

THE EFFECT OF MODIFICATION OF COORDINATING GROUPS ON THE CATALYTIC BEHAVIORS OF POLYMER CATALYSTS

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ABSTRACT

Several polymer-supported palladium complex catalysts containing two different coordinating groups were prepared and the cooperative effect of the coordinating groups on the catalytic behaviors of polymer catalysts was studied. It was found that poly(acrylic acid-co-acrylonitrile)-Pd complex (PAA-AN-Pd) is a more active and stable catalyst for hydrogenation than both poly(acrylic acid)-Pd and poly(acrylonitrile)-Pd complexes. A marked change of catalytic behaviors of poly(N-substituted maleamic acid-co-styrene)-Pd complexes was observed in comparison with poly(maleic acid-co-styrene)-Pd complex. Acetophenone was reduced to 1-phenyl ethanol by poly(N-phenyl maleamic acid-co-styrene)-Pd complex (N-1-Pd), but ethylbenzene was obtained using poly(maleic acid-co-styrene)-Pd complex as a catalyst. The influence of solvents, additives and N/Pd gram atomic ratio on the catalytic behaviors of the polymer complexes was investigated.

INTRODUCTION

Many heterogeneous catalysts for hydrogenation of nitro-compounds and alkenes have been generally used, but only a few homogeneous catalysts, for example, $\text{Co}(\text{CN})_5^{3[1]}$ and $\text{RuCl}(\text{PPh}_3)_3^{[2, 3]}$, have been reported. Bis(dimethylglyoximate)cobalt (II) can catalyze the hydrogenation of nitrobenzene at room temperature and atmospheric pressure, but the catalytic activity is very low^[4]. Moreover, these homogeneous catalysts are unstable in air and difficult to be recovered from the reaction products. In order to overcome these disadvantages, a number of polymer-supported metal catalysts have been synthesized^[5-7]. Most of these polymer catalysts are more stable and selective for the hydrogenation reaction than homogeneous catalysts. For instance, nitrobenzene can be reduced to aniline in 100% yield at room temperature and atmospheric pressure by silica-supported polyvinylpyrrolidone-Pd complex^[5], but in the case of $\text{Pd}_2(\text{PPh}_2)_3\text{Cl}_4^{[8]}$, by-products azobenzene (5%) and azoxybenzene (15%) are obtained in addition to aniline (75%).

We have reported poly(maleic acid-co-styrene)-Pd complex as a highly active and stable

catalyst for hydrogenation of nitro-compounds^[9]. Recently we have prepared several polymer-supported Pd-complex catalysts containing two different coordinating groups and the cooperative effect of these coordinating groups on the catalytic behaviors of polymer catalysts was investigated.

RESULTS AND DISCUSSION

1. Polymer ligands from copolymerization

The silica-supported crosslinked homopolymer and copolymers of acrylic acid, and their complexes containing palladium have been prepared. The catalytic activities of these complexes for the hydrogenation of nitrobenzene and 1-heptene are summarized in Table 1. Among these complexes poly(acrylic acid-co-acrylonitrile)-Pd complex (abbr. as PAA-AN-Pd) is the most active and highly stable catalyst for hydrogenation reaction. As shown in Fig. 1, the catalytic activity of PAA-AN-Pd is higher than those of Pd-complexes of the homopolymers, i.e., poly(acrylic acid)-Pd (PAA-Pd) and polyacrylonitrile-Pd (PAN-Pd)^[10].

Table 1 Initial rate of hydrogenation of nitrobenzene catalyzed by poly(acrylic acid)-Pd and the Pd-complexes of copolymers

Catalysts	Initial rate (ml/min)
PAA-Pd	22.5
PAA-St-Pd	13.7
PAA-AN-Pd	27.1
PAA-AM-Pd	14.1
PAA-VP-Pd	22.2

Conditions: Amount of complexes: 0.01 mmol of Pd; amount of nitrobenzene: 5 mmol; 20 ml of methanol; $T=30^{\circ}\text{C}$; hydrogen pressure: 1 atm.

St: styrene; AN: acrylonitrile; AM: acrylamide; VP: vinylpyrrolidone.

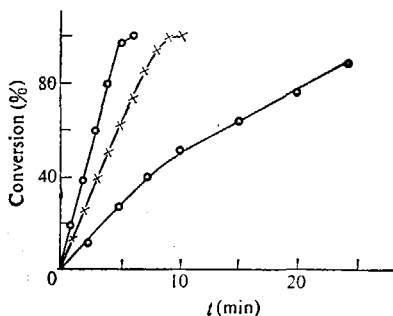


Fig. 1 Comparison of catalytic activities of PAA-AN-Pd (●) with PAA-Pd (×) and PAN-Pd (○) for the hydrogenation of nitrobenzene
Conditions: amount of Pd in the complexes: 0.05 mmol; 5 mmol of nitrobenzene; 20 ml of methanol; $T=30^{\circ}\text{C}$; $p=1$ atm.

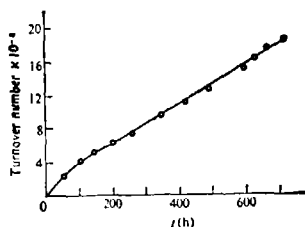


Fig. 2 Relationship between turnover number and reaction time in the hydrogenation of nitrobenzene catalyzed by PAA-AN-Pd

Conditions: amount of Pd in PAA-AN-Pd: 0.001 mmol; 5 mmol of nitrobenzene was added at interval of several hours; 20 ml of methanol; $T=30^{\circ}\text{C}$; $p=1$ atm.

As to the stability of this complex, it is surprising that PAA-AN-Pd is much more stable than PAA-Pd and PAN-Pd. Its catalytic activity for the hydrogenation of nitrobenzene does not decrease as the turnover number is up to 1.8×10^5 (Fig. 2). The extraordinarily high stability of PAA-AN-Pd may be attributed to the cooperative effect of coordinating groups $-\text{COOH}$ and $-\text{CN}$ in the same polymer chain. The product of hydrogenation was detected with gas chromatography, it consisted of aniline and unreacted nitrobenzene without by-product.

The initial rates of hydrogenation of various substrates catalyzed by PAA-AN-Pd are shown in Table 2. Terminal alkenes were almost hydrogenated with the same rate in spite of their different chain lengths. Cyclic alkenes, internal alkenes and alkenes with complicated structure were hydrogenated more slowly than terminal alkenes. In the case of various nitroanilines, the rate decreased in the order: $p > m > o$ as a result of steric effect. Moreover, hydrogenolysis of benzaldehyde and acetophenone occurred when catalyzed by PAA-AN-Pd to give ethyl benzene and toluene.

Table 2 Initial rate of hydrogenation of various substrates catalyzed by PAA-AN-Pd

Substrates	Initial rate (ml/min)	Substrates	Initial rate (ml/min)
Nitrobenzene	27.1	Cyclohexene	6.5
p-Nitroaniline	21.2	β -Pinene	0.1
m-Nitroaniline	11.4	Squalene	2.0
o-Nitroaniline	3.1	Allyl alcohol	10.8
1-Hexene	20	Allyl ethyl ether	26.2
1-Heptene	20.5	Acrylonitrile	31
1-Tetradecene	23	Benzaldehyde	15
Acetophenone	5		

Conditions as given in Table 1.

2. Polymer ligands from polymer reaction

Four kinds of silica-supported crosslinked polymer-Pd complexes, i.e., N-1-Pd, N-2-Pd, N-3-Pd and N-4-Pd have been prepared by reactions of several amines with poly(maleic anhydride-co-styrene) followed by Pd-complex formation. The polymer ligands contain both carboxylic and amide groups (Table 3). A marked change of their catalytic behavior was observed by comparison of these four complexes with the Pd-complex of the hydrolyzed product of this copolymer, i.e., poly(maleic acid-co-styrene)-Pd complex (PMS-Pd). N-1-Pd is more active than PMS-Pd for catalytic hydrogenation of nitrobenzene, but the activities of the other three complexes are lower than that of PMS-Pd (Table 3).

Table 3 Catalytic activities of several polymer-Pd complexes for the hydrogenation of nitrobenzene and 1-heptene

Complexes	Polymer ligands	Content of nitrogen (%)	Initial rate (ml/min)	
			Nitrobenzene	1-Heptene
PMS-Pd	$\text{P}-\text{OH}^*$	—	31.3	30.0
N-1-Pd	$\text{P}-\text{NHC}_6\text{H}_5$	3.38	34.0	33.0
N-2-Pd	$\text{P}-\text{N}$ 	3.30	6.0	8.0
N-3-Pd	$\text{P}-\text{NCH}_2\text{C}_6\text{H}_5$	2.42	17.0	19.0
N-4-Pd	$\text{P}-\text{N}$ 	1.94	7.6	11.0

Conditions as given in Table 1.

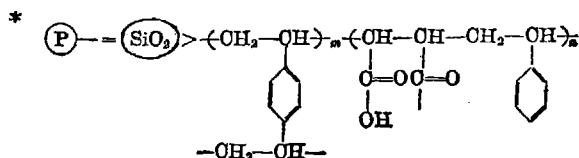


Table 4 Initial rates of hydrogenation of various substrates catalyzed by N-1-Pd complex

Substrates*	Initial rate (ml/min)	Substrates	Initial rate (ml/min)
p-Nitroaniline	17.5	1-Hexene	19.5
m-Nitroaniline	6.5	Cyclohexene	8.0
o-Nitroaniline	3.0	1-Tetradecene	15.0
Acetophenone**	2.5	Squalene	1.5
Benzaldehyde**	8.0	β -Pinene	0

Conditions as given in Table 1.

* Products detected by gas chromatography.

** Amount of N-1-Pd: 0.02 mmol of Pd.

Table 4 illustrates the initial rates of hydrogenation of various substrates catalyzed by N-1-Pd. It is interesting to notice that acetophenone can be reduced to 1-phenyl ethanol, no ethylbenzene is found in the product, and benzaldehyde can be reduced to phenyl methanol with a small amount of toluene, but acetophenone and benzaldehyde are converted into ethylbenzene and toluene by PMS-Pd respectively. The results show the effect of the modification of coordinating groups on the catalytic behaviors of the polymer-Pd complexes.

3. Influence of solvents, gram atomic ratio N/Pd and additives on the activities of the polymer catalysts

The effect of solvents on the catalytic activities of PAA-AN-Pd and N-1-Pd has been studied. The results (Table 5) indicate that alcohols are good solvents for the hydrogenation of nitrobenzene, among them methanol is the best and those with long alkyl groups decrease the reaction rate. Nonpolar solvents such as CCl_4 and solvents with strong coordinating power such as dimethyl sulfoxide lead to complete loss of catalytic activities of PAA-AN-Pd and N-1-Pd.

Table 5 Influence of different solvents on the initial rate of hydrogenation of nitrobenzene catalyzed by PAA-AN-Pd and N-1-Pd

Solvents	Initial rate (ml/min)	
	PAA-AN-Pd	N-1-Pd
Methanol	27.1	34.0
Ethanol	23.0	23.0
n-Butanol	17.1	15.0
n-Octanol	6.6	6.5
Ethyl acetate	6.6	—
Tetrahydrofuran	7.0	4.0
Benzene*	10.0	10.0
Acetone	1.9	7.0
Carbon tetrachloride	0	0
Dimethyl sulfoxide	0	0

Conditions as given in Table 1.

* With induction period.

The influence of gram atomic ratio N/Pd and additives on the activities of the catalysts has also been examined. The peak of catalytic activity appears in these polymer complexes. for example, an optimum rate of the hydrogenation of nitrobenzene arises when the N/Pd ratio of N-1-Pd is about 25. The catalytic activities of PAA-AN-Pd and N-1-Pd are greatly affected by additives. The hydrogenation rates of nitrobenzene increase when a small amount of acetic acid is added, but aqueous solution of NaOH, hydrochloric acid and ammonia solution lower the reaction rates. The reason for the change of the catalytic activities of the polymer complexes is not clear yet, it may be due to the coordination of Pd in the complex with

additives.

EXPERIMENTAL

Polymerization

In the presence of silica gel, the monomers were homopolymerized and copolymerized respectively according to the methods reported in literatures^[11-15]. For example, to a 250 ml three-necked flask equipped with a reflux condenser, mechanical stirrer, and thermometer were added 100 ml of dioxane and 11 g of silica gel (surface area $370\text{ m}^2\text{g}^{-1}$), then, 7.2 g (0.105 mol) of acrylic acid, 5.6 g (0.105 mol) of acrylonitrile, divinylbenzene (0.03 mol) and AIBN (2.1 mmol) were added with stirring. Polymerization was carried out at 60°C for 6 hr. 21 g of product was obtained after being extracted with solvent and dried.

Polymer reaction

With reference to the methods in literatures^[16, 17], we obtained the polymer ligands containing both carboxylic and amide groups by the reaction of silica-supported crosslinked poly-(maleic anhydride-co-styrene) with excess of various amines respectively. For instance, 12 g of silica-supported crosslinked poly(maleic anhydride-co-styrene) was mixed with 100 ml of freshly distilled aniline. The reaction mixture was stirred with a magnetic stirrer and heated at about 100°C for 5 hr under nitrogen atmosphere. The gross product was filtered, washed with dilute hydrochloric acid and extracted with benzene, and then 12.4 g of product was obtained. Nitrogen contents of these polymer ligands were listed in Table 3. The $\text{C}=\text{O}$ absorption bands of IR spectra at 1770 cm^{-1} , 1710 cm^{-1} and $1650\text{--}1700\text{ cm}^{-1}$ show that both carboxylic and amide groups are present in these polymer ligands.

Complex formation

PAA-AN-Pd was obtained by reaction of PAA-AN and $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ in boiling acetone. The polymer ligands N-1 to N-4 were allowed to react with $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ in ethanol at 60°C for 7-8 hr to yield their Pd-complexes.

Determination of stability of complexes

Under 30°C and atmospheric pressure of hydrogen, 5 mmol of nitrobenzene was catalytically hydrogenated by PAA-AN-Pd (Pd: 0.001 mmol) in methanol, then every 5 mmol of nitrobenzene was added to the reaction mixture at interval of several hours, and the quantities of hydrogen uptake was calculated.

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