POLYMERS FOR ADVANCED TECHNOLOGIES
Polym. Adv. Technol. **11**, 258–261 (2000)

Catalytic Behaviors of Silica-supported Natural Biopolymer–Oxalic Acid–Pt Complexes in Hydrogenation†

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ABSTRACT

Three kinds of natural biopolymers, gelatin, alginic acid and sodium carboxymethylcellulose (NaCMC), were reacted with oxalic acid in the presence of silica to yield complexes on the surface of silica, followed by reaction with H_2PtCl_6 $6H_2O$ to form Pt complexes, SiO_2–gelatin–$(COOH)_2$–Pt, SiO_2–alginic acid–$(COOH)_2$–Pt, and SiO_2–NaCMC–$(COOH)_2$–Pt, respectively. These complexes were able to catalyze the hydrogenation of 1-heptene to give n-heptane and that of nitrobenzene to give aniline at 25°C and under 1 atm H_2 in 100% yields. Experimental data show that the catalysts were very stable and could be reused without any remarkable change in catalytic activity. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: biopolymer; oxalic acid; Pt complex catalyst; hydrogenatiorr, nitrobenzene

INTRODUCTION

Many polymer–metal complexes have been used to catalyze the hydrogenation of various organic compounds [1]. In general, synthetic polymers have been used as the polymer ligands. In the previous papers, some natural biopolymers and their derivatives such as chitin [2], wool [3] and carboxymethylcellulose [4] have been found to be useful as effective ligands. It is well known that enzymes are natural biopolymeric catalysts and have extremely high activity and selectivity in mild conditions. In addition, an enzyme consists of several kinds of polymers of amino acids, and has a higher-order structure. In order to imitate the function of enzyme, the useful application of natural biopolymers may be one of the effective courses.

Four kinds of natural biopolymers, gelatin, alginic acid, sodium carboxylmethylcellulose (NaCMC) and casein were employed to react with oxalic acid in the presence of silica to yield complexes on the surface of silica, followed by the reactions with $H_2PtCl_6{\cdot}6H_2O$ to produce Pt complexes (Fig. 1). These silica-supported biopolymer–oxalic acid–Pt complexes, SiO_2–gelatin–$(COOH)_2$–Pt, SiO_2–alginic acid–$(COOH)_2$–Pt, SiO_2–NaCMC–$(COOH)_2$–Pt, SiO_2–casein–$(COOH)_2$–Pt, were found to catalyze the hydrogenation of 1-heptene to give *n*-heptane and that of nitrobenzene to give aniline in 100% yields at 25°C and under 1 atm H_2, respectively. These catalysts were very stable and could be reused without obvious loss in catalytic activities.

EXPERIMENTAL

Preparation of Silica-supported Oxalic Acid

In a typical experiment, 0.45 g of oxalic acid dihydrate was dissolved in 40 ml of H_2O to prepare oxalic acid aqueous solution, to which 4 g of silica

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† This paper was presented at the 2nd International Symposium on Hi-tech Polymers and Polymeric Complexes (HPPC-II), Zhengzhou University, China on 13–19 September 1999.

Received 12 September 1999
Revised 1 November 1999
Accepted 10 December 1999

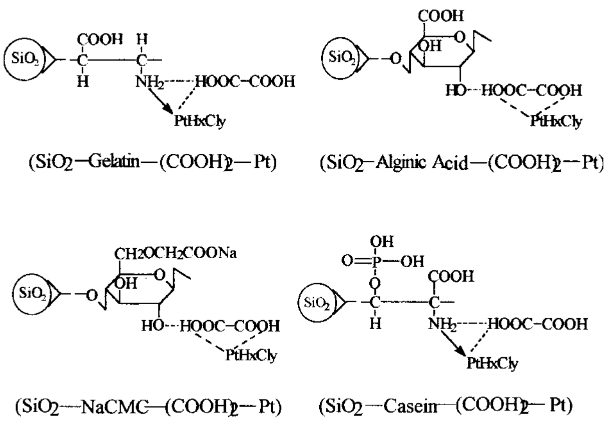

FIGURE 1. Structures of silica-supported bio-polymer–oxalic acid–Pt complexes.

(specific surface area, $90\,m^2/g$) was added. The mixture was dried, and milled and sieved to produce silica-supported oxalic acid, SiO_2–$(COOH)_2$ (4.3 g, particles > 100 mesh).

Preparation of Silica-supported Biopolymer–Oxalic Acid

In a beaker, 1 g of gelatin was dissolved in 40 ml of water at 60 °C, 1 g of alginic acid was dissolved in 40 ml of water in a beaker at 50 °C, 1 g of sodium carboxymethylcellulose (NaCMC) was dissolved in 40 ml of water by stirring in a beaker for 3 hr, and 1 g of casein was dissolved in 40 ml of 1% NaOH aqueous solution by stirring for 1 hr in a beaker.

To these beakers containing gelatin, alginic acid, sodium carboxymethylcellulose or casein aqueous solution, SiO_2–$(COOH)_2$ was added, and mixed to form a paste, dried, milled and sieved to obtain about 5.3 g of >100 mesh particles of SiO_2–gelatin–$(COOH)_2$, SiO_2–alginic acid–$(COOH)_2$, SiO_2–NaCMC–$(COOH)_2$ and SiO_2–casein–$(COOH)_2$, respectively.

Preparation of Silica-supported Biopolymer–Oxalic Acid–Pt Complexes

Silica-supported biopolymer–oxalic acid was reacted with $H_2PtCl_6{\cdot}6H_2O$ to produce Pt complexes of differing Pt content. For instance, 1 g of SiO_2–gelatin–$(COOH)_2$, 0.077 mmol $H_2PtCl_6{\cdot}6H_2O$ dissolved in small amounts of ethanol, and 10 ml ethanol were placed in a 25 ml flask equipped with a magnetic stirrer and reflux condenser. The mixture was stirred and refluxed under nitrogen atmosphere for 12 hr. The reaction mixture was filtered, washed with ethanol, and dried to obtain about 1 g of gray powder, SiO_2–gelatin–$(COOH)_2$–Pt (Pt content: 0.077 mmol/g).

Hydrogenation

In 25 ml flask equipped with a magnetic stirrer and a hydrogen inlet tube connected to a hydrogen volume measuring burette and a hydrogen storage cylinder, catalyst, SiO_2–gelatin–$(COOH)_2$–Pt, SiO_2–alginic acid–$(COOH)_2$–Pt, SiO_2–NaCMC–$(COOH)_2$–Pt or SiO_2–casein–$(COOH)_2$–Pt, and the substrate 1-heptene or nitrobenzene, as well as solvent, were placed. The hydrogenation reaction system was alternately evacuated and flushed with hydrogen several times. The hydrogenation was carried out at room temperature and under atmospheric hydrogen pressure. During the hydrogenation, the volume of hydrogen absorbed was measured. After the reaction, the reaction mixture was filtered to separate the catalyst. The recovered catalyst may be reused. The hydrogenation products were analyzed by gas chromatography (GC).

RESULTS AND DISCUSSION

Silica-supported biopolymer–oxalic acids were prepared simply by mixing silica, oxalic acid and biopolymer which are very cheap commercial materials [5]. Gelatin is a copolymer of various amino acids with an average molecular weight of 60,000. It can be obtained from skins and bones of various animals, and is usually used as hemostatic, food, adhesive, medicine, capsule etc. Alginic acid is similar to cellulose in chemical structure except for the presence of —COOH groups in molecules. It can be obtained from various brown seaweeds, and is used as the raw material of fiber, emulsifying agent of medicines and cosmetics, sizing material for paper, etc. Sodium carboxymethylcellulose is a derivative of cellulose produced from cellulose in a large scale, and commonly used as an additive in soap, synthetic washing agents, papers, foods, medicines and cosmetics. Casein is a copolymer of various amino acids containing phosphoric acid with a molecular weight of 75,000–375,000. It is produced from milk, and used as the raw material of cheese, adhesive water paint, emulsifying agent, entrophic medicine, etc.

These natural biopolymers, gelatin, alginic acid, NaCMC oxalic acid and casein are all soluble in water. When gelatin or casein is reacted with oxalic acid, a complex connected by ionic bonds is formed. Similarly, when alginic acid or NaCMC is reacted with oxalic acid, a complex connected by hydrogen bonds is produced. These complexes are insoluble in water and any solvents, probably because of the crosslinking in the reaction of the preparing polymer ligand.

The structures of biopolymer–oxalic acid–Pt complexes shown in Fig. 1 are probable examples, in which COOH, NH_2, OH and $P(O)(OH)_2$ groups in biopolymer–$(COOH)_2$ ligands are connected with Pt ion in $H_2PtCl_6{\cdot}6H_2O$ by coordinate bond or ionic bond. These functional groups can also connect with each other by ionic bond or hydrogen bond. Hence, the structures of biopolymer–oxalic acid–Pt complexes should be very complicated which may be varified by Pt content in the complexes.

Experimental results of hydrogenation of 1-heptene catalyzed by the silica-supported bio-

TABLE 1. Hydrogenation of 1-Heptene Catalyzed by Silica-supported Bio-polymer–Oxalic Acid–Pt Complexes

Catalyst	*Pt content*		*1-Heptene (mmol)*	*Initial hydrogenation rate (ml/min)*	*n-Heptane yield(%)*
	(mmol/g)	*(mmol/0.2 g)*			
SiO_2–gelatin–$(COOH)_2$–Pt	0.145	0.029	4.63	0.3	100
	0.116	0.023	3.68	1.2	100
	0.077	0.015	2.41	1.9	100
	0.048	0.010	1.60	0.8	100
SiO_2–Alginic acid–$(COOH)_2$–Pt	0.145	0.029	4.63	0.6	100
	0.116	0.023	3.68	1.7	100
	0.077	0.015	2.41	2.8	100
	0.048	0.010	1.60	1.4	100
SiO_2–NaCMC–$(COOH)_2$–Pt	0.145	0.029	4.63	0.5	100
	0.116	0.023	3.68	1.6	100
	0.077	0.015	2.41	3.0	100
	0.048	0.010	1.60	1.2	100
SiO_2–casein–$(COOH)_2$–Pt	0.145	0.029	4.63	0	0
	0.116	0.023	3.68	0.4	87
	0.077	0.015	2.41	0.7	91
	0.048	0.010	1.60	0	0

Catalyst, 0.2 g; 1-heptene/Pt molar ratio, 160/1; solvent, 5 ml ethanol; 25 °C, 1 atm H_2, 6 hr.

TABLE 2. Hydrogenation of Nitrobenzene Catalyzed by Silica-supported Biopolymer–Oxalic Acid–Pt Complexes

Catalyst	*Pt content*		*Nitrobenzene (mmol)*	*Initial hydrogenation rate (ml/min)*	*Aniline yield(%)*
	(mmol/g)	*(mmol/0.2 g)*			
SiO_2–gelatin–$(COOH)_2$–Pt	0.145	0.029	6.96	0.6	100
	0.116	0.023	5.52	1.5	100
	0.077	0.015	3.60	2.5	100
	0.048	0.01	2.40	1.1	100
SiO_2–Alginic acid–$(COOH)_2$–Pt	0.145	0.029	6.96	0.5	100
	0.116	0.023	5.52	1.4	100
	0.077	0.015	3.60	3.3	100
	0.048	0.010	2.40	1.3	100
SiO_2–NaCMC–$(COOH)_2$–Pt	0.145	0.029	6.96	0.5	100
	0.116	0.023	5.52	1.8	100
	0.077	0.015	3.60	3.2	100
	0.048	0.010	2.40	1.4	100
SiO_2–casein–$(COOH)_2$–Pt	0.145	0.029	6.96	0	0
	0.116	0.023	5.52	0.5	90
	0.077	0.015	3.60	0.8	92
	0.048	0.010	2.40	0	0

Catalyst, 0.2 g; nitrobenzene/Pt molar ratio, 240/1; solvent, 5 ml ethanol 25 °C, 1 atm H_2, 18 hr.

polymer–oxalic acid–Pt complexes are shown in Table 1. It can be seen that the initial hydrogenation rate is greatly affected by Pt content in the complex catalyst. At 0.077 mmol/g Pt content, the catalysts are more active. When SiO_2–gelatin–$(COOH)_2$–Pt, SiO_2–alginic acid–$(COOH)_2$–Pt or SiO_2–NaCMC–$(COOH)_2$–Pt is used as catalyst for this reaction, *n*-heptene can be converted into *n*-heptane in 100%

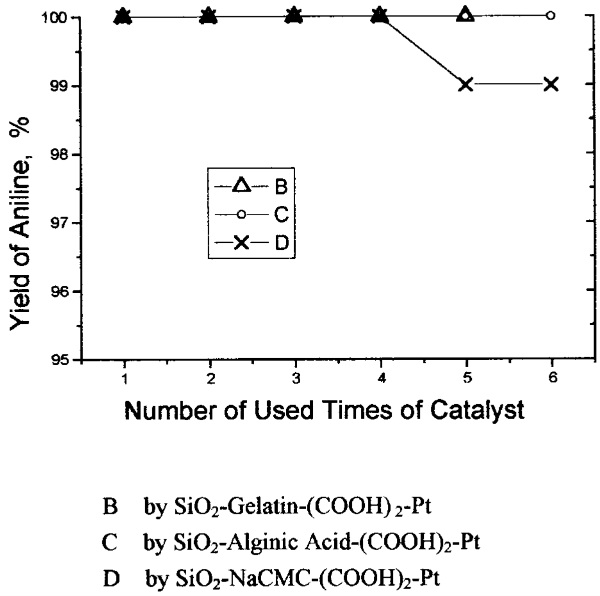

FIGURE 2. Reuse stability of catalyst in the hydrogenation of nitrobenzene: (B) by SiO_2–gelatin–$(COOH)_2$–Pt; (C) by SiO_2–alginic acid–$(COOH)_2$–Pt; (D) by SiO_2–NaCMC–$(COOH)_2$–Pt. Catalyst (Pt content, 0.077 mmol/g), 0.05 g (Pt, 0.0037 mmol); nitrobenzene, 0.98 mmol; nitrobenzene/Pt molar ratio, 265/1; solvent, 10 ml ethanol; 25 °C, 1 atm H_2, 18 hr.

yield. However, when SiO_2–casein–$(COOH)_2$–Pt is used as catalyst, it has no activity at 0.145 and 0.048 mmol/g Pt content, and 90 and 92% yield are obtained at 0.145 and 0.048 mmol/g Pt content. This example shows that the catalytic activity is greatly affected by the Pt content in the complex. As shown above the structure of the polymer–Pt complex may be changed by changing the Pt content.

Table 2 shows the hydrogenation of nitrobenzene catalyzed by silica-supported biopolymer–oxalic acid complexes. The results are similar to the hydrogenation of 1-heptene shown in Table 1.

In order to determine the stability of the catalysts, SiO_2–gelatin–$(COOH)_2$–Pt, SiO_2–alginic acid–$(COOH)_2$–Pt and SiO_2–NaCMC–$(COOH)_2$–Pt, the catalysts were recovered and reused. The results are shown in Fig 2, in which the catalytic activities do not change obviously regardless of reuse.

CONCLUSIONS

Silica-supported biopolymer–oxalic acid–Pt complexes, SiO_2–gelatin–$(COOH)_2$–Pt, SiO_2–alginic acid–$(COOH)_2$–Pt and SiO_2–NaCMC–$(COOH)_2$–Pt, have been prepared and employed to catalyze the hydrogenation of 1-heptene to *n*-heptane and nitrobenzene to aniline at 25 °C, 1 atm H_2 in 100% yields respectively. These catalysts could be reused without obvious changes in catalytic activity.

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