

## Effect of Calcinated Temperature on the Performance of Nickel Supported on Active Carbon Catalyst for Hydrogenation of *p*-Nitro phenol to *p*-Amino phenol

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The catalytic hydrogenation of *p*-nitro phenol to produce *p*-amino phenol was carried out over the catalyst nickel supported on active carbon. The calcinated temperature was one of the most important technical conditions: temperature higher than 450 °C would result in the reduction of NiO to Ni phase by activated carbon and the loss of support. The surface area and nickel dispersion over catalyst decreased obviously after 450 °C calcinated temperature because of the loss of support and the Ni phase sintering.

**Key Words:** *p*-Nitrophenol, *p*-Aminophenol, Nickel, Active carbon, Calcinated temperature.

### INTRODUCTION

*p*-Amino phenol (PAP) is an important pharmaceutical intermediate for the manufacture of paracetamol, a widely used analgesic and antipyretic drug. Conventionally, *p*-amino phenol is manufactured by iron-acid reduction of *p*-nitro chloro benzene or *p*-nitro phenol, which are multistep processes. The major disadvantage of iron-acid reduction is the generation of large amount of Fe-FeO sludge which causes a serious pollution problem<sup>1,2</sup>. A single-step catalytic hydrogenation of nitro benzene to *p*-amino phenol using supported noble metal catalyst in the presence of aqueous acid medium is gaining more importance because (i) it is a single-step process, (ii) environmentally acceptable, (iii) more efficient since the work up of reaction crude is simple<sup>3</sup>. However, lower selectivity of *p*-amino phenol is a major disadvantage, because the aniline is produced during catalytic hydrogenation of nitro benzene<sup>4</sup>. With the growing demand for *p*-amino phenol, direct catalytic hydrogenation of *p*-nitro phenol to *p*-amino phenol becomes important, because it is an efficient and greener route<sup>5,6</sup>. Up to now, some works have been reported on the liquid phase *p*-nitro phenol hydrogenation over Raney nickel<sup>7</sup>, nano-sized nickel<sup>1,8,9</sup> and several noble metal catalysts such as Pt/C<sup>6,10-12</sup>. However, there are few reports on the catalytic hydrogenation of *p*-nitro phenol over supported nickel catalysts<sup>13,14</sup>. Because of low cost and high catalytic activity, supported nickel catalysts are widely used in various reactions<sup>15,16</sup>. Therefore, this work is attempted to perform the catalytic hydrogenation of

*p*-nitro phenol to *p*-amino phenol over Ni/activated carbon catalysts and the effect of calcinated temperature and K<sub>2</sub>O addition was investigated.

### EXPERIMENTAL

Ni/activated carbon catalyst with a Ni loading of 3.0 wt % was prepared by incipient wetness impregnation method, using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as precursor and a high specific surface area active carbon as support. Ni-K/activated carbon catalyst (loading of Ni and K being 3 wt % and 1 wt %, respectively) was prepared by co-impregnation of active carbon with an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and KNO<sub>3</sub>. Both impregnations lasted for 24 h at room temperature and then the catalysts were dried at 393 K for 12 h and calcined at 450 °C in N<sub>2</sub> atmosphere for 3 h and then reduced by hydrogen at 450 °C for 2 h.

Thermogravimetric analyses (TGA) were carried out on the apparatus TGA92 (Setaram Co., France) under an nitrogen flow of 30 mL min<sup>-1</sup> within the temperature range 20-750 °C at a heating rate of 10 °C/min.

Nickel dispersion was evaluated by means of hydrogen chemisorption. Analysis was carried out on a multi-purpose adsorption apparatus (TP-5080, Tianjin-Xianquan, China). Prior to the chemisorption measurements, 100 mg of each catalyst was reduced with a mixed stream of 5 vol % H<sub>2</sub> in Ar (30 mL/min) at 400 °C for 2 h and it was purged under Ar (30 mL/min) at the same temperature for 0.5 h, the catalyst was cooled to room temperature under a flow of argon (30 mL/min).

Then, H<sub>2</sub> pulses were injected at regular interval times (5 min). Dispersion is calculated using the following equation<sup>17,18</sup> by assuming that one hydrogen atom is adsorbed per nickel atom<sup>19-21</sup>:

$$D (\%) = \frac{2P_{H_2} V_{H_2} M_{Ni}}{RTx_m m_{cat}}$$

with P<sub>H<sub>2</sub></sub>, hydrogen pressure (1.01 × 10<sup>5</sup> Pa); V<sub>H<sub>2</sub></sub>, volume adsorbed (mL); M<sub>Ni</sub>, nickel molar weight (58.7 g/mol); R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup>; T = 295 K; x<sub>m</sub>, nickel loading (3.0 wt %); m<sub>cat</sub>, catalyst weight (0.1 g).

The Brunauer-Emmett-Teller (BET) surface area of the catalysts was measured by nitrogen adsorption at -195.8 °C with a TriStar 3000 Gas Absorption Analyzer (Micromeritics Instrument Co., USA). The samples were degassed at 300 °C for 3 h, under flow of helium prior to analysis.

The catalytic hydrogenation of *p*-nitro phenol to *p*-amino phenol was investigated in a 500 mL stainless steel autoclave equipped with a magnetically driven impeller. After given amounts of Ni/activated carbon (or Ni-K<sub>2</sub>O/activated carbon) catalyst and *p*-nitro phenol in ethanol were introduced, the autoclave was sealed and nitrogen was fed to the reactor and purged three times. Then, nitrogen was replaced with hydrogen and purged three times. The agitation was started and maintained at 800 rpm and the autoclave was heated to 80 °C, under 1.6 MPa H<sub>2</sub>. During the progress of reaction, pressure was kept at 1.6 MPa by periodical introducing hydrogen into the autoclave. Samples were periodically withdrawn to monitor the progress of reaction. At the end of the reaction, the reaction mixture was dissolved in ethanol in order to obtain a homogeneous solution and analyzed to determine the conversions and selectivities. The reactants and products were analyzed by HPLC using a C18 column and a solution of acetonitrile (30 %) in water as eluent.

## RESULTS AND DISCUSSION

In order to understand the effects of calcinated temperature on the catalytic performance, we have studied the *p*-nitro phenol conversion and *p*-amino phenol selectivity on the Ni/activated carbon catalyst calcinated under different temperatures. The results are shown in Fig. 1.

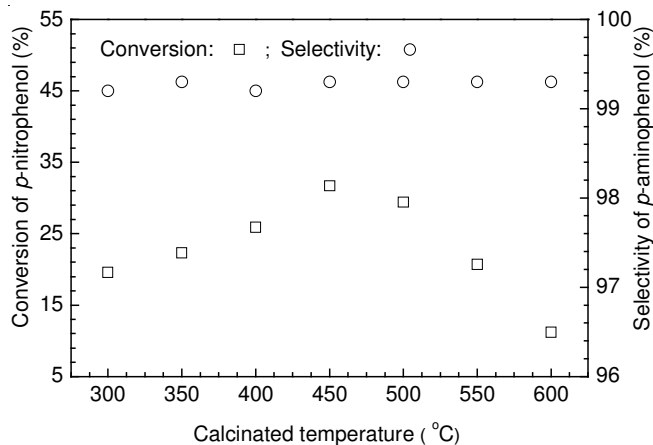


Fig. 1. Performance of catalysts calcinated at different temperatures. Reduced temperature: 450 °C; Reaction conditions: 80 °C, 1.6 MPa; reaction time: 1 h

It is observed that the *p*-nitro phenol conversion increased successively as calcinated temperature increasing before 450 °C (Fig. 1). The *p*-nitro phenol conversion increased from 19.6 % (300 °C) to 31.7% (450 °C). However, it decreased obviously as calcinated temperature increasing after 450 °C. The *p*-amino phenol selectivity did not increase or decrease obviously during the process of catalytic hydrogenation under different calcinated temperatures.

In order to understand the reason for effect of different calcinated temperatures on the catalytic performance, we characterized the catalyst calcinated under different temperatures by TGA, BET and hydrogen chemisorption.

According to the TG-DTG profiles<sup>22</sup> of Ni(NO<sub>3</sub>)<sub>2</sub>/activated carbon in Ar shown in Fig. 2.

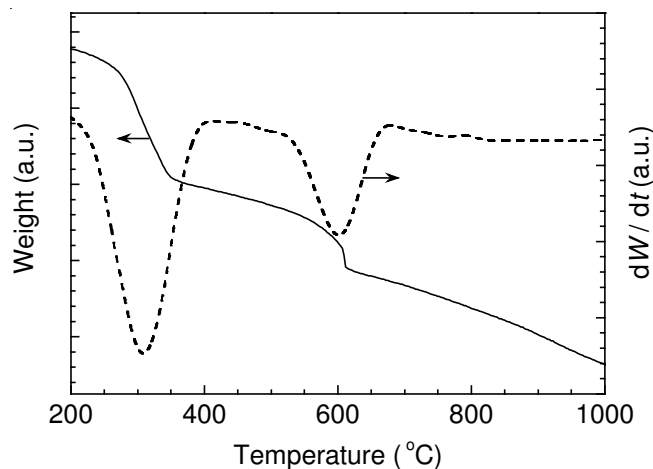


Fig. 2. TG-DTG profiles of Ni(NO<sub>3</sub>)<sub>2</sub>/activated carbon in argon

Two peaks of weight loss are observed: the first peak between 200 and 400 °C is attributed to the decomposition of Ni(NO<sub>3</sub>)<sub>2</sub> to NiO and the second peak between 450 and 650 °C is ascribed to the reduction of NiO to Ni by activated carbon. Therefore, NiO phase began to be reduced by activated carbon after the calcinated temperature higher than 450 °C and the activated carbon support was destroyed seriously.

The surface area of catalyst calcinated at different temperatures was characterized by BET method. The results were shown in Table-1.

Calcinated temperature (°C)	Surface area (m <sup>2</sup> /g)
300	630
350	639
400	647
450	650
500	518
550	445
600	372

It is observed that the surface area of catalysts improved as calcinated temperature increasing before 450 °C. However, the surface area of catalysts began to decrease after 450 °C. According to the result of TGA of Ni(NO<sub>3</sub>)<sub>2</sub>/activated carbon catalyst, the reason for the surface area of catalysts decreasing

after 450 °C may be that the support of active carbon would react with NiO phase as the calcinated temperature increasing, thereby the number of active carbon decreased.

From Table-2, we can see that the nickel dispersion over catalyst improved continuously as calcinated temperature increasing. However, the nickel dispersion over catalyst began to decrease abruptly after the calcinated temperature reached 450 °C. According to the result of TGA of Ni(NO<sub>3</sub>)<sub>2</sub>/activated carbon catalyst, the reason may be that the reaction of NiO phase and activated carbon support resulted in the loss of support and Ni phase is prone to sintering under higher temperature<sup>23</sup>.

TABLE-2  
NICKEL DISPERSION OF CALCINATED CATALYSTS  
UNDER DIFFERENT TEMPERATURES

Calcinated temperature (°C)	Nickel dispersion (%)
300	11.2
350	18.5
400	25.1
450	25.7
500	11.6
550	10.9
600	7.3

## Conclusion

In conclusion, the catalytic hydrogenation of *p*-nitro phenol to *p*-amino phenol over Ni/activated carbon catalyst performed the high conversion and selectivity. During the process of catalyst preparation, the calcinated temperature of Ni(NO<sub>3</sub>)<sub>2</sub>/activated carbon precursor catalyst is a very important factor: calcinated temperature higher than 450 °C would result in the reaction of NiO phase and activated carbon support, which would result in the loss of activated carbon support and the decrease of the surface area and the Ni phase over catalyst is prone to sintering under higher temperature, which would result in the decrease of the nickel dispersion over catalyst. These factors would result in the decrease of hydrogenation performance of Ni/activated carbon catalyst.

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## REFERENCES

1. Y. Du, H.L. Chen, R.Z. Chen and N.P. Xu, *Appl. Catal. A*, **277**, 259 (2004).
2. S.P. Bawane and S.B. Sawant, *Appl. Catal. A*, **293**, 162 (2005).
3. C.V. Rode, M.J. Vaidya, R. Jaganathan and R.V. Chaudhari, *Chem. Eng. Sci.*, **56**, 1299 (2001).
4. A. Deshpande, F. Figueras, M.L. Kantam, K.J. Ratnam, R.S. Reddy and N.S. Sekhar, *J. Catal.*, **275**, 250 (2010).
5. M.J. Vaidya, S.M. Kulkarni and R.V. Chaudhari, *Org. Process Res. Dev.*, **7**, 202 (2003).
6. Y. Du, H.L. Chen, R.Z. Chen and N.P. Xu, *Chem. Eng. J.*, **125**, 9 (2006).
7. H.C. Yao and P.H. Emmett, *J. Am. Chem. Soc.*, **84**, 1086 (1962).
8. R.Z. Chen, Q.Q. Wang, Y. Du, W.H. Xing and N.P. Xu, *Chem. Eng. J.*, **145**, 371 (2009).
9. A.L. Wang, H.B. Yin, H.H. Lu, J.J. Xue, M. Ren and T.S. Jiang, *Catal. Commun.*, **10**, 2060 (2009).
10. N. Bhanudas, H. Subhenjit, S.P. Vadakkethonippurathu and N.G. Narendra, *Catal. Commun.*, **12**, 1104 (2011).
11. Y.C. Chang and D.H. Chen, *J. Hazard. Mater.*, **165**, 664 (2009).
12. H.C. Yao and P.H. Emmett, *J. Am. Chem. Soc.*, **83**, 799 (1960).
13. J. Xiong, J.X. Chen and J.Y. Zhang, *Catal. Commun.*, **8**, 345 (2007).
14. H.H. Lu, H.B. Yin, Y.M. Liu, T.S. Jiang and L.B. Yu, *Catal. Commun.*, **10**, 313 (2008).
15. P.A. Rautanen, J.R. Aittamaa and A.O.I. Krause, *Chem. Eng. Sci.*, **56**, 1247 (2001).
16. M.P. Kapoor and Y. Matsumura, *J. Mol. Catal. A*, **178**, 169 (2002).
17. D. Duprez, *J. Chim. Phys.*, **80**, 487 (1983).
18. A. Baylet, S. Royer, P. Marécot, J.M. Tatibouët and D. Duprez, *Appl. Catal. B*, **81**, 88 (2008).
19. V. Maurice, Yu.A. Ryndin, G. Bergeret, L. Savary, J.P. Candy and J.M. Basset, *J. Catal.*, **204**, 192 (2001).
20. G.A. Martin, P. de Montgolfier and B. Imelik, *Surf. Sci.*, **36**, 675 (1973).
21. R. Stockmeyer, H.M. Conrad, A. Renouprez and P. Fouilloux, *Surf. Sci.*, **49**, 549 (1975).
22. J.F. Ding, Z.F. Qin, X.K. Li, G.F. Wang and J.G. Wang, *J. Mol. Catal. A*, **315**, 221 (2010).
23. S.J. Tauster, *Acc. Chem. Res.*, **20**, 389 (1987).