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PREPARATION OF Pd/C CATALYSTS VIA DEPOSITION OF PALLADIUM HYDROXIDE ONTO SIBUNIT CARBON AND THEIR APPLICATION TO PARTIAL HYDROGENATION OF RAPESEED OIL

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Abstract

Pd/Sibunit catalysts were prepared by deposition of palladium hydroxide onto the support surface in an alkaline medium. It was found that the palladium distribution throughout the catalyst grain, and the dispersion of Pd particles depend on (*i*) the order of the addition of H_2PdCl_4 and Na_2CO_3 to carbon suspension, (*ii*) Na_2CO_3 to H_2PdCl_4 ratio, and (*iii*) aging time of the mixture $H_2PdCl_4 + Na_2CO_3$ before its addition to the carbon. The catalysts were tested in the hydrogenation of cyclohexene and rapeseed oil under static conditions. The yield of *trans*-isomers as products of partial hydrogenation of rapeseed oil was found to decrease with decreasing the Pd particle size in the catalysts, as well as with increasing the Pd concentration on the periphery of the support grains.

Keywords: Pd/C catalysts, vegetable oil hydrogenation, *cis-trans* isomerization

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INTRODUCTION

Ni and Pd catalysts are employed for partial or total hydrogenation of C=C double bonds of vegetable oils [1-4]. The partial hydrogenation yields cis- and trans-isomers of unsaturated products, the last being able to affect negatively the health [5]. The severe conditions of hydrogenation unavoidable while using silica supported Ni catalysts [6-9] (473 K, 15 atm) promote the formation of *trans*-isomers and that of products of thermal decomposition of fatty acids. Application of palladium catalysts in this reaction promises many advantages due to the lower temperature of the process (373-423 K), and higher selectivity toward cis-isomers of fatty acids. Moreover, the trans-isomer formation can be diminished by decreasing the palladium particle size [2]. Carbon materials possessing tunable chemical and textural surface properties are most suitable for use as supports for palladium catalysts [10].

Conventional approaches for the Pd/C catalyst preparation are impregnation of the support with solutions of the catalyst precursors, as well as their adsorption or deposition. The last seems to be the most convenient way for the production of Pd/C catalyst via the control of the palladium particle size and distribution through the support grain [11, 12]. For that, any water-soluble salt of Pd^{II} is appropriate [13-15], but the most usable are H_2PdCl_4 or Na_2PdCl_4. Basic agents, such as nitrogen-containing bases, or hydroxides, carbonates or bicarbonates of alkali metals (usually Na_2CO_3), are employed for the palladium deposition. The Pd/C catalyst preparation method based on the hydrolysis of H_2PdCl_4 at pH $\leq$ 5-6 and deposition of palladium hydroxide onto a carbon support were thoroughly studied in [13-16]. It was found that the higher is the pH of the catalyst precursor solution contacting with the support grains, the more palladium is located on their periphery [12]. However, there is insufficient information available in the literature on the properties of Pd/C catalysts obtained via palladium hydroxide deposition at pH $\geq$ 7. Supposedly, the egg-shell distribution of Pd in the support grain at these conditions may be narrower than for palladium deposition at pH $\leq$ 6.

In this paper, we describe the effects of the Pd hydroxide deposition onto the carbon surface at pH > 7 on (i) the Pd particle size and their distribution in the carbon grains in the final Pd/C catalysts and (ii) on the catalytic activity and selectivity of these catalysts in hydrogenation of rapeseed oil.

EXPERIMENTAL

Carbon support

A powdered mesoporous carbon of the Sibunit family [17] with S_{BET} of 450 m^2/g, average pore volume of 0.819 cm^3/g, average pore diameter of 9.9 nm, and grain size between 0.07 and 0.09 mm was used as a support.

Preparation of Pd/Sibunit catalysts

1 (wt.%) Pd/Sibunit catalysts were prepared by deposition of Pd hydroxide onto the support surface at room temperature. Pd hydroxide was generated by mixing aqueous solutions of Na_2CO_3 and H_2PdCl_4, with Na/Pd atomic ratio denoted further as χ, being changed from 5 to 21. The deposition was carried out by three different methods as described below.

I. Addition of a Na_2CO_3 solution to the carbon powder suspended in aqueous H_2PdCl_4. 0.2 g of Sibunit was suspended in 5 cm^3 of distilled water by agitating for 30 minutes. 1 cm^3 of 0.019 M H_2PdCl_4 solution was added to the slurry with a peristaltic pump (0.33 cm^3/min) followed by the addition of 2 cm^3 of a Na_2CO_3 solution (χ = 5-21). Finally, the mixture was agitated for 6 h.

II. Addition of a H_2PdCl_4 solution to the carbon powder suspended in aqueous Na_2CO_3 (χ = 5-21). The deposition was performed analogously to method **I**, but the sequence of the reagents' addition was altered.

III. Addition of a mixture of aqueous H_2PdCl_4 and Na_2CO_3 (χ = 5-21) to the carbon slurry. The solutions of H_2PdCl_4 and the alkali agent were preliminary mixed. After aging for 15 min, the mixture was added to the suspended support and left under agitation for 6 h.

In all cases, the final slurries were alkaline with pH values as high as 7.5-8.5 depending on χ. The carbon samples with supported palladium hydroxide were thoroughly washed with distilled water, dried at 373 K and reduced in a hydrogen flow at 423 K for 1 h.

Catalysts characterization and testing

The dispersion D of Pd particles in the Pd/C catalysts was determined by pulse CO-chemisorption. CO was chemisorbed from the hydrogen flow at 298 K, and a CO:Pd = 1:1 stoichiometry was assumed. The mean particle size d_s was calculated as $d_s(nm) = 1.08/D$ [18].

X-Ray Photoelectron Spectroscopy (XPS) was adapted to investigate the metal distribution in the catalyst grain. For this purpose, a VG ESCA HP device was used. The Pd/C atomic ratios detected for the as-prepared and pre-ground catalyst were compared with the theoretical value calculated for uniform metal distribution.

The liquid-phase hydrogenation of cyclohexene (5% vol. solution in isopropyl alcohol) at 273 K, which is known to be a structure-insensitive reaction [19], was used for catalytic testing of the Pd/Sibunit catalysts. Efficiency η of the catalyst was evaluated as the ratio $\eta = W_g/W_i$, where W_g is the reaction rate for the pre-ground catalysts and W_i is the rate for the non-ground (initial) catalyst. Grinding was performed with an agate mortar to carbon particle sizes of 1-5 μm.
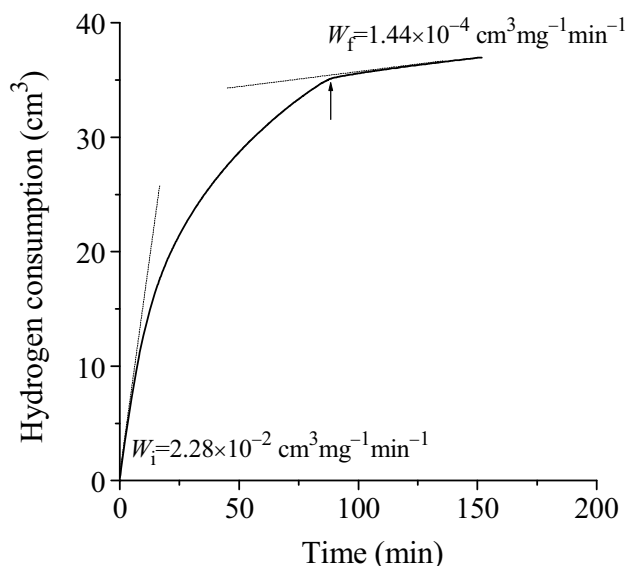
Fig. 1. Typical shape of the kinetic curve of rapeseed oil hydrogenation (catalyst: method **II**, Na/Pd = 21). A break on the curve (shown with the arrow) can be considered as a border between the regions of fast and slow hydrogen consumption

Procedure of rapeseed oil hydrogenation

Rapeseed oil supplied by Nefis Cosmetics Company (Russia) without preliminary distillation was hydrogenated at 373 K and hydrogen pressure of 6 atm in a stainless steel autoclave (150 ml in volume). 20-50 mg of a 1% Pd/C catalyst (the product of the catalyst weight by metal dispersion $m_{Pd/C} \times D$, which is proportional to the palladium surface, was kept constant) and 14 g of rapeseed oil was loaded into the autoclave, which was then sealed. The air inside the autoclave was successively replaced with nitrogen and hydrogen at ambient pressure. After heating the autoclave to 373 K, the hydrogen pressure was brought to 6 atm. An electromagnetic stirrer working at 1000 rpm and an automatic recorder of hydrogen uptake were turned on simultaneously as soon as the pressure required was attained. The experiment was finished within 2.5-3 h, when the rate of hydrogen uptake decreased by a factor of *ca*. 150 (Fig. 1). After cooling the autoclave, the products of rapeseed oil hydrogenation were filtrated and analyzed.

Analysis of the hydrogenated rapeseed oil

Products of rapeseed oil hydrogenation were etherified with sodium methylate $NaOCH_3$, and the methyl ethers obtained were analyzed by IR techniques and gas-liquid chromatography (GLC) in accordance with [20-23].
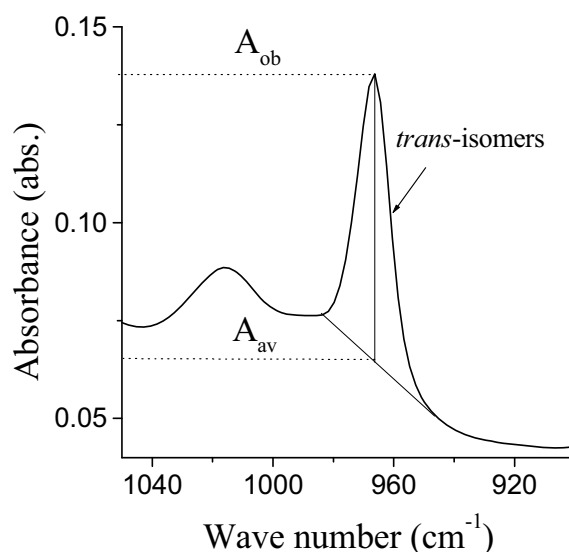
Fig. 2. Typical IR spectrum of partially hydrogenated rapeseed oil and the method of determination of A_{ob} and A_{av}, which are necessary to calculate the concentration of trans-isomers

Infrared transmission spectra were recorded in the 400-6000 cm^{-1} region with a resolution of 4 cm^{-1} using a Shimadzu FTIR 8300 spectrometer equipped with the diffusion reflection accessories DRS-8000. The mode of calculation of the amount of trans-isomers among the products of the partial hydrogenation of rapeseed oil is shown in Fig. 2. The absorbance A_{ob} of the IR irradiation at 966 cm^{-1} by a probe can be attributed to the absorbance of trans-isomers A_{tr} and the absorbance of other unsaturated compounds A_{av} and expressed as $A_{ob} = A_{av} + A_{tr}$. The concentration of trans-isomers C_{tr} was calculated by the following empirical equation derived from the Bouguer-Lambert-Beer law [20, 24-26]:

$$C_{tr} = 0.37 \times \left(\frac{A_{ob}}{A_{av}} - 1 \right), \quad \text{mole fraction}$$

GLC (using a 15 m×0.25 mm×0.25 μm quartz capillary column with Carbowax-DVB) was employed to detect the amounts of saturated and unsaturated products of rapeseed oil hydrogenation, and to calculate the ratio between the total numbers of C-C and C=C bonds in a sample. Outlet times of main products at 453 K were as follows: methyl palmitate 250 s, methyl stearate 350 s, methyl oleate 400 s, methyl arachidate 570 s.

The iodine number of the oils was determined by a standard method described elsewhere [27].

RESULTS AND DISCUSSION

The state of the active component in the Pd/C catalysts

Table 1

Influence of the preparation method and the Na/Pd ratio χ on the dispersion of the supported metal in 1% Pd/Sibunit catalysts, their catalytic activities before and after grinding, and efficiencies η of the catalyst grain in the liquid-phase hydrogenation of cyclohexene

Preparation mode	**I** $Na_2CO_3+\{C+H_2PdCl_4\}$			**II** $H_2PdCl_4+\{C+Na_2CO_3\}$			**III** $\{H_2PdCl_4+Na_2CO_3\}+C$		
χ	5	9	21	5	9	21	5	9	21
CO/Pd	0.43	0.57	0.60	0.45	0.54	0.68	0.34	0.29	0.31
Average particle size, d_s (nm)	2.5	1.9	1.8	2.4	2.0	1.6	3.2	3.7	3.5
W_i, $cm^3_{H_2}/mg_{cat}\cdot min$	0.068	0.081	0.076	0.103	0.152	0.215	0.040	0.054	0.056
W_g, $cm^3_{H_2}/mg_{cat}\cdot min$	0.133	0.162	0.180	0.145	0.215	0.266	0.079	0.077	0.079
TOF, sec^{-1} (±25%)	2.45	2.25	2.38	2.55	3.15	3.10	1.84	2.10	2.02
η	0.51	0.50	0.42	0.71	0.71	0.81	0.51	0.70	0.71

Results of the CO-chemisorption studies of the catalysts prepared are shown in Table 1. Analysis of this data leads to the conclusion that a successive addition of the reagents during the catalyst synthesis (methods **I** and **II**) provides higher dispersions of Pd particles than the addition of the preliminarily mixed reagents to the carbon slurry (method **III**). As a rule, the metal dispersion increases with increasing parameter χ, except for method **III,** which gives the

lowest dispersion nearly independent of χ. This means that the higher is the pH of the final suspension, the smaller are the Pd particles formed at the support surface. The blank experiments (deposition of palladium hydroxide in the absence of the support at the same conditions) showed that mixing of H_2PdCl_4 and Na_2CO_3 yields dark-brown colloidal solutions of palladium hydroxocomplexes, whose stability to coagulation increases with χ. Thus, a higher rate of growth and coagulation of the colloidal particles at χ = 5 leads to a lower dispersion of the metal in Pd/C catalysts, and the adsorption of just-formed colloids onto the carbon surface results in better palladium dispersion than the adsorption of the aged ones at any value of χ.

Table 2

XPS data on the palladium concentration on the periphery of support grains for the 1% Pd/C catalysts prepared by methods **I-III** (at χ = 21) and some characteristics of the products of rapeseed oil hydrogenation over these catalysts [1]

Properties of 1% Pd/C catalysts				Products of rapeseed oil hydrogenation			
Synthesis method	Sample	Pd\C atomic ratio (XPS)	d_s(Pd), nm	Trans/Cis ratio	$\dfrac{(C-C)}{(C=C)}$ ratio	Unsaturated acids, mole fraction	Iodine number
				0.174 [2]	0.07 [2]	0.932 [2]	108.2 [2]
I	ground	0.00114 [3] 0.0028					
I	initial	0.0055	1.8	2.7	0.32	0.758	64.9
II	initial	0.0121	1.6	1.7	0.65	0.604	51.8
III	initial	0.0097	3.5	3.0	0.54	0.649	55.6

[1] Surface area of palladium loaded into the reactor and duration of the hydrogenation were kept constant in all cases.
[2] The characteristics of the initial rapeseed oil.
[3] The theoretical value for the uniform distribution of palladium through the support grains.

The results of the XPS investigation of the metal concentration on the periphery of the support grains are given in Table 2. As is evident from these data, the palladium concentration on the support surface exceeds the theoretical value calculated for uniform metal distribution. Since this method provides a scanning depth not exceeding 10 nm, one can conclude that all the catalyst samples studied possess an egg-shell distribution of the active component in the Sibunit grain. The data in Table 2 allow for the conclusion that the width of the palladium concentration profile (PCP) depends on the catalyst preparation mode and increases in the order:

Width of PCP (by XPS):   **II < III < I**   (1)

Hence, the higher is the pH of the carbon suspension at the beginning of palladium deposition, the narrower is the width of PCP on the support grains. This conclusion is also confirmed by catalytic testing of the Pd/C samples prepared in the liquid-phase hydrogenation of cyclohexene, whose rate is usually controlled by the internal diffusion of reagents. In this connection, the efficiency η of the catalyst grain increases with increasing the concentration of the active component at the outer rim of the support grains. As it is seen from Table 1, for the Pd/C catalysts with $\chi = 21$, the catalytic data on η give the same qualitative estimate of the width of PCP (**II < III < I**) as the XPS data (**1**) discussed above. The data in Table 1 testify also that the calculated values of the turn-over frequency (TOF) in cyclohexene hydrogenation are similar for all mortared catalysts within experimental error. This suggests that the chemical state of the supported palladium in these catalysts was not altered due to differences in the deposition procedures.

Rapeseed oil hydrogenation over 1% Pd/Sibunit catalysts

Some characteristics of the products of partial hydrogenation of rapeseed oil over this catalyst are listed in Table 2. The determined amounts of unsaturated species (unsaturated acids or double C=C bonds) in these products point out that the catalysts can be ranged in accordance with their hydrogenation activity per unit palladium surface as

Specific catalytic activity: **II > III > I**   (**2**)

Comparing orders (**1**) and (**2**) leads to the deduction that the specific rate of rapeseed oil hydrogenation increases with decreasing width of PCP in the catalyst. Hence, hydrogenation seems to be diffusion-controlled (the internal diffusion region).

Studies on the selectivity of rapeseed oil hydrogenation by FTIR and GLC show that the catalysts prepared by method **II** yield lower amounts of *trans*-isomers than the catalysts prepared by methods **I** and **III** (Fig. 3, Table 2). The calculated values of the trans/cis ratio are as follows:

Trans/Cis ratio: 1.7 (**II**) < 2.7 (**I**) ≤ 2.9 (**III**)   (**3**)
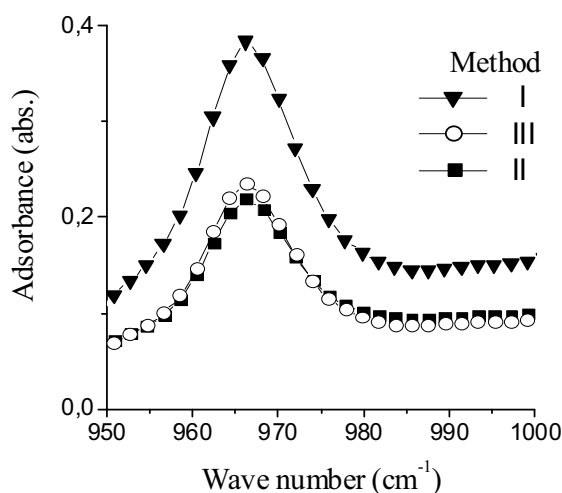
Fig. 3. IR-spectra of the products of rapeseed oil hydrogenation on the
1 wt.%Pd/C catalysts prepared by methods **I-III** ($\chi = 21$)

Analyzing the data of Table 2 one can conclude that the concentration of
trans-isomers in the reaction products depends on both the Pd particle size and
the character of the distribution of palladium in the support grain. Comparison
of the catalysts prepared by methods **II** and **III** allows one to conclude that the
coarse metal particles produce higher amounts of trans-isomers than the fine
particles do, which confirms the finding of the work [2]. Besides, comparison of
the catalysts prepared by methods **I** and **II** points out that a Pd/C catalyst with a
broader PCP yields more trans-isomers than one with a narrower PCP does.
Consequently, the condition of the accumulation of the trans-isomers of fatty
acids in the products of partial hydrogenation of rapeseed oil is a prolonged
contact of its molecules with the palladium surface, owing to *i*) multiple-point
mode of their adsorption, which is more probable on large metal particles, and
is much stronger than one-point adsorption, or *ii*) long time of diffusion out of
the carbon pores loaded with palladium particles for the catalyst with the broad
palladium concentration profile in the support grain.

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