ISSN 0965-5441, Petroleum Chemistry, 2017, Vol. 57, No. 12, pp. 1024–1030. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © N.A. Magdalinova, M.V. Klyuev, 2017, published in Neftekhimiya, 2017, Vol. 57, No. 6, pp. 645–650.

Hydrogenation of Nitro and Unsaturated Organic Compounds over Catalysts Containing Nanosized Palladium Particles

N. A. Magdalinova* and M. V. Klyuev**
Ivanovo State University, Ivanovo, 153025 Russia
**e-mail: mn2408@mail.ru*
***e-mail: klyuev@inbox.ru*

Received November 25, 2016

Abstract—The activity of palladium catalysts prepared on the basis of ZnO modified with polyethylene glycol (1 wt % Pd–PEG/ZnO) with molecular weights of 4000 and 6000 in the hydrogenation reaction of a series of nitro and unsaturated organic compounds has been studied. The catalysts are characterized by the formation of small metal particles with a size from 3 to 8 nm which uniformly coat the support surface. The results obtained have been compared to the catalytic properties of palladium-containing nanodiamonds and activated carbon under similar conditions.

Keywords: palladium, catalysts, polyethylene glycol, hydrogenation, nitro compounds, nanodiamonds, activated carbon

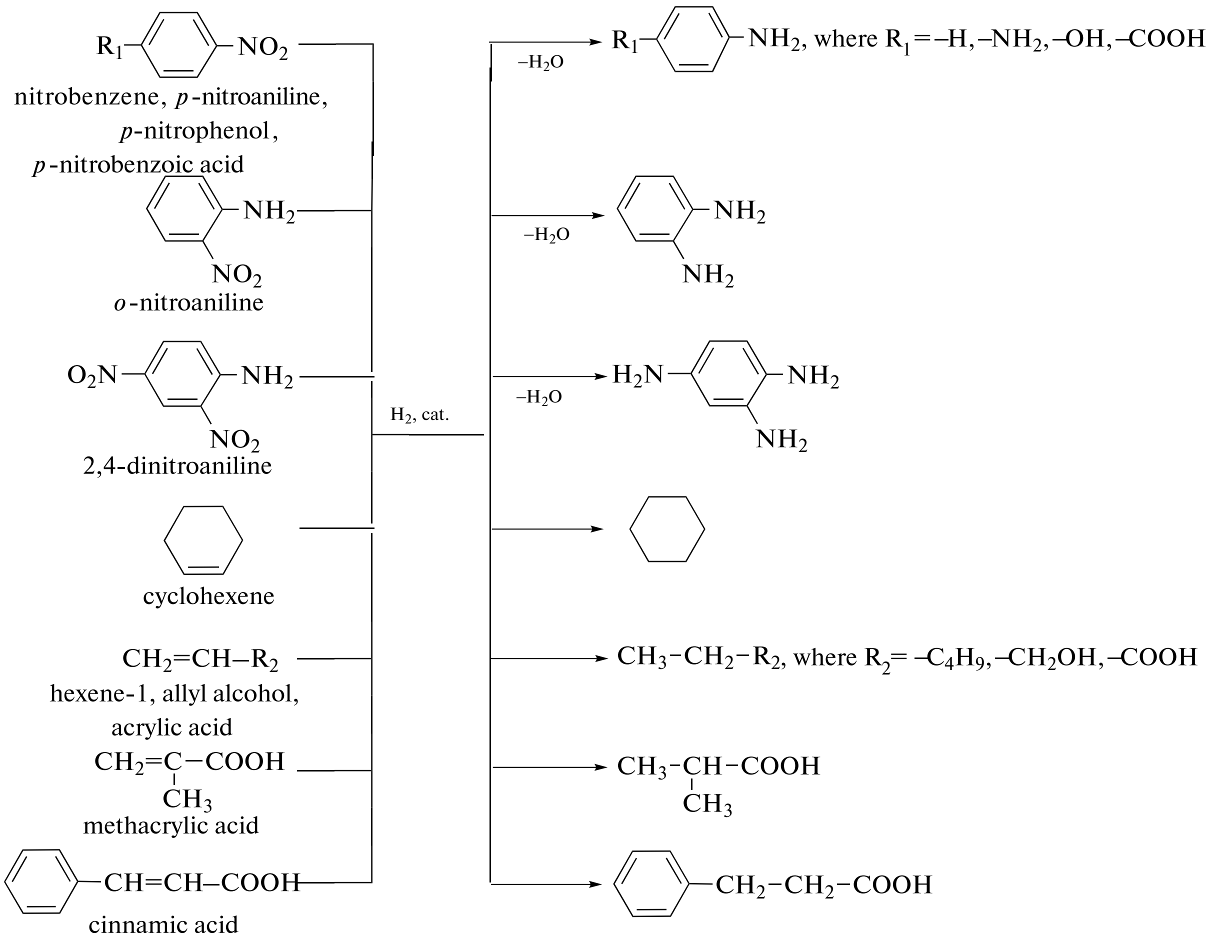
DOI: 10.1134/S0965544117120064

INTRODUCTION

The active part of most catalysts for hydrogenation is transition metal particles which are bound to a support in one way or another. Over the recent years, solutions which make it possible to obtain nanosized metal sites have been found. For this, carbon (activated carbon, carbon nanofibers and nanotubes, and nanodiamonds) and noncarbon (Al_2O_3, CeO_2, TiO_2, ZnO, ZrO_2, MgO, and CaO) supports, as well as various stabilizing agents such as ionic liquids, dendrimers, and polymers are used [1], which prevent the aggregation of metal nanoparticles and, hence, promote its more effective use. In connection therewith, it is promising to use cheap and nontoxic polyethylene glycol (PEG), the molecular weight of which can change within a quite wide range, as the modifying agent.

Catalysts on the basis of nanosized palladium nanoparticles stabilized with PEG have already been tested in hydrogenation reactions of various organic compounds: Pd/PEG (400, 800, 1000, 2000, 4000, and 6000) (hereinafter, numbers in brackets correspond to the average molecular weight of PEG used) in the hydrogenation of styrene and nitrobenzene [2], Pd/PEG (1000, 6000, 15000, 20000, and 40000) in the hydrogenation of acetylene alcohols [3], Pd–Co/PEG [4] and Pd/PEG (2000, 4000, and 6000) [5] in the hydrogenation of crotonic aldehyde, Pd/PEG (400) [6] in the hydrogenation of 1,5-cyclooctadiene, and Pd/PEG (4000) [7] and Pd/PEG (400, 800, 1000, 2000, and 4000) in the hydrogenation of a series of other olefins [8]. A Pt/PEG (1000, 2000, 6000, and 12000) catalyst has been studied in the hydrogenation of *o*-chloronitrobenzene with the formation of *o*-chloroaniline [9].

Harraz et al. [2] revealed the necessary conditions for the formation of palladium nanoparticles with an average size of 5 nm in a set of experiments (varying the metal loading (1.2, 2.5, 3.75, and 4.8%), temperature (50, 75, 100, 125, and 150°C), synthesis time (1, 2, 3, and 4 h), and PEG molecular weight (400, 800, 1000, 2000, 4000, and 6000)). It turned out that a small size of particles with high density and high Pd(0) dispersion is obtained in the case of using PEG with higher molecular weights of 4000 and 6000 (3.75 wt % Pd, $T = 75°C$, 2 h). When PEG with a low molecular weight of 400, 800, or 1000 was used under the given experimental conditions, no reduction reaction of Pd(II) ions to Pd(0) was observed. For PEG-2000, only partial reduction of Pd particles was observed.



Scheme 1. The hydrogenation reactions studied.

In this work, the catalytic activity of palladium-containing samples prepared on the basis of ZnO with the surface modified with PEG with molecular weights of 4000 and 6000 (1 wt % Pd–PEG-4000/ZnO and 1 wt % Pd–PEG-6000/ZnO, respectively) in the hydrogenation reactions of a number of aromatic nitro compounds and some unsaturated organic compounds (Scheme 1) has been studied. The results obtained have been compared with the catalytic properties of palladium-containing nanodiamonds (1 wt % Pd/ND) and activated carbon (1 wt % Pd/C) experimentally determined under similar conditions.

The choice of zinc oxide is determined by its stability, wide application as the support and structural and textural modifier of the catalysts for organic synthesis processes, and a low cost. The choice of the substrates is determined by different mechanisms of reduction of functional groups ($-NO_2$ and $>C=C<$) which differ in nature and position, as well as by the practical value of the products formed as a result of hydrogenation.

EXPERIMENTAL

Preparation of Samples

1 wt % Pd–PEG-4000/ZnO and 1 wt % Pd–PEG-6000/ZnO catalysts were prepared according to the procedure [10] at Sokolskii Institute of Organic Catalysis and Electrochemistry, Almaty, Republic of Kazakhstan.

An aqueous polymer solution containing 0.0011 g of PEG in 5 mL of water was added to an aqueous suspension of the support (0.2 g of zinc oxide in 5 mL of water) at room temperature under constant stirring, and it was vigorously stirred for 2 h. Then 5 mL of an aqueous H_2PdCl_4 solution containing 0.002 g of Pd was added, and it was stirred for 3 h until complete binding of palladium chloride. The system obtained was kept in the mother liquor for at least 10 h, after which the precipitate was washed with water and dried in air. As a result, a catalyst containing 1.0 wt % Pd, 0.54 wt % PEG, and 98.46 wt % ZnO was obtained.

To compare catalytic properties, 1 wt % Pd/ND (ND are detonation nanodiamonds with a specific surface area of 307–314 $m^2 g^{-1}$, an average size of the crystalline diamond core of particles of about 4 nm, and a total concentration of noncarbon impurities of no more than 0.2 wt %) synthesized according to the procedure described in the patent [11] and in [12, 13] and 1 wt % Pd/C prepared according to the procedure described in [12, 13] on the basis of activated carbon of the PHO M200 brand (prepared on the basis of the coconut shell) (Eurocarb, the United Kingdom) were used.

Hydrogenation Procedure

The hydrogenation reaction of aromatic nitro compounds and unsaturated organic compounds (see Scheme 1) was carried out as follows: 30 mg of a catalyst and 10 mg of sodium tetrahydroborate $NaBH_4$ were placed under a solvent layer (10 mL of ethanol) into a glass reactor equipped with a thermostatting jacket and a magnetic stirrer, the activation was carried out for 10 min, and then 1 mmol of a substrate (cyclohexene (CH), hexene-1 (H-1), allyl alcohol (AAl), acrylic acid (AA), methacrylic acid (MA), cinnamic acid (CA), nitrobenzene (NB), *p*-nitrophenol (*p*-NP), *p*-nitrobenzoic acid (*p*-NBA), *o*-nitroaniline (*o*-NA), *p*-nitroaniline (*p*-NA), or 2,4-dinitroaniline (2,4-DNA)) was introduced in a hydrogen flow. The hydrogenation was carried out at $T = 45°C$ and $P_{H_2} = 0.1$ MPa. The reaction mixture was stirred at a constant rate of 1250 stir bar revolutions/min during all the experiments, which is sufficient for the process to occur in the kinetic region. This value was determined experimentally.

In studying the effect of $NaBH_4$ on the hydrogenation rate, the amount of the reducing agent was varied from 0 to 25 mg.

The apparent reaction rate was measured volumetrically by the absorption of hydrogen. Under the reaction conditions, a turnover number (TON, min^{-1}), which shows how many moles of the substrate is converted per mole of Pd per minute, was used for the comparison of the catalytic activity of the objects under study.

Under the given experimental conditions, the reactions of interest were zero-order with respect to the substrate and first-order with respect to the catalyst and hydrogen [14]. To confirm that the processes occurred in the kinetic region, the Thiele criterion (Φ) was used [15]:

$$\Phi = R\sqrt{\frac{W}{CD}},$$

where R is the average particle size of the catalyst, cm; W is the reaction rate, mol/(L s), during the period of time corresponding to the linear portion of the kinetic curve until a 10% conversion of the theoretically value calculated for each substrate; C is the concentration of the substrate, mol/L; and D is the diffusion coefficient, 10^{-5} cm^2/s. In the conducted experiments, the Thiele criterion turned out to be substantially smaller than 1 ($\Phi = 1.9 \times 10^{-6}$–$1.9 \times 10^{-5}$), which is indeed the evidence for the fact that the reaction proceeds in the kinetic region.

The products of the hydrogenation reaction were analyzed on a Series 3700 commercial chromatograph equipped with a flame ionization detector: a glass column of a 3 mm diameter and a 2000 mm length packed with 5% LucoPrene G-1000-coated Chromaton N-AW-DMCS, the carrier gas was nitrogen, the evaporator temperature was 80–230°C, the column temperature was 50–180°C (depending on the analyte), the carrier-gas flow rate was 1.6 ± 0.02 L/h, and the injection volume was 0.5–1 μL.

Investigation Methods

The structure and composition of synthesized 1 wt % Pd/C and 1 wt % Pd/ND were studied by a set of instrumental techniques, namely, X-ray microanalysis (a VEGA TS 5130MM fully PC-controlled scanning electron microscope), X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD), and scanning electron microscopy (Zeiss LEO SUPRA 25) [12, 13].

The 1 wt % Pd–PEG-4000/ZnO and 1 wt % Pd–PEG-6000/ZnO catalysts were examined using transmission electron microscopy (Jeol JSM-6610LV) [3].

RESULTS AND DISCUSSION

Characterization of the Catalysts

Based on the data of transmission electron microscopy, it was shown [3] that the systems applied onto zinc oxide from an aqueous palladium chloride solution are metal particles with a rather broad size spread (20–40 nm). The palladium catalyst prepared using PEG is characterized by the formation of small metal particles with sizes from 3 to 8 nm which quite uniformly cover the support surface.

Preliminary Activation of the Catalysts

The samples under study were subjected to preliminary activation using sodium tetrahydroborate. The essence of the activation process in the case of palladium-containing catalysts consists in the transition of Pd^{2+} to Pd^0; it is over the latter species that the activation of an H_2 molecule occurs. The effect of the amount of $NaBH_4$ on the catalytic properties of 1 wt % Pd–PEG-6000/ZnO and 1 wt % Pd/C_{act} (M 200) was examined in a model hydrogenation reaction of nitrobenzene ($P_{H_2} = 0.1$ MPa, $T = 45°C$, solvent: ethanol).

Figure 1 shows the diagram of the dependence of the average rate constant of the model nitrobenzene hydrogenation reaction on the weight of $NaBH_4$ (0, 0.05, 0.10, 0.15, 0.20, 5, 10, 15, 20, and 25 mg) for 1 wt % Pd–PEG-6000/ZnO. A similar dependence

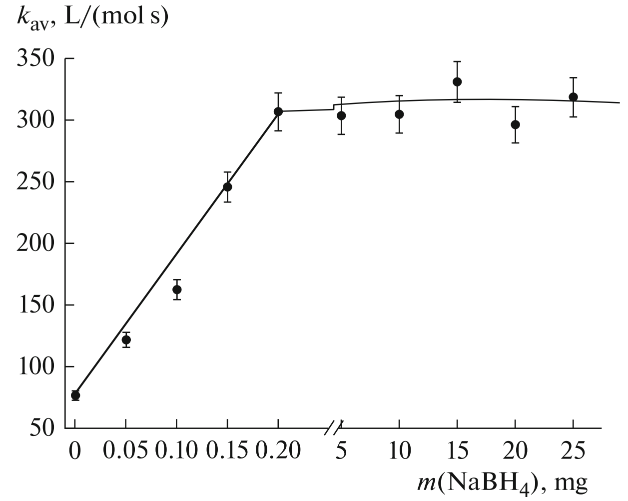


Fig. 1. The dependence of the average rate constant of the nitrobenzene hydrogenation reaction on the amount of $NaBH_4$ used to activate 1 wt % Pd–PEG-6000/ZnO.

was obtained for 1 wt % Pd/C as well. It turned out that the preliminary activation of the catalyst with $NaBH_4$ resulted in a fourfold increase in the nitrobenzene hydrogenation rate on 1 wt % Pd–PEG-6000/ZnO (Fig. 1) and a 4.6-fold increase on 1 wt % Pd/C as compared to the preliminary activation by molecular hydrogen alone. The values of the rate constant of nitrobenzene hydrogenation increased with an increase in the amount of $NaBH_4$ uses up to 0.20 mg. During further increase in the weight of the activator, the values of the rate constants remained unchanged and fell within the limits of the experimental error. It can be assumed that the addition of 0.20–5 mg of $NaBH_4$ is sufficient for the reduction of all the Pd^{2+} ions.

Table 1. Influence the molecular weight of polyethylene glycol on the activity of 1 wt % Pd–PEG/ZnO in the hydrogenation of organic compounds

Substrate	TON, min^{-1}	
	PEG-4000	PEG-6000
Nitrobenzene	85.3	109.1
p-Nitroaniline	26.6	141.6
p-Nitrophenol	17.1	47.6
p-Nitrobenzoic acid	11.7	118.6
o-Nitroaniline	15.3	61.3
2,4-Dinitroaniline	19.2	126.6
Hexene-1	28.7	40.4
Cyclohexene	45.7	62.5
Allyl alcohol	93.6	75.8
Acrylic acid	134.4	101.0
Methacrylic acid	105.8	80.4
Cinnamic acid	3.5	2.9

Experimental conditions: $T = 45°C$, $P_{H_2} = 0.1$ MPa, 30 mg of the catalyst (1 wt % Pd–PEG/ZnO), 10 mg of $NaBH_4$, 10 mL of ethanol, and 1 mmol of the substrate.
The error in the determination of TON does not exceed 7%.

Studying the Activity of the Catalysts Prepared with PEG

Table 1 presents the results of the hydrogenation of nitroarenes and unsaturated organic compounds in the presence of 1 wt % Pd–PEG-4000/ZnO and 1 wt % Pd–PEG-6000/ZnO.

An increase in the reaction rate constant and the turnover number is observed in the hydrogenation reaction of nitro compounds on the 1 wt % Pd–PEG-6000/ZnO catalyst, as compared to 1 wt % Pd–PEG-4000/ZnO (Table 1), by a factor of 5.3 for *p*-nitroaniline, 2.8 for *p*-nitrophenol, or 10 for *p*-nitrobenzoic acid. During the hydrogenation of the double C=C bond in the unsaturated organic compounds, the same trend is observed for cyclohexene. In the cases of allyl alcohol and unsaturated acids, there is an inverse dependence; thus, the reaction rate constant and TON over 1 wt % Pd–PEG-6000/ZnO are lower than in the presence of 1 wt % Pd–PEG-4000/ZnO. Obviously, during the hydrogenation of the nitro compounds and unsaturated organic compounds, which proceeds via different mechanisms, intermediate substrate–active site complexes are formed which are screened to different extents by PEGs with molecular weights of 4000 and 6000. A similar trend was noted during the hydrogenation of alkynyl alcohols in [3]; thus, the highest rate was observed using PEG with a molecular weight of 1000, the rate decreased with an increase in the PEG molecular weight to 6000 and further to 15000 g/mol, and the catalysts with molecular weights of 20000 and 40000 g/mol turned out to be inactive.

Comparing the Activity of the Catalysts Prepared Using PEG with That of 1 wt % Pd/C and 1 wt % Pd/ND

The results obtained in the hydrogenation reactions of aromatic nitro compounds and unsaturated organic compounds on 1 wt % Pd–PEG-6000/ZnO were compared to the data on the activity of the 1 wt % Pd/C [12] and 1 wt % Pd/ND [12] catalysts (Figs. 2, 3). The catalytic activity of the test 1 wt % Pd–PEG-6000/ZnO sample in the hydrogenation of nitrobenzene, 2,4-dinitroaniline, *p*-nitroaniline, or *p*-nitrobenzoic acid was found to be higher by a factor of 2.5, 3.2, 3.5, or 5.2, respectively, than that of 1 wt % Pd/C (Fig. 2).

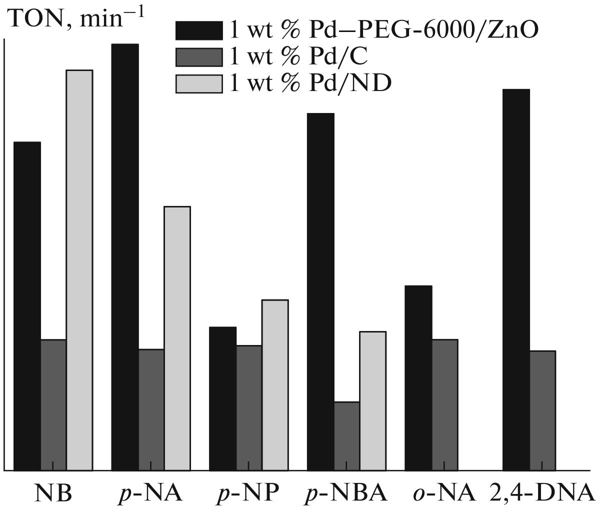


Fig. 2. The activity of 1 wt % Pd–PEG-6000/ZnO, 1 wt % Pd/C, and 1 wt % Pd/ND in the hydrogenation reaction of nitroarenes. The values of TON for the 1 wt % Pd/ND catalyst are borrowed from [12].

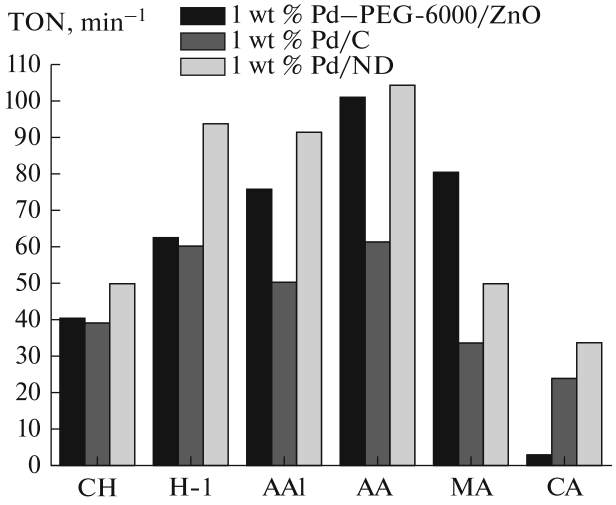


Fig. 3. The activity of 1 wt % Pd–PEG-6000/ZnO, 1 wt % Pd/C, and 1 wt % Pd/ND in the hydrogenation reaction of unsaturated organic compounds. The values of TON for the 1 wt % Pd/C and 1 wt % Pd/ND catalysts are borrowed from [12].

In the hydrogenation of *p*-nitroaniline and *p*-nitrobenzoic acid, 1 wt % Pd–PEG-6000/ZnO was 1.6-fold and 2.6-fold more active, respectively, than 1 wt % Pd/ND. It is also seen from Fig. 2 that 1 wt % Pd–PEG-6000/ZnO is more sensitive towards the nature of the substrate than 1 wt % Pd/C. However, the yield of target amines with 1 wt % Pd–PEG-6000/ZnO did not exceed 30%, while the target amines can be obtained in a quantitative yield in the presence of 1 wt % Pd/C and 1 wt % Pd/ND.

In the case of hydrogenation of unsaturated organic compounds, the activity of 1 wt % Pd–PEG-6000/ZnO is higher than that of 1 wt % Pd/C in the hydrogenation of allyl alcohol, acrylic acid, and methacrylic acid, but it is higher than that of 1 wt % Pd/ND only in the reaction with methacrylic acid (Fig. 3). In the hydrogenation of the other substrates (cyclohexene, hexene-1, and cinnamic acid), the test sample on the basis of PEG is inferior to the catalysts on carbon supports (Fig. 3). It is also noteworthy that the catalysts differ in the "sensitivity" towards the change of the nature of substrate molecules. This is well seen by the example of three acids, namely, acrylic, methacrylic, and cinnamic acids. Acrylic acid is hydrogenated best of all over all the catalysts, while cinnamic acid, worst of all. The activity of 1 wt % Pd/C and 1 wt % Pd/ND decreases almost threefold on passing from one acid to another, whereas it drops as dramatically as by a factor of 35 in the case of 1 wt % Pd–PEG-6000/ZnO. Apparently, such structural sensitivity of 1 wt % Pd–PEG-6000/ZnO can be explained only by the presence of polyethylene glycol macromolecules in this catalyst. The presence of the polymer poses additional constraints on the contact of substrate molecules with the active sites of the catalyst.

The 1 wt % Pd–PEG-6000/ZnO catalyst turned out to be quite stable (Fig. 4), thus, in the case of repeated use, the rate of the hydrogenation reaction of nitrobenzene changed within the limits of the measurement error. During the hydrogenation of the second portion, the effect of catalyst "conditioning" was observed. The effects can be due to the fact that some of the palladium has not been reduced during the initial activation (treatment with $NaBH_4$) because of the steric hindrances created by PEG. When being on stream, palladium is reduced, the amount of zerovalent palladium capable of activating molecular hydrogen increases, and the reaction rate grows.

Figure 5 shows the plots of the activation energy versus the change in the entropy of activation for the 1 wt % Pd–PEG-6000/ZnO and 1 wt % Pd/C catalysts. For both the catalysts, a linear dependence between the values of the activation energy and the change in the entropy of activation is observed, which gives evidence for the presence of a compensation effect [16, 17] in the following series of nitroarenes: nitrobenzene–*p*-nitroaniline–*o*-nitroaniline–2,4-dinitroaniline. The correlation coefficient for the aggregate relationship is also close to unity, which confirms the similarity of the active sites in both the catalysts. Apparently, these are zerovalent palladium particles.

It should also be noted that the value of the change in the entropy of activation for 2,4-dinitroaniline over 1 wt % Pd–PEG-6000/ZnO is positive, unlike that for 1 wt % Pd/C. It is known that the entropy of activation

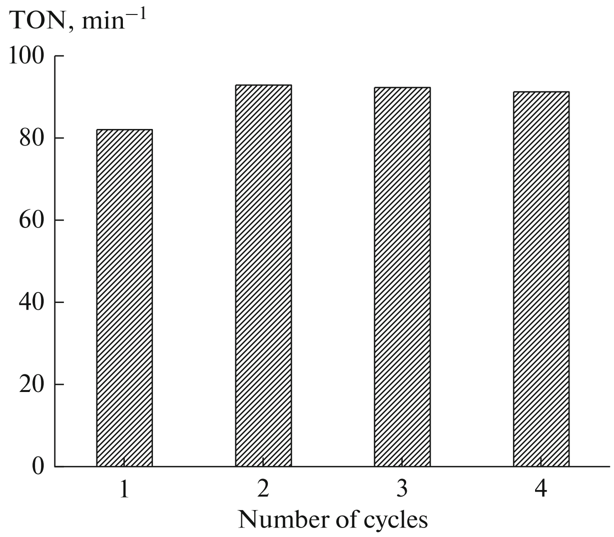


Fig. 4. Stability of 1 wt % Pd–PEG-6000/ZnO in the nitrobenzene hydrogenation reaction.

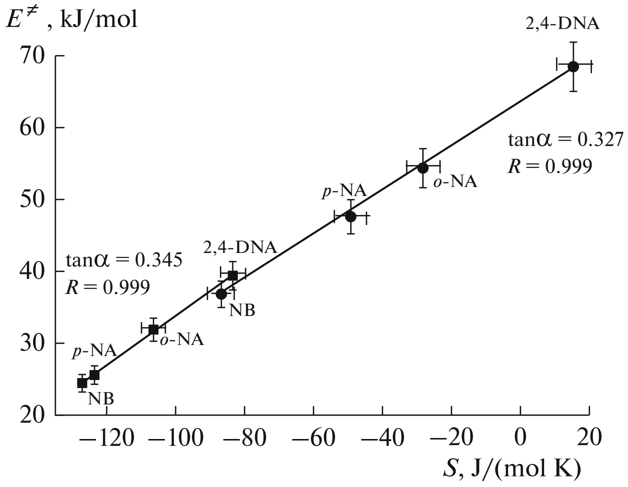


Fig. 5. The compensation effect for (●) 1 wt % Pd–PEG-6000/ZnO and (■) 1 wt % Pd/C.

varies to a greater extent depending on the structure of the reactant molecule and the activated complex, unlike the enthalpy of activation. The change in the entropy of activation can be both positive and negative. The positive value of the entropy for 2,4-dinitroaniline over 1 wt % Pd–PEG-6000/ZnO can be explained as follows: the Pd active sites of the metal–polymer catalyst can be both on the surface and inside the polymer matrix, thereby creating certain steric hindrances to the nitro groups of 2,4-dinitroaniline approaching the active sites of the catalyst.

The values of the activation energy and entropy of activation (Fig. 5) for 1 wt % Pd/C are below those for 1 wt % Pd–PEG-6000/ZnO for all the nitroarenes examined, suggesting a more ordered structure of Pd nanoparticles in 1 wt % Pd/C. This can be explained by the fact that the polymer matrix can immobilize palladium clusters of different sizes, whereas palladium particles are more uniform when palladium is deposited on activated carbon.

In summary, the results of the study of the activity of 1 wt % Pd–PEG/ZnO shows that the catalyst modified with PEG-6000 is more effective in the hydrogenation of nitro compounds and the catalyst modified with PEG-4000, in the hydrogenation reaction of unsaturated organic compounds. Under similar conditions, 1 wt % Pd–PEG-6000/ZnO is superior in catalytic properties to 1 wt % Pd/C and, in some cases, to 1 wt % Pd/ND; however, the yields of the target products are almost quantitative over the two latter catalysts, not the catalysts prepared using PEG. This difference can also be explained by the steric hindrances due to the presence of the polymer in the catalyst composition.

ACKNOWLEDGMENTS

The authors are grateful to Prof. A.K. Zharmagambetova (at Sokolskii Institute of Organic Catalysis and Electrochemistry, Almaty, Republic of Kazakhstan) for kindly providing the samples of the 1 wt % Pd–PEG-4000/ZnO and 1 wt % Pd–PEG-6000/ZnO catalysts. We also thank I.S. Kiseleva, a student, for assistance in conducting the experimental work.

REFERENCES

1. M. V. Klyuev, N. A. Magdalinova, and P. A. Kalmykov, *Hydrogenation Catalysts Based on Carbon Nanomaterials* (Ivanovskii Gos. Univ, Ivanovo, 2015) [in Russian].
2. F. A. Harraz, S. E. El-Hout, H. M. Killa, and I. A. Ibrahim, J. Catal. **286**, 184 (2012).
3. A. K. Zharmagambetova, A. T. Zamanbekova, and B. K. Dyusenalin, Izv. Nats. Akad. Nauk RK, Ser. Khim., No. 6, 62 (2009).
4. A. K. Zharmagambetova, A. S. Auezkhanova, E. T. Talgatov, et al., Izv. Nats. Akad. Nauk RK, Ser. Khim. Tekhnol., No. 3, 44 (2014).
5. F. A. Harraz, S. E. El-Hout, H. M. Killa, and I. A. Ibrahim, J. Mol. Catal. A: Chem. **370**, 182 (2013).
6. U. R. Pillai and E. Sahle-Demessie, J. Mol. Catal. A: Chem. **222**, 153 (2004).
7. T. S. Huang, Y. H. Wang, J. Y. Jiang, and Z. L. Jin, Chin. Chem. Lett. **19**, 102 (2008).
8. X. Ma, T. Jiang, B. Han, et al., Catal. Commun. **9**, 70 (2008).
9. H. Cheng, C. Xi, X. Meng, et al., J. Colloid Interface Sci. **336**, 675 (2009).
10. A. K. Zharmagambetova and I. A. Kurmanbaeva, RU Patent No. 12356 (2006).

11. N. N. Vershinin and O. N. Efimov, RU Patent No. 2348090 (2009).
12. P. A. Kalmykov, N. A. Magdalinova, and M. V. Klyuev, Pet. Chem. **55**, 64 (2015).
13. P. A. Kalmykov and M. V. Klyuev, Pet. Chem. **56**, 32 (2016).
14. M. V. Klyuev, Doctoral Dissertation in Chemistry (Moscow, 1991).
15. *Collection of Questions and Problems on Analytical Chemistry*, Ed. by V. P. Vasil'ev (Vysshaya Shkola, Moscow, 1976) [in Russian].
16. M. V. Klyuev, L. V. Tereshko, and E. F. Vainshtein, Vestn. Mosk. Univ., Ser. 2: Khim. **32**, 198 (1991).
17. M. V. Klyuev and E. F. Vainshtein, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. **34**, 76 (1991).

Translated by E. Boltukhina