Effect of electron beam irradiation on the structure and catalytic performance of Pd nanoparticles supported on Al₂O₃ and carbon.

A. S. Pribytkov, O. P. Tkachenko, A.Yu. Stakheev, K.V. Klementiev^{**}, W. Grunert^{*}, M. W. E. van den Berg^{*}, L.M. Kustov, V. N. Golubeva^{***} и A. V. Tel'nov^{***}

N.D. Zelinsky Institute of Organic Chemistry, Moscow, Russia

^{*} Ruhr-University Bochum, Germany

^{**} Hasylab at DESY, Hamburg, Germany

^{***} RFYaTs-VNIIF, Sarov, Russia

Electron beam irradiation of Pd/Al₂O₃ and Pd/C increased dispersion of Pd nanoparticles and activity in toluene hydrogenation by a factor 3-4.

Nontraditional methods of catalyst activation (plasma treatment, microwave irradiation) attract significant attention of researchers working in the field of heterogeneous catalysis. Use of these non traditional methods allows obtaining of the new types of active sites on the catalyst surface possessing higher activity and/or selectivity.

One of the promising methods is the irradiation catalysts by an electron beam [1 - 3]. However, the literature data on studying an impact of the electron irradiation is scarce. The aim of this study consists in an evaluation of an impact electron beam on the structure and activity of Pd catalysts in toluene hydrogenation.

1%Pd/Al₂O₃ catalyst was prepared using γ -Al₂O₃ (BET surface area 120 m²/g). 1%Pd/C catalyst was prepared from carbon support «Sibunit» (BET surface area 330 m²/g). The catalysts were prepared by incipient wetness impregnation with water solution of [Pd(NH₃)₄]Cl₂ [4].

The activation of the catalysts by the electron beam irradiation was carried out using a LU-10-24 linear resonance electron accelerator in flowing air. The electron energy was 7.7 MeV. The irradiation dose was varied from 120 to 600 Mrad. The catalyst activity in the gas-phase toluene hydrogenation was evaluated using a flow type reactor operated at the atmospheric pressure at 100 – 200⁰C. The analysis of the reaction products was performed by gas chromatography. Before catalytic runs the catalyst was reduced in the catalytic reactor at 250⁰C in the flowing hydrogen.

Apparent activation energy of toluene hydrogenation was evaluated within a range of low toluene conversion (<15%).

EXAFS measurements were carried out at HASYLAB (DESY, Hamburg) on the beam line X1 with the use of the double-crystal Si(311) monochromator. The EXAFS spectra were recorded in transmission mode in He flow at 80 K. Initial catalyst (before reduction) were studied. The catalysts after toluene hydrogenation were studied after the re-reduction in 5%vol H₂ in He in-situ special EXAFS cell at 250°C. Before spectra acquisition the samples were purged with He for 30 min in order to destroy Pd hydride formed in the course of the reductive treatment. The analysis of the EXAFS spectra was performed using the program VIPER for Windows [6]. The details of quantitative information extraction from EXAFS data and Pd particles size estimation are given in [7].

The data on the impact of the electron irradiation on the catalytic activity of 1%Pd/Al₂O₃ catalyst in the gas-phase toluene hydrogenation are given in Table 1. It is evident, that the catalyst activity is significantly improved with increasing irradiation dose from 10 to 600 Mrad. The toluene conversion at 200 °C increases from 32 % over parent catalyst to 58 and 100% with increasing electron irradiation dose to 240 and 600 Mrad respectively. Noteworthy that apparent activation energies of toluene hydrogenation for the parent catalyst and e-beam irradiated samples are essentially identical (49.3 – 51.7 kJ/mol).

Similar results were obtained for 1%Pd/C catalysts. For these catalysts we also observed an enhancing in the toluene conversion with increasing irradiation dose. The toluene conversion at 200°C increases from 22% for initial catalyst to 35% for the catalyst irradiated by 120 Mrad and to 100% for catalyst after irradiation with the dose of 600 Mrad. Note that apparent activation energies of toluene hydrogenation are also similar for irradiated and parent catalysts.

Our preliminary study of a stability of the observed effect indicates that “time-on-stream” behavior of irradiated catalysts is rather stable. The observed enhancement of the catalyst activity caused by e-beam irradiation was retained during 20h of reaction performed at 200°C.

It is noteworthy that the catalysts were prepared using [Pd(NH₃)₄]Cl₂ complex. Therefore we can expect that some deviations in the activity may result from chlorine presence in the catalysts. However XPS study of the catalysts after e-

beam irradiation and reduction treatment indicates that chlorine is not detected on the catalyst surface. Therefore we can presume that chlorine does not significantly affect the catalytic properties of the catalysts [5].

Low temperature N₂ BET measurements of parent and irradiated Pd/Al₂O₃ and Pd/C catalyst indicates that total surface area remains constant (120 and 330 m²/g respectively) and was not affected by irradiation with electron beam.

In order to reveal a reason of the enhanced catalytic activity of irradiated samples we studied structure of metal Pd particles in irradiated and parent samples after catalytic experiments by EXAFS. EXAFS spectra of 1%Pd/Al₂O₃ catalysts reduced at 250°C are shown in Fig 1. The peak at ~ 2.2 Å (uncorrected distance), which corresponds to Pd-Pd distance, dominates in the spectra of both samples indicating a complete reduction of Pd species to metallic state.

It is important that the intensity of this peak is notably lower in the case of irradiated samples and gradually diminishes with increase of the irradiation dose. A calculation of an average Pd coordination number and Pd particles size on the basis of EXAFS data indicated that increasing of the irradiation dose results in the significant enhancement of Pd dispersion: the Pd particles size decreases from 12.5 to 8.5 Å. The similar effect was observed for 1%Pd/C catalysts (table 2).

The results obtained demonstrated that a preliminary electronic irradiation of Pd/Al₂O₃ and Pd/C resulted in an increase of Pd particles dispersion upon the reduction of the catalyst with hydrogen. We can hypothesize that increasing Pd particles dispersion leads to the observed the activity in toluene hydrogenation. This is a tentative suggestion since enhancement of the catalyst activity may be significantly effected by changes in metal-support interaction caused by electron beam irradiation.

In order to find out an origin of the enhancement of Pd dispersion we studied a catalyst after the electron beam irradiation but before their reduction with hydrogen.

EXAFS spectra of the initial of 1%Pd/Al₂O₃ and the catalyst irradiated by with 120 Mrad electron beam dose are given in Fig 2. In the EXAFS spectra of the initial samples we observed the peak at distance < 1.6 – 1.8 Å which is indicative of a presence of oxygen atoms in a close vicinity to Pd. It is noteworthy that a signal which corresponds to Pd-Pd distance in this spectrum of the initial catalyst did not observe. EXAFS data of unreduced samples suggest that 4-5 oxygen atoms are the

nearest neighbors of the central Pd atom, 1-2 at a distance of 2.07-2.08 Å, others are at a distance of 2.19-2.22 Å (table 2).

However, after the electron beam irradiation an additional peak at the distance about 2.3 Å appeared. This peak is characteristic of Pd-Pd distance in metal Pd. The similar results were obtained for Pd/C sample. Calculations indicated that in irradiated by e-beam samples 2-3 Pd atoms at a distance of 2.74-2.75 Å are the nearest neighbors of the central Pd atom. The presence of these Pd atoms in first coordination shell points to a partial reduction of Pd during irradiation process and a formation of small metallic Pd particles with formal average diameter of 4-5 Å (despite the fact that irradiation was performed in the flowing air in the absence of reductants).

According to the results obtained we conclude that the pre-activation of 1%Pd/Al₂O₃ and 1%Pd/C catalysts by electron beam irradiation results in a partial reduction of Pd and formation of metal particles of high dispersion. It is possible to hypothesize that Pd particles formed on upon irradiation may play a role of nucleation sites in the course of the reduction of the catalysts with hydrogen. As a result, Pd dispersion increases, which in turn leads to an increase in the catalyst activity.

ACKNOWLEDGEMENT

The support of the International Science and Technology Center ISTC-1764 Grant is gratefully acknowledged.

Thank is due to HASYLAB at DESY for an opportunity to EXAFS measurements.

REFERENCES

1. Zhong-Yong Yuan, Wuzong Zhou, Viorica Parvulescu, Bao-Lian Su // J. Electron Spectrosc. Relat. Phenom. 2003, V. 129, p. 189.
2. Jin Jun, Jo-Chun Kim, Joong-Hyeok Shin, Ki-Wan Lee, Young Soon Baek. // Radiat. Phys. Chem. 2004. 71 (6). p.1095-1101
3. Muska V., Otahal B., Silber R. // Radiat. Phys. Chem. 2002, V. 65, p.177.
4. A. Yu. Stakheev, G. N. Baeva, N. S. Telegina, A. B. Volynsky, L. M. Kustov, Kh. M. Minachev.// Mendeleev Comm.. 2000, N 2, p. 99.
5. A.S. Pribytkov, G. N. Baeva, N. S. Telegina, A.L. Tarasov, A. Yu. Stakheev, L. M. Kustov, A.V. Tel'nov, V.N. Golubeva, Kinetics and catalysis, 2006, 47, 4, 1
6. K.V. Klementiev VIPER for Windows (Visual Processing in EXAFS Researches), freeware, www.desy.de/~klmn/viper.html
7. A.Yu. Stakheev, O.P. Tkachenko, G.N. Baeva, T.R. BruevaK.V. Klementiev, W. Grunert, L.M. Kustov. *Russ.Chem.Bull.*, 2004, 3, p.502.

Таблица 1. The effect of irradiation dose on the catalytic activity of Pd/Al₂O₃ and Pd/C catalysts in the toluene hydrogenation at 200°C.

Irradiation dose, Mrad	Toluene conversion, %	Apparent E _{act} , kJ/mol
Pd/Al ₂ O ₃		
0	32	51.7 +/- 1.5
240	58	49.3 +/- 1.5
600	100	50.5 +/- 1.5
Pd/C		
0	22	52.6 +/- 1.6
120	35	51.4 +/- 1.6
240	100	50.8 +/- 1.6
600	100	51.1 +/- 1.6

Таблица 2. EXAFS results for 1%Pd/Al₂O₃ and 1%Pd/C irradiated catalysts, reduced at 250 °C.

Irradiation dose, Mrad	Path	r (Å)	CN	D _{Pd cluster} (Å)
1% Pd/Al ₂ O ₃				
as received	Pd-Pd	2.757 ± 0.001	8.1 ± 0.2	12.5 ± 0.7
120 Mrad	Pd-Pd	2.745 ± 0.002	7.2 ± 0.2	10.0 ± 0.5
600 Mrad	Pd-Pd	2.745 ± 0.019	6.4 ± 0.2	8.5 ± 0.3
1% Pd/C				
as received	Pd-Pd	2.740 ± 0.002	10.6 ± 0.4	35.2 ± 14
120 Mrad	Pd-Pd	2.742 ± 0.002	9.9 ± 0.3	24.6 ± 5.4
600 Mrad	Pd-Pd	2.743 ± 0.002	9.5 ± 0.3	21.4 ± 3.2

Таблица 3. EXAFS results for 1%Pd/Al₂O₃ and 1% Pd/C irradiated catalysts before reduction procedure.

Irradiation dose, Mrad	Path	r (Å)	CN	D _{Pd cluster} (Å)
1% Pd/Al ₂ O ₃				
as received	Pd-O	2.079 ± 0.014	1.7 ± 0.3	-
	Pd-O	2.216 ± 0.012	2.0 ± 0.3	-
120 Mrad	Pd-O	2.067 ± 0.002	2.3 ± 0.5	-
	Pd-O	2.201 ± 0.017	2.6 ± 0.5	-
	Pd-Pd	2.743 ± 0.007	3.4 ± 0.5	5.2 ± 0.4
600 Mrad	Pd-O	2.069 ± 0.023	1.2 ± 0.4	
	Pd-O	2.189 ± 0.013	2.4 ± 0.4	
	Pd-Pd	2.748 ± 0.017	1.7 ± 0.5	4.1 ± 0.3
1% Pd/C				
as received	Pd-O	2.072 ± 0.003	1.4 ± 0.5	-
	Pd-O	2.223 ± 0.001	3.3 ± 0.5	-
600 Mrad	Pd-O	2.081 ± 0.003	0.7 ± 0.4	
	Pd-O	2.223 ± 0.001	3.3 ± 0.4	
	Pd-Pd	2.740 ± 0.003	0.8 ± 0.4	3.5 ± 0.3

Fig.1. Fourier transform of the Pd K-edge EXAFS spectra of the reduced 1%Pd/Al₂O₃ sample: initial (solid), irradiated by e-beam 600 Mrad (dash dot) and Pd-foil (dot).

Fig. 2. Fourier transform of the Pd K-edge EXAFS spectra of the unreduced 1%Pd/Al₂O₃ sample: initial (solid), irradiated by e-beam 120 Mrad (dash dot) and Pd-foil (dot).