Palladium Hydrogenation Catalyst Based on a Porous Carbon Material Obtained upon the Dehydrochlorination of a Chloro Polymer

R. M. Mironenko[a, b, *, O. B. Belskaya[a, c], V. S. Solodovnichenko[a, d], T. I. Gulyaeva[a],
Yu. G. Kryazhev[a, d], and V. A. Likholobov[a, d]**

[a] *Institute of Hydrocarbons Processing, Siberian Branch, Russian Academy of Sciences, Omsk, 644040 Russia*
[b] *Dostoevsky Omsk State University, Omsk, 644077 Russia*
[c] *Omsk State Technical University, Omsk, 644050 Russia*
[d] *Omsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Omsk, 644024 Russia*
*e-mail: ch-mrm@mail.ru
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Abstract—The applicability of a porous carbon material obtained as a result of the "chemical" dehydrochlorination of chlorinated polyvinyl chloride as a support for palladium hydrogenation catalysts was demonstrated. The efficiency of the catalyst was evaluated in the liquid-phase reactions of nitrobenzene hydrogenation and chlorobenzene hydrodechlorination. Although the specific activity of the catalyst was lower by a factor of 3–4 than that of the samples based on Sibunit and carbon nanotubes, the complete conversion of the initial compounds with the selective formation of end products under mild conditions was achieved at a relatively low palladium content (1.5%).

INTRODUCTION

Polymeric chlorine-containing materials are in wide current use because of their performance characteristics. Polyvinyl chloride (PVC), the world output of which is greater than 35 million tons per year [1], is one of these materials. Although the products based on PVC exhibit a prolonged service life, the amount of environmentally hazardous wastes obtained from them is growing every year. The problem is acute because all of the chlorine-containing organic compounds are xenobiotics, and the unqualified combustion of chlorine-bearing wastes or their spontaneous combustion unavoidably lead to the formation of highly toxic compounds such as phosgene and dioxins [1, 2]. Currently, attention has been focused on the utilization and repeated use of chlorine-containing plastics [1–3]. Among many methods for the conversion of chloro polymers, those which make it possible to obtain called-for products upon the utilization of wastes are especially attractive [2, 3]. One of these methods is the dehydrochlorination of chloro polymers with the production of porous carbon materials. Thus, as a result of the heat treatment of the polymers and copolymers of 1,1-dichloroethylene for many hours, their thermal dehydrochlorination occurs with the formation of porous carbon materials with an ultramicroporous structure and a narrow unimodal pore-size distribution, which makes it possible to use them for the separation of small molecules in gas separation processes [4]. Another method for the production of porous carbon materials with large micropore and mesopore volumes is based on the "chemical" dehydrochlorination of chlorinated carbon-chain chloro polymers, such as chlorinated PVC (CPVC), under the action of alkalis in organic media. A porous carbon material is formed after the carbonization of the resulting product under relatively mild conditions and subsequent activation [5]. In this case, the porous structure of the material obtained can be regulated over a wide range depending on the structure of a polymer precursor and the conditions of carbon formation. The porous carbon materials thus obtained are promising adsorbents, in particular, for medical purposes [5].

Carbon materials are frequently used as supports in the synthesis of heterogeneous catalysts. The wide application of carbon supports in catalysis is caused by their large specific surface areas and the presence of a developed pore system, which facilitate the transfer of reactants and reaction products. The supports of this type possess tunable surface chemical properties and chemical inertness, especially in strong acidic and basic media [6, 7]. Among them are various forms of

Table 1. Porous structure parameters of the carbon supports

Support	S_{BET}, m^2/g	V_Σ, cm^3/g	V_{micro}, cm^3/g	d_{av}, nm
C-CPVC	756	0.71	0.23	3.8
CNT	196	1.49	0.01	30.3
Sibunit	354	0.60	0.03	6.7

porous carbon materials: activated carbons, carbon black of different grades, carbon nanotubes (CNT), carbon nanofibers, etc.

Here, we consider the applicability of a porous carbon material obtained by the "chemical" dehydrochlorination of CPVC as a palladium catalyst support for the reactions of nitrobenzene hydrogenation and chlorobenzene hydrodechlorination. The liquid-phase catalytic hydrogenation of nitrobenzene was studied in sufficient detail. This reaction is an industrial method for the production of aniline, a large-scale product of organic synthesis [8–10]. The hydrodechlorination of chlorobenzene is frequently used as a model reaction in the studies of the hydrogenolysis of C–Cl bonds in organochlorine compounds. Furthermore, this reaction can be used for the testing of metallic catalysts, which are potentially capable of manifesting high efficiency in hydrogenation processes for the neutralization of toxic organochlorine compounds [11–16].

EXPERIMENTAL

The porous carbon material obtained by the "chemical" dehydrochlorination of CPVC under the action of KOH in a dimethyl sulfoxide solution followed by heat treatment was used as a support for a palladium catalyst. Henceforth, this material is referred to as C-CPVC.

Baytubes C 150 HP multiwall CNT and a Sibunit carbon material were also used for the preparation of catalysts. These supports are radically different in morphology, and they are frequently used in research works for the preparation of hydrogenation catalysts. The porous structure characteristics of the carbon supports, namely, the BET specific surface area (S_{BET}), the total adsorption pore volume (V_Σ), the micropore volume (V_{micro}), and the average pore diameter (d_{av}), were found by an analysis of the isotherms of nitrogen adsorption–desorption at 77 K, which were measured on an ASAP-2020 surface area and porosimetry analyzer (Micromeritics, United States).

The supported palladium catalysts containing 1.5 wt % Pd were prepared by the incipient wetness impregnation of carbon supports with aqueous solutions of H$_2$PdCl$_4$. The preliminary treatment of the catalysts included their drying in a flow of argon at a temperature of 423 K for 0.5 h and reduction in a flow of hydrogen at 523 K for 2 h. The dispersion (D) of the supported metal in the reduced Pd/C samples was determined by the pulse chemisorption of CO at room temperature on an AutoChem II 2920 chemi-

sorption analyzer (Micromeritics). Before the measurement of dispersion, the reduced samples were pretreated in a flow of a mixture containing 10% H$_2$ in Ar under temperature-programmed conditions in a temperature range of 303–393 K (rate of heating, 10 K/min), and the signals of the thermal-conductivity detector were measured.

The liquid-phase hydrogenation of nitrobenzene (10 mmol) was performed in the presence of Pd/C catalysts (200 mg) in a steel autoclave at a temperature of 323 K and a pressure of 0.5 MPa in an ethanol solution (100 mL). Before each particular experiment, the catalyst was activated with hydrogen (323 K, 0.5 MPa) for 0.5 h under conditions of stirring. The course of the reaction was judged from the volume of hydrogen consumed in a specific time interval.

The hydrodechlorination of chlorobenzene (10 mmol) was performed analogously at a temperature of 363 K and a pressure of 0.5 MPa in the presence of Pd/C (200 mg); however, in this case, an ethanol–water mixture (1 : 1) with an additive of NaOH (for the binding of hydrogen chloride formed upon the hydrodechlorination) served as a reaction medium.

After the completion of reactions (i.e., after the cessation of hydrogen consumption), the products were analyzed by gas chromatography–mass spectrometry (on an Agilent 5973N/6890N instrument) and gas–liquid chromatography (on a Hewlett Packard 5890 Series II instrument). The activity of the catalysts was expressed as a turnover frequency (TOF) in $mol_{H_2} \, mol_{Pd}^{-1} \, s^{-1}$.

RESULTS AND DISCUSSION

The study of the carbon supports by the low-temperature adsorption–desorption of nitrogen showed that the porous carbon materials chosen for comparison have a mesoporous structure with relatively uniform pores. The difference between CNT and Sibunit consists in a smaller specific surface area of CNT at a considerably larger average pore size (Table 1).

The carbon material obtained upon the dehydrochlorination of CPVC was essentially different in texture from CNT and Sibunit. In contrast to the latter, C-CPVC possessed a much higher specific surface area with a small average pore diameter. The high specific surface area of C-CPVC is caused by an increased fraction of micropores (more than 30% on an V_Σ basis) (Table 1). Note that the porous structure of a support

Table 2. Catalytic properties of Pd/C samples in the liquid-phase reactions of nitrobenzene hydrogenation and chlorobenzene hydrodechlorination under a pressure of hydrogen

Catalyst	D	Nitrobenzene hydrogenation*			Chlorobenzene hydrodechlorination**		
		x_{NB}, %	S_a, %	TOF, s^{-1}	x_{CB}, %	S_b, %	TOF, s^{-1}
1.5%Pd/C-CPVC	0.22	100	98	1.4	100	99	1.3
1.5%Pd/CNT	0.52	100	98	5.5	100	98	4.2
1.5%Pd/Sibunit	0.54	100	98	5.8	100	97	3.4

 * Reaction conditions: T = 323 K; P = 0.5 MPa; 100 mL of ethanol; 10 mmol of $C_6H_5NO_2$; 200 mg of catalyst; $C_6H_5NO_2$: Pd = 353 (mol/mol); x_{NB} is the conversion of nitrobenzene; and S_a is the selectivity of aniline formation (based on the chromatographic analysis data).

 ** Reaction conditions: T = 363 K; P = 0.5 MPa; 100 mL of a mixture of ethanol−water (1 : 1); 10 mmol of NaOH; 10 mmol of C_6H_5Cl; 200 mg of catalyst; C_6H_5Cl : Pd = 353 (mol/mol); x_{CB} is the conversion of chlorobenzene; and S_b is the selectivity of benzene formation (based on the chromatographic analysis data).

plays an important role in the formation of metal sites and their stabilization on the support surface and in the mass transfer of reactants and products within a catalyst grain in the course of reaction [6, 7].

According to the results of chromatographic analysis, all of the 1.5%Pd/C catalysts tested in the reaction of nitrobenzene hydrogenation under a pressure of hydrogen ensured the complete conversion of nitrobenzene with the selective formation of aniline (Table 2). In this case, the amount of consumed hydrogen was nearly stoichiometric for the reaction of nitrobenzene conversion into aniline (Fig. 1a). The yield of heavy unidentified products was about 2%.

The study of the catalysts in the liquid-phase reaction of chlorobenzene hydrodechlorination under a pressure of hydrogen also showed their high efficiency (Table 2): the complete conversion of chlorobenzene with the selective formation of benzene (cyclohexane and biphenyl were detected among the by-products) was achieved. However, the amount of consumed hydrogen was noticeably smaller than that corresponding to the reaction stoichiometry of chlorobenzene conversion into benzene, especially, on the Pd/C-CPVC catalyst, in the presence of which it did not exceed 54% on a calculated basis (Fig. 1b).

The reason for this can be the participation of hydrogen, which was previously absorbed by the catalyst in the process of its activation before conducting the experiments, in the reaction. Indeed, in the course of the preliminary reduction of catalysts under temperature-programmed conditions, a peak due to the release of hydrogen with a maximum at 352 K was detected (Fig. 2). In this case, the amount of hydrogen desorbed from the Pd/C-CPVC sample was considerably greater than those desorbed from the Pd/CNT and Pd/Sibunit samples with the same supported metal contents. This may be related to the different dispersion of palladium, which was lower for Pd/C-CPVC by a factor of >2 than that for Pd/CNT and Pd/Sibunit. Coarse palladium particles absorb hydrogen with the
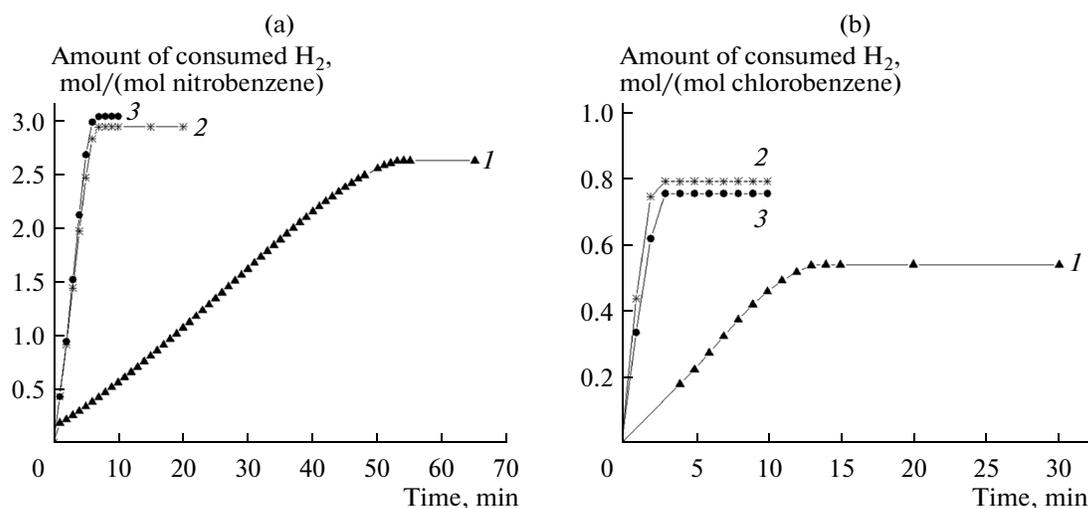
Fig. 1. Curves of hydrogen consumption in the course of the reactions of (a) nitrobenzene hydrogenation and (b) chlorobenzene hydrodechlorination in the presence of the following catalysts: (*1*) 1.5%Pd/C-CPVC, (*2*) 1.5%Pd/CNT, and (*3*) 1.5%Pd/Sibunit.

Thermal-conductivity
detector signal, arb. units
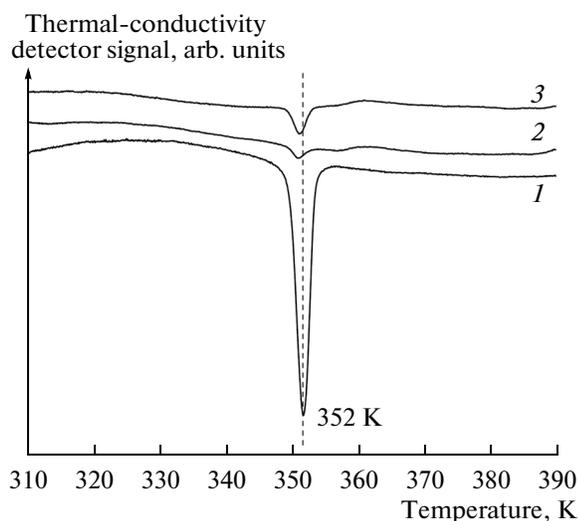
Fig. 2. Desorption of hydrogen under the conditions of the preliminary reduction of the (*1*) 1.5%Pd/C-CPVC, (*2*) 1.5%Pd/carbon nanotubes, and (*3*) 1.5%Pd/Sibunit catalysts with a mixture of 10% O_2 in Ar in the temperature-programmed mode in a range of 303−393 K.

formation of hydride even at room temperature and a partial pressure of H_2 of 2.27 kPa [17]. The release of hydrogen, which was frequently observed under the conditions of the temperature-programmed reduction of palladium catalysts at $T < 393$ K, was related to the decomposition of palladium hydride [14, 18]. The much more intense release of previously absorbed hydrogen from the Pd/C-CPVC sample (Fig. 2) can be the reason for the lower degree of H_2 conversion in the hydrodechlorination reaction. The same effect was also observed in the hydrogenation of nitrobenzene in the presence of Pd/C-CPVC (Fig. 1a); however, in this case, it was much smaller (the amount of consumed hydrogen was 87% on a calculated basis) because, at this reaction temperature (323 K), it seems likely that the desorption of hydrogen absorbed in the course of activation was insignificant.

We also cannot exclude the solvent effect. The deviations of hydrogenation and, especially, hydrodechlorination reactions from stoichiometry can also be explained by the participation of ethanol in the reactions. It is well known that aliphatic alcohols can serve as the donors of hydrogen, thus facilitating the reduction of a substrate [12, 15]. Thus, in a study of the hydrodechlorination of chlorobenzene on a Pd/C catalyst in an ethanol solution, Yakovlev et al. [12] found that an additional quantity of hydrogen, which participated in the transformations of chlorobenzene, was generated as a result of the dehydrogenation of ethanol to the acetate ion.

From an analysis of the results obtained, it follows that the catalyst based on C-CPVC with the low dispersity of supported palladium ($D = 0.2$) is less active by a factor of 3–4 (in terms of a surface Pd atom) in

the test reactions than the samples of Pd/Sibunit and Pd/CNT, which differ from each other only slightly in catalytic activity at close metal dispersity values ($D = 0.5$) (Table 2). The reason for the lowered specific catalytic activity of Pd/C-CPVC can be the localization of metal particles in the micropores of the support, as a result of which the working surface area of the metal decreases and a portion of supported Pd becomes inaccessible to substrate (nitrobenzene and chlorobenzene) molecules. The effect of blocking the supported metal in the narrow pores of the support was described earlier [19, 20] in a study of Pt/C and Pd/C catalysts prepared with the use of different carbon supports. Thus, according to Okhlopkova et al. [19], coarsely dispersed palladium particles ($D = 0.19$) were formed on a carbon support with the developed system of micropores (activated carbon), and the resulting catalyst manifested specific catalytic activity lower by a factor of almost 2 than that of a sample based on mesoporous Sibunit, which was characterized by the value of $D = 0.51$, in the reaction of nitrobenzene hydrogenation.

The lower dispersion of the supported metal in the sample of Pd/C-CPVC can also be explained by the presence of residual chlorine on the support surface. Earlier, it was established [21] that the presence of different halide ions on the surface of a carbon support affects both the size of palladium particles formed and the particle size distribution. For example, after the preliminary adsorption of chloride ions on activated carbon, the resulting Pd particles acquired a larger size than that without the use of this adsorption.

CONCLUSIONS

Thus, the C-CPVC carbon material obtained by the dehydrochlorination of CPVC can be used as a support for the synthesis of palladium catalysts for hydrogenation. A comparatively high specific surface area and the presence of a considerable fraction of micropores (more than 30% on a total pore volume basis) are its special features. The complete conversion of starting compounds with the selective formation of target products was achieved on the 1.5%Pd/C-CPVC catalyst in the reactions of nitrobenzene hydrogenation (323 K, 0.5 MPa) and chlorobenzene hydrodechlorination (363 K, 0.5 MPa). In contrast to the samples of Pd/CNT and Pd/Sibunit, the above catalyst exhibited lower (by a factor of 3–4) specific catalytic activity. Furthermore, with the use of Pd/C-CPVC, the deviation of hydrogenation and hydrodechlorination reactions from stoichiometry was observed; this fact can be explained by the presence of a considerable amount of previously accumulated hydrogen in the catalyst or by the participation of ethanol as a donor of hydrogen in the reaction. In the future, we intend to examine the reasons for these special features of the Pd/C-CPVC system.

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