

Highly Dispersed Palladium on Carbon Nanofibers for Hydrogenation of Nitrocompounds to Amines

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Abstract

The effect of palladium dispersion and nature of the support on catalytic performance in hydrogenation of nitrobenzene to aniline was studied. It was shown that the type of the support and modification of palladium with phosphorus make it possible to stabilize highly dispersed (1.5–2 nm) palladium particles in the metallic state, thus increasing the efficiency of new catalysts.

1. Introduction

The development and study of highly efficient and selective catalysts for hydrogenation of aromatic nitrocompounds to the corresponding amines are of considerable scientific and practical interest because amines are widely used to produce various dyes, medicinal preparations, corrosion inhibitors, antiknock additives in gasolines and motor fuels, etc. [1–5]. The appearance of physical methods for the control of nanoscale properties of supports and active component particles leads to radically new approaches to the synthesis of highly active and selective catalysts.

This is the first work where a highly active catalyst for hydrogenation of nitrobenzene to aniline was synthesized using the nitrogen-doped carbon nanofibers (N-CNFs) with well-characterized properties and surface structure and the modification of palladium with triphenylphosphine. The novel approach made it possible to stabilize palladium particles in a highly dispersed state (1.5–2 nm) with a narrow size distribution. Due to a synergistic effect of two factors (the use of N-CNFs and modification of palladium with triphenylphosphine), the synthesized catalysts are much more active than the analogs reported in the literature.

Recently, we have performed a series of studies

on modification of CNFs with nitrogen atoms and synthesis of catalysts [6–14].

2. Experimental

In this work, CNFs and N-CNFs were examined as supports, while activated carbon and alumina were used for comparison purposes. Palladium was introduced by deposition or impregnation from K_2PdCl_4 and $Pd(OAc)_2$ compounds; for deposition, palladium was modified with triphenylphosphine (PPh_3). Activity of the synthesized catalysts and palladium black was tested in hydrogenation of nitrobenzene by molecular hydrogen. The catalytic testing was carried out by the volumetric method in a static system at a constant atmospheric pressure and a temperature of 40 °C [15].

Results and Discussion

Figure 1 displays the kinetic curves for the volume of absorbed hydrogen (VH_2) versus the reaction time (τ) of nitrobenzene hydrogenation to aniline for the synthesized palladium catalysts. According to their activity, the catalysts can be arranged in the following order: 2% $Pd_{mod}/7\%$ N-CNFs \geq 2% $Pd_{mod}/$ CNFs \gg 4% Pd/Al_2O_3 $>$ Pd-black $>$ 1% $Pd/CNFs$, Table 1.

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Table 1
Properties of palladium catalysts and their activity in hydrogenation of nitrobenzene to aniline

Catalyst	Synthesis method	S_{BET} , m^2/g	$D_{\text{Pd}}^{\text{TEM}}$, nm	Activity, $\text{L H}_2/\text{g Pd} \cdot \text{min}$
2% Pd _{mod} /7%N-CNFs	deposition	230	1.5	13.2
2% Pd _{mod} /CNFs	deposition	190	2.0	11.6
1% Pd/CNFs	deposition	210	10	2.1
4% Pd/C	impregnation	400-500	20	1.8*
4% Pd/Al ₂ O ₃	impregnation	110	25	0.31
Pd-black	reduction by hydrazine	35	30	0.05

* a mean value for known Pd/C catalysts (C – activated carbon [16-18]).

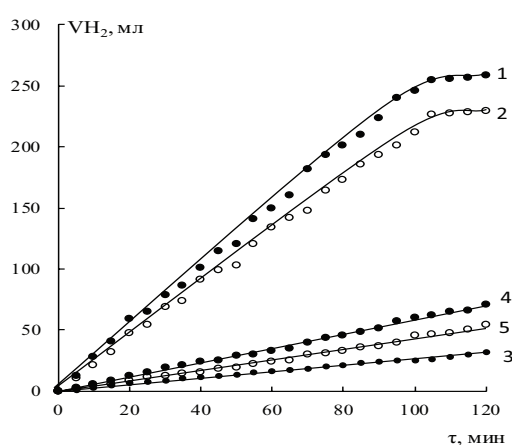


Fig. 1. The kinetic curves for hydrogenation of nitrobenzene on palladium catalysts deposited on different supports: 1 – 2% Pd_{mod}/7% N-CNFs, 2 – 2% Pd_{mod}/CNFs, 3 – 1% Pd/CNFs, 4 – 4% Pd/Al₂O₃, 5 – Pd-black. Weight of the catalyst sample – 10 mg (1-3, 5), 50 mg (4); amount of nitrobenzene – 0.3 mL.

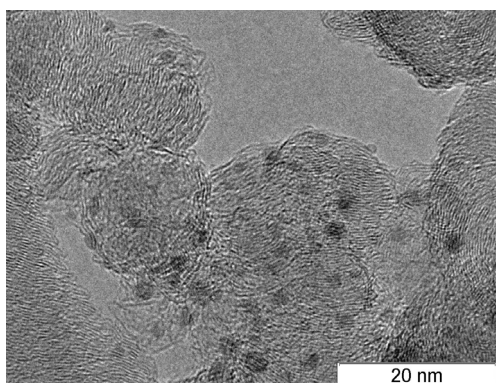


Fig. 2. TEM image of 2% Pd_{mod}/7%N-CNFs.

As seen from Table 1, the particle size of supported palladium varies from 1.5 to 25 nm depending on the type of support and the method of metal deposition. In the most active catalysts supported on CNFs or N-CNFs, the size of palladium particles is 2.0 and 1.5 nm, respectively, Fig. 2.

The high dispersion of palladium in the indicated catalysts is confirmed also by the XPS data displayed in Fig. 3. The Pd3d spectra can be described by two main components with the binding energy $E_b \sim 335.8$ eV and ~ 337.7 - 337.8 eV. The doublet with a lower binding energy is predominant and can be attributed to small clusters of metallic palladium. The component with $E_b(\text{Pd}3d_{5/2}) \sim 337.7$ - 337.8 eV can be assigned to the oxidized palladium particles. The E_b values observed for the components are by ~ 0.5 - 0.8 eV higher than the typical values for metallic and oxidized states of palladium [19]. Such shift of the lines can be caused by the formation of small particles and clusters. In this case, electron relaxation upon photoionization is less efficient than for bulk samples, which is commonly reflected by shifting of the photoelectron line toward higher binding energies [20]. The shift of spectral lines can be related also to a partial encapsulation of the particles by carbon nanofibers. As the samples were synthesized with the use of triphenylphosphine, it cannot be ruled out that the peak in Pd3d spectra with the binding energy 337.7-337.8 eV is partially induced by the formation of palladium compounds with triphenylphosphine [21].

A correlation between palladium particle size in the catalyst and catalytic activity has been found. When the size of Pd particles increases from 1.5 to 30 nm, the catalytic activity decreases by 2.5 orders of magnitude. The formation of highly dispersed Pd particles (1.5-2.0 nm) is caused by their stabilization with triphenylphosphine, which also inhibits the migration of Pd atoms over the support surface and their aggregation. It should be noted that doping of CNFs with nitrogen is accompanied by an additional decrease in the size of palladium particles as compared to undoped CNFs; this confirms the role of nitrogen in increasing the dispersion of metallic particles supported on carbon nanomaterials [22]. Most likely, the high activity of the 1.5-2.0 nm palladium particles is related to a substantial increase in the fraction of sur-

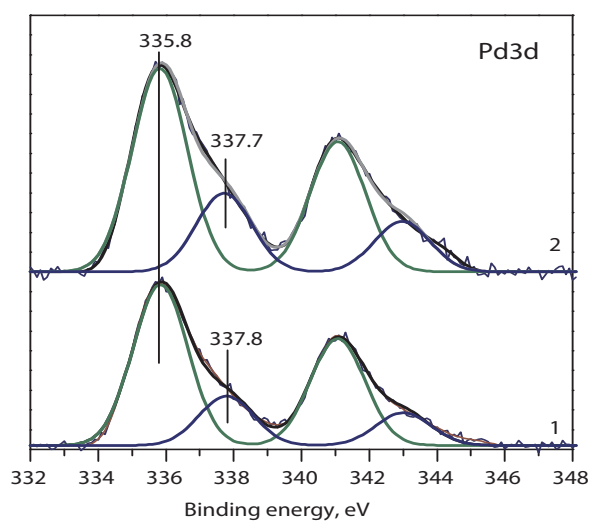


Fig. 3. Pd3d spectra of the samples: 1 – 2% Pd_{mod}/CNFs; 2 – 2% Pd_{mod}/7%N-CNFs.

face Pd atoms (~ 50% for the 2 nm particles), which determine the catalytic activity. For palladium particles with the size of 10-30 nm, the fraction of surface atoms does not change significantly, thus producing only moderate changes in the catalytic properties of other catalysts under consideration.

4. Conclusions

Thus, the use of N-CNFs and modification of palladium with triphenylphosphine enable stabilization of highly dispersed palladium particles in the metallic state. Most probably, these are the factors that determine high activity of the synthesized catalysts in the production of amines by hydrogenation of nitrocompounds.

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References

- [1]. E.A. Gelder, S.D. Jackson and C.M. Lok, *Catal. Lett.* 84 (2002) 205–208.
- [2]. W. Chuntiag, V.G. Dorokhov, G.A. Boiko, B.S. Bal'zhinimaev, and V.V. Barelko, *Dokl. Chem.* 402 (2005) 111–113.
- [3]. I.I. Obraztsova, and O.A. Efimov, *Russ. J. Appl. Chem.* 77 (2004) 511–512.
- [4]. A.I. Kozlov, and V.L. Zbarsky, *Russ. Chem. J.* 50 (2006) 131–139.
- [5]. I.I. Obraztsova, N.K. Eremenko, G.Yu. Simenyuk, and A.N. Eremenko, *Russ. J. Natural and Technical Sciences* 6 (2010) 91–94.
- [6]. A.E. Shalagina, Z.R. Ismagilov, O.Yu. Podyacheva, et al. *Carbon* 45 (2007) 1808–1820.
- [7]. Z.R. Ismagilov, A.E. Shalagina, O.Yu. Podyacheva et al. *Kinetics and Catalysis* 48 (2007) 581–588.
- [8]. Z.R. Ismagilov, A.E. Shalagina, O.Yu. Podyacheva et al. *Carbon* 47 (2009) 1922–1926.
- [9]. O.Yu. Podyacheva, A.N. Shmakov, Z.R. Ismagilov, *Carbon* 52 (2013) 486–492.
- [10]. L. Jia, D.A. Bulushev, O.Yu. Podyacheva, A.I. Boronin, L.S. Kibis, E.Yu. Gerasimov, S. Beloshapkin, I.A. Seryak, Z.R. Ismagilov, and J.R.H. Ross, *J. Catal.* 307 (2013) 94–102.
- [11]. A. Ayusheev, O. Taran, I. Seryak, O. Podyacheva, C. Descorme, M. Besson, L. Kibis, A. Boronin, A. Romanenko, Z. Ismagilov, and V. Parmon, *Appl. Catal., B* 146 (2014) 177–185.
- [12]. O.Yu. Podyacheva, A.N. Stadnichenko, S.A. Yashnik, O.A. Stonkus, E.M. Slavinskaya, A.I. Boronin, A.V. Puzynin, and Z.R. Ismagilov, *Chin. J. Catal.* 35 (2014) 960–969.
- [13]. O.A. Stonkus, L.S. Kibis, O. Yu. Podyacheva, E.M. Slavinskaya, V.I. Zaikovskii, Z.R. Ismagilov, A.S. Noskov, and A.I. Boronin, *Chem. Cat. Chem.* 6 (2014) 2115–2128.
- [14]. O.Yu. Podyacheva, Z.R. Ismagilov, *Catal. Today* 249 (2015) 12–22.
- [15]. I.I. Obraztsova, N.K. Eremenko, and Yu.N. Velyakina, *Kinetics and Catalysis* 49 (2008) 422–427.
- [16]. A.A. Nasibulin, and M.V. Klyuev, *Russ. J. Petrochemistry* 38 (4) (1998) 277–281.
- [17]. Y. Nakao, and S. Fujishige, *J. Catal.* 68 (1981) 406–410.
- [18]. M.V. Klyuev, *Russ. J. Organic Chemistry* 23 (3) (1987) 581–585.
- [19]. T. Pillo, R. Zimmermann, P. Steiner, and S. Hüfner, *J. Phys. Condens. Matter.* 9 (1997) 3987–3999.
- [20]. M.G. Mason, *Electronic structure of supported small metal clusters*, *Phys. Rev. B.* 27 (1983) 748–762.
- [21]. D. Briggs, M.P. Seah, Eds. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, John Wiley & Sons: New York (1983).
- [22]. O.Yu. Podyacheva, Z.R. Ismagilov, A.I. Boronin, L.S. Kibis, E.M. Slavinskaya, A.S. Noskov, N.V. Shikina, V.A. Ushakov, and A.V. Ischenko, *Catal. Today* 186 (2012) 42–47.