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A homogeneous catalyst made of poly(4-vinylpyridine-*co*-*N*-vinylpyrrolidone)-Pd(0) complex for hydrogenation of aromatic nitro compounds

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Abstract

Poly(4-vinylpyridine-*co*-*N*-vinylpyrrolidone)(VPy-*co*-NVP) and its palladium complex (VPy–NVP–Pd) were prepared. The *palladium* complex was used as catalyst for the hydrogenation of some nitroaromatics. The molar content of VPy units in VPy-*co*-NVP was determined as 31.25% by ^{1}H NMR. VPy–NVP–Pd can be easily resolved in ethanol forming a homogeneous catalytic hydrogenation system together with substrates. The optimum catalytic activity for hydrogenation of nitrobenzene appeared when VPy/Pd molar ratio was 2. The catalytic behavior of the catalyst was found to be greatly affected by the type and concentration of added alkalies. The highest hydrogenation rate for nitrobenzene was found in a 0.1 mol/l ethanol solution of potassium hydroxide. The catalytic stability was examined by using nitrobenzene and 4-nitroanisole as substrates. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic hydrogenation is a very important process in the chemical industry, especially in the production of aromatic aniline compounds from corresponding aromatic nitro compounds. Conventionally, Raney-Ni is widely used as the catalyst in such a hydrogenation process. While, Raney-Ni is very sensitive toward the moisture in air and may cause burning, which is quite dangerous for a hydrogenation plant. On the other hand, macromolecule–metal complexes as catalysts have been extensively investigated in recent years, and many of them have been found suitable for catalyzing the above hydrogenation process with good catalytic activity and selectivity. Most research works have been focused on heterogeneous catalyst systems [1–7] and their results are somewhat exciting. While in some cases, a homogeneous catalyst is desired. For example, when a hydrogenation product is poorly soluble in the reaction medium, the catalyst might be encapsulated in the product and lose its catalytic activity. Such situation has been found in the hydrogenation of 4-

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nitrophenol catalyzed by a heterogeneous catalyst [8]. Therefore, we have investigated a homogeneous catalyst made of macromolecule–palladium complex. The macromolecule selected was a copolymer (VPy-*co*-NVP) made from the free radical copolymerization of 4-vinylpyridine (VPy) with *N*-vinylpyrrolidone (NVP). The copolymer is easily soluble in ethanol and its Cu(II) complex has been used for the oxidation of hydroquinone in methanol/water medium [9]. The palladium complex of poly(4-vinylpyridine-*co*-*N*-vinylpyrrolidone) (VPy–NVP–Pd) can also form a homogeneous system in ethanol. The optimum catalytic activity for the hydrogenation of nitrobenzene was found when VPy/Pd molar ratio was 2 in the catalyst. Several factors affecting the catalytic activity were examined. It was found that the catalytic activity can be greatly improved by adding alkalies. The highest hydrogenation rate for nitrobenzene was found in a 0.1 mol/l ethanol solution of potassium hydroxide. The catalytic behaviors of VPy–NVP–Pd for hydrogenation of various nitroaromatics and the catalytic stability were also examined.

2. Experimental

2.1. Materials and measurements

VPy was purchased from Merck-Schuchardt and purified by being stirred over solid potassium hydroxide pellets for 24 h and distilled under nitrogen at a reduced pressure. NVP was also a Merck-Schuchardt product and was purified by distillation before polymerization. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization twice from methanol, and diethyl sulfoxide (DMSO) was purified by distillation. 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}H NMR (nuclear magnetic resonance) was recorded on a Bruker DPX-400 NMR spectrometer by using $CDCl_3$ as solvent. HPLC (high performance liquid chromatography) analysis was carried out by using a Shimadzu LC-10A liquid chromatograph with μBondapak™ C18 column using methanol/water (70/30) as eluent.

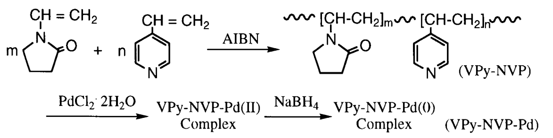
2.2. Catalyst preparation

2.2.1. Preparation of VPy-co-NVP

The radical copolymerization of VPy with NVP was proceeded under nitrogen protection in the presence of AIBN at 65°C. The active monomer VPy was added dropwise into a DMSO solution of the less active monomer NVP during the process of polymerization. After a required time of polymerization, the reaction mixture was poured into excess amount of diethyl ether to precipitate the copolymer. The copolymer was purified twice by reprecipitation from methanol/ether system. The molar ratio of VPy units in the copolymer VPy-*co*-NVP was determined as 31.25% by ^{1}H NMR.

2.2.2. Preparation of VPy–NVP–Pd

For a typical catalyst preparation, 130 mg of VPy-*co*-NVP copolymer [containing 0.038 mmol of VPy monomer unit] was resolved in 5 ml of absolute ethanol, 2.2 ml of $PaCl_2$ $2H_2O$-ethanol solution [containing 0.038 mmol of Pa(II)] was added dropwise under stirring to form a yellowish-brown solution. The reaction mixture was stirred for 5 h to ensure a complete complexation. Then, a stoichiometric amount of sodium borohydride ($NaBH_4$) ethanol solution was added. At the same time, the reaction mixture changed to black indicating a reduction of Pd(II) to Pd(0). After being precipitated from diethyl ether and dried in vacuo, 125 mg of VPy–NVP–Pd [VPy/Pd molar ratio is 1 as calculated] was obtained. The preparation of VPy–NVP–Pd with different VPy/Pd molar ratio was conducted in a similar manner. The procedure for the preparation of VPy-*co*-NVP



Scheme 1. A schematic illustration for VPy–NVP–Pd preparation.

copolymer and VPy–NVP–Pd complex is illustrated in Scheme 1.

2.3. Hydrogenation

Catalytic hydrogenations were carried out with a classical hydrogenation apparatus as described in [Ref. 12] under mild conditions in a 100-ml flask. For a typical hydrogenation procedure, VPy–NVP–Pd containing 0.02 mmol of Pd, 10 mmol of substrate and 15 ml of absolute ethanol were charged in the flask. The hydrogenation was taking place under magnetic stirring and an atmospheric hydrogen pressure at 30°C. The hydrogen uptakes were measured through a hydrogen storage bottle. Product characterization was performed by using HPLC.

3. Results and discussion

3.1. Copolymerization of VPy with NVP

The copolymerizability ratios of monomers VPy and NVP are rVPy = 9.06 and rNVP = 0.05, [10] respectively. Therefore, the less active non-conjugated monomer NVP should be hardly participated in the copolymer at the early stage of the copolymerization with a conjugated monomer VPy. However, as the copolymerization proceeded, the NVP content in the copolymers would be increased as the increased consumption of the less active NVP monomer. Apparently, the composition of the copolymer prepared at the early stage of copolymerization would be greatly different from the copolymer prepared at the final stage. The composition distribution of the copolymer could affect the catalytic activity of its metal complex [11]. Therefore, the copolymerization was carried out by adding the active monomer VPy dropwise to a DMSO solution of the less active monomer NVP in getting a copolymer with narrow composition distribution.

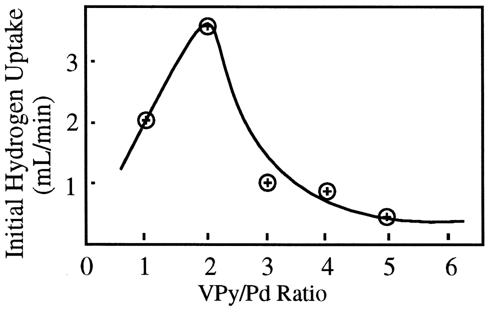


Fig. 1. Hydrogenation of nitrobenzene catalyzed by VPy–NVP–Pd with different VPy/Pd ratios (10 mmol of nitrobenzene; 15 ml of ethanol; 0.02 mmol of Pd; 30°C and 1 atm H_2).

3.2. Optimum VPy / Pd molar ratio

For most catalysts of the macromolecule–metal complexes, there exists an optimum ratio of the ligand atom to the metal atom. It was reported that a Cu(II) complex of VPy-*co*-NVP has a much higher catalytic activity than poly(4-vinylpyridine) homopolymer for the oxidation of hydroquinone. While, poly(*N*-vinyl-

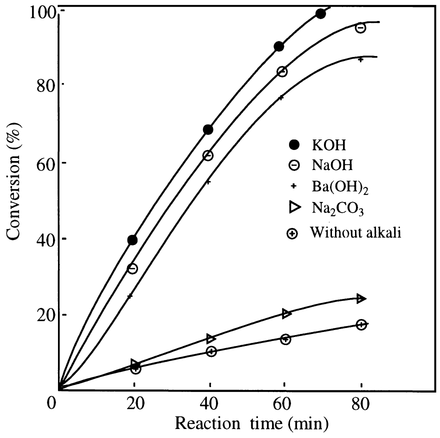


Fig. 2. The activity comparison for the hydrogenation of nitrobenzene catalyzed by VPy–NVP–Pd in different kinds of alkali (10 mmol of substrate; 0.02 mmol of Pd; 15 ml of ethanol; 30°C; 1 atm of H_2; 0.1 mol/l of alkali).

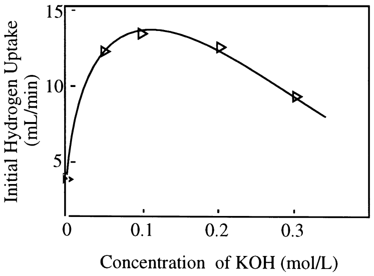


Fig. 3. Hydrogenation of nitrobenzene catalyzed by VPy–NVP–Pd in different concentration of KOH (10 mmol of nitrobenzene; 15 ml of ethanol; 0.02 mmol of Pd; 30°C and 1 atm H_2).

pyrrolidone) homopolymer does not form a complex with Cu(II). It was believed that the NVP units near VPy units in the copolymer would affect VPy not to form a stable complex with Cu(II) and the unstable complex would become a more reactive unsaturated complex center [9]. Therefore, when the content of VPy in VPy-*co*-NVP was determined, the catalytic activity of its palladium complex could be evaluated in terms of VPy/Pd molar ratio. In fact, as it can be found from Fig. 1 that an optimum catalytic activity for VPy–NVP–Pd in the hydrogenation of nitrobenzene appeared when VPy/Pd molar ratio was 2.

3.3. Influence of alkalies

The influence of different alkalies on the hydrogenation rate of nitrobenzene is shown in Fig. 2. It can be seen that the catalytic activity of the complex increased significantly by the addition of strong alkalies such as potassium and sodium hydroxides, whereas sodium carbonate gave almost no influence.

The hydrogenation rate of nitrobenzene can also be altered by the concentration of added potassium hydroxide as shown in Fig. 3. With the concentration of potassium hydroxide increased, the hydrogenation rate of nitrobenzene increased considerably at first, up to a concentration of 0.1 mol/l, and then decreased. This may be due to the removal of protons from the medium by the added hydroxy anion and from the quaternized pyridine with a consequent increase of electron density in the copolymer. This may also increase the electron density on the metal to favor substrate coordination. In the presence of excess alkali, the substrate coordination would be hindered due to the preoccupation of vacant metal coordination sites by hydroxy anion, which resulted in a decreased rate as experimentally observed. This phenomenon is similar to a reported result for the palladium

Table 1
Hydrogenation results of various substrates catalyzed by VPy–NVP–Pd[a]

Substrate	Initial hydrogen uptake (ml/min)	Product	Composition[b] (%)
nitrobenzene	13.3	aniline	100.0
4-chloronitrobenzene	5.1	4-chloroaniline	92.0
2-chloronitrobenzene	3.6	2-chloroaniline	13.6
4-nitrophenol	1.0	4-aminophenol	93.3
4-nitrobenzaldehyde	0.6	4-aminobenzaldehyde	2.0
4-nitroacetophenone	0.3	4-aminoacetophenone	3.0
2-nitroanisole	9.9	2-aminoanisole	98.3
3-nitroanisole	9.7	3-aminoanisole	95.8
4-nitroanisole	10.0	4-aminoanisole	97.5
2-nitroaniline	5.9	2-phenylenediamine	99.0
3-nitroaniline	5.7	3-phenylenediamine	97.0
4-nitroaniline	7.0	4-phenylenediamine	92.0

[a] 10 mmol of substrate; 0.02 mmol of Pd; 15 ml of ethanol; 0.1 mol/l of KOH; 30°C; 1 atm of H_2.

[b] Determined by HPLC.

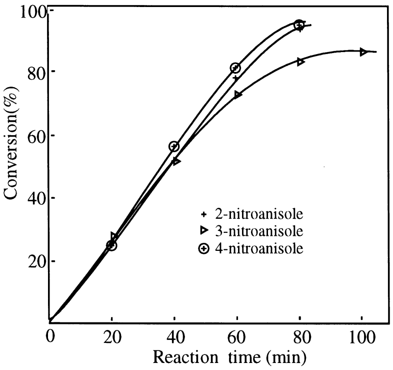


Fig. 4. The activity comparison for the hydrogenation of different isomers of nitroanisole (10 mmol of substrate; 0.02 mmol of Pd; 15 ml of ethanol; 30°C; 1 atm of H_2; 0.1 mol/l of KOH).

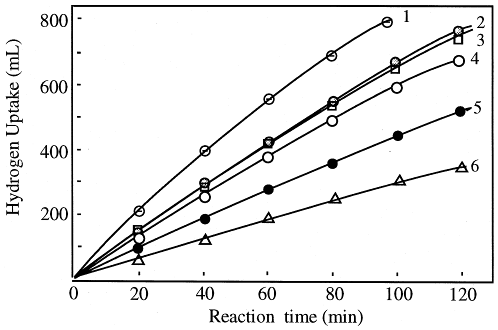


Fig. 6. The activity comparison for the hydrogenation of nitrobenzene catalyzed by VPy–NVP–Pd in each cycle (10 mmol of substrate in each cycle; 0.02 mmol of Pd; 15 ml of ethanol; 30°C; 1 atm of H_2; 0.1 mol/l of KOH).

and platinum complexes of poly(vinylpyridine) homopolymers [13].

3.4. Hydrogenation of various substrates

The catalyst of VPy–NVP–Pd and some substrates can form a homogeneous system in ethanol. Table 1 shows the hydrogenation results of different substrates catalyzed by VPy–NVP–Pd. For all the nitro-compounds, the order of initial hydrogenation rate was nitrobenzene > electron-donating group substituted ≫ electron-withdrawing group substituted nitrobenzenes. Amino and methoxy groups, which may increase the electron density of nitro-group, favor the substrate coordination with palladium, while the electron-withdrawing groups are not favorable to the activation of the nitro-group. On the other hand, steric effect may also be an important factor. The comparison of the hydrogenation rate of different isomers of nitroanisoles and nitroanilines is shown in Figs. 4 and 5, respectively. The two figures gave a similar phenomenon, the rate order at lower conversion was *p*- > *m*- > *o*-substituted nitrobenzenes, while at higher conversion was *p*- > *o*- > *m*-substituted nitrobenzenes.

3.5. Catalytic stability

The catalytic stability was evaluated in terms of the number of reaction cycles and the reaction rate comparison for each cycle. The experi-

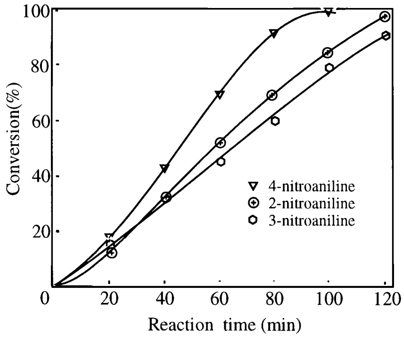


Fig. 5. The activity comparison for the hydrogenation of different isomers of nitroaniline (10 mmol of substrate; 0.02 mmol of Pd; 15 ml of ethanol; 30°C; 1 atm of H_2; 0.1 mol/l of KOH).

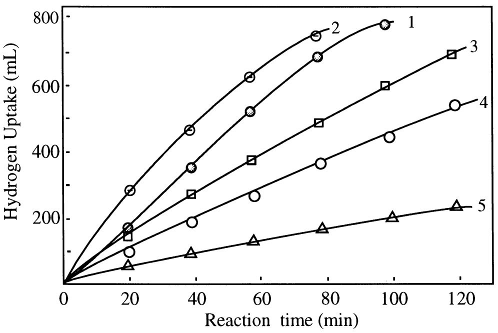


Fig. 7. The activity comparison for the hydrogenation of 4-nitroanisole catalyzed by VPy–NVP–Pd in each cycle (10 mmol of substrate; 0.02 mmol of Pd; 15 ml of ethanol; 30°C; 1 atm of H_2; 0.1 mol/l of KOH).

ment was carried out in an unseparated system. 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. 6 shows the catalyst stability evaluation of the hydrogenation of nitrobenzene. After four cycles, the turnover number of nitrobenzene was amounted to 2000 within a total reaction time of 7.7 h, and the hydrogenation rate was not found to decrease very much. When the turnover number amounted to 3000, the hydrogenation rate was still considerably fast. Fig. 7 shows the catalyst stability evaluation of the hydrogenation of 4-nitroanisole. When the turnover number was 2000, the total reaction time was 8.3 h. The hydrogenation rate was fastest in the second cycle, which is a common phenomenon for some macromolecule–metal catalysts. The reason may be the microstructure of polymer has had slight regulation in the reaction solution [14].

Acknowledgements

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