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The Influence of the Dispersion of Metals on the Activity of Pt/C and Pd/C Catalysts in the Dehydrogenation of Perhydroterphenyl

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Abstract—The activity of Pt/C and Pd/C catalysts in the dehydrogenation of perhydroterphenyl was studied at conversions lower than 30% depending on the dispersion of platinum and palladium metals, which was estimated by two independent methods (adsorption of CO and X-ray diffraction).

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INTRODUCTION

Hydrogen and systems for its storage attract ever increasing interest in relation to the search for new energy sources and creation of environmentally friendly transport and fuel cells. One of the methods for the storage of hydrogen [1] is based on performing reversible hydrogenation-dehydrogenation of condensed aromatic compounds in catalytic composite systems. Substrates can be accessible chemical compounds containing aromatic nuclei (condensed and polycyclic and aromatic polymers, for instance, polyphenylenes) capable of being reversibly and multiply hydrogenated-dehydrogenated. Perhydroterphenyl (PHT) is most promising in this respect [2]. These materials have exceedingly high capacities with respect to hydrogen, of ~6–8 wt %.

In was shown [3] that catalysts containing noble metals (Pt, Pd, etc.) on carbon carriers with high specific surface areas (for instance, Sibunite and activated carbon) are of the greatest interest for the storage of hydrogen in catalytic composite materials. A high activity of catalysts, which provides a short time of hydrogen discharge from devices for its storage and the possibility of decreasing the temperature of the process, is most important. A high selectivity is the condition of the possibility of multiply using these systems without substrate loss, which is possible if side cracking, hydrogenolysis, and coke formation processes occur. The catalytic activity of Pt and Pd catalysts in the hydrogenation [3] and dehydrogenation [4] of some substrates depends on the dispersion of the supported metal. The question of the influence of the size of metal nanoparticles on their catalytic activity in the dehydrogenation of polycyclic naphthene hydrocarbons is therefore of considerable interest for both fundamental science (for the determination of the mechanism of the reaction) and practical applications, because this dependence is one of the main parameters determining the effectiveness of a catalyst for use in devices for hydrogen storage and should be taken into account in its development.

The specific catalytic activity of metallic supported catalysts can change substantially as the size of metal nanoparticles changes depending on the type of the reaction. For structurally sensitive reactions, which supposedly occur on ensembles of atoms on the surface of metals, and which include aromatic compound hydrogenation-dehydrogenation reactions, the activity of a catalyst depends on the structure of the surface of the metal and is determined not only by the total number of surface metal atoms accessible to the reaction.

The purpose of this work was to compare catalytic activity in the dehydrogenation of perhydroterphenyl with the results of physicochemical studies of catalysts and reveal the rules that governed the influence of the size of nanoparticles on specific catalytic activity. The catalysts were synthesized using original procedures developed by the authors.

EXPERIMENTAL

Catalysts and Preparation

The influence of the dispersion of platinum and palladium on the dehydrogenation of PHT was studied using a series of catalysts containing 1 wt % platinum or palladium on Sibunite carbon carrier. All the methods for depositing palladium and platinum were based on the deposition of metal precursors from aqueous solutions of chloride complexes followed by reduction with hydrogen. The dispersion of metals was varied by the method and conditions of the deposition of the corresponding metal salt (Table 1). The initial reagents were $PdCl_2$ and a solution of H_2PtCl_6 ($\omega(Pt) = 36.3\%$) of ch. (pure) grade. Solutions of H_2PdCl_4 were pre-

Table 1. Conditions of catalyst preparation

Sample	Method for precursor deposition	Concentration, composition, and pH of initial working solutions	Preliminary reduction
		1%Pt/C	
1	Deposition on carrier surface	0.001 M H_2PtCl_6, pH 6.9 ($Na_2CO_3 : H_2PtCl_6 = 2.1$)	Gas-phase, 180°C, 1 h,
2	Adsorption from dilute solutions	0.0004 M H_2PtCl_6	Gas-phase, step: 150°C, 1 h; 250°C, 2 h
		1%Pd/C	
3	Impregnation according to incipient wetness capacity	0.145 M $[Pd(NH_3)_4]Cl_2$, pH 6.9	Calcining in a flow of air at 350°C, 2 h
4	Impregnation in excess solution	0.012 M H_2PdCl_4, pH 1.97	Liquid-phase
5	Deposition on carrier surface	Solution of PHC, pH 7.0 ($Na_2CO_3 : H_2PtCl_6 = 2.2$), concentration Pd 0.004 mol/l	Liquid-phase
6	Impregnation according to incipient wetness capacity	0.145 M $[Pd(NH_3)_4]Cl_2$, pH 6.9	Gas-phase, at 150°C, 4 h
7	Deposition on carrier surface	Solution of PHC, pH 10.2 ($Na_2CO_3 : H_2PtCl_4 = 10$), concentration Pd 0.004 mol/l	Liquid-phase

pared by dissolving $PdCl_2$ in 4.6 M HCl taken in a 1 : 2.55 molar ratio with subsequently bringing the mixture to the required concentration. A solution of $[Pd(NH_3)_4]Cl_2$ was prepared as described in [5], by the addition of a 1 M solution of ammonia to a 0.146 M solution of H_2PdCl_4 with heating to 40–78°C.

To prepare catalysts by deposition on the surface of the carrier, Sibunite powder (0.1–0.25 mm fraction) was added to the initial working solution formed after the addition of a 1 M solution of Na_2CO_3 to a solution of H_2PtCl_6 at 19°C or to a solution of H_2PdCl_4 at 4°C. The concentration and pH were selected on the basis of the data obtained in [6]. pH of solutions and suspensions was controlled by a pH-meter. Suspensions were intensely mixed by a magnetic stirrer for 1 h at the same temperatures and then at 80°C (Pt) and 60°C (Pd) also for 1 h. The completeness of deposition (or adsorption) was checked by qualitative reactions with KI (Pt, sensitivity 2 μg/ml) or dimethylglyoxime (Pd, sensitivity 0.2 μg/mol) [5].

For liquid-phase reduction, the flask with the suspension was purged with hydrogen. Mixing was then switched on, and the suspension was held at a weak hydrogen flow for ~1 h until hydrogen absorption ceased. Gas-phase reduction was performed in a U-shaped tube by passing hydrogen (0.7 cm/s) over a thin layer of a preliminarily dried catalyst. The rate of heating was about 10 K/min.

The preparation of sample 2 by adsorption from dilute solutions, including the preliminary treatment of Sibunite and step sample reduction after the deposition of the platinum compound, was performed as described in [3].

After suspension filtration, samples 1, 2, 4, 5, and 7 were many times washed with distilled water on a filter and held in water for 12 h to more completely remove ions from the pore space. Sample 6 obtained by impregnation according to its incipient wetness capacity was washed from ions after gas-phase reduction. All catalysts were dried in a desiccator at 115°C.

The Determination of Catalytic Activity

A catalyst sample (100 mg) and perhydroterphenyl (400 mg) were loaded into a reactor, which was a quartz ampule 9 mm in diameter and 100 mm long (Fig. 1). The substrate/catalyst weight ratio was 4. Per-

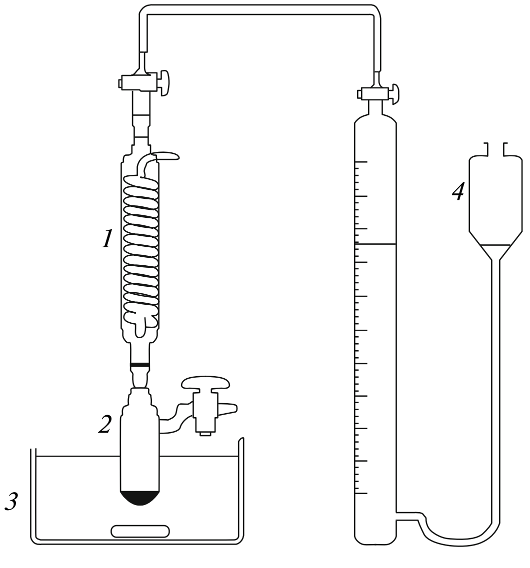

Fig. 1. Catalytic unit: (*1*) reflux condenser, (*2*) reactor, (*3*) heater, and (*4*) gas burette.

Table 2. Composition of a mixture of terphenyls (*t* is the boiling temperature)

Composition	Content, wt %	Formula	*T*, °C
Biphenyl	4	$C_{12}H_{10}$	
o-Terphenyl	23	$C_{18}H_{14}$	337
m-Terphenyl	35		379
p-Terphenyl	20		389
Polyphenylenes	18	–	–

hydroterphenyl was prepared by the complete hydrogenation of terphenyl (Santowax-R, Solutia). The composition of initial terphenyl is given in Table 2.

Within the reactor, a thermocouple was placed into a substrate layer in a thin-walled beaker; the thermocouple recorded the temperature of the reaction mixture. The reactor was placed into a furnace and heated to 350°C. At the top of the reactor, there was a reflux condenser, which prevented organic substrate loss with a flow of hydrogen. The temperature profile of the reaction mass (*T*) during reactor heating is shown in Fig. 2. This method allowed the dehydrogenation reaction to be performed while the boiling temperature of the multicomponent mixture of organic substrates (perhydroterphenyl isomers and partially hydrogenated terphenyl isomers formed in the reaction) changed as the reaction proceeded. The volume of released hydrogen was measured using a gas burette (Fig. 1). The amount of hydrogen (ml) released during the first 10 min of the reaction at PHT conversion less than 50% (see Table 2) can be used as a conventional measure of catalyst activity. At the reactor load that we used and complete perhydroterphenyl conversion into terphenyl, the amount of released hydrogen should be 340 ml, which corresponds to a 7.25 wt % capacity of the naphthene substrate with respect to hydrogen.

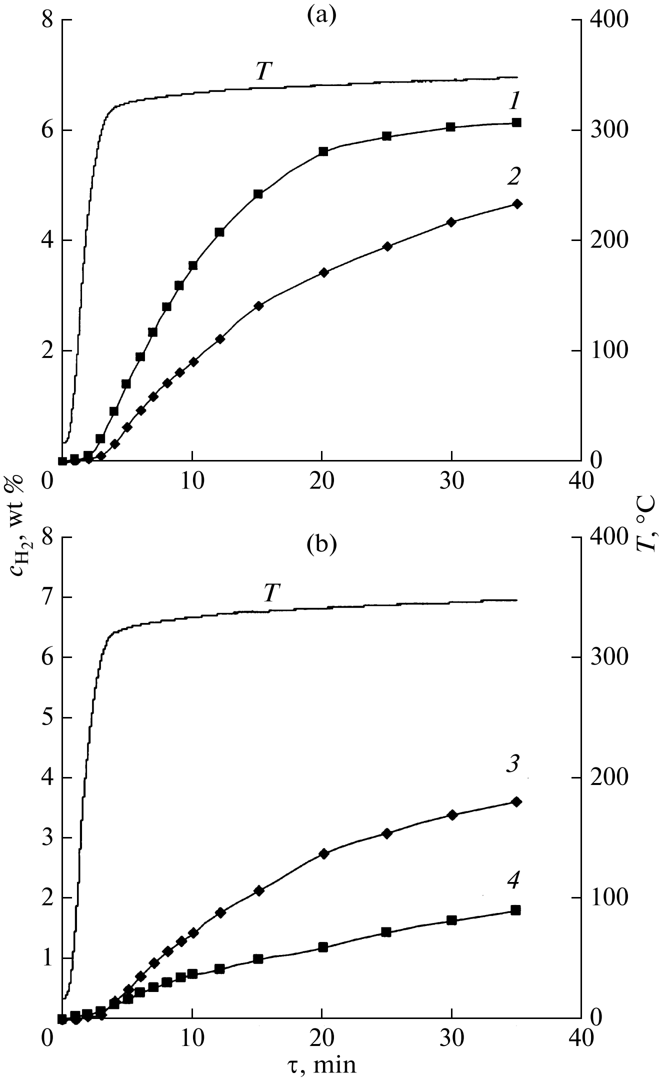

Fig. 2. Kinetic curves of hydrogen release during the dehydrogenation of tercyclohexane for (*1, 2*) 1% Pt/C, (*3, 4*) 1% Pd/C catalysts.

The Determination of the Dispersion of Metals

Adsorption method. We used catalyst titration at room temperature by carbon oxide pulses (the loop volume corresponded to the introduction of 3.2 × 10^{17} CO molecules per pulse) to measure the dispersion of metals in catalysts. A catalyst sample (200 mg) was placed into a reactor at the exit of which nonadsorbed CO in a carrier gas (He) flow passed into an analyzer cell (katharometer). Pulses were produced every 10 s. The content of metals in the samples was 6.14×10^{18} Pt atoms and 1.13×10^{9} Pd atoms.

Before titration, the catalysts were subjected to standard treatment, they were reduced in a 5% H_2/Ar flow (heating to 300°C, 30 K/min, 10 min at 300°C), blown off in a flow of helium at 300°C (5 min), and cooled in a flow of helium to room temperature during 20 min.

The temperature of preliminary reduction in H_2 was selected to be 300°C because the activity of catalysts in the dehydrogenation of PHT was compared at 300–350°C.

X-ray diffraction. X-ray analysis of the samples was performed on a DRON-2 diffractometer over the 2θ range 6°–60° at a 0.5 deg/min goniometer rotation rate using CuK_α radiation. The size of platinum crystallites was calculated from diffraction line broadenings using the Debye–Scherer equation and the strongest reflections at 39.8° from the Pt [111] plane and 40.1° from the Pd [100] plane.

RESULTS AND DISCUSSION

The activity of catalysts. The kinetic curves of the release of hydrogen during the dehydrogenation of perhydroterphenyl are shown in Figs. 2. The rates of hydrogen release are substantially different (by ~2 times) along the initial curve portions for two Pt/C and Pd/C samples. For all the samples, values taken to conventionally represent activity (ml H_2 per 10 min of the reaction) are listed in Table 2. Clearly, different sample activities are only related to the dispersion of platinum and palladium in catalysts, because the catalysts were prepared using the same carbon carrier (Sibunite).

Note that some catalyst stirring in a mixture of organic substrates in the microreactor that we used is provided by substrate convection caused by boiling and, additionally, intense hydrogen release. During a short time of experiments (40–60 min), complete release of hydrogen (7.25 wt %) could be attained without mechanical reaction mass stirring.

Table 3 contains the results of titration with carbon monoxide of Pt/C samples 1 and 2 and Pd/C samples 3 and 4 preliminarily reduced in H_2; the activities of these samples in the dehydrogenation of perhydroterphenyl differed most strongly (see Figs. 2 and 3).

The mean size of metal particles in catalysts can most simply be estimated by representing particles on the surface of a carrier in the form of cubes with five accessible faces and one face in contact with the surface of the carrier. According to this simple model, the ratio between the fraction of surface atoms (S) and the total number of metal atoms (V) depending on the size of particles is calculated. The calculated curve is shown in Fig. 3. According to [7], the size of noble metal atoms is $R_{at}(Pt) = 1.39$ Å and $R_{at}(Pd) = 1.37$ Å, and the crystal structure of platinum and palladium metals is face-centered cubic.

Data on the adsorption of CO and the model of construction of particles on the surface of the carrier were used to calculate the mean size of metal particles (with insignificant errors) in the catalysts. The dispersion of Pt and Pd particles obtained this way was compared with the results of catalytic tests of the samples in the dehydrogenation of PHT (Table 3).

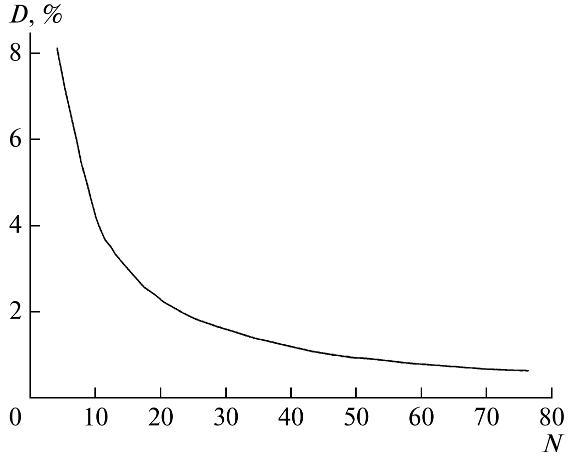

Fig. 3. Ratio between the fraction of surface atoms (accessible to adsorption of CO) and the total number of metal atoms in a cubic particle depending on its size.

Note that, as distinct from platinum, where there are only linear forms of CO adsorption (Pt–CO), bridge CO adsorption forms (Pd–CO–Pd) are possible and, according to [8], predominant for palladium. For palladium catalysts, dispersion was therefore calculated on the assumption that CO was adsorbed on palladium metal particles as bridge forms only.

Table 3 shows that the results of dispersion determination from the adsorption of CO closely agree with the data on catalytic activity. Among platinum catalysts, sample 1 with the highest activity has the maximum Pt dispersion (particle size ~2 nm). A similar trend is observed for palladium catalysts. Sample 3 with the highest Pd dispersion is most active (Table 3). Moreover, the numerical values of activity and dispersion of all Pt/C and Pd/C samples well agree to within measurement errors.

Table 3. Activity of Pt and Pd catalysts versus active phase dispersion

Sample	A	D	N	σ_{ad}, nm	σ_{XRD}, nm
1% Pt/C					
1	147	0.66	7	2	A
2	75	0.24	20	6	7.5
1% Pd/C					
3	60	0.10	25*	7.5*	A
4	31	0.063	40*	12*	9
5	41				6
6	36				8
7	55				A

Note: A is the activity with respect to H_2 (H_2 (ml) released in 10 min), D is the dispersion of CO/at Pt(Pd) molecules, N is the number of atoms in the base of a particle in the form of a cube, σ_{ad} is the mean size of particles determined from the adsorption of CO, σ_{XRD} is the radius of particles according to the X-ray diffraction data, and A is the amorphous state of the substance. Asterisked values were calculated on the assumption that palladium predominantly formed bridge structures in the adsorption of CO.

Note (see Table 1) that, as distinct from somewhat less active sample 6 prepared using a similar procedure, sample 3 was not subjected to preliminary prolonged (4 h at 150°C) reduction in a flow of hydrogen. Before Pd dispersion measurements, sample 3 was for a short time (10 min at 300°C) reduced in a dilute 5% H_2/Ar mixture. The somewhat lower activity of sample 6 could be caused by partial sintering of Pd metal particles.

X-ray studies of catalysts were also used to estimate the dispersion of metal particles from Pt and Pd line broadenings. The results were compared with the size of active components determined from the data on adsorption of CO. An analysis of the X-ray data showed that the metallic phase (Pt and Pd) in three samples (1, 3, and 7) was in the amorphous state, which was evidence that the size of metal particles in them was less than 5 Å. The high dispersion of metals in these samples is responsible for the highest activity of these catalysts in the dehydrogenation of PHT.

To summarize, we observe a direct correlation between the activities of Pt/C and Pd/C catalysts in the dehydrogenation of perhydroterphenyl at conversion degrees below 30% and the dispersion of platinum and palladium metals, which was estimated by two independent methods (adsorption of CO and X-ray diffraction).

The method for the determination of the dispersion of metals in catalysts on carbon carriers from the adsorption of CO showed a fairly high convergence of the results.

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