Preparation and catalytic oxidation by polymer supported 4-(2-pyridylazo) rosorcinol–metal complexes

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Abstract

Polymer-supported 4-(2-pyridylazo) rosorcinol–metal complexes (PS-PAR-M, M = Cu, Co, Ni, Fe) were prepared and characterized by IR, ICP, XPS, and used in the oxidation of ethylbenzene as catalyst. In comparison with their catalytic activities, PS-PAR-Cu was a more effective catalyst for the oxidation of ethylbenzene without solvent. The influences of reaction temperature, the amount of catalyst and substrate concentration, as well as reaction time on the oxidation of ethylbenzene have been investigated. The reaction optimum conditions have been obtained. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst; Polymer-supported azo metal complex; Oxidation

1. Introduction

The oxidation of hydrocarbons catalyzed by polymer-supported transition metal complexes have been studied extensively as they have the advantages of excellent selectivity, separation and recovery easier [1–4]. The oxidation of ethylbenzene is an important reaction in the chemical industry. Study on polymer-supported metal complexes as catalysts has been interestedly focused on. Ernst et al. [5] and Cloark [6] independently studied the oxidation reaction of ethylbenzene, using inorganic polymer-supported cobalt complexes as catalysts and oxygen or hydrogen peroxide as oxidant. However, the system had a need for co-reductant. In our previous researches [7,8], the polymer bound N,N,N,N-type metal complexes shows the certain catalytic activity and selectivity in the oxidation of ethylbenzene carried out at atmospheric pressure without co-reductant and any solvent. In this paper, we will discuss the catalytic behavior of polymer-supported 4-(2-pyridylazo) rosorcinol–metal complexes, especially when metal is copper, in the oxidation of ethylbenzene in the presence of molecular oxygen.

The reaction of chloromethylated polystyrene with azo-type ligand and formation of its complex are shown in Scheme 1.

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2. Experimental

2.1. Material and equipment

Chloromethylated polystyrene (containing 5.7 mmol Cl/g of resin and 2% cross-linked divinybenzene), 4-(2-pyridylazo) rosorcinol, anhydrous ethanol, ethyl benzene and metal salts were obtained commercially. Solvents were purified according to standard methods before using.

The IR spectra were recorded in KBr on an Alpha-centauri FT-IR spectraphotometer. Small area X-ray photoelectron spectroscopy (XPS) data were recorded with the PHI-5702 Multi-Technique System, Power Source by MgK_α line and $Ag_{3d5/2}$ FWHM ≤ 0.48 eV. Elemental analysis was performed on Itali Carbo-Erba 1106 elemental auto-analyzer. The content of metal was obtained by using ARL-3520 ICP.

2.2. Preparation of polymer-supported 4-(2-pyridylazo) rosorcinol ligand (PS-PAR)

Chloromethylated polystyrene (2.0 g) was added to anhydrous ethanol (20 ml) and was allowed to stand for 30 h. To this ethanol solution, 4-(2-pyridylazo) rosorcinol (2.45 g) was added followed by triethylamine (1.5 g). The mixtures were heated under reflux for 30 h.

After cooling, a red–purple polymer precipitated out, which was filtered and washed, respectively, with water and anhydrous ethanol. Dried in vacuum at room temperature for 24 h. Elemental analysis of the product gave 0.37 mmol N/g of resin.

2.3. General method for the synthesis of PS-PAR-M

The polymer-supported 4-(2-pyridylazo) rosorcinol ligand (PS-PAR) (1.2 g) was allowed to swell in anhydrous ethanol (30 ml) for 1 h. An ethanol solution of $Cu(Ac)_2 \cdot 2 H_2O$ (0.7 g) was added to the above suspension. The mixture was heated at 313 K for 24 h with stirring and was then cooled to room temperature. The red resin was filtered, washed with ethanol and dried in vacuum. PS-PAR-Co, PS-PAR-Ni and PS-PAR-Fe were prepared similarly.

2.4. Oxidation of alkybenzene

Catalyst and substrate were added in a glass reactor with a gas inlet tube connected to a gas burette and an oxygen storage bottle, a gas outlet tube, which can opened to the air [9]. After alkybenzene and polymer-supported 4-(2-pyridylazo) rosorcinol complex were added to the reactor, repeatedly exchanged the oxygen in
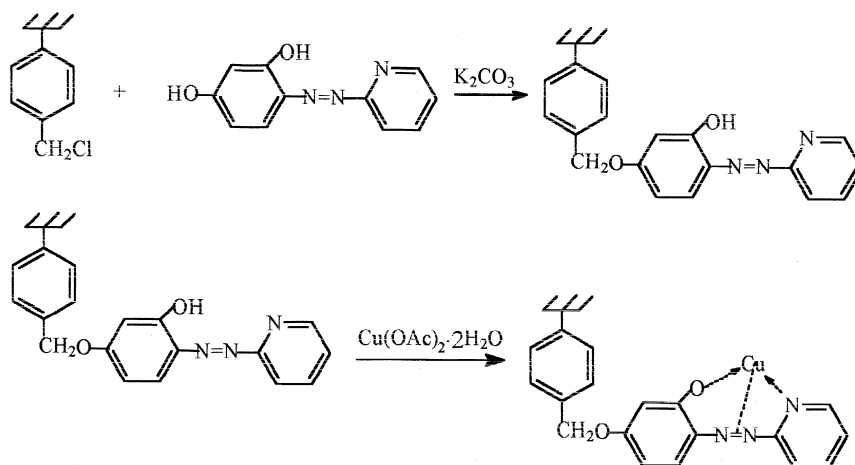
Scheme 1.

Table 1
XPS data of PS-PAR, PS-PAR-Cu and metal salt

| Compound	Binding energy (eV)			
	$O_{1s\,1/2}$	$N_{1s\,1/2}$		$Cu_{2p\,3/2}$
		$N1_{1s\,1/2}$	$N2_{1s\,1/2}$	
PS-PAR	532.0	398.3	401.8	–
PS-PAR-Cu	531.7	399.8	401.4	932.7
$Cu(Ac)_2 \cdot H_2O$	–	–	–	931.8

order to fill up the glass reactor. The mixture was heated to 353 K in oil bath and stirred with a magnetic stirrer. The volume of oxygen consumed was measured from the burette. The reaction products were analyzed on SHIMADZU QP-1000A GC/MS system and GC-16A model.

3. Results and discussion

3.1. Characterization

IR spectrum showed a band at 1436 cm^{-1} due to the $\gamma_{N=N}$. In the polymer-supported complexes, this band undergoes a negative shift by 14 cm^{-1} indicating the involvement of the nitrogen atom of pyridylazo in coordination. The stretching vibrations of C=N and C=C double bands appeared as follows: 1574–1577 cm^{-1} and 1650 cm–1655 cm^{-1} for PS-PAR-M, 1578 and 1662 cm^{-1} for PS-PAR, respectively. The different in IR spectra is that the pyridylazo backbone is influenced by the metal ion.

In order to prove the coordination of polymer-supported complexes, small area XPS data of polymer ligand and its complex have been studied (Table 1).

R=CH$_3$,   CH$_2$CH$_3$
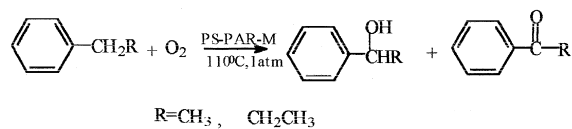
Scheme 2.

Compared with copper acetate, the binding energy of $Cu_{2p\,3/2}$ increases 0.9 eV. The change of the $Cu_{2p\,3/2}$ binding energy means a decrease of its election density. On the other hand, $O_{1s\,1/2}$ binding energy of polymer complex decreases 0.3 eV than that of the corresponding polymer-supported ligand. The electronic state of the oxygen atom in the polymer complex is of higher electron density and, therefore, the electrons in the copper atom may flow into the oxygen atom to form an O–Cu coordination bond. The nitrogen peak in the complex could be divided into three peaks including two nitrogen atoms of azo-group, which are similar, and a nitrogen atom of pyridine. The $N_{1s\,1/2}$ binding energy of the polymer complex is raised 1.5 eV than that of the corresponding support. These results show that coordination bonds are formed between the copper atom and the nitrogen atoms (as seen in Scheme 1). According to ICP, the copper content is 0.03 mmol Cu/g catalyst.

3.2. Oxidation reactions

The polymer-supported azo copper complex (PS-PAR-Cu) as a catalyst has been investigated in the oxidation of ethlybenzene and propylbenzene by molecular oxygen. The oxidation takes place on the α-carbon of the alkybenzene, the main products are α-alcohol (α-ol) and α-ketone (α-one) (the structure was shown in Scheme 2).

Table 2
Oxidation of substituted benzene catalyzed by PS-PAR-Cu

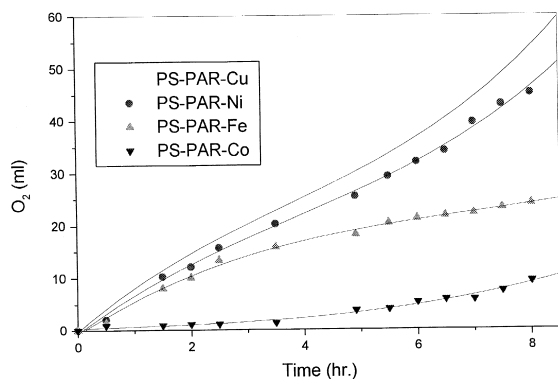| Substrate (mmol)	Catalyst (mg)	Temperature (K)	Time (h)	Conversion (%)	Products selectivity (%)		
					α-ol	α-one	Total
Ethylbenzene(24)	3	363	10	10.7	26.2	68.2	94.4
n-Propylbenzene(36)	5	383	10	5.4	35.2	31.5	66.7

Fig. 1. Effect of various metal ions of catalytic oxidation. Catalyst: 2 mg; substrate: 1 ml; temperature: 373 K; 1 atm.

Table 2 shows that conversion of ethylbenzene is higher than that of *n*-propylbenzene under the respective conditions. The selectivity of product is, for ethylbenzene, α-one is higher than α-ol, and for *n*-propylbenzene, it is nearly equal.

3.3. Effect of metal ions

The oxygen consumption are shown as a function of time in the ethylbenzene oxidation, which is carried out in the same reaction condition (Fig. 1), 1 ml of ethylbenzene, at 373 K, 2 mg of catalyst and oxygen pressure of 101.3 kPa. The oxygen adsorbed of PS-PAR-Co is
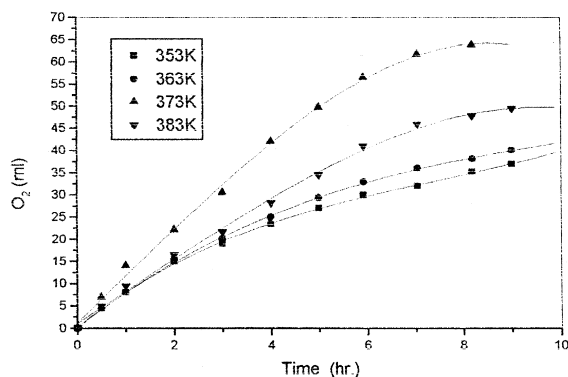

Fig. 2. The relationship of consumption of O_2 and the reaction time on the different temperature. Catalyst: 0.5 mg, substrate: 1 ml.

Table 3
Product distribution of oxidation of ethylbenzene in the presence of PS-PAR-Cu at various temperatures
Catalyst: 0.5 mg, substrate: 1 ml, reaction time: 7 h.

Temperature (K)	Conversion (%)	Selectivity (%)	
		α-ol	α-one
353	11.2	66.8	32.4
363	19.2	51.2	40.3
373	23.1	46.6	47.6
383	8.9	18.8	65.5

lower and it does not catalyze the ethylbenzene oxidation reaction. But, in the presence of PS-PAR-Cu, the highest adsorbed oxygen and the shortest inducement period have been observed. Therefore, PS-PAR-Cu is an effective catalyst for the ethylbenzene oxidation reaction.

3.4. Effect of temperature

The catalytic activity of PS-PAR-Cu is investigated as a function of temperature at 353, 363, 373 and 383 K. The consumption of oxygen with 0.5 mg PS-PAR-Cu as a function of the temperature is shown in Fig. 2. It is clear that the oxygen consumption is the highest at the temperature of 373 K. The conversion and selectivity at the different temperatures are also collected in Table 3. At 373 K, the conversion of ethylbenzene is 2.6 times than that at 383 K. And the selectivity of α-ol and α-one is almost equal. From 353 to 383 K, the selectivity of α-ol is decreased while the selectivity of α-one is increased.

Table 4
Effect of amount of catalyst on the oxidation reaction
Substrate: 1 ml, temperature: 373 K, reaction time: 7 h.

Catalyst (mg)	Conversion (%)	Selectivity (%)	
		α-ol	α-one
0.5	23.1	46.6	47.6
1.0	28.1	57.2	38.3
2.0	13.9	39.1	41.9
4.0	11.2	50.9	23.4

Table 5
Effect of concentration of ethylbenzene on the oxidation reaction
Catalyst: 1 mg, temperature: 373 K, reaction time: 7 h.

Substrate (ml)	Conversion (%)	Selectivity(%)	
		α-ol	α-one
0.5	23.8	30.1	49.5
1.0	28.1	57.2	38.3
2.0	8.5	25.9	56.4
3.0	4.8	39.1	46.1
5.0	2.3	19.2	61.5

3.5. Effect of the amount of catalyst

At 373 K, the results of oxidation of ethylbenzene in the presence of various amount of PS-PAR-Cu are collected in Table 4. When the amount of catalyst increase from 0.5 to 4.0 mg/1 ml of ethylbenzene, the conversion of ethylbenzene decrease from 23.1% to 11.2%. It indicates that the amount of catalyst has the best quantity when the amount of substrate is fixed. Otherwise, increasing or decreasing the amount of catalyst, the conversion of substrate will decrease.

3.6. Effect of concentration of substrate

Table 5 shows the conversion of substrate does not rise with rising concentration of substrate when the reaction temperature and amount of catalyst are fixed. The conversion of substrate is the highest only the appropriate proportion relationship between catalyst and substrate exist. The result of calculation is cat.:sub. = 1:290,000 (mol/mol).

4. Conclusion

The polymer-supported 4-(2-pyridylazo) rosorcinol copper complex (PS-PAR-Cu) is an effective catalyst for the oxidation of ethylbenzene by molecular oxygen. This oxidation takes place on the α-carbon of the ethylbenzene, the major products are α-ol and α-one. The optimum condition of oxidation reaction is as followed: temperature: 373 K, cat.: sub. = 1:290,000 (mol/mol).

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