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The use of ion exchange resins in the recycle of palladium catalysts for the synthesis of polyketones

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Abstract

In the present work, three methods were employed to find ways of recycling palladium catalysts. Ion exchange resins were used as carriers to prepare resin-supported palladium catalysts and the reusability of this catalyst in the preparation of polyketone by copolymerization of carbon monoxide and styrene was investigated. Additionally, the feasibility of recycling the expensive palladium catalysts was examined by two methods: (1) absorbing the effective components in the after-treatment solution of polyketone and reusing them; (2) condensing the after-treatment solution of polyketone and reusing it as a catalyst to investigate its catalytic activity. The structure of the copolymer was determined by IR, TGA, DSC, etc. The results showed that the resin-supported palladium catalyst was active and could be reused. Furthermore, the ion exchange resin D-72 can adsorb Pd^{2+} , Cu^{2+} , etc., in the after-treatment solution of the copolymerization. The catalytic activity of reused catalyst reached about 474 g/g h. The condensed after-treatment solution showed good catalytic activity in the copolymerization of carbon monoxide and styrene.

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Keywords: Carbon monoxide; Styrene; Ion exchange resin; Palladium catalyst; Recycle

1. Introduction

Environmental pollution by polymer materials is a global problem that needs to be addressed. Polyketone [1–4] attracted considerable interest from both academic and industry in recent years as it can be degraded in the environment. Since 1980s, an increasing number of reports have ap-

peared on the synthesis of polyketone copolymers of carbon monoxide and styrene [5–18]. Palladium (Pd) complexes are the most commonly used catalysts [19–21]. The catalytic activity of these complexes are relatively high but not so high that the catalyst embedded in the product has to be removed. Generally, the Pd catalyst is removed from the copolymer by dilution in alcohol and disposed of in the after-treatment solution. It cannot be reused in the next reaction, which results in an increase in the production cost.

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In this work, in order to find out how to recycle Pd catalyst, three methods were chosen and the recycled Pd catalyst was used as a catalyst in the copolymerization of CO and styrene. The structure of copolymer was characterized by IR, TGA and DSC.

Ion exchange resins, particularly the macroporous ones, play an important role in the manufacture of petrochemicals. Resins can be applied in the removal of metal ions even in large-scale operations [22,23]. In this way, cation exchange resins were chosen as the carrier in preparing the recycled resin-supported Pd catalyst and its reusability was investigated. The feasibility to recycle Pd catalyst was discussed through two methods: (1) absorbing the effective components in the after-treatment solution of polyketone and reuse them; (2) condensing the treatment solution of polyketone and reuse it as catalyst to investigate its catalytic activity.

2. Experimental procedure

2.1. Starting materials

Carbon monoxide (>99.9%) was purchased from Beijing Analysis Instrument Company, China. Styrene and *o*-chlorophenol were vacuum distilled before use. Cupric *p*-toluenesulphonate was prepared in our laboratory. Palladium acetate, 2,2'-bipyridine, *p*-toluenesulphonic acid, 1,4-quinone, methanol, potassium acetate and acetic acid were all Analytical Pure and used directly without further purification. Cation exchange resins of polystyrene and polyacrylate were supplied by the Resins Factory of Nankai University, Tianjin, China.

2.2. Preparation of resin-supported catalyst

A cation exchange resin of polystyrene, D-72, was reacted with water solution of CuSO_4 . Then the resin was placed into acetonitrile (the ratio of potassium acetate to acetonitrile (g/g) was 0.015:1) with palladium acetate, and dried under vacuum. So the resin-supported catalyst was obtained.

2.3. Copolymerization of CO and styrene

Polyketone, the copolymer of styrene and CO, was prepared by using a catalyst composed of: palladium acetate 0.5×10^{-4} mol, 2,2'-bipyridine 1.5×10^{-4} mol, *p*-toluenesulphonic acid 1.5×10^{-4} mol, 1,4-quinone 1.0×10^{-4} mol, cupric *p*-toluenesulphonate 0.25×10^{-4} mol. Into a 100 ml autoclave, 4 ml methanol, 15 ml distilled styrene, 10 ml *o*-chlorophenol and the catalyst were added. The reactor was then filled with 3.0 MPa CO at room temperature, and heated to the desired temperature (60 °C). The reactor was cooled to room temperature and CO was vented when the copolymerization was finished. The copolymer was precipitated with ethanol, filtered, rinsed, extracted in a Soxhlet extractor and dried. Finally the dried polyketone was obtained in the form of white fine powder. Experimental value: C, 81.75%; H, 6.47%; O, 11.78%; theoretical value: C, 81.82%; H, 6.06%; O, 12.12%.

When the resin-supported Pd catalyst was used, the copolymerization was carried out under the same conditions mentioned above.

2.4. Recycling of noble Pd catalyst

There were two methods to recycle Pd^{2+} :

- (1) The D-72, ion exchange resin, was used to absorb Pd^{2+} in the after-treatment solution obtained from the after-treatment of the copolymer.
- (2) The after-treatment solution was condensed and reused in the copolymerization of CO and styrene.

2.4.1. Absorbing Pd^{2+} in the after-treatment solution using D-72 resin

The D-72 resin was added into a column and the after-treatment solution was added through slowly. Velocity was kept as 2–3 drops per second. The addition of after-treatment solution was stopped when the color of the resin turned to pink. Then the resin was washed with acetic acid–potassium acetate as effluent. The effluent was condensed to remove the solvent of ethanol and it (composed of potassium acetate, cupric acetate,

acetic acid, etc.) was used in the copolymerization. The catalyst palladium was thus recycled.

2.4.2. Condensing of the after-treatment solution

The after-treatment solution was condensed to remove ethanol and water. Then the condensed solution was used as catalyst in the copolymerization of CO and styrene.

2.5. Measurement

The content of palladium in the resin or condensed solution was determined by plasma emission spectrograph ICP-9000(N+M) (T.J.A. company, USA). The infrared spectrum was performed by using the potassium bromide pellet technique with a BIO-RAD FTS3000 infrared spectrometer. Thermogravimetric analysis was performed in a Shimadzu TGA-50H thermal analysis system with nitrogen at the heating rate of 10 °C/min.

3. Results and discussion

3.1. Characterization of copolymer

The copolymers of CO and styrene using resin-supported Pd and condensed solution as catalysts were both almost insoluble in common solvents and the IR analysis results of copolymer were summarized in Table 1 and Fig. 1.

The thermal stabilities of the polymers were investigated by thermogravimetric analysis (TGA) in a nitrogen stream at a heating rate of 10 °C/min. In Fig. 2, the TGA thermograms of polymers were shown. As can be seen, the loss of mass started at about 379 °C. The maximum decomposition occurred at about 401 °C, the same as that of the CO/styrene copolymer prepared by using fresh homogeneous Pd catalyst.

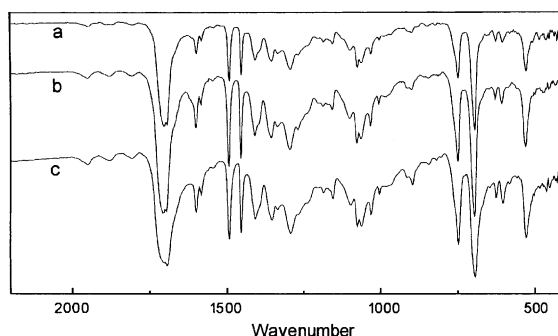


Fig. 1. IR spectra of CO/styrene copolymer: (a) resin-supported Pd catalyst; (b) recycled resin-supported Pd catalyst; (c) condensed recycled solution catalyst.

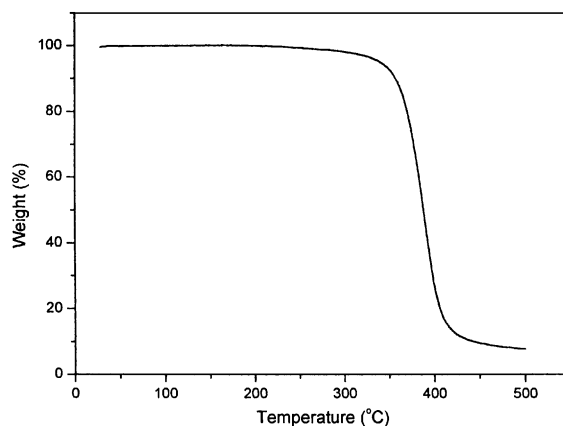


Fig. 2. TGA curve of the CO/styrene copolymer (Note: sample weight, 4.400 mg; cell, quartz; atmosphere, nitrogen; flow rate, 10.00 ml/min).

3.2. Resin-supported Pd catalyst

3.2.1. Catalytic activity of resin-supported Pd catalyst

The resin-supported Pd catalyst prepared by reacting benzoquinone cation exchange resin with palladium acetate was used in the copolymerization

Table 1
IR analysis results of CO/styrene copolymer using different catalyst

Catalyst	$\nu_{\text{C=O}}$ (cm^{-1})	$\nu_{\text{C=C}}$ (cm^{-1})	$\delta = \text{C-H}$ (cm^{-1})
Resin-supported Pd catalyst	1706	1493	696
Recycled resin-supported Pd catalyst	1706	1493	696
Condensed recycled solution catalyst	1698	1492	695

of CO and styrene. The effect of the composition of resin-supported Pd catalyst on the copolymerization of CO and styrene were shown in Table 2.

Considering the intrinsic $-\text{SO}_3^-$ group in the cation-exchange resin of polystyrene, *p*-toluenesulphonic acid and cupric *p*-toluenesulphonate were not added into the copolymerization.

It can be seen from Table 2 that there was no product when the catalyst was composed of composition 1 (basic composition), which had no *p*-toluenesulphonic acid ions in the system. Based on composition 1, when cupric *p*-toluenesulphonate was added (as composition 2), there were some product but the yield was still very low. This showed that $-\text{SO}_3^-\text{H}^+$ in the carrier could not take the place of *p*-toluenesulphonic acid which can produce weak coordinating action with Pd^+ center. Therefore, some *p*-toluenesulphonic acid was added into the reaction system (as composition 3). In composition 2, there were $-\text{SO}_3^-\text{H}^+$ ions and thus the product formed. The yield of composition 3 came close to composition 4. Comparing composition 3 with composition 4, the only difference was that there was no additional Cu^{2+} added in composition 3. These data showed that Cu^{2+} absorption played a limited role in the reaction. From there, only some *p*-toluenesulphonic acid was needed to be added in the copolymerization catalyzed by Pd^{2+} resin-supported catalyst. In composition 5, there was no solvent and the catalytic activity of palladium in this system was lower than that in homogenous system, and the catalyst was less embedded. Without any solvent, the concentration of active

center was increased and the reaction rate was also improved.

3.2.2. Reuse of resin-supported catalyst

Table 2 showed that the resin-supported catalyst displayed some catalytic activity for the copolymerization of CO with styrene. The purpose of using the resin-supported catalyst was to recycle the palladium. Hence, it was necessary to investigate the usable life of the resin-supported catalyst. The catalytic activity of the reused catalyst was listed in Table 3.

It can be seen from Table 3 that the yield and catalytic activity for the first run were much higher than those of the second, third or fourth run. The yield and catalytic activity of the second, third and fourth runs were nearly the same. It can be deduced that part of Pd^{2+} was gradually lost and entered into the system. While part of the Pd^{2+} kept the close catalytic activity along with the reuse of the resin-supported catalyst. It can be concluded that the resin-supported catalyst prepared

Table 3
Effect of reused times of resin-supported catalyst on copolymerization

Used times	Yield (mg)	Catalytic activity (g STCO/g Pd h)
1	1513	143
2	222	20
3	217	21
4	180	17
No the resin-supported catalyst	4855	459

Reaction condition: temperature, 60 °C; pressure, 3.0 MPa; time, 2 h; 2-chlorophenol, 10 ml; styrene, 15 ml.

Table 2
Effect of composition of resin-supported Pd catalyst on copolymerization

Composition	Yield (mg)	Catalytic activity (g STCO/(g Pd h))
(1) Basic composition	0	0
(2) Basic composition + A	152	14
(3) Basic composition + B	1215	115
(4) Basic composition + A + B	1512	143
(5) Basic composition + A + B – solvent	2873	272

Basic composition: resin-supported catalyst, 2,2'-bipyridyl, benzoquinone, styrene, 2-chlorophenol, methanol; A – cupric *p*-toluenesulphonate; B – *p*-toluenesulphonic acid.

Reaction condition: temperature, 60 °C; pressure, 3.0 MPa; time, 2 h; 2-chlorophenol, 10 ml; styrene, 15 ml.

in this work had some reusability. Whereas the loading pattern and loading amount of Pd^{2+} still need to be further improved.

Table 3 also showed that the catalytic activity of resin-supported catalyst was lower than that of the homogeneous catalyst. Potential explanations for this effect are: (1) The optimum composition of the homogeneous catalyst had been found after many experiments, hence the catalytic activity was higher. At the same time, investigation of the resin-supported resin catalyst was still underway and the optimal composition has not yet been found. (2) The resin-supported catalyst is solid. It has a high density and remains in the bottom of the autoclave. Although reactor was stirred, the resin-supported catalyst could not be dispersed homogeneously in the copolymerization and this resulted in low reaction rate. Some resins at the bottom of the autoclave were ground into powder by the magnetic stirrer and cannot be reused. This also needs further improvement.

3.3. The adsorption of resin

Two kinds of resins (strong acid cation exchange resin of polystyrene and weak acid cation exchange of polyacrylate) were used as carriers to absorb the effective component, Pd^{2+} , in the catalyst.

When cation exchange resin of polystyrene was used, the Pd^{2+} in the after-treatment solution could be absorbed onto the resin and the resin column turned from yellow to pink gradually.

While when cation exchange resin of polyacrylate was used, the Pd^{2+} could not be strongly absorbed onto the resin and it can be seen that in the resin column, the layer enriched with Pd^{2+} moved slowly down to the column.

The above two kinds of resins enriched with Pd^{2+} were dried and added into the reaction system, into which all the other components but palladium acetate were placed. It was found that polyketone could be obtained when the cation exchange resin of polystyrene was used, and no polyketone was found when cation exchange resin of polyacrylate was used.

Thus, further researches were concentrated on the absorbing Pd^{2+} using cation exchange resin of polystyrene.

3.3.1. Effect of amount of resin-supported catalyst on catalytic activity of copolymerization

The effect of the amount of resin-supported Pd catalyst on catalytic activity of copolymerization is shown in Fig. 3.

From Fig. 3, it can be seen that the catalytic activity reached the highest when 4 g resin-supported catalyst (content of Pd was 11.6×10^{-3} mmol) was used. The reason was that with increasing the resin dosage, the volume of the resin in autoclave grew. Due to the use of the magnetic stirrer, the resin cannot be thoroughly stirred to form an homogeneous effective active center with increasing the amount of solid substance in the autoclave.

3.3.2. Effect of other components of catalyst adsorbing after-treatment solution on the catalytic activity

During Pd^{2+} is adsorbed by the resin, it is also possible that other components in the after-treatment solution could also be adsorbed. Hence, the effect of the other components in the adsorbent resin on the catalytic activity was investigated. The copolymerization was carried out with the other

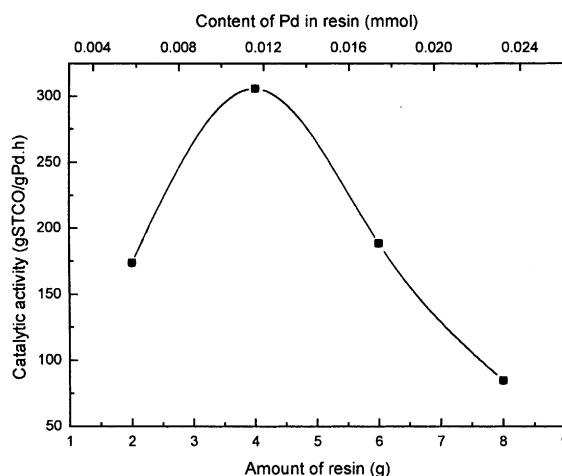


Fig. 3. Effect of amount of resin on catalytic activity of copolymerization.

Table 4

Effect of the special components of catalyst on the catalytic activity

Other material	Palladium ($\text{mol} \times 10^{-7}$)	Yield (mg)	Catalytic activity ($\text{g STCO} (\text{g Pd h})^{-1}$)
All added ^a	116	2257	306
No 2,2'-bipyridyl	116	599	81
No <i>p</i> -toluenesulfonic copper	116	2013	273

Reaction condition: temperature, 60 °C; pressure, 3.0 MPa; time, 2 h; 2-chlorophenol, 10 ml; styrene, 15 ml.

^a Include 2,2'-bipyridyl, benzoquinone, cupric *p*-toluenesulphonate, *p*-toluenesulphonic acid.

components in the catalyst system removed and the result was listed in Table 4.

Thin-layer chromatography was used to analyze the effluent of the resin column and no bidentate ligand of 2,2'-bipyridine was found. From this it was known that 2,2'-bipyridine might be absorbed in the resin with Pd^{2+} in the form of a complex. It was found that polyketone could be obtained when 2,2'-bipyridine and palladium acetate were not added into the copolymerization, but the catalytic activity was lower and it was just one fourth of the original. This showed that part of 2,2'-bipyridine had lost the catalytic activity.

During the detection of effluent, no Cu^{2+} (comes from cupric *p*-toluenesulphonate) was found. From Table 4 it was seen that without cupric *p*-toluenesulphonate in the copolymerization (see Table 4) the catalytic activity was less. This proved that Cu^{2+} could also be absorbed in the resin with Pd^{2+} and took part in the catalytic action in the copolymerization. This could also be proved from the color change of the resin during the absorption and by a plasma emissive spectrograph. From this, it was unnecessary to add cupric *p*-toluenesulphonate when the resin was used as carrier.

3.3.3. Reusability of resin-supported catalyst

The effective components in the after-treatment solution of the copolymerization of CO with styrene were fully reused by using the resin as the absorbent. Because of the intrinsic functional group in the resin, some of the components were adsorbed in the resin and made the resin reuse possible. The results of the reusability of resin-supported catalyst were listed in Table 5.

From Table 5, it was seen that the catalytic activity (*R*) of the resin was the highest when 8 g resin was reused for the first time in the copolymerization, and *R* was more than 470 g/(g Pd h). The reason was that the content of Pd^{2+} in the resin decreased gradually with the reuse of resin. It was shown that when 4 g resin was used during the second time as the catalyst, the content of Pd^{2+} decreased to 36×10^{-7} mol from 116×10^{-7} mol, i.e., if 8 g such resins was added, the content of Pd^{2+} was only 71×10^{-7} mol and the catalytic activity was 474 g STCO/g Pd h.

When 8 g resin was reused as catalyst in the repeated reactions, polyketone obtained from the third time catalyst was low and was close to that of the fourth run. The data of plasma emissive

Table 5

Effect of reuse of resin on copolymerization

Used times	Dosage of resin (g)	Pd^{2+} ($\text{mol} \times 10^{-7}$)	Yield (mg)	Catalytic activity (g STCO/g Pd h)
1	4	116	2257	306
2	4	36	386	170
2	6	54	1233	362
2	8	71	2154	474
3	6		192	
3	8		247	
4	8		187	

Reaction condition: temperature, 60 °C; pressure, 3.0 MPa; time, 2 h; 2-chlorophenol, 10 ml; styrene, 15 ml.

Table 6
Effect of the condensed liquid on copolymerization

Volume of condensed liquid (ml)	The other component	Yield (mg)	Catalytic activity (g STCO/g Pd h)
20	All added	1357	219
20	No 2,2'-bipyridine	0	0
20	No <i>p</i> -toluenesulphonic acid	2591	419
20	No cupric <i>p</i> -toluenesulphonate	2953	477

Reaction condition: temperature, 60 °C; pressure, 3.0 MPa; time, 2 h; 2-chlorophenol, 10 ml; styrene, 15 ml.

spectrograph showed that Pd^{2+} adsorbed in resin changed from 116×10^{-7} mol (first run) to 36×10^{-7} mol (second run) to that undetectable (third run). So Pd^{2+} got lost heavily after the resin was reused three times. The yields of polyketone after the third run usage of resin were low. Hence, twice usage of the resin was reasonable.

Acetic acid–potassium acetate solution was used to remove the Pd^{2+} from the sulfonic resin and a pink solution was obtained. Then the solution was distilled to remove ethanol and water solvent. The red condensed solution, in which there were palladium acetate, potassium acetate, acetic acid, cupric acetate, etc., was thus obtained. This solution was added into the reaction with/without 2,2'-bipyridine and 1,4-quinone, no polyketone was formed. So this method was not found to be feasible.

3.4. Effect of condensed after-treatment solution on copolymerization

The after-treatment solution was distilled at 1 atm to remove ethanol, it was then distilled again under vacuum to get rid of water by boiling with benzene. Finally, a condensed liquid was obtained, which contained *o*-chlorophenol, Pd^{2+} , 2,2'-bipyridine, *p*-toluenesulphonic acid, 1,4-quinone, cupric *p*-toluenesulphonate. This condensed liquid was added into the reaction to catalyze the copolymerization of CO and styrene. The results of this experiment were listed in Table 6.

From Table 6, it can be seen that if the concentrated liquid was used as catalyst, polyketone could be obtained. No 2,2'-bipyridine, no polyketone was found. This demonstrated that 2,2'-bipyridine in the concentrated liquid had lost its

activity and bidentate ligand of 2,2'-bipyridine should be compensated in the repeating experiment.

The catalytic activity of the reaction became higher when *p*-toluenesulphonic acid and cupric *p*-toluenesulphonate were not added into the system. Because *p*-toluenesulphonic acid is strong acid, it could react with bipyridine. The coordinating action between 2,2'-bipyridine and Pd^{2+} was lowered and this led to a lower catalytic activity. During the repeated reaction, no more *p*-toluenesulphonic acid and the cocatalyst cupric *p*-toluenesulphonate should be put into the system.

4. Conclusion

The resin-supported resin catalyst prepared in this work had catalytic activity and reusability in the copolymerization of CO and styrene. The catalytic activity of reused catalyst can reach 474 g/g.h. The ion exchange resin can adsorb Pd^{2+} , Cu^{2+} , etc., in the after-treatment solution of the copolymerization and no cupric *p*-toluenesulphonate and Pd^{2+} were needed to be added into the copolymerization of CO/styrene.

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