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Carbon-palladium catalytic systems based on Kazakhstan shungite ore for liquid-phase nitrobenzene hydrogenation

The carbon concentrate (C = 40% by the weight) based on shungite ore has been obtained by chemical enrichment. The concentrate is used as carbon-metal carrier of catalyst. It has been established that the best affinity of the C-Pd is due to the high content of carbon. A partial recovery of palladium due to electron-donor centers of the surface of the carbon matrix occurs on the shungite carrier as a result of chemisorption on H_2PdCl_4 . The carbon-metal catalysts have been researched by electron microscopy and X-ray fluorescence analysis.

Keywords: shungite, catalytic systems, carbon-palladium.

Introduction

Palladium catalysts based on carbon substrates are widely used in industrial important reactions of organic synthesis.

At present, much attention is paid to the development of new methods for the preparation of porous carbon materials and palladium catalysts based on carbon carriers [1-2], in particular, to the influence of the nature of the carbon substrate on the catalytic properties of supported palladium [3].

The high cost and lack of raw materials for producing carbon carriers limit scope of their industrial application. Therefore, it is important to develop new methods of producing porous carbon materials with desired combination properties of the available types of industrial raw materials [4]. One type of this kind of carbon carriers may be shungite.

The researches of condition effects of chemical modification and heat treatment of natural shungite to the structure of the obtained porous carbon

materials have been carried out in the given work. The nature of distribution of ionic complexes of applied palladium has been also carried out. The catalytic properties in reactions of liquid phase hydrogenation of nitrobenzene have been determined.

Materials and methods

Shungite ore was used from the tailings of the mining of polymetallic ores of the "Bolshevik" field of East Kazakhstan.

The first stage the shungite ore enrichment has been carried out by froth flotation method [5]. The carbon content in the concentrate achieves 40% in one stage. Dehydrated concentrate with a moisture content of 15% has been treated sequentially by concentrated acids HNO_3 , HF, respectively. After that the concentrate has been washed to neutral. The chemical composition of the initial ore and shungite products are given in Table 1.

Table 1 – Element composition of shungite samples

№	Chemical composition, % by weight										
	C	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	Na ₂ O	K ₂ O	M _{Al}
1*	19,1	50,7	0,6	12,3	4,6	2,0	3,3	2,8	1,0	2,2	0,28
2**	43,8	32,1	0,5	8,6	2,6	2,2	2,8	0,9	1,5	1,8	0,19

* – Shungite ore

** – Shungite concentrate

The carriers of carbon metal catalysts have been prepared by briquetting the pasty mass through drawplate with diameter 2 mm. Further shungite briquettes have been treated by heat in an inert atmosphere of argon at 800 °C. The next stage

of carrier preparation was a gas-steam activation with acute water vapor at temperature 800-850 °C. Specific surface area (up to 180-270 m²/g) has been increased on account of gas-steam activation.

3 types of carriers have been obtained (Table 2).

Table 2 – Treatment regimens of carrier

Sample	Processing by acids		Activation temperature, °C	Media
	HNO ₃	HF		
1	-	-	800	Argon
2	+	-	800	Argon
3	+	+	800	Argon

The carbon metal catalysts have been prepared in a such way:

Sample №1. Impregnation of the shungite carrier with hydroalcoholic solution H₂PdCl₄, with the next heat activation at temperature 800°C under argon.

The sample № 2. Impregnation of the carrier with an aqueous alcohol solution of H₂PdCl₄, with the next evaporation to dry salt and heat activation at temperature 800°C under argon.

Sample № 3. Direct shungite mixing with a hydroalcoholic H₂PdCl₄ solution and further briquetting with the next heat activation at a temperature of 800°C under argon.

The palladium content in all the prepared catalysts was 3-5 % by weight, which has been controlled by X-ray fluorescence analysis.

Structure of shungite carrier has been researched by electron microscopy Quanta 3D 200i in the

Nanolaboratory of the al-Farabi Kazakh National University.

The depth reaction of the liquid phase hydrogenation of nitro compounds under hydrogen pressure has been determined on the high-pressure kinetic installation. Hydrogenation has been carried out under by the next conditions : P = 20 atm , t = 50 °C, the solvent – isopropyl alcohol, q = 0,2 g The analys of the hydrogenation products has been carried out on the gas chromatography with a mass spectrometer detector, Agilent, Santa Clara, USA.

Results and discussion

The results of electron – microscopic examination of samples shungite ore and shungite concentrates have shown that the structure of the particles shungite were presented flocculent inclusions in a carbon matrix with a particle size of 500 nm ÷ 4 microns.

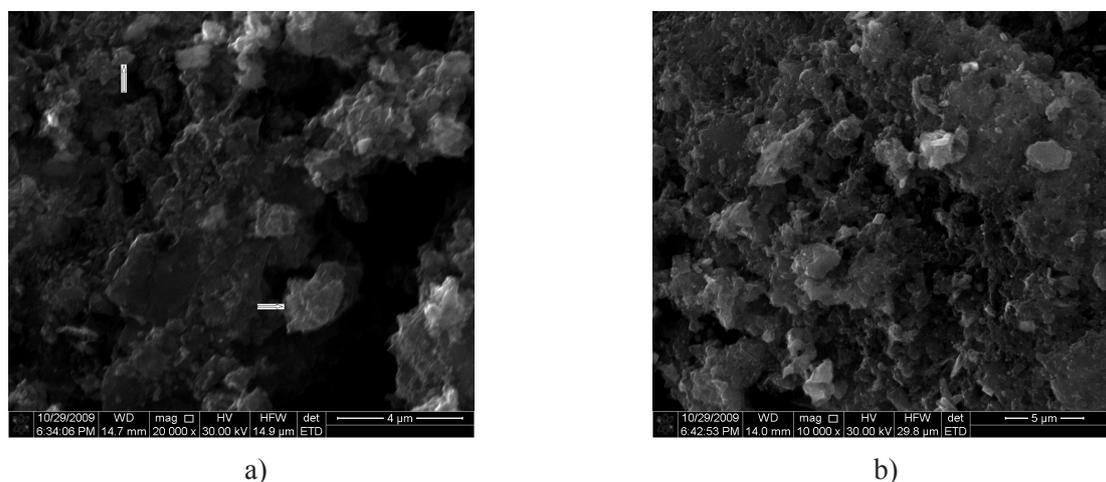


Figure 1 – The results of scanning electron microscopic analysis: a) Shungite ore «Bolshevik»; b) Shungite processed by the acids

Sample № 3 (Figure 1b) which has been processed sequentially with concentrated acids HNO_3 , HF, respectively, with subsequent briquetting has a fundamental difference from the original shungite. It has a uniform surface with many small pores distributed uniformly on the carrier surface, in contrast to sample №1 (Figure 1a). The pore size does not exceed 40 nm. In the sample № 3 due to sequential acid treatment has achieved the highest percentage of the carbon concentration, which

contributes to a better affinity of the C – Pd link in the catalyst in the further impregnation of the carbon carrier by water – alcohol solution H_2PdCl_4 . Great importance has the formation of the carrier surface, the removal from the surface irregularities and disclosure of “corked” pores, which is important for the catalytic activity of the carrier.

The obtained palladium – carbon catalysts have been tested in liquid phase hydrogenation reactions of nitrobenzene (Figure 2).

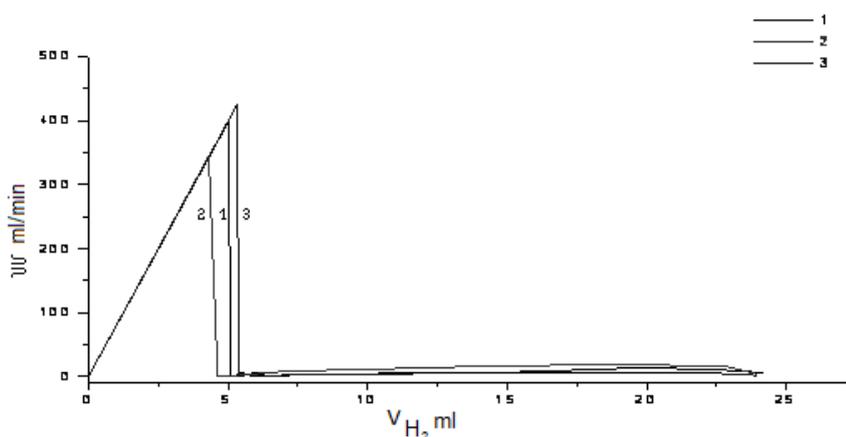


Figure 2 – Kinetic curves of the nitrobenzene recovery: 1 – catalyst №1; 2 – catalyst №2; 3 – catalyst №3

At the initial stage of the hydrogenation reaction proceeds with high speed for 15 seconds. Then the process decreases down slowly. Rate decrease of the hydrogenation process can be explained by the fact that competitive interaction of the nitrobenzene starting molecules and the reaction product – aniline take place on the catalyst surface.

In particular, it can be said that the molecules of the aniline do not immediately leave active catalyst sites and thereby inhibit the hydrogenation process. Also, the graph shows that the method of catalyst preparation affects the hydrogenation rate. To confirm these data the dependence of nitrobenzene hydrogenation over time has been tracked (Figure 3).

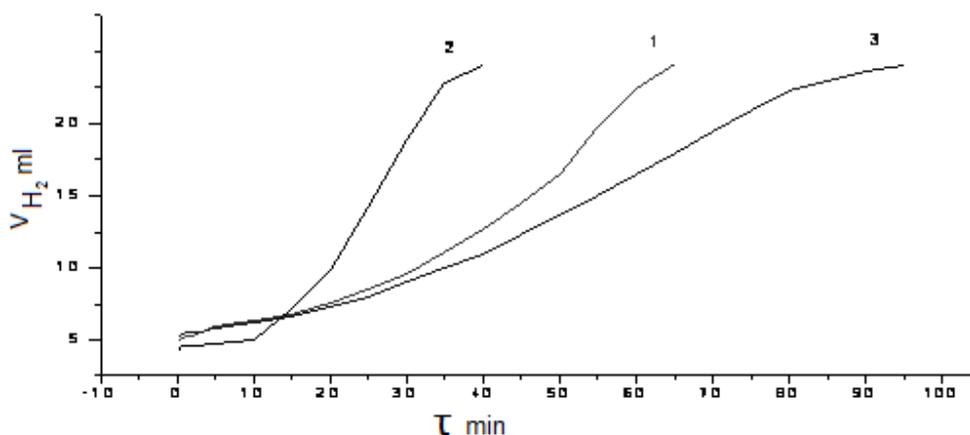


Figure 3 – Kinetic curves of the nitrobenzene recovery:
1 – catalyst №1; 2 – catalyst №2; 3 – catalyst №3

The analysis of the kinetic curves of the nitrobenzene recovery has been established that the catalyst № 3 spends more time for allocation of the same amount of hydrogen as compared with the catalyst № 2. Consequently catalyst №2 is the best

option for the nitrobenzene hydrogenation under specified conditions.

The results of the chromatographic analysis are given in Figure 4 and Table 3.

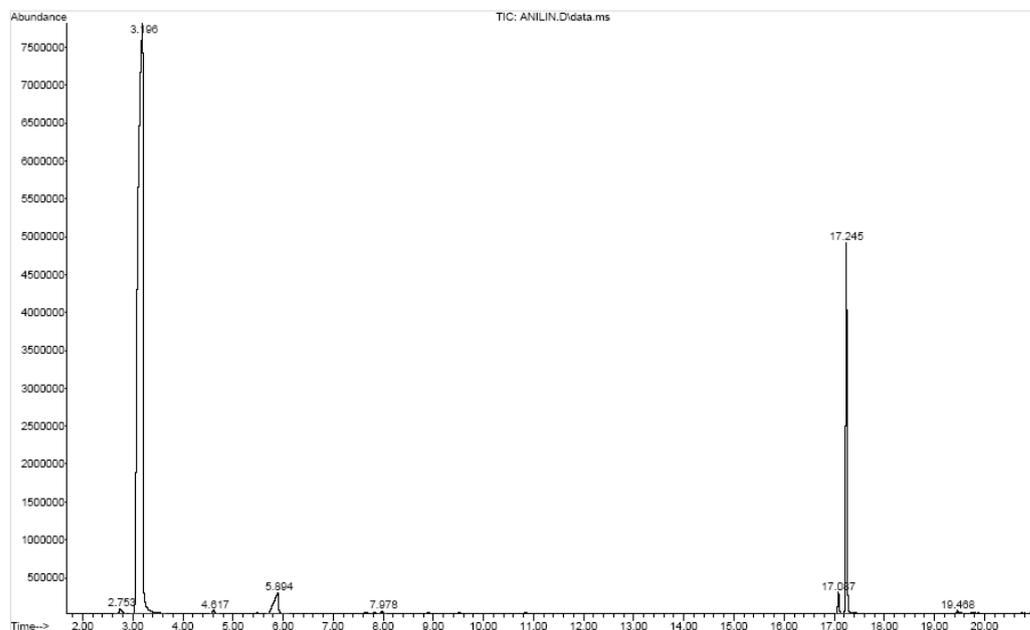


Figure 4 – The chromatogram of products of nitrobenzene recovery

Table 3 – Products of nitrobenzene recovery

№	Elements	%
1	2 – propanol	0,37
2	Isopropyl *	82,43
3	methyl isobutyl ketone	0,22
4	ammonia, water	2,70
5	p – xylene	0,11
6	benzene	0,74
7	Aniline	13,33
8	ethanol	0,10

*- solvent

The above data have shown that nitrobenzene was not detected in the solution after the hydrogenation. It indicates that its complete hydrogenation to aniline and other minor by products.

Conclusion

1. The method of sequential treatment of shun-

gite by acids (HNO_3 and HF) is the optimal method for carbon substrate obtaining for catalyst carrier.

2. As a result of H_2/PdCl_4 chemisorption on the shungite carrier is a partial recovery of palladium with electron – donor centers of the surface of the carbon matrix. The presence and percentage of palladium catalysts has been established by scanning elec-

tron microscopy and X-ray fluorescence analysis.

3. It has been established that the most effective for the nitrobenzene hydrogenation in the laboratory is a carbon-palladium catalyst by treated HNO_3 at $800\text{ }^\circ\text{C}$ for 40 min under argon impregnation with $1\text{ mg/ml H}_2\text{PdCl}_4$ with evaporating the solution to dry salts.

4. The products of the nitrobenzene reduction of by gas chromatography have been researched. It has been established that the nitrobenzene in isopropyl alcohol to form the rebuilding of fully aniline has been established.

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