

# Palladium complex of poly(4-vinylpyridine-*co*-acrylic acid) for homogeneous hydrogenation of aromatic nitro compounds

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## Abstract

Copolymers, poly(4-vinylpyridine-*co*-acrylic acid) (PVPA), with different composition were synthesized, and their palladium complexes were prepared. The catalytic properties of the palladium complex for the hydrogenation of aromatic nitro compounds were investigated. The palladium complex of PVPA can form a homogeneous system in ethanol. The optimum catalytic activity for hydrogenation of nitrobenzene was obtained when the molar content of 4-vinylpyridine (VPy) units in PVPA was 57.5% and VPy/Pd molar ratio was 6. The presence of 0.1 mol/l KOH can promote the catalytic activity to a great extent. In most cases, the hydrogenation of aromatic nitro compounds yields the corresponding aniline compounds almost quantitatively. The catalyst shows especially good activity for the hydrogenation of nitrophenols and nitroanisoles. The catalytic stability was also examined.

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*Keywords:* Palladium complex; Hydrogenation; Nitro compounds; 4-Vinylpyridine; Acrylic acid; Copolymer

## 1. Introduction

Macromolecule-metal complexes as catalysts have been extensively studied for many years, and many excellent results were achieved [1,2]. However, the interaction between the macromolecule ligand and metal remains still not so clear in most cases. Although synthetic catalysts have many advantages, their activity and selectivity as well as working conditions still could not be compared with their natural counterparts, the enzymes. Most research works in the area of macromolecule-metal complexes as catalysts have focused on heterogeneous catalyst systems. Heterogeneous catalysts provide a convenience for easier

separation from the reaction system, while in some cases, a homogeneous catalysts is desired, such as for gaining a clearer understanding on the interaction of macromolecule with metal, and when a hydrogenation product is poorly soluble in the reaction medium, the heterogeneous catalyst might be encapsulated in the product and lose its catalytic activity. Such a situation has been found in the hydrogenation of 4-nitrophenol catalyzed by a heterogeneous catalyst [3].

Catalytic hydrogenation is usually carried out in an alcohol medium to give an ideal performance of the catalyst. For the purpose of making hydrogenation system homogeneous, the polymeric ligand selected for forming the macromolecule-metal complex catalyst should be soluble in an alcohol. Poly(4-vinylpyridine), an alcohol soluble synthetic polymer, has been well investigated for preparing a heterogeneous catalyst and has been proved to have good coordination ability

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with many transition metals. Palladium complexes usually exhibit good catalytic performance for hydrogenation. Therefore, we started our research project with the palladium complex of poly(4-vinylpyridine). Since the palladium complex of 4-vinylpyridine homopolymer is easily aggregated from ethanol forming a gel-like particle, the catalyst provides less surface and the palladium atom could not provide enough activation sites for the substrate and hydrogen [4]. Hence, its catalytic activity is rather poor. Such an aggregation may be due to the strong coordination ability of the pyridine nitrogen atom leading to a formation of crosslinked structure by the inter-molecular chain coordination through the palladium atom. Based on these considerations, several efforts have been made on minimizing the inter-chain interaction through metal complexation. To introduce a spacer within pyridine units in the molecular chain through copolymerization was found to be an effective way. The spacer units introduced should be unable or less able to coordinate with the palladium atom, which contributes to the catalyst in two ways. Firstly, owing to the decrease in the inter-molecular chain interaction, the solubility of the catalyst in ethanol would be greatly improved forming a homogeneous catalytic system. Secondly, owing to the less coordination ability of introduced spacer units, the micro-environment of the palladium atom would be in a better state for the activation of substrate and hydrogen, which would impart a better activity and a unique selectivity to the catalyst. In our previous paper, poly(4-vinylpyridine-*co-N*-vinylpyrrolidone) (PVPN) and its palladium complex (PVPN-Pd) has been found to form a homogeneous catalytic hydrogenation system in ethanol and catalyze the hydrogenation of aromatic nitro compounds to corresponding aniline compounds at room temperature [4].

For gaining a clearer understanding on the interaction of macromolecule with metal, we prepared another copolymer in the present paper, poly(4-vinylpyridine-*co*-acrylic acid) (PVPA), and its palladium complex (PVPA-Pd), which has not been employed as a polymeric ligand to the Pd catalyst for hydrogenation. The PVPA copolymer is a polyampholyte, i.e. containing both basic and acidic units in the polymer chain [5]. In most publications [6–8], it was mentioned that the acrylic acid unit might form inter-polymer complex with the 4-vinylpyridine units through cationic/anionic interaction and hy-

drogen bonding. The formation and structure of an inter-polymer complex have been found to depend on several factors such as the composition of copolymer and conditions such as solvent and temperature. Copolymers with different molar contents of 4-vinylpyridine were synthesized. The palladium complex of PVPA forms a homogeneous system in ethanol.

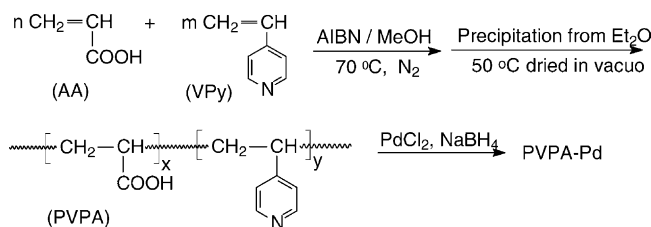
## 2. Experimental

### 2.1. Materials and measurements

4-Vinylpyridine (VPy) was purchased from Merck–Schuchardt and purified by being stirred over solid potassium hydroxide pellets for 24 h followed by distillation under nitrogen at a reduced pressure. Acrylic acid was purified over CuCl and distilled. AIBN was purified by recrystallization twice from methanol. Hydrogen gas (99.999% pure), palladium chloride (99.8% pure) and other chemicals were all purchased from Chinese chemical or reagent companies and directly used as supplied.  $^1\text{H-NMR}$  was recorded on a Bruker DPX-400 NMR spectrometer by using  $\text{CDCl}_3$  as solvent. High performance liquid chromatography (HPLC) analysis was carried out by using a Shimadzu LC-10A liquid chromatograph with a  $\mu$ -Bondapak<sup>TM</sup> C18 column using methanol/water (70/30) as eluent. Elemental analysis was measured on an MOD-1106 instrument (Italy).

### 2.2. Preparation of PVPA

The radical copolymerization of VPy with acrylic acid (AA) conducted under nitrogen protection in the presence of AIBN at 70 °C. The copolymerizability ratios of monomers VPy and acrylic acid are  $r_{\text{VPy}} = 0.0925$  and  $r_{\text{AA}} = 0.879$  [9], respectively. Therefore, for making an even distributed copolymer, the active monomer AA was added dropwise into a methanol solution of the less active monomer VPy with mechanical stirring during the process of polymerization. After 10 h of polymerization, the reaction mixture was poured into excess amount of diethyl ether to precipitate the copolymer. The copolymer was purified twice by reprecipitation of the methanol solution by adding diethyl ether. Several copolymers with different VPy



Scheme 1. Preparation of PVPA copolymer and its palladium complex.

molar contents were prepared. The molar ratio of VPy units in the copolymer PVPA was determined by using elemental analysis and  $^1\text{H-NMR}$ .

### 2.3. Preparation of PVPA-Pd complex

The preparation of PVPA-Pd complex with different Pd contents was conducted in a method similar to that described for the preparation of PVPN-Pd [4]. The procedure for the preparation of PVPA-Pd is illustrated in Scheme 1.

### 2.4. Hydrogenation

Catalytic hydrogenation was carried out in a 50 ml flask with a classical hydrogenation apparatus [10] under mild conditions. For a typical hydrogenation procedure, PVPA-Pd containing 0.02 mmol of Pd, 10 mmol of substrate and 15 ml of absolute ethanol were charged into the flask. The hydrogenation took place under magnetic stirring and an atmospheric hydrogen pressure at 35 °C. The hydrogen uptakes were measured through a hydrogen storage bottle. The hydrogenation product was analyzed by using HPLC.

## 3. Results and discussion

### 3.1. The influence of the molar content of VPy in PVPA

The influence of the molar content of VPy on the hydrogenation rate of nitrobenzene is shown in Fig. 1. It can be seen that an optimum catalytic activity for hydrogenation of nitrobenzene was obtained when the molar content of VPy units in PVPA was 57.5%. When the VPy content in PVPA is higher than 57.5%,

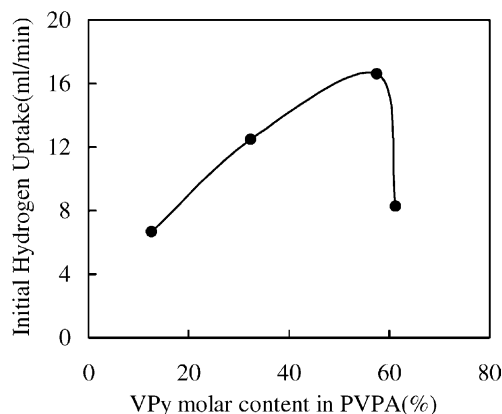


Fig. 1. Hydrogenation of nitrobenzene catalyzed by PVPA-Pd with different VPy molar content in PVPA (10 mmol of substrate, 15 ml of ethanol, 0.02 mmol of Pd, 35 °C and 1 atm  $\text{H}_2$ ).

the dilution of VPy units with AA units would not be sufficient. Hence, the inter-molecular crosslinking through coordination with palladium would not be avoided sufficiently. When the VPy content in PVPA is less than 57.5%, the relative density of hydrogen bonding between VPy and AA would be increased, which would result in the lowering solubility of PVPA in ethanol. On the other hand, the ability of the carboxyl group to coordinate with palladium atom is weaker than that of the pyridine nitrogen. Thus, the proper ratio of the two units would provide a suitable environment for the formation of an active coordination center. It was reported that in a copper complex of VPy-*N*-vinyl-pyrrolidone (NVP) copolymer, the NVP units near VPy units would prohibit VPy from forming a stable complex with copper, giving a more reactive unsaturated complex center for catalytic oxidation [11]. A similar consideration was found for a rhodium complex containing PVPA as the ligand

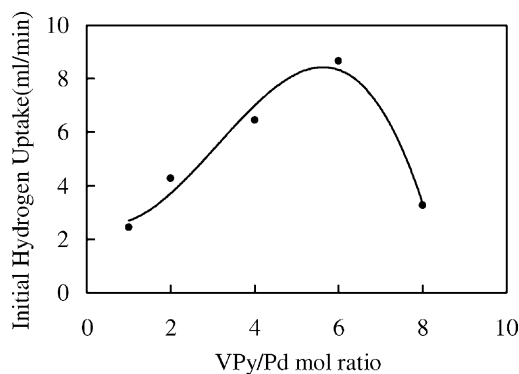


Fig. 2. Hydrogenation of nitrobenzene catalyzed by PVPA-Pd with different VPy/Pd ratios (10 mmol of substrate, 15 ml of ethanol, 0.02 mmol of Pd, 35 °C and 1 atm H<sub>2</sub>).

polymer in catalytic carbonylation of methanol to acetic acid [9]. In the present PVPA-Pd complex, except for the solubility factor discussed above, the molar content of VPy in PVPA much lower or higher than 57.5% may not be in favor of an active coordination center formation.

### 3.2. Optimum VPy/Pd molar ratio

For PVPA-Pd catalyst, as it can be seen from Fig. 2, an optimum catalytic activity in the hydrogenation of nitrobenzene was obtained when VPy/Pd molar ratio was 6. We believe that the coordination of the basic ligand atom nitrogen with palladium was greatly

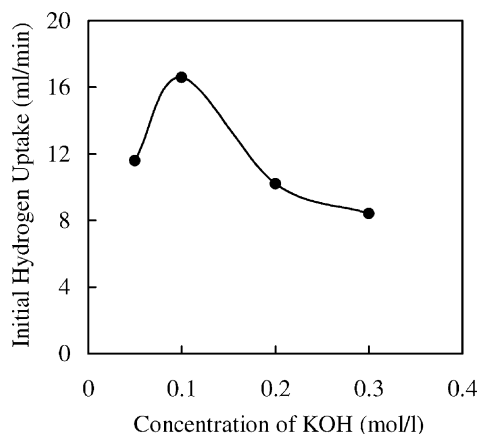


Fig. 4. Hydrogenation of nitrobenzene catalyzed by PVPA-Pd in different concentration of KOH (10 mmol of substrate, 15 ml of ethanol, 0.02 mmol of Pd, 35 °C and 1 atm H<sub>2</sub>).

affected by the introduction of hydrogen bonding and acid/base interaction between VPy and AA.

### 3.3. Influence of alkalis

On a similar manner to PVPN-Pd, the catalytic activity of the PVPA-Pd complex was significantly affected by the addition of a strong alkali such as potassium and sodium hydroxides as illustrated in Fig. 3. However, weak alkali such as potassium carbonate did not make any contribution. Fig. 4 shows the effect

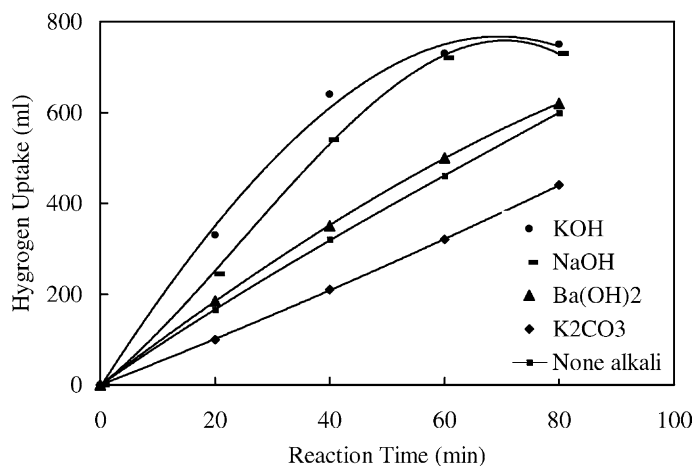


Fig. 3. The activity comparison for the hydrogenation of nitrobenzene catalyzed by PVPA-Pd in different kinds of alkali (10 mmol of substrate, 15 ml of ethanol, 0.02 mmol of Pd, 35 °C and 1 atm H<sub>2</sub>).

Table 1  
Hydrogenation of various substrates catalyzed by PVPA-Pd

Substrate	Initial hydrogen uptake (ml/min)	Product	Yield <sup>a</sup> (%)
Nitrobenzene	16	Aniline	100
4-Nitroaniline	5.5	4-Phenylenediamine	98.1
3-Nitroaniline	4.54	3-Phenylenediamine	97.2
2-Nitroaniline	2.85	2-Phenylenediamine	99.5
4-Nitrophenol	40.0	4-Hydroxyaniline	83.5
3-Nitrophenol	15.6	3-Hydroxyaniline	68.4
2-Nitrophenol	10.8	2-Hydroxyaniline	59.8
4-Nitroanisole	17.8	4-Methoxyaniline	98.8
3-Nitroanisole	16.4	3-Methoxyaniline	95.7
2-Nitroanisole	14.3	2-Methoxyaniline	96.3
4-Nitrobenzaldehyde	0.1	4-Aminobenzaldehyde	80.7

Reaction conditions: 10 mmol of substrate, 0.02 mmol of Pd, 15 ml of ethanol, 0.1 mol/l of KOH, 35 °C, 1 atm H<sub>2</sub>.

<sup>a</sup> Determined by HPLC.

of the concentration of KOH on the catalytic activity of PVPA-Pd, the highest activity was found when the concentration was 0.1 mol/l.

### 3.4. Hydrogenation of various substrates

Table 1 shows the hydrogenation results of different substrates catalyzed by PVPA-Pd. For all the *p*-substituted nitrobenzenes investigated, the order of initial hydrogenation rate was *p*-OH > *p*-OCH<sub>3</sub> > H > *p*-NH<sub>2</sub> > *p*-CHO. Hydroxy and methoxy groups, which may increase the electron density of nitro group, favor the substrate coordination with palladium, while the -CHO group is not favorable to the activation of the nitro group. While the -NH<sub>2</sub> group is also an electron donating group, its hydrogenation rate is even lower than that of nitrobenzene catalyzed by PVPA-Pd. Such an unusual phenomenon must be attributed by a special interaction between the amino groups in the substrate and the pyridine or acid groups in the macromolecule ligand. On the other hand, steric effect may also be an important factor. The comparison of hydrogenation rate of different isomers of nitroaniline gives an order of *p*- > *o*- > *m*-substituted nitrobenzenes.

Table 2 shows that the palladium complex with different polymeric ligands gives totally different catalytic behavior for the hydrogenation of substituted nitrobenzene. MEFO-Pd, a heterogeneous catalyst composed of palladium complex of MgO-supported melamino-formaldehyde polymer [3,12], exhibited excellent activity for the sequential hydrogenation of

Table 2  
Hydrogenation catalyzed by different complexes

Substrate	Initial H <sub>2</sub> uptake (ml/min)			
	Catalyst <sup>a</sup>	MEFO-Pd	PVPN-Pd	PVPA-Pd
Nitrobenzene		11.1	13.3	16.6
4-Nitroaniline		13.0	7.0	5.6
3-Nitroaniline			5.7	4.5
2-Nitroaniline			5.9	2.9
4-Nitrophenol		11.4	1.0	40.0
3-Nitrophenol				15.6
2-Nitrophenol				10.8
4-Nitroanisole		12.2	10.0	17.8
3-Nitroanisole			9.7	16.4
2-Nitroanisole			9.9	14.3
4-Nitrobenzaldehyde		19.0	0.6	0.1

Reaction conditions: 10 mmol of substrate, 0.02 mmol of Pd, 15 ml of ethanol, 35 °C, 1 atm H<sub>2</sub>.

<sup>a</sup> MEFO-Pd: palladium complex of MgO-supported melamino-formaldehyde polymer [3,12]; PVPN-Pd: palladium complex of a random copolymer of 4-vinylpyridine with *N*-vinyl-pyrrolidone [4]; PVPA-Pd: palladium complex of a random copolymer of 4-vinylpyridine with acrylic acid.

4-nitrobenzaldehyde. PVPN-Pd, the palladium complex of a random copolymer of 4-vinylpyridine with *N*-vinyl-pyrrolidone [4], showed higher activity for nitrobenzene than MEFO-Pd. In contrast, PVPA-Pd, the palladium complex of a random copolymer of 4-vinylpyridine with acrylic acid, showed even higher activity for nitrobenzene. Interestingly, neither PVPN-Pd nor PVPA-Pd works for the hydrogenation of nitrobenzaldehyde. PVPA-Pd showed extremely high activity for the hydrogenation of 4-nitrophenol. Therefore, knowledge about the morphological study

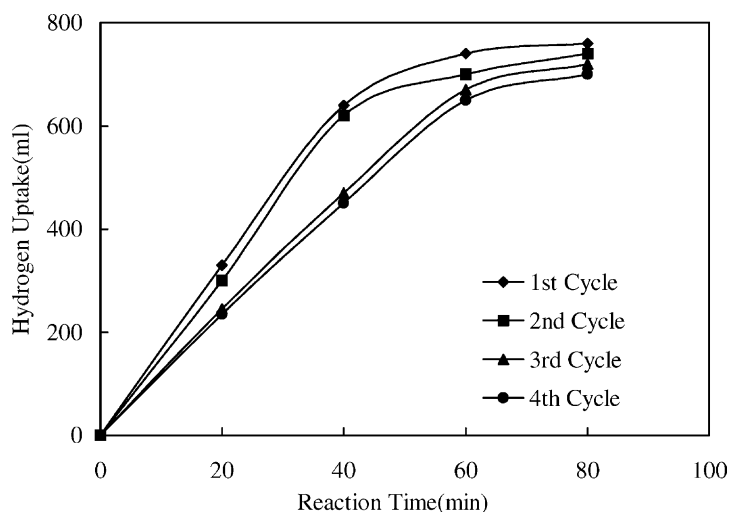


Fig. 5. The activity comparison for the hydrogenation of nitrobenzene catalyzed by PVPA-Pd in each cycle (10 mmol of substrate, 15 ml of ethanol, 0.02 mmol of Pd, 35 °C and 1 atm H<sub>2</sub>).

on these complexes would be quite necessary, which would be a subject of our future work.

### 3.5. Catalytic stability

The catalytic stability was evaluated in terms of the number of reaction cycles. For each reaction cycle, the turnover number of the substrate was 500. The catalyst was kept unseparated, and the substrate for

the next reaction cycle was directly added to the reaction system. Fig. 5 shows the catalyst stability for the hydrogenation of nitrobenzene. After four cycles, the turnover number of nitrobenzene was amounted to 2000 within a total reaction time of 4.5 h, and the hydrogenation rate was decreased a little only in the third cycle, in the fourth cycle the hydrogenation rate was still considerably fast. Fig. 6 shows the catalyst stability evaluation for the hydrogenation of

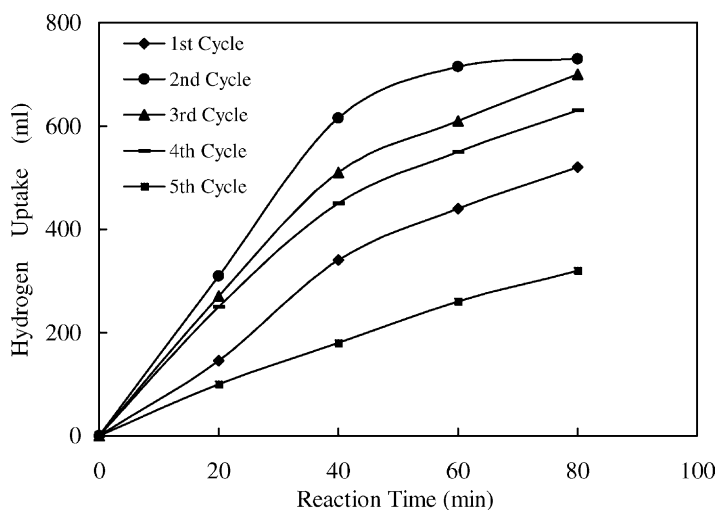


Fig. 6. The activity comparison for the hydrogenation of 4-nitroanisole catalyzed by PVPA-Pd in each cycle (10 mmol of substrate, 15 ml of ethanol, 0.02 mmol of Pd, 35 °C and 1 atm H<sub>2</sub>).

4-nitroanisole. When the turnover number was 2000, the total reaction time was 2.3 h. It was found in these experiments that the 4-nitroanisole hydrogenation rate was the fastest in the second cycle, which is a common phenomenon for some macromolecule-metal catalysts.

#### 4. Conclusion

The palladium complex of poly(4-vinylpyridine-*co*-acrylic acid) with different comonomer ratios were prepared. The complex of PVPA forms a homogeneous system in ethanol. An optimum catalytic activity for hydrogenation of nitrobenzene was obtained when the molar content of VPy units in PVPA was 57.5% and VPy/Pd molar ratio was 6. The catalytic behavior was greatly affected by the type and concentration of added alkalis. The highest hydrogenation rate for nitrobenzene was found in a 0.1 mol/l ethanol solution of potassium hydroxide. In most cases, the hydrogenation of aromatic nitro compounds yields the corresponding aniline compounds almost quantitatively. The catalyst exhibited good stability as examined by using nitrobenzene and 4-nitroanisole as substrates. By just changing the comonomer for the copolymerization with 4-vinylpyridine, the palladium complex showed

very different catalytic behavior and the PVPA-Pd complex showed extremely high activity for the hydrogenation of 4-nitrophenol. Therefore, knowledge about the morphological study on these complexes would be quite necessary.

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