The solid was dried in vacuum at 323 K for 24 h to obtain chloromethylated polystyrene supported 2,4-dihydroxyacetophotone.

Chloromethylated polystyrene supported 2,4-dihydroxyacetophotone (2 g, 9.0 mmol) was added to 2-aminopyridine (0.84 g, 9.0 mmol) in 50 ml of anhydrous ethanol. The mixture was heated and refluxed for 24 h and then cooled to room temperature. The products obtained were filtered off and washed with ethanol and dried at 323 K in vacuum for 24 h to give polymer-supported tridentate Schiff-base (PS–DA).

PS–DA was added to Cu^{2+} solution dissolved in 50 ml of absolute ethanol, and then the mixtures were refluxed for 24 h. After the reaction, the solids were collected by filtration, washed with ethanol and dried at 353 K in vacuum to give chloromethylated polystyrene supported tridentate Schiff-base copper (II) complex (PS–DA–Cu). The synthesis routine of PS–DA–M was shown in Scheme 1. PS–DA–Co, PS–DA–Ni and PS–DA–Mn were prepared as the same way, respectively.

2.3. *Oxidation reaction*

Typical oxidation of substrate was performed according to the procedure described in the literature [30]. The substrate and the catalyst (chloromethylated polystyrene supported tridentate Schiff-base metal complexes) were added to the special glass reactor. The oxygen was filled from the gauge glass and the atmosphere was discharged out of the glass reactor with the gas outlet tube. After the gas outlet tube was closed, the reactor was put into a paraffin oil path and heated to certain temperature. The consumption of oxygen was measured by the gauge glass. After the reaction, the products were analyzed by gas chromatograph and GC/MS.

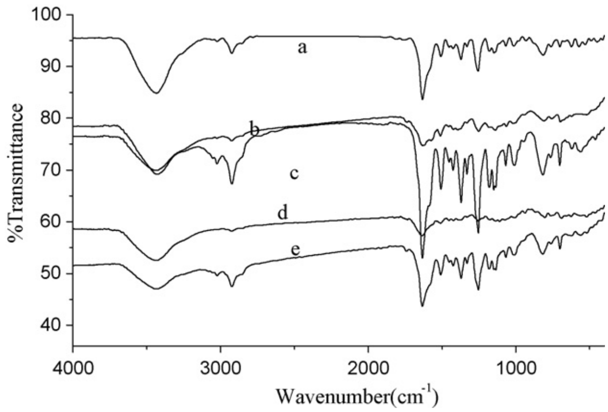

Fig. 1. IR spectra of complexes (a) PS–DA, (b) PS–DA–Cu, (c) PS–DA–Mn, (d) PS–DA–Ni, and (e) PS–DA–Co.

3. Results and discussion

3.1. *Characterization*

The IR spectra of chloromethylated polystyrene supported tridentate Schiff-base ligand show sharp bands around 3428 cm^{-1} due to the ν_{O-H} vibrations. It gets a shift of 11–12 $cm^{-1}$to the lower wave number after chelated with metal ions, showing coordination is through phenol oxygen atom in the complexation (Fig. 1). Meanwhile, the band 1642 cm^{-1} due to $\nu_{C=N}$ in the free ligand gets shifted to the lower wave number ($\delta\nu = 11–20\ cm^{-1}$) in the metal complexes, indicating coordination is through pyridine nitrogen. Several new bands in the complexes at 489–520 cm^{-1}, 411–419 cm^{-1} are due to ν_{O-M} and ν_{N-M}, respectively, which are absent in the spectrum of the ligand, further supporting the participation of the oxygen atom and the nitrogen atom in complexation.

In order to prove the coordination of polymer-supported tridentate Schiff-base ligand with metal ion, corresponding small area X-ray photoelectron spectroscopy of copper acetate, ligand and its complex have been studied (Fig. 2). Compared to copper acetate, the binding energy of $Cu_{2p3/2}$ of complex increases 3.0 eV. The change of binding energy of the $Cu_{2p3/2}$ means a decrease of its election density. On the other hand, binding energy of $N_{1s1/2}$ of polymer complex decreases 5.1 eV than that of the corresponding ligand of PS–DA. The electronic state of the nitrogen atom in the polymer complex is of higher electron density and, therefore, the electrons in the copper atom may flow into the nitrogen atom to form an N–Cu coordination bond. The $O_{1s1/2}$ binding energy of the polymer complex is raised of 0.6 eV than that of the corresponding support, which indicates that oxygen atom in hydroxy group is bound with metal ion. The structure of complex can be ensured as in Scheme 1.

The thermogravimetric analyses (TG) of the PS–DA and PS–DA–Cu were measured under nitrogen atmosphere in the temperature range from 293 K to 1023 K in order to investigate the thermal stability. It was showed that degradation of the polymer ligand (PS–DA) was from 484 K to 1023 K (Fig. 3). And the polymer-supported copper complex (PS–DA–Cu) was gradually from 462 K to 1023 K. The corresponding weight loss for PS–DA, PS–DA–Cu in above temperature range was 86%, 67%, respectively.