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Effect of electron beam-irradiation on the structure and catalytic performance of Pd nanoparticles supported on Al_2O_3 and carbon

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The electron-beam irradiation of Pd/Al_2O_3 and Pd/C increased dispersion of Pd nanoparticles and activity in toluene hydrogenation by a factor of 3–4.

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

A promising method is the irradiation of catalysts by an electron beam.[1–3] The aim of this work was to study the effect of an electron beam on the structure and activity of Pd catalysts in toluene hydrogenation.

The 1% Pd/Al_2O_3 catalyst was prepared using γ-Al_2O_3 (BET surface area of 120 $m^2\,g^{-1}$). The 1% Pd/C catalyst was prepared from the carbon support Sibunit (BET surface area of 330 $m^2\,g^{-1}$). The catalysts were prepared by incipient wetness impregnation with an aqueous solution of $[Pd(NH_3)_4]Cl_2$.[4]

The activation of the catalysts by 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 atmospheric pressure and 100–200 °C. The analysis of the reaction products was performed by gas chromatography. Before catalytic runs the catalyst was reduced in the catalytic reactor at 250 °C in flowing hydrogen. The apparent activation energy of toluene hydrogenation was evaluated at low toluene conversions (< 15%).

The 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 a He flow at 80 K. Initial catalysts (before reduction) were studied. The catalysts after toluene hydrogenation were studied after re-reduction in 5 vol% H_2 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 VIPER program for Windows.[6] The details of quantitative information extraction from EXAFS data and Pd particles size estimation are given elsewhere.[7]

The data on the impact of electron irradiation on the catalytic activity of the 1% Pd/Al_2O_3 catalyst in 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. Toluene conversion at 200 °C increases from 32% over the parent catalyst to 58 and 100% with increasing electron irradiation doses to 240 and 600 Mrad, respectively. Note that the apparent activation energies of toluene hydrogenation for the parent catalyst and electron-irradiated samples are identical (49.3–51.7 kJ mol^{-1}).

Similar results were obtained for 1% Pd/C catalysts. We also observed an enhancing in the toluene conversion with increasing irradiation dose. The toluene conversion at 200 °C increases from 22% for the initial catalyst to 35% for the catalyst irradiated

Table 1 The effect of irradiation dose on the catalytic activity of Pd/Al_2O_3 and Pd/C catalysts in toluene hydrogenation at 200 °C.

Catalyst	Irradiation dose/ Mrad	Toluene conversion (%)	Apparent E_{act}/ kJ mol^{-1}
Pd/Al_2O_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

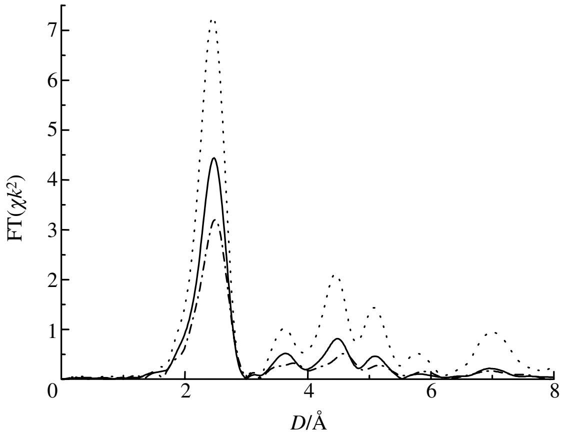

Figure 1 Fourier transform of the Pd K-edge EXAFS spectra of the reduced 1% Pd/Al_2O_3 sample: initial (solid), irradiated at 600 Mrad (dash dot) and Pd foil (dot).

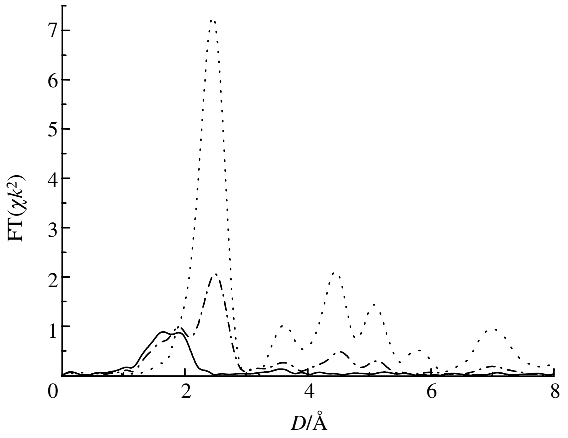

Figure 2 Fourier transform of the Pd K-edge EXAFS spectra of the unreduced 1% Pd/Al_2O_3 sample: initial (solid), irradiated at 120 Mrad (dash dot) and Pd foil (dot).

at 120 Mrad and to 100% for the catalyst after irradiation at 600 Mrad. Note that apparent activation energies of toluene hydrogenation are also similar for irradiated and parent catalysts.

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

It is noteworthy that the catalysts were prepared using the $[Pd(NH_3)_4]Cl_2$ complex. Therefore, we can expect that some deviations in the activity may result from the presence of chlorine in the catalysts. However, the XPS study of the catalysts after electron irradiation and reduction 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}

The low-temperature N_2 BET measurements of parent and irradiated Pd/Al_2O_3 and Pd/C catalysts indicate that the total surface area remains constant (120 and 330 $m^2\,g^{-1}$, respectively) and was not affected by irradiation with an electron beam.

In order to reveal a reason for the enhanced catalytic activity of irradiated samples, we studied the structure of Pd metal particles in irradiated and parent samples after catalytic experiments by EXAFS. The EXAFS spectra of 1% Pd/Al_2O_3 catalysts reduced at 250 °C are shown in Figure 1. The peak at ~2.2 Å (uncorrected distance), which corresponds to the Pd–Pd distance, dominates in the spectra of both samples indicating a complete reduction of Pd species to a metallic state.

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

The results demonstrated that the preliminary electron irradiation of Pd/Al_2O_3 and Pd/C resulted in an increase of Pd particle dispersion upon the reduction of the catalyst with hydrogen. We can hypothesise that increasing Pd particles dispersion leads to the observed activity in toluene hydrogenation. This is a tentative suggestion since the enhancement of catalyst activity may be significantly affected by changes in metal-support interactions caused by electron-beam irradiation.

Table 2 EXAFS results for 1% Pd/Al_2O_3 and 1% Pd/C irradiated catalysts reduced at 250 °C (path, Pd–Pd).

Catalyst	Irradiation dose/Mrad	r/Å	CN	$D_{\text{Pd cluster}}$/Å
1% Pd/Al_2O_3	as received	2.757±0.001	8.1±0.2	12.5±0.7
	120	2.745±0.002	7.2±0.2	10.0±0.5
	600	2.745±0.019	6.4±0.2	8.5±0.3
1% Pd/C	as received	2.740±0.002	10.6±0.4	35.2±14
	120	2.742±0.002	9.9±0.3	24.6±5.4
	600	2.743±0.002	9.5±0.3	21.4±3.2

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

The EXAFS spectra of the initial 1% Pd/Al_2O_3 and the catalyst electron-irradiated at 120 Mrad are given in Figure 2. In the EXAFS spectra of the initial samples, we observed a peak at a distance of < 1.6–1.8 Å, which is indicative of the presence of oxygen atoms in a close vicinity to Pd. Note that a signal, which corresponds to the Pd–Pd distance in this spectrum of the initial catalyst, was not observed. EXAFS data of unreduced samples suggest that 4–5 oxygen atoms are the nearest neighbours of the central Pd atom, 1–2 at a distance of 2.07–2.08 Å, the others are at a distance of 2.19–2.22 Å (Table 2).

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

According to the results obtained, we conclude that the preactivation of 1% Pd/Al_2O_3 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 hypothesise that Pd particles formed 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.

Table 3 EXAFS results for 1% Pd/Al_2O_3 and 1% Pd/C irradiated catalysts before reduction.

Catalyst	Irradiation dose/Mrad	Path	r/Å	CN	$D_{\text{Pd cluster}}$/Å
1% Pd/Al_2O_3	as received	Pd–O	2.079±0.014	1.7±0.3	—
		Pd–O	2.216±0.012	2.0±0.3	—
	120	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	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	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

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