ISSN 0023-1584, Kinetics and Catalysis, 2006, Vol. 47, No. 5, pp. 765–769. © MAIK "Nauka/Interperiodica" (Russia), 2006.
Original Russian Text © A.S. Pribytkov, G.N. Baeva, N.S. Telegina, A.L. Tarasov, A.Yu. Stakheev, A.V. Tel'nov, V.N. Golubeva, 2006, published in Kinetika i Kataliz, 2006, Vol. 47, No. 5, pp. 788–792.

Effect of Electron Irradiation on the Catalytic Properties of Supported Pd Catalysts

A. S. Pribytkov[a], **G. N. Baeva**[a], **N. S. Telegina**[a], **A. L. Tarasov**[a],
A. Yu. Stakheev[a], **A. V. Tel'nov**[b], **and V. N. Golubeva**[b]
[a] *Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
[b] *Russian Federal Nuclear Center, All-Russia Research Institute of Experimental Physics,*
Sarov, Nizhegorodskaya oblast, 607200 Russia
e-mail: st@ioc.ac.ru

Received December 5, 2005

Abstract—The effect of electron irradiation on the properties of the systems 1% Pd/C, 1% Pd/Al_2O_3, and 1% Pd/TiO_2 is studied in gas-phase and liquid-phase toluene hydrogenation. An increase in the irradiation dose to 120–900 Mrad increases the catalytic activity by a factor of 2–8 relative to that of the original system. XPS data for the Pd/C catalyst suggest that, after irradiation with high-energy electrons, the metal particles are stabilized on the surface of the carbon support, their degree of dispersion is increased, and their sintering is suppressed. These inferences are consistent with the observed changes in catalytic properties.

DOI: 10.1134/S0023158406050168

INTRODUCTION

Along with conventional thermal treatment, unconventional activation procedures are finding increasing use in the activation of heterogeneous catalysts. Thermal treatment and high-temperature reduction and oxidation in various gases do not often provide the desired activity, selectivity, and stability of a catalyst, because such treatments produce active sites varying widely in nature and strength, including sites catalyzing undesired side reactions.

A possible way of solving this problem is to take unconventional approaches to the activation of heterogeneous systems at the preparation stage in order to change the catalyst activity and selectivity. These approaches include the treatment of a catalyst with low-temperature plasmas of various origins (glow-discharge plasma, microwave afterglow plasma, or barrier discharge), microwave irradiation, gamma irradiation, and exposure to a neutron or electron beam [1–7].

Irradiation with accelerated electrons is one of the least studied methods. Note that, when a catalyst is exposed to a high-energy electron beam, the combined physical and chemical effect of accelerated electrons can produce new types of active sites with unusual and valuable catalytic properties, such as enhanced activity and stability [8–12].

Here, we report a study of the effect of high-energy electron irradiation on the catalytic properties and structure of palladium catalysts. These systems are chosen because highly active and selective palladium catalysts are widely used in commercial hydrogenation reactions [13].

EXPERIMENTAL

Palladium catalysts supported on graphitized carbon Sibunit (330 m^2/g), alumina (79.4 m^2/g), and titania (48.5 m^2/g) were studied. Palladium was supported by incipient-wetness impregnation from a solution of the ammine complex $[Pd(NH_3)_4]Cl_2$ at room temperature.

Catalysts were exposed to the electron beam of an LU-10–20 linear resonance accelerator in an air flow. The electron beam consisted of 3.8-μs-long pulses. The pulse-repetition frequency was 1000 Hz. The mean electron energy was 7.7 MeV. The irradiation dose was varied by changing the sample exposure time (Table 1). The dose was monitored by measuring the accelerator current with a digital current integrator. Furthermore, the irradiation dose was measured on the sample surface.

The catalytic activity of 1% Pd/C, 1% Pd/Al_2O_3, and 1% Pd/TiO_2 in gas-phase toluene hydrogenation was studied in a flow reactor under atmospheric pressure in

Table 1. Irradiation dose as a function of irradiation time for the Pd/C catalyst

Electron irradiation time, s	Dose, Mrad
0	0
111	30
610	120
960	240
3000	600
4500	900

Table 2. Effect of the irradiation dose on the activity of the catalysts Pd/C, Pd/Al_2O_3, and Pd/TiO_2 in liquid-phase toluene hydrogenation at 95°C

Irradiation dose, Mrad	Toluene conversion, %
Pd/C	
0	4.3
240	10.7
900	19.9
Pd/Al_2O_3	
0	0.9
240	3.3
600	3.3
Pd/TiO_2	
0	2.1
240	3.3
900	16.1

Table 3. Effect of the irradiation dose on the activity of the catalysts Pd/C, Pd/Al_2O_3, and Pd/TiO_2 in gas-phase toluene hydrogenation at 160°C

Irradiation dose, Mrad	Toluene conversion, %
Pd/C	
0	15.0
240	30.5
900	86.9
Pd/Al_2O_3	
0	22.1
240	29.0
600	39.5
Pd/TiO_2	
0	11.3
240	19.1
900	27.5

the temperature range 100–200°C. The initial sample and samples irradiated with doses of 240, 600, and 900 Mrad were examined.

A 0.20- to 0.63-mm fraction of a catalyst (0.5 g of Pd/C, 0.35 g of Pd/Al_2O_3, or 0.35 g of Pd/TiO_2) was loaded to the reactor.

Before hydrogenation, the catalysts were reduced in a hydrogen flow at 200°C for 1 h. Hydrogen from a cylinder was purified to remove traces of O_2 and H_2O by passing it through columns packed with MnO/Al_2O_3 and zeolite 5A, respectively. Next, H_2 was passed through a mixing evaporator simultaneously fed with toluene. The mixture was fed into the heated reactor with a catalyst (the hydrogen and toluene feed rates were 40 ml/min and 0.12 ml/h, respectively). The reaction products were identified on a VLKhM-80 chromatograph (flame-ionization detector, PONA capillary column, column length 50 m, inner diameter 0.22 mm, film thickness 0.53 μm, chromatographic phase SE-54). The reaction was initiated at 200°C, the temperature was then decreased to 160°C over 1 h, and measurements were taken at this temperature. The carrier gas was nitrogen. Catalytic activity was estimated from toluene conversion data. Methylcyclohexane was found to be the only reaction product. The activity of samples in our experiments remained constant for 10 h.

Liquid-phase toluene hydrogenation was carried out in an autoclave with a volume of 300 ml. A catalyst (40 mg) and toluene (0.6 ml) were loaded into a glass ampoule ($d = 1$ cm, $h = 4$ cm). The toluene-to-catalyst weight ratio was 13. The autoclave was purged with hydrogen and was kept under an H_2 pressure of 50 atm at 95°C for 2.5 h without being agitated. The autoclave was heated from room temperature to 95°C over 20 min.

To study the effect of electron irradiation on the structure of the Pd/C catalyst, we compared, by XPS measurements, an unirradiated sample to a sample irradiated with a dose of 900 Mrad. XPS spectra were recorded on an XSAM-800 spectrometer using Al$K_{\alpha 1,2}$ radiation with an energy of 1486.6 eV. The C 1s line of the support ($E_b = 285.0$ eV) was used as the reference.

In addition, the reduction of the irradiated and unirradiated catalysts was studied by XPS during successive hydrogen treatments in the reactor at 20, 200, 250, and 300°C.

The samples were reduced in a special-purpose reactor attached to a spectrometer. The reduced samples were transferred to the spectrometer chamber without being exposed to air.

RESULTS AND DISCUSSION

Liquid-Phase Toluene Hydrogenation

Table 2 presents toluene conversion data for unirradiated Pd/C, Pd/Al_2O_3, and Pd/TiO_2 catalysts and for the same catalysts irradiated with doses of 240, 600, and 900 Mrad. For all of these systems, exposure to an electron beam raises the toluene conversion by a factor of 3 to 8.

Gas-Phase Toluene Hydrogenation

Table 3 lists toluene conversion data as a function of irradiation dose for the original Pd/C catalyst and the same catalyst irradiated with doses of 240 and 900 Mrad. As can be seen, the catalytic activity increases substantially with increasing irradiation dose. For instance, the toluene conversion on the unirradiated catalyst Pd/C is 15%, whereas the toluene conversion on the sample irradiated with a dose of 900 Mrad is at least 85%.

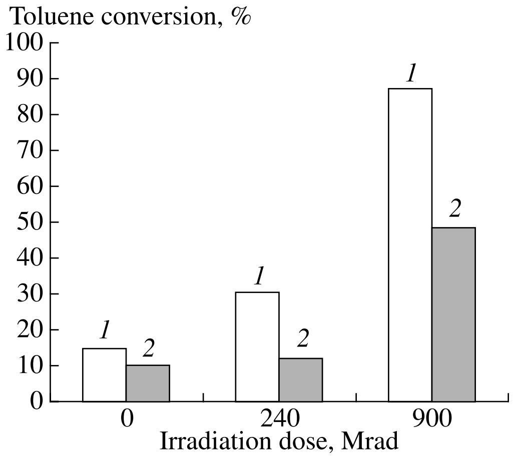

Fig. 1. Effect of the H_2 reduction temperature ((*1*) 200 and (*2*) 300°C) and irradiation dose on the activity of the Pd/C catalyst in gas-phase toluene hydrogenation at 160°C.

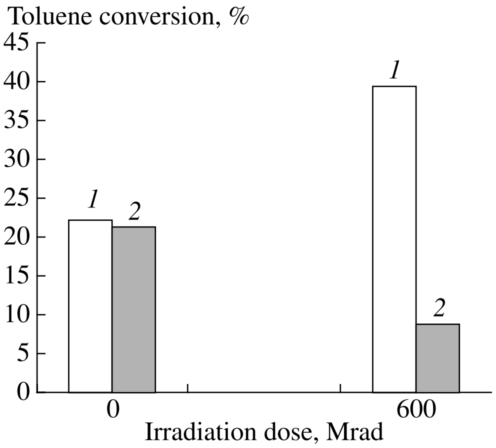

Fig. 2. Effect of the H_2 reduction temperature ((*1*) 200 and (*2*) 400°C) and irradiation dose on the activity of the Pd/Al_2O_3 catalyst in gas-phase toluene hydrogenation at 160°C.

Similar results were obtained for the Pd/Al_2O_3 and Pd/TiO_2 catalysts: the activities increased 2–2.5 times as the irradiation dose was increased (Table 3).

To estimate the stability of this effect, we studied the activity of the irradiated and unirradiated Pd/C and Pd/Al_2O_3 catalysts after reduction with H_2 for 1 h at 300 and 400°C, respectively.

Figure 1 plots toluene conversion versus irradiation dose for the original Pd/C catalyst and for the catalysts that were irradiated with doses of 240 and 900 Mrad and were then reduced at 200 and 300°C. Note that, for any irradiation dose, the catalyst reduced with H_2 at 300°C is less active than the catalyst reduced at 200°C and is, however, essentially more active than the original sample. Hence, the enhancing effect of electron irradiation on the catalytic activity is sufficiently stable in this system. The high activity of the irradiated catalysts is likely due to an increase in the degree of dispersion of Pd under the action of accelerated electrons.

The hydrogen treatment of Pd/Al_2O_3 irradiated with a 600-Mrad dose at 400°C diminishes the toluene conversion by a factor of 4, whereas the activity of the original, unirradiated sample remained virtually unchanged (Fig. 2).

XPS Data

The Pd 3*d* spectra for both irradiated and unirradiated catalysts are shown in Fig. 3. The binding energy of the Pd 3*d* electrons in the original sample, 338.4 eV, is relatively high. High values of binding energy are typical of isolated Pd^{2+} ions occurring on the surface of oxide supports or occupying cationic sites in a zeolite matrix (“ionic” palladium) [14]. The binding energy of the Pd 3*d* electrons in the irradiated sample is shifted by 0.5 eV to lower energies. In addition, the corresponding spectral line is somewhat broader. The changes in the XPS spectra are evidence of a change in the state of palladium on the catalyst surface upon electron irradiation. The decrease in binding energy can be due to the conversion of part of the support-bound cationic palladium species to oxide species with lower Pd 3*d* binding energies. The increase in peak half-width observed for the irradiated sample is also indirect evidence of the appearance of a new Pd state.

A comparison of the XPS spectra of the unirradiated (Fig. 4a) and irradiated (Fig. 4b) catalysts recorded during their reduction with hydrogen has revealed a substantial difference between the behaviors of these catalysts. The reduction of the unirradiated catalyst begins at 200°C. However, reduction at this temperature is incomplete, as is indicated by the shoulder on the higher binding energy side (Fig. 4a).

The reduction of the electron irradiated catalyst begins at room temperature, as is suggested by a shoul-

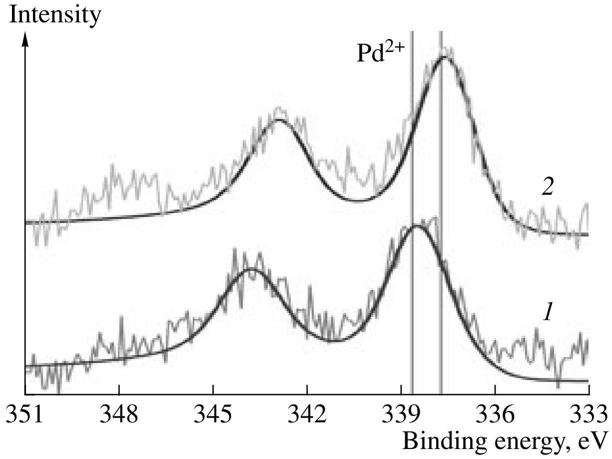

Fig. 3. Pd 3*d* XPS spectra of the Pd/C catalyst: (*1*) unirradiated sample and (*2*) sample irradiated with a dose of 900 Mrad.

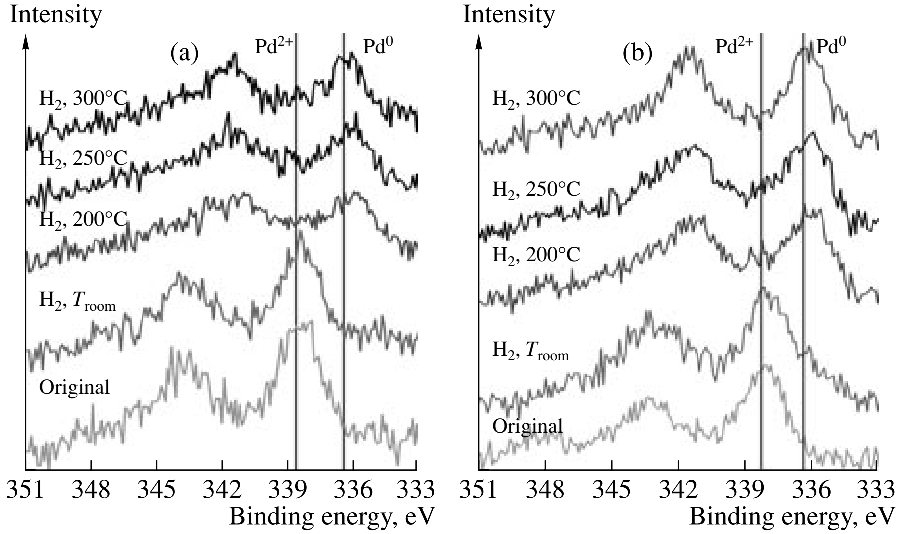

Fig. 4. Pd 3*d* XPS spectra of the Pd/C catalyst: (a) unirradiated sample and (b) sample irradiated with a dose of 900 Mrad and reduced with H_2 at various temperatures.

der appearing at E_b = 336.4 eV (Fig. 4b). The line of metallic palladium appearing upon H_2 treatment at room temperature confirms the assumption that part of the palladium ions aggregate into oxide species, since the fact of palladium oxide reduction in the temperature range 0–20°C is well known [15]. Raising the reduction temperature to 200°C gives rise to an intense line due to metallic palladium at E_b = 336.3 eV, and an examination of the line shape suggests that reduction is complete at 200°C.

Another significant distinction between the behaviors of these two samples manifests itself as a change in the intensity of the Pd 3d line during the high-temperature reduction treatment. It is clear from the XPS spectra that the line intensity does not change in the case of the electron-irradiated sample (Fig. 4b). By contrast, the signal intensity for the unirradiated sample decreases significantly as the reduction temperature is increased to 200–300°C (Fig. 4a). The surface Pd/C atomic ratio in the unirradiated sample calculated from the XPS data (Table 4) decreases systematically as the reduction temperature is increased to 200–300°C, whereas this ratio in the irradiated sample remains nearly constant.

Note that, after reduction at 300°C, the atomic Pd/C ratio for the irradiated sample is twice that for the original sample. One can assume that, during electron treatment, the energy of the palladium–support bond increases, resulting in an increase in the degree of dispersion and sintering resistance of palladium.

Table 4. Pd $3d_{5/2}$ binding energy and Pd/C atomic ratio as a function of reduction temperature according to XPS data

Reduction temperature, °C	E_b Pd $3d_{5/2}$, eV	Pd/C
	Unirradiated catalyst	
– (Original)	338.4	0.0020
20	338.4	0.0019
200	336.1	0.0022
250	336.1	0.0018
300	336.1	0.0014
	Irradiated catalyst (900 Mrad)	
– (Original)	337.9	0.0023
20	337.7	0.0030
200	336.1	0.0025
250	336.1	0.0023
300	336.1	0.0025

ACKNOWLEDGMENTS

This work was supported by the International Science and Technology Center, project no. 1764.

REFERENCES

1. Tian, Y.J., Zhang, Y.L., Yu, Q., et al., *Catal. Today*, 2004, vol. 89, p. 233.
2. Vissokov, G., *Catal. Today*, 2004, vol. 89, p. 245.
3. Berry, F.J., Smart, L.E., Prasad, P.S.S., Lingaiah, N., and Rao, P.K., *Appl. Catal., A*, 2000, vol. 204, p. 191.
4. Prasad, P.S.S., Lingaiah, N., Rao, P.K., Berry, F.J., and Smart, L.E., *Catal. Lett.*, 1995, vol. 35, p. 345.
5. Wada, Y., Kuramoto, H., Sakata, T., Mori, H., Sumida, T., Kitamura, T., and Yanagida, S., *Chem. Lett.*, 1999, p. 607.
6. Vileno, E., Zhou, H., Zhang, Q., Suib, S.L., Corbin, D.R., and Koch, T.A., *J. Catal.*, 1999, vol. 187, p. 285.
7. Liu, C.-J., Vissokov, G.P., and Jang, B.-W.L., *Catal. Today*, 2002, vol. 72, p. 173.

8. Gotec, F., *Surf. Sci.*, 2000, vol. 448, p. 188.
9. Yuan, Z.-Y., Zhou, W., Parvulescu, V., and Su, B.L., *J. Electron Spectrosc. Relat. Phenom.*, 2003, vol. 129, p. 189.
10. Jun, J., Kim, J.-Ch., Shin, J.-H., Lee, K.-W., and Baek, Y.S., *Radiat. Phys. Chem.* (in press).
11. Muska, V., Otahal, B., and Silber, R., *Radiat. Phys. Chem.*, 2002, vol. 65, p. 177.
12. Pikaev, A.K., *Sovremennaya radiatsionnaya khimiya. Tverdoe telo i polimery. Prikladnye aspekty* (Modern Radiation Chemistry of Solids and Polymers: Applied Aspects), Moscow: Nauka, 1987.
13. Krylov, O.V., *Geterogennyi kataliz* (Heterogeneous Catalysis), Moscow: Nauka, 2004.
14. Stakheev, A.Yu., Baeva, G.N., Telegina, N.S., Volynsky, A.B., Kustov, L.M., and Minachev, Kh.M., *Mendeleev Commun.*, 2000, vol. 10, no. 3, p. 99.
15. Sachtler, W.N.H. and Zhang, Z., *Adv. Catal.*, 1993, vol. 39, p. 129.