ISSN 0023-1584, Kinetics and Catalysis, 2016, Vol. 57, No. 5, pp. 586–591. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © T.I. Akchurin, N.Z. Baibulatova, S.A. Grabovskii, P.P. Talipova, E.G. Galkin, V.A. Dokichev, 2016, published in Kinetika i Kataliz, 2016, Vol. 57, No. 5, pp. 592–597.

Alkene Hydrogenation over Palladium Supported on a Carbon–Silica Material

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Received July 8, 2015

Abstract—Palladium catalysts supported on a carbon–silica material were synthesized. Hydrogenation by molecular hydrogen was studied in the presence of straight-chain and cyclic olefins. As distinct from what is observed for olefins having a phenyl substituent, for aliphatic alkenes the reaction rate decreases with an increasing conversion due to the accumulation of hydrogenation products. The synthesized palladium catalysts show a higher hydrogenation activity than Pd/C.

Keywords: heterogeneous catalysis, palladium, carbon–silica support, hydrogenation reaction, molecular hydrogen, olefins

DOI: 10.1134/S0023158416050025

INTRODUCTION

In the catalytic hydrogenation of unsaturated compounds with molecular hydrogen in the presence of heterogeneous catalysts, choice of support plays a major role because it has a significant effect on the activity and selectivity of the catalyst. The most commonly used supports for Pd-catalysts are activated carbon, Al_2O_3, and zeolites [1]. In a number of studies [2–4], microheterogeneous palladium catalysts consisting of palladium phosphides and Pd(0) clusters were used in hydrogenation. In recent years, there have been data on the deposition of palladium on carbon materials, namely, fullerenes, carbon nanotubes and nanofibers, and nanodiamonds [5–9] and on its encapsulation in polypropylenimine dendrimers [10]. However, the literature contains no information on the catalytic activity of heterogeneous palladium catalysts on carbon–silica supports that combine the properties of silica and hydrophobic carbon materials [11–15].

The purpose of this work was to develop Pd-containing catalysts on a carbon–silica support and to study their usability in the hydrogenation of olefins with straight-chain and cyclic structures by molecular hydrogen.

EXPERIMENTAL

Materials

We used 99% pure $PdCl_2$ and the following olefins: 1,1-diphenylethylene (97%), indene (98%), norbornene (99%), and cyclopentene (96%) from Aldrich, as well as 98% pure allylbenzene, vinylbenzene, hexadecene-1, 1-heptene, 1-decene, 1-nonene, 1-octene, cyclohexene, and cyclooctene.

The supports were a carbon–silica adsorbent produced by Pilot Co. (Ufa) and activated carbon (BAU-A brand, USSR State Standard GOST 6217–74) produced by Forus Co. Cherepovets.

Catalyst Synthesis

$Pd/C–SiO_2$ catalysts with a metal content of 1, 2, 3, 4 and 5% were synthesized via a procedure developed for the synthesis of palladium on carbon [16]. For example, for the preparation of a 5% Pd sample, a mixture of 1.0 g of $PdCl_2$, 2.4 mL of HCl_{conc} and 6 mL of water was refluxed for 1.5 h until a clear solution was obtained, which was diluted with 17 mL of water and thoroughly stirred with 11.4 g of the carbon–silica support. The resulting material was evaporated in a water bath and dried in an oven at 100°C (Table 1).

A 5%Pd/C reference catalyst was was synthesized by the same method [16].

The weight of the sample obtained from 0.50 g of $PdCl_2$ and 6.60 g of activated carbon was 6.05 g

To synthesize a $5\%Pd/C\text{-}SiO_2$ catalyst reduced with diazomethane, 100 mL of a 0.5 M solution of diazomethane in diethyl ether was added in small portions to 1 g of $5\%Pd/C\text{-}SiO_2$. After gas evolution had ceased, the catalyst was filtered and dried at room temperature in a vacuum (1 Torr). This yielded 0.88 g of the final product.

Characterization Methods

The static adsorption capacity of the support was determined by the desiccator method based on complete saturation of the sample with adsorbate vapor (water, benzene, *n*-heptane) under standard conditions at a temperature of 20–25°C. The sample (0.2–0.3 g) was dehydrated in a muffle furnace at 200 and 350°C for 2–3 h, placed in a desiccator with adsorbate, and incubated for 24–48 h at room temperature until complete saturation with adsorbate vapor [17]. The static adsorption capacity of the sample for the condensed adsorbate vapor was calculated from the formula

$$C = m_2 \Big/ m_1 d_4^{20},$$

where m_1 is the weight of the calcined sample (g), m_2 is the weight of the adsorbate adsorbed (g), and d_4^{20} is the adsorbate density (g/cm^3). The discrepancy between the results of replica measurements did not exceed 0.02 cm^3/g.

The specific surface area (S_{BET}) of the support was determined by the BET method by measuring the equilibrium amount of nitrogen adsorbed at 77 K [18]. Adsorption isotherm in the relative equilibrium nitrogen vapor pressure (P/P_0) range from 0.05 to 0.33 were obtained using a Sorptomatic-1900 automated volumetric vacuum static analyzer (Fisons, Italy).

The IR spectra of the carbon–silica support were recorded on a Vertex 70V Fourier spectrometer (Bruker, Germany) in the 4000–400 cm^{-1} wavenumber range. The sample, pressed into a KBr pellet, was placed in a cuvette and was calcined at 200°C for 25 min to remove physically bound water.

The elemental composition of the carbon–silica support was determined using an EDX-800 HS energy-dispersive X-ray (EDX) microprobe (Shimadzu, Japan).

The microstructure of the samples was studied using field emission scanning electron microscopy (FE-SEM) on an SU-8000 (Hitahi, Japan) electron microscope. Imaging was performed in secondary-electron detection mode at an accelerating voltage of 2 kV and a working distance of 4–5 mm. The measurement results were optimized using the approach described previously in Ref. [19]. The sample to be examined was placed on the surface of an aluminum stage 25 mm in diameter and wass secured with conductive glue. The morphology of the samples tested under native conditions to rule out the surface effects arising from the deposition of the conductive layer [20].

Table 1. Synthesis of the palladium catalysts Pd/C–SiO$_2$

Pd, wt %	Amounts of the initial components, g		Weight of the resulting catalyst, g
	PdCl$_2$	support	
1	0.25	14.85	15.30
2	0.50	14.70	15.40
3	0.60	11.64	12.34
4	0.80	11.50	12.60
5	1.00	11.40	12.42

Olefins Hydrogenation Experiments

The volumetric hydrogenation setup [21] consisted of a thermostatically controlled jacketed glass reactor and a gas burette. Ethanol (10 mL 95%), 5%Pd/C–SiO$_2$ (50 mg) containing 2.5 mg (0.024 mmol) if Pd, and olefin (2.34 mmol) were placed in the jacketed reactor, whose volume was 30 mL. The reaction was performed under magnetic stirring at atmospheric pressure and a temperature of 23 ± 1°C. The volume of hydrogen consumed during the reaction was measured at a constant pressure, by comparing the levels of the liquid in the burette and leveling vessel. Upon the completion of hydrogenation (when the volume of hydrogen ceased to change), 0.27 g (2.34 mmol) of octane was added as a standard and the catalyst was filtered out. The kinetics of olefin hydrogenation was studied by a volumetric method, recording the change in the amount of hydrogen. To determine reaction rate constants, we plotted the absorbed amount of hydrogen as a function of the reaction time up to a conversion of over 96%. The initial rate was calculated from the slope of the tangent to the initial segments of kinetic curves.

The product composition and yield were determined in a GC-2014 gas chromatograph (Shimadzu, Japan) with a 30 m × 0.25 mm × 0.25 μm capillary column (HP-INNOWAX phase), raising the temperature from 50 to 250°C at a rate of 12°C/min. An MAT 95 XP gas chromatograph–mass spectrometer system (Thermo Finnigan, Germany; voltage of 70 eV, ionization chamber temperature of 250°C, temperature-programmed mode, 50–250°C, heating rate of 10°C/min) was also used. Mixture components were identified using the NIST 05 mass spectral library.

RESULTS AND DISCUSSION

Below, we report the results for the hydrogenation, with molecular hydrogen, of the C=C bond in a series of straight-chain and cyclic olefins over Pd/C–SiO$_2$ catalysts with a metal content of 1 to 5% and over 5%

Table 2. Static adsorption capacity of the carbon-silica support

Temperature, °C	Pore volume, cm^3/g		
	for benzene	for heptane	for water
200	0.02	0.02	0.01
350	0.04	0.06	0.01

$Pd/C–SiO_2$ pre-reduced with diazomethane. The 5%Pd/C sample was used as the reference catalyst.

The support was a hydrophilic low-porosity carbon–silica material with a particle size of 0.1–0.63 mm, a bulk density of 1.25 g/cm^3, a specific surface area of 7.0 m^2/g, and a water absorption capacity of 10%. Static adsorption capacity data for the support are presented in Table 2.

EDX microanalysis showed that the carbon–silica support contains 71.78% C, 24.01% SiO_2, and 3.91% Al_2O_3.

Absorption bands characteristic of both carbons [22] and silica [23] were observed in the IR spectrum of the support (Fig. 1). The absorption band at 3425 cm^{-1} is due to the stretching vibrations of OH-groups bound by hydrogen bonds. The absorption bands at 2920 and 2940 cm^{-1} are assignable to the stretching vibrations of C–H bond in CH_3 and CH_2 groups. The weak peaks at ~1700 cm^{-1} arise from the stretching vibrations of the carbonyl group in the aromatic acids. The absorption bands at ~1630 cm^{-1} are characteristic of the stretching vibrations of the C=C bonds in the aromatic rings of the carbons. The shift of the maximum of this band to 1635 cm^{-1} may be due to the support being similar in structure to the low metamorphosed coals or to the presence of olefinic C=C groups on the surface. However, the presence of this absorption band in the spectrum of the carbon–silica support is most likely fue to bending vibrations of water on the surface of SiO_2. The broad low-intensity absorption band at ~1400 cm^{-1} can be assigned to bending vibrations of COOH groups. The broad absorption band in the 1250–900 cm^{-1} range characterizes the stretching vibrations of the C–OH bonds in the carbons. The band at ~800 cm^{-1} can be assigned to out-of-plane bending vibrations of C–H bonds in the substituted benzene rings. In addition, in the 1250–400 cm^{-1} range there are absorption bands corresponding to Si–O–Si stretching and bending vibrations: the intense band is characteristic of the asymmetric stretching vibrations of Si–O–Si (1090 cm^{-1}); the medium-intensity band at ~800 cm^{-1}, to the symmetric stretching vibrations of SiO_4 tetrahedra; the band at ~500 cm^{-1}, to bending SiO_4 vibrations.

In the FE-SEM images (Fig. 2), palladium particles can not be seen even at a very high magnification. This may indicate that the particle size of Pd is less than 3 nm and the distribution of palladium on the support is relatively uniform, since the resolution limit of the electron microscope is almost ~3 nm. The data of X-ray microanalysis of the $Pd/C-SiO_2$ catalyst indicate the presence of palladium therein.

The catalysts prepared were tested in the hydrogenation of 1-heptene, 1-octene, 1-nonene, 1-decene, 1-hexadecene, allylbenzene, vinylbenzene, 1,1-

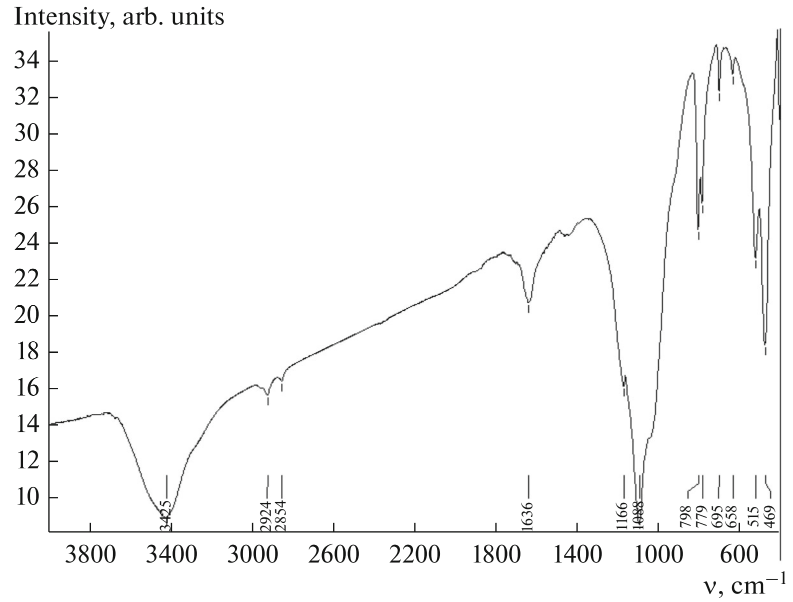

Fig. 1. IR spectrum of the carbon–silica support.

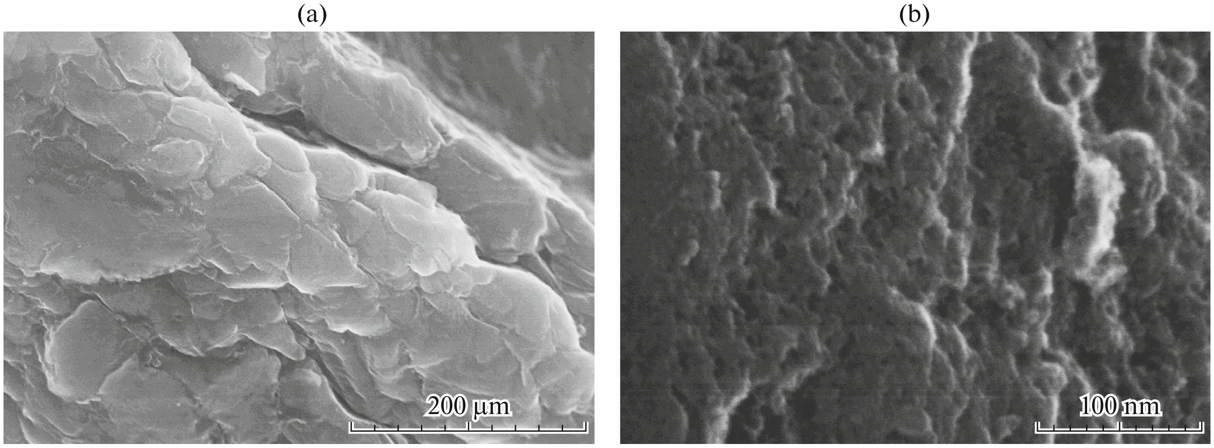

Fig. 2. FE-SEM images of the (a) support surface and (b) 5%Pd/C–SiO_2 catalyst.

diphenylethylene, cyclopentene, cyclohexene, cyclooctene, norbornene, and indene with molecular hydrogen. Their activity was characterized in terms of the initial hydrogenation rate and 98% hydrogen consumption time. The order of the reaction was determined by the integral method.

The relative catalytic activity of the catalysts on the carbon–silica support was determined using 1-decene hydrogenation at a 1-decene : Pd ratio of 100: 1 (Fig. 3a). According to hydrogenation rate, the catalysts are arranged in the following order: 5%Pd/C–SiO_2 > 3%Pd/C–SiO_2 > 4%Pd/C–SiO_2 > 1%Pd/C–SiO_2 > 2%Pd/C–SiO_2 > 5%Pd/C–SiO_2 reduced with diazomethane. The low activity of the latter is probably due to the neutralization of its Brønsted acid sites (AlOH) by diazomethane.

A comparison of the 5%Pd/C–SiO_2 and 5%Pd/C catalysts showed that, when the carbon–silica support is used, the reduction of 1,1-diphenylethylene takes place 2.9 times more rapidly than in the case of 5%Pd/C ($k_{\text{eff}} = 0.75 \pm 0.06$ μmol L^{-1} s^{-1}). The hydrogenation of 1-hexadecene over 5%Pd/C–SiO_2 (initial rate of $w_0 = 1.06 \pm 0.09$ μmol L^{-1} s^{-1}) also occurs 1.4 times more rapidly than over 5%Pd/C. However, the reaction rate over the 5%Pd/C–SiO_2 catalyst is lower and, at 90% conversion, it is 0.41 ± 0.06 μmol L^{-1} s^{-1}, 1.9 times lower than over 5%Pd/C. As a result, the time to 98% conversion for both catalysts is the same and is ~57 min (Fig. 3b).

Since the 5%Pd/C–SiO_2 sample showed the highest catalytic activity, it is this catalyst that was used in all subsequent studies.

Among the straight-chain α-olefins, the alkenes having a phenyl substituent are hydrogenated at the highest rate (Fig. 4). The consumption of hydrogen under the conditions examined is described by a zeroth-order equation (correlation coefficient of >0.98), and the rate of its consumption remains constant throughout the experiment. Thus, the rate constant decreases in the 1,1-diphenylethylene > allylbenzene > vinylbenzene order (ralkene : Pd = 100 : 1, 50 mg of 5%Pd/C–SiO_2) and it is 2.2 ± 0.1, 1.16 ± 0.09 and 1.07 ± 0.09 μmol L^{-1} s^{-1}, respectively.

In the hydrogenation of straight-chain alkenes (1-heptene, 1-octene, 1-nonene, 1-decene, and 1-hexadecene), the initial reaction rate was almost independent of the length of the alkyl chain and was (1.1 ± 0.1)–(0.9 ± 0.1) μmol L^{-1} s^{-1}. However, with an increasing substrate conversion, the hydrogenation rate gradually decreased and, at 90% conversion, it became 1.7–2.0 times lower than the initial rate; the time to 95% conversion was 78–83 min. Apparently, the observed deceleration was due to the accumulation of the hydrogenation product in the reaction mixture.

To verify this hypothesis, a series of experiments was performed, in which 1-octene containing different amounts of octane was hydrogenated. It was found that the initial reaction rate does depend on the concentration of octane (Fig. 5), but when its content was two times higher than the olefin concentration, the hydrogen consumption rate became independent on the substrate conversion and was described by a zeroth-order equation (correlation coefficient of >0.98). In the hydrogenation of alkenes containing a phenyl substituent, the reaction products do not affect the rate of the reaction. For vinylbenzene : ethylbenzene = 1 : 2, $k = 0.90 \pm 0.08$ μmol L^{-1} s^{-1}, and at the same ratio of vinylbenzene to *n*-octane, the constant is 1.02 ± 0.08 μmol L^{-1} s^{-1}, which within the error coincides with the rate constant of hydrogen consumption in the absence of ethylbenzene and octane, respectively. The effect of the concentration of the hydrogenation product of the aliphatic olefins is probably caused by the slightly higher static adsorption capacity of the support for heptane versus benzene (Table 2).

The reactivity of monocycloalkenes in the hydrogenation reactions over 5%Pd/C-SiO_2 was the smaller

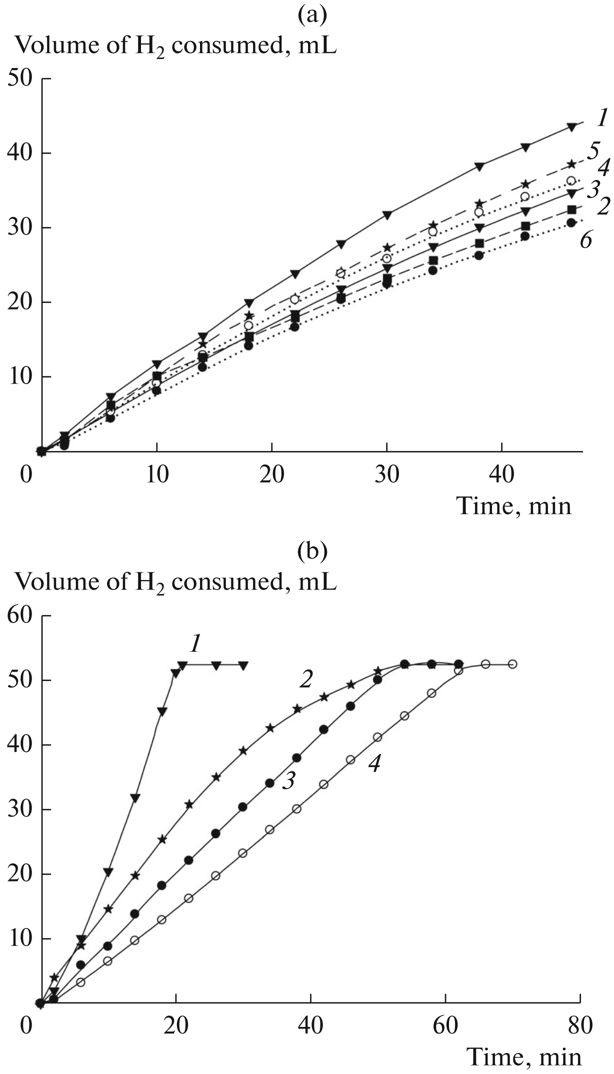

Fig. 3. (a) Time dependence of the volume of hydrogen consumed for 1-decene hydrogenation over (*1*) 5%Pd/C–SiO_2, (*2*) 3%Pd/C–SiO_2, (*3*) 4%Pd/C–SiO_2, (*4*) 1%Pd/C–SiO_2, (*5*) 2%Pd/C–SiO_2, and (*6*)5%Pd/C–SiO_2 reduced with diazomethane. (b) The same curves for the hydrogenation of (*1*) 1,1-diphenylethylene and(*2*) 1-hexadecene over 5%Pd/C–SiO_2 and for the hydrogenation of (*3*) 1-hexadecene and (*4*) 1,1-diphenylethylene over 5%Pd/C.

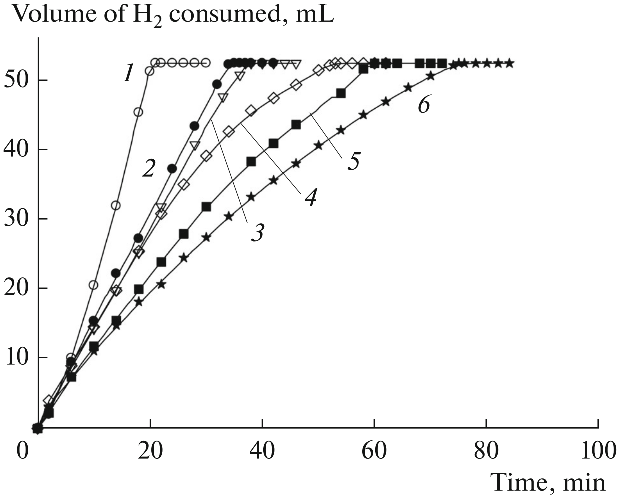

Fig. 4. Time dependence of the volume of hydrogen consumed for α-olefins hydrogenation oover 5%Pd/C–SiO_2: (*1*) 1,1-diphenylethylene, (*2*) allylbenzene, (*3*) vinylbenzene, (*4*) 1-hexadecene, (*5*) 1-decen, and (*6*) 1-octene.

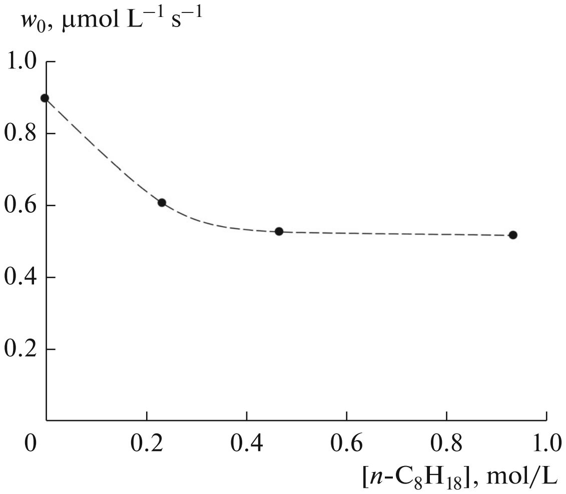

Fig. 5. Dependence of the initial rate of the hydrogenation of 1-octene over the 5%Pd/C–SiO_2 catalyst on the octane concentration in the reaction mixture.

the greater the size of the ring. As in the case of phenyl-substituted alkenes, the hydrogen uptake is described by a zerothe-order equation (correlation coefficient of >0.98), and the rate of hydrogen consumption remains constant throughout the experiment. The rate constant decreases in the cyclopentene > cyclohexene > cyclooctene order and is $1.2 \pm 0.1 \times 10^{-6}$, $7.6 \pm 0.1 \times 10^{-7}$, and $4.8 \pm 0.1 \times 10^{-7}$ μmol L^{-1} s^{-1}, respectively, while the 98% conversion of the initial olefins is reached in 45, 59, and 80 min, respectively (Fig. 6).

The 5%Pd/C-SiO_2 catalytic system is also suitable of effectively hydrogenating bicyclic olefins, such as norbornene and indene. Norbornene is hydrogenated at a higher rate ($k = 2.1 \pm 0.1 \times 10^{-6}$ μmol L^{-1} s^{-1}, and 96% conversion is reached in 34 min) than monocycloalkenes. The hydrogenation rate of the double bond in the cyclopentene ring of indene is two times lower than in the case of norbornene: the rate constant is $7.5 \pm 0.1 \times 10^{-7}$ μmol L^{-1} s^{-1} and is comparable with the rate constant of cyclohexene hydrogenation.

Thus, in the present work new palladium catalysts on the carbon–silica support were first synthesized.

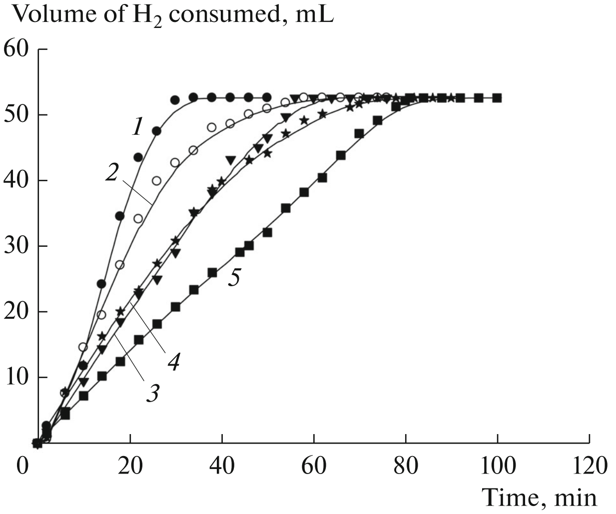

Fig. 6. Time dependence of the volume of hydrogen consumed for the hydrogenation of cyclic olefins over the 5%Pd/C–SiO_2 catalyst: (*1*) norbornene, (*2*) cyclopentene, (*3*) indene, (*4*) cyclohexene and (*5*) cyclooctene.

They demonstrate a higher activity in the hydrogenation reactions of straight-chain and cyclic olefins than Pd/C.

ACKNOLEDGEMENTS

The authors are grateful to the Department of Structural Research of the Zelinsky Institute of Organic Chemistry for the examination of the catalysts by electron microscopy.

Structural studies were supported by the Russian Scientific Foundation (project no. 14-33-00022).

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Translated by A. Pashigreva