

# Catalytic behaviors of the palladium complex of MgO-supported melamino-formaldehyde polymer for hydrogenations of different substrates

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## Abstract

The palladium complex of MgO-supported melamino-formaldehyde polymer (MEFO-Pd) has been prepared and used as catalyst for the hydrogenation of some nitroaromatics and aldehydes. The catalyst showed high activity for the hydrogenation of nitroaromatics producing the corresponding aminoaromatics in most cases. Besides the nitro group reduction, dechlorination was found in the hydrogenation of chloro-substituted nitroaromatics. The hydrogenation of benzaldehyde and furfuraldehyde proceeded in yielding the corresponding alcohols, while the latter catalytic activity is much lower than that for nitro group reduction. Stability of the catalyst is fairly good and can be used for several times without apparent activity loss. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrogenation; Palladium complex; Magnesium oxide support; Melamino-formaldehyde polymer; Catalysis

## 1. Introduction

Catalytic hydrogenation of nitroaromatics is an effective way to produce corresponding aminoaromatics and has been widely used in production scale. The use of heterogeneous catalyst has provided an easy isolation procedure and the product is much cleaner than other reduction techniques. As we previously reported, the palladium complex of MgO-supported melamino-formaldehyde polymer (abbreviated as MEFO-Pd) has been prepared and

used for the hydrogenation of nitroaromatics containing a carbonyl group. The catalyst was found to be very effective for the hydrogenation of nitro group and less effective or not active for the hydrogenation of carbonyl group at ambient conditions. Through such catalysis, the nitro group in *o*-nitrobenzaldehyde, *m*-nitrobenzaldehyde and *p*-nitroacetophenone can be selectively hydrogenated yielding the corresponding aminoaromatic compound, while the nitro and carbonyl groups in *p*-nitrobenzaldehyde can sequentially be hydrogenated forming *p*-aminobenzaldehyde (or its self-condensation product) at first and then *p*-aminobenzyl alcohol (or the self-condensation followed reduction product) [1]. For a better understanding of this

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catalyst, different substrates has been applied for the hydrogenation and the catalyst stability has also been examined.

## 2. Experimental

Hydrogen gas is 99.999% pure. Light MgO (with a specific volume of  $\geq 8$  ml/g), melamine, water solution of formaldehyde (with a concentration of 37.0–40.0%), palladium chloride (99.8%), nitrobenzene, benzaldehyde, furfuraldehyde and *p*-methoxynitrobenzene are all analytically pure. *o*-Chloronitrobenzene, *p*-chloronitrobenzene, *p*-hydroxynitrobenzene and *p*-nitroaniline are all chemically pure. All the chemicals were purchased from Chinese chemical or reagent companies and directly used as supplied.  $^1\text{H}$  NMR was recorded on a Bruker DPX400 NMR spectrometer by using DMSO- $d^6$  as solvent. High performance liquid chromatographic (HPLC) analysis was carried out by using a Shimadzu LC-10A liquid chromatograph with  $\mu\text{Bondapak}^{\text{TM}}$  C18 column using methanol/water (70/30) as eluent.

MEFO-Pd catalyst preparation has been described in Ref. [1]. The catalytic hydrogenation was carried out with a classical hydrogenation apparatus as described in Ref. [2]. For a typical

hydrogenation procedure, MEFO-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 the hydrogen storage bottle. Product analysis were mainly conducted by using HPLC after separating the catalyst through filtration.

## 3. Results and discussion

Table 1 shows the hydrogenation results of different substrates catalyzed by MEFO-Pd. For all the nitro-compounds, the catalyst shows good activity for the hydrogenation of the nitro group. Nitrobenzene, *p*-nitroaniline, *p*-hydroxynitrobenzene and *p*-methoxynitrobenzene were hydrogenated to form the corresponding aniline almost quantitatively. Dechlorination was found in the hydrogenation of chloro substituted nitrobenzenes. The carbonyl group in benzaldehyde and furfuraldehyde can also be hydrogenated forming the corresponding alcohol product, while the reaction rate was fairly slow. All the product composition analysis were carried out by using HPLC after separating the

Table 1  
The hydrogenation results of various substrates catalyzed by MEFO-Pd

Substrate	Initial hydronation uptake (ml/min)	Product	Composition <sup>a</sup> (%)
Nitrobenzene	11.1	aniline	100
<i>p</i> -Chloronitrobenzene	18.8	aniline <i>p</i> -chloroaniline	43.6 56.3
<i>o</i> -Chloronitrobenzene	11.8	aniline <i>o</i> -chloroaniline	39.7 58.4
<i>p</i> -Nitroaniline	13.0	1,4-benzenediamine	100
<i>p</i> -Hydroxynitrobenzene	11.4	<i>p</i> -hydroxyaniline	96.4 <sup>b</sup>
<i>p</i> -Methoxynitrobenzene	12.2	<i>p</i> -methoxyaniline	100
Benzaldehyde	2.1	benzyl alcohol	90
Furfuraldehyde	1.2	furfuryl alcohol	99

10 mmol of substrate; 0.334 g of catalyst, 0.02 mmol of Pd; 15 ml of ethanol; 30°C; 1 atm of H<sub>2</sub>.

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

<sup>b</sup>Determined by  $^1\text{H}$  NMR.

catalyst through filtration except for the hydrogenation product of *p*-hydroxynitrobenzene. *p*-Hydroxylaniline, the hydrogenation product of *p*-hydroxynitrobenzene, is poorly soluble in and easily crystallized from the reaction medium ethanol. Therefore, the product composition was determined by  $^1\text{H}$  NMR.

Conversion curves for the hydrogenation of some nitroaromatics catalyzed by MEFO-Pd are illustrated in Fig. 1. It was realized that the hydrogenation rate of nitrobenzenes with an amino-, hydroxy- or methoxy substituent is faster than the unsubstituted one. From the results we have previously reported [1], it was found that the hydrogenation rate of nitrobenzenes with a carbonyl group catalyzed by the same MEFO-Pd catalyst is in the order of *p*-nitroacetophenone > *p*-nitrobenzaldehyde > *o*-nitrobenzaldehyde > *m*-nitrobenzaldehyde, and all of them are slower than that of the unsubstituted nitrobenzene. Such hydrogenation rate variation may have resulted from the nature of the substituent. Amino-, hydroxy- and methoxy-groups are electron-donating, which may give help to the activation of the nitro-group over the catalyst, while the carbonyl group is electron-withdrawing, which is not favorable to the activation of the nitro-group.

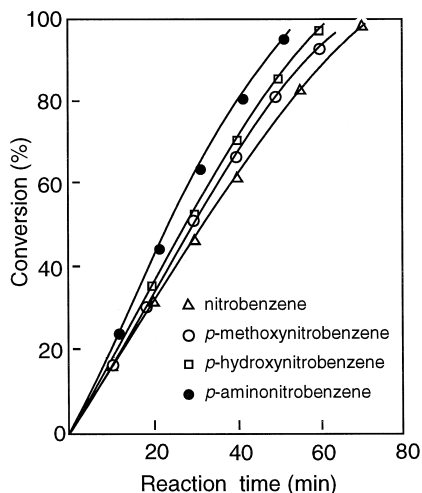


Fig. 1. Hydrogenation of different substrates catalyzed by MEFO-Pd (10 mmol of substrate; 0.02 mmol of Pd; 15 ml of ethanol; 30°C; 1 atm of  $\text{H}_2$ ).

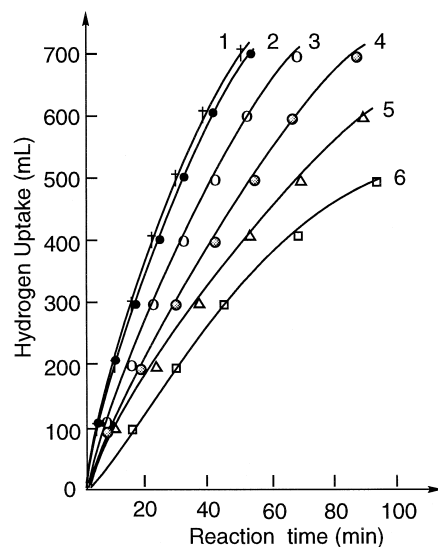


Fig. 2. The activity comparison for the hydrogenation of nitrobenzene catalyzed by MEFO-Pd (10 mmol of substrate in each cycle; 0.02 mmol of Pd; 15 ml of ethanol; 30°C; 1 atm of  $\text{H}_2$ ).

The catalyst stability was evaluated in terms of the number of reaction cycles and the reaction rate comparison for each cycle. The experiment was conducted in an unseparated system. For each reaction cycle, the turnover number of

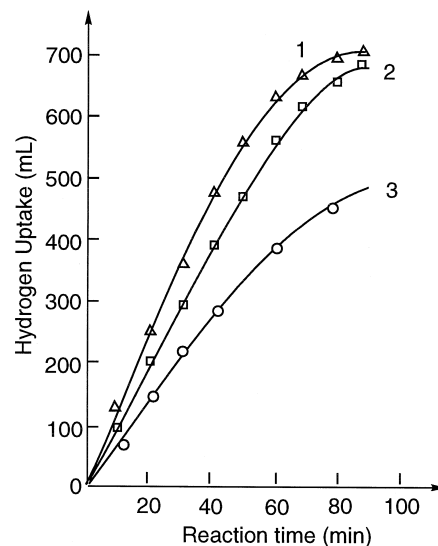


Fig. 3. The activity comparison for the hydrogenation of *p*-hydroxynitrobenzene catalyzed by MEFO-Pd (10 mmol of substrate in each cycle; 0.04 mmol of Pd; 15 ml of ethanol; 30°C; 1 atm of  $\text{H}_2$ ).

the substrate was 250 for *p*-hydroxynitrobenzene, and was 500 for nitrobenzene. The catalyst was kept unseparated, and the substrate for the next reaction cycle was directly added to the reaction system. Fig. 2 shows the catalyst stability evaluation of the hydrogenation of nitrobenzene. After six cycles, the turnover number of nitrobenzene has amounted to 3000 within a total reaction time of 12 h, and the hydrogenation rate was not found to decrease very much. The slight slow-down may be derived from concentration increase of the product and from the bulk increase of the reaction solution, while for the hydrogenation of *p*-hydroxynitrobenzene, as it can be seen from Fig. 3, the drop of the reaction rate was very obvious. The reason could come from the low solubility of the product, *p*-hydroxyaniline, in the reaction medium. As the concentration increases, *p*-hydroxy-

aniline is crystallized from the solution, and the catalyst may also be encapsulated in the product crystals.

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