

Pretreatment of Polymer-Supported Pd-Co and Its Catalytic Activity

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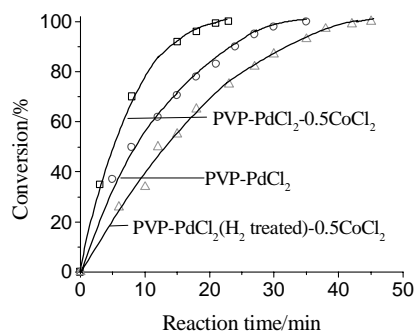
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Abstract: Various pretreatments of poly (N-vinyl-2-pyrrolidone) (PVP) protected palladium-cobalt system result in different catalytic activities in the hydrodechlorination of chlorobenzene.

Keywords: Pretreatment, polymer supported Pd-Co, catalytic activity.

For a heterogeneous catalyst, it is common that different methods of preparation result in a difference in the catalytic activity, although its composition is the same. For a traditional homogeneous catalyst with fixed composition, its catalytic activity usually does not change with the method of preparation. Polymer-supported catalysts are called the heterogenized homogeneous catalysts that combine the merits of homogeneous and heterogeneous catalysts and have been proved to be effective in many reactions¹⁻⁹. In this letter, we show that the method of preparation of the polymer-supported system has significant effect on the catalytic activity.

Figure 1 Effect of addition sequence of CoCl₂ on the catalytic activity



(Reaction conditions are described in note 11.)

PVP supported PdCl₂-0.5CoCl₂ was used as catalyst precursor with the hydrodechlorination of chlorobenzene as a model reaction. The effects of various pretreatments of catalyst precursor on the catalytic activity were investigated. The addition sequence of CoCl₂ displays influence on the catalytic activity of PVP-PdCl₂-0.5CoCl₂ as illustrated in **Figure 1**. It shows that PVP-PdCl₂-0.5CoCl₂ reduced by H₂ exhibits a high catalytic activity, while the PVP-PdCl₂ (H₂ treated)-0.5CoCl₂ formed by the addition of CoCl₂ into PVP-PdCl₂ reduced by hydrogen is not so active, which exhibits even a lower catalytic activity than PVP-PdCl₂ itself. The addition sequence of CoCl₂ changes its effect on the catalytic activity of the PVP

supported Pd. Base on the redox potential, Co^{2+} is not reduced under hydrogen atmosphere and exhibits no catalytic activity, while Pd^{2+} is reduced and forms nano-scale particles which has been confirmed by TEM test. In the first case, Co^{2+} may exist inside the Pd particles and form new catalytic active species with higher catalytic activity. While for PVP-PdCl₂ (H₂ treated)-0.5CoCl₂, Co^{2+} is added into the solution of the already preformed nano-scale Pd particles. In this case, Co^{2+} is dissolved in the solvent and interferes with the catalytic reaction produced by the PVP-Pd system. Reduction temperature for the catalyst also influences the catalytic activity. The experimental results are listed in **Table 1** in which the other reaction conditions are kept the same and only the reduction temperature for PVP-PdCl₂-0.5CoCl₂ system is different. It shows that at a lower reduction temperature, the catalyst results in a higher catalytic activity. At a lower temperature, the reduction of catalyst takes place slower than at a higher reduction temperature and forms smaller particles. As a result, it gives a higher catalytic activity. In addition, the rate of agitation and different reduction methods for PVP-PdCl₂-0.5CoCl₂ also affect the catalytic activity. A strong agitation for the catalyst reduction gives a higher catalytic activity. The activity of catalyst reduced by NaBH₄ is higher than that by H₂.

Table 1 Influence of reduction temperature of catalyst precursor on the catalyst activity

Entry	Reduction temperature /°C	Time for 100% dechlorination of PhCl /min
1	28	20
2	55	23
3	78	42

Other reaction conditions are described in note 11.

In summary, the pretreatment of PVP-PdCl₂-0.5CoCl₂ system strongly influences its catalytic activity in the hydrodechlorination of chlorobenzene.

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References and notes

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10. PVP-PdCl₂-0.5CoCl₂ (0.004 mmol Pd/mL, N/Pd=20) was prepared as follows: To a solution of 0.056 g PdCl₂ in 1 mL 5 mol/L HCl were added 75 mL ethanol and 0.724 g PVP. After stirring at room temperature for 48 h, half amount of CoCl₂ was added and stirred for 24 h.
11. A typical reaction procedure was conducted as follows: 0.41 mmol NaOAc was added into a 30 mL reaction bottle. After flushing with hydrogen, 6.5 mL absolute ethanol was introduced. Under the given reaction conditions, 1 mL catalyst solution was introduced and reduced for 15 min. At 55 °C, 4 mmol PhCl was added at a rate of agitation 1100 rpm. Determined by hydrogen uptake and GC analysis and when the percentage of dechlorination was 100%.

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