Platinum Nanoparticles Supported on Reduced Graphite Oxide as Hydrogenation Catalyst

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Platinum nanoparticles supported on reduced graphite oxide are produced by reduction of a slurry including graphite oxide and $H_2PtCl_6 \cdot xH_2O$, and pyridine as modifying agent. Four compounds as a formate-ion or ethylene glycol or hydrazine or sodium borohydride as reducing agents were used. Both initial graphite oxide and Pt-containing compositions reduced were investigated by elemental analysis, thermogravimetric analysis, IR- and Raman spectroscopies. Reduced compositions are tested as catalysts of decene-1 and nitrobenzene hydrogenation at hydrogen atmospheric pressure and 45°C.

In the result of reduction Pt^{4+} is converted to Pt metal and graphite oxide loses of oxygen. The symbasis Pt loading with C/O ratio is observed. Compositions Pt - reduced graphite oxide catalyze the hydrogenation of decene-1 and nitrobenzene in a solution. The greatest activity is shown composition reduced by sodium borohydride with the particle size of 2.0 nm, however it is substantially lower than it for Pt/fullerene black catalyst. Some inhibiton of hydrogenation by incompletely reduced graphite oxide is shown.

Keywords: Graphite oxide, Platinum nanoparticles, Catalyst, Hydrogenation.

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1. INTRODUCTION

Carbon nanomaterials with graphene structure attract attention as potential catalysts or electrocatalysts supports in recent years. A dominant causes of this interest to nanomaterials with graphene structure are associated with substrate possibility to coordination with aromatic fragments of their structure and availability of the conjugate bonds system, and the abnormal wide two-sided surface and high (comparable with graphite) conduction that is necessary for catalysts of the reactions proceeding with electron transfer from metal to a substrate [1].

The perspective support for catalysts for reactions with electron transfer from these points of view may be the graphene, i.e. the graphite inclucive one layer and being, thus, a two-dimensional conductor.

At the same time, an effective catalyst support includes anchor functional groups, suitable for covalent bonds formation with metal ions. In a structure of carbon nanomaterials with aromatic conjugation system as recently noted [2-4] it is difficult to introduce functional groups into carbon nanomaterials to the extent sufficient for the formation of covalent bonds with platinum. In fact, substitution reactions involving aromatic ring protons are impossible in this case because of the absence of protons and extremely small (of the order 10^{-4} g^{-1}) amount of dangling bonds.

Widely used for graphite functionalization methods of oxidation by various agents allows to introduction carbonyl-, carboxyl-, epoxy- and hydroxyl (phenolic) groups, but leads to destruction of conjugation system and conduction degradation. One of products of graphite deep oxidation as graphite oxide may be reduced to graphene and this method is discussed as graphene preparation methods in the appreciable quantities [5, 6].

It seemed tempting to produce platinum particles supported on graphene since appears possible to fix of platinum by means of functional groups graphite oxide and to combine of platinum reduction with graphite oxide reduction to graphene.

2. RESULTS AND DISCUSSION

The graphite oxide produced by oxidation of graphite by sulfuric or nitric acids or their mixture, includes, except carbon, significant amounts of oxygen and characterised by C/O ratio equal of 2.544 (Tab. 1).

Table 1 − Properties of graphite oxide and Pt-containing compositions based on it

A sample	Content of , % wt.				Gross formula	C/O ratio	I_D/I_G
	C	H	N	O			
GO	49.31	2.42	0.03	45.02	$C_8H_{4.68}O_{5.48}$	1.459	0.964
Pt/RGO_F	49.48	2.85	0.44	40.92	1.81 % $Pt/C_8H_{5.49}O_{4.97}N_{0.06}$	1.610	1.008
Pt/RGO_{EG}	70.77	1.53	0.73	17.96	3.70 % $Pt/C_8H_{2.06}O_{1.52}N_{0.07}$	5.263	1.037
Pt/RGO_H	79.64	0.94	2.82	6.02	8,82 % $Pt/C_8H_{1.125}O_{0.45}N_{0.24}$	17.622	1.106
Pt/RGO_B	71.14	1.91	1.52	12.41	8,22 % $Pt/C_8H_{2.56}O_{1.05}N_{0.148}$	7.636	1.034

As per a conventional nonstoichiometric models by Lerf and Klinovski, graphite oxide includes mainly hydroxylic and epoxy- (1,2-ethers) functional groups. Carboxyl groups are present along the edges graphene

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sheets. Besides, oxygen is present as 5 and 6-membered lactols. The presence of such functional groups agrees with the thermogravimetric analysis of graphite oxide in Ar (Fig. 1) according to which the basic products of decomposition are carbon oxide with m/e 28, water (m/e 18) and carbon dioxide (m/e 44), escaping with ekzo-effect mainly to 200°C.
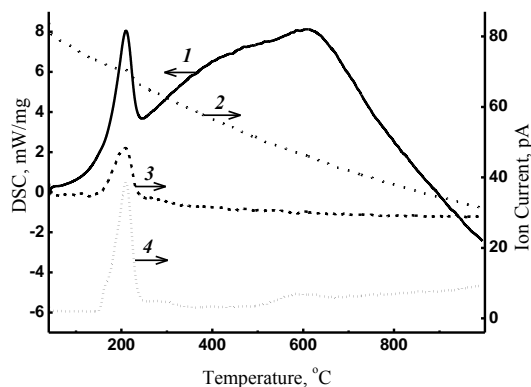

Fig. 1 - Thermogram in Ar of (*1*) graphite oxide combined with the mass spectrometric analysis of gas products with mass numbers, *m/e*: (*2*) 28, (*3*) 18, (*4*) 44

The presence of these functional groups in a graphite oxide structure proves to be true also by IR- data wherein the absorbtion peaks can be assigned to the O–H stretching vibrations at 3430 cm^{-1}, C–O stretching at 1070 cm^{-1}, the C = O carbonyl stretching at 1727 cm^{-1}, the C = C ring stretching at 1624 cm^{-1}, the phenol O–H deformation vibration at 1407 cm^{-1} and C-OH at 1226 cm^{-1}).

The introduction of hydroxyl and epoxy-groups into graphene structure with sp^2- hybridization of carbon atoms causes reorganisation of planar conjugate system into spacial system with sp^3- hybrid carbon atoms. As a result of it in Raman-spectra graphite oxide (Fig. 3) both G - and D-mode in the ID/IG ratio of 0.964 are observed.

Compositions platinum - reduced graphite prepared by platinum addition to graphite oxide by covalent bonds and the subsequent reduction. The presence of hydroxyl and epoxy (1,2-ether) groups in graphite oxide structure assumes some possibility of Pt^{4+} addition to graphite oxide. Replacement of chloride acido ligand onto oxyl-fragment of hydroxyl group demands a presence of platinum in cation part of its compound that is reached by introduction of amine, in particular pyridine, to reaction system. Recently [2-4] pyridine role in platinum fixation with use of carboxyl groups of support was discussed., one of which aspects is rearrangement of a complex of platinum to cationic complex formation. On the other hand, pyridine disacidifies of acid formed by proton replacement of hydroxyl group on platinum-containing cation. The hydroxyl group of graphite oxide as opposed to carboxyl is monodentate ligand that is a little suitable for platinum bonding. Additional use of epoxy (1,2-ether) group of graphite oxide as ligand is unproductively as platinum-containing anion reacts with epoxide by trans-addition, i.e. add to reverse side with regard to hydroxyl group.

A reducing agent able to both Pt^{4+}, and graphite oxide reduction is required for preparation of compositions on the base of graphite oxide (GO). Four compounds as a formate-ion or ethylene glycol or hydrazine or sodium

borohydride as a reducing agents were used. The reduced bases of these compositions after reduction in the depending on reductant is called as RGO$_F$, RGO$_{EG}$, RGO$_H$, and RGO$_B$ respectively.

A composition bases after its reduction lose of oxygen (Tabl. 1). In result of this the amounts of decomposition products are decrease (Fig. 2).
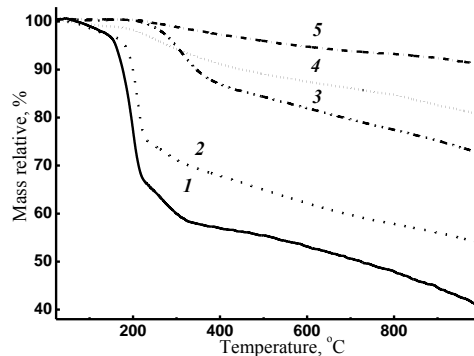

Fig. 2 - Thermograms in Ar of (*1*) GO and compositions (*2*) Pt/ RGO$_F$, (*3*) Pt/RGO$_{EG}$, (*4*) Pt/RGO$_B$, and (*5*) Pt/RGO$_H$

The observed after reduction increases in comparison with GO of C/O ratio (Tabl. 1) and I$_D$/I$_G$ ratio (Fig. 3), and the temperatures of decomposition (Fig. 2) and oxidation (Fig. 4) point out to a change of non-conjugating sp^3-hybridised graphite oxide in ordered sp^3-hybridised system.
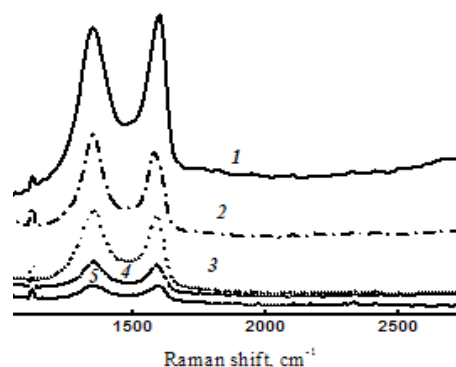

Fig. 3 – Raman spectra of (*1*) GO, (*2*) Pt/RGO$_H$, (*3*) Pt/RGO$_B$, (*4*) Pt/ RGO$_F$ and (*5*) Pt/RGO$_{EG}$

Moreover, in Raman spectra of platinum-reduced graphite oxide compositions against to graphite pristine D-mode are present and 2G-mode about of 2700 cm^{-1} are absent (Fig. 3) *i.e.* product of reduction of graphite oxide is not graphene and right call as reduced graphite oxide.

Thus, hydrazine react with carbonyl compounds (Wolff–Kishner reaction) with deoxygenation and carbohydrates formation. Epoxides ineract with hydrazine yielded aminoalcohols (Wharton reaction). High nitrogen content observed for Pt/RGO$_H$ (Tabl. 1) very likely is associated with aminoalcohols formation and/or the transient formation of hydrazones in these reactions [7]. Interactions of both carbonyl- and epoxy- compounds with formate-ion or ethylene glycol with oxygen loss not associate.
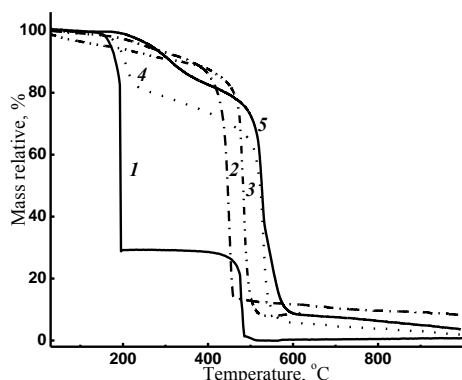
Fig. 4 - Oxidative thermograms of (*1*) GO and compositions (*2*) Pt/RGO$_B$, (*3*) Pt/RGO$_H$, (*4*) Pt/RGO$_F$, and (*5*) Pt/RGO$_B$

The reduced compositions contained platinum (0) were produced, but only at the use of hydrazine or NaBH$_4$ as a reducing agent in contrast to a formate-ion or ethylene glycol its Pt loading correspond to calculated value (Tabl. 1). The symbatic change of Pt loading with C/O ratio (Tabl. 1), i.e. slope opposition of Pt loading with oxygen content is observed.
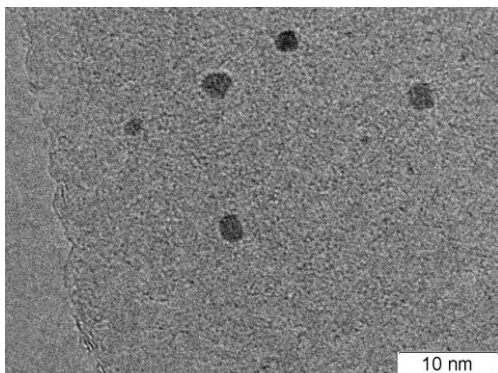

Fig. 5 - Pt/RGO$_B$ TEM image

Thus, platinum fixation by means covalent bonds formation and its reduction to metal are carried out within one process and platinum is supported on the surface of graphite oxide subjected to interaction with reductant. Platinum particles in Pt - reduced graphite oxide compositions prepared by reduction by formate-ion or ethylene glycol or hydrazine are distributed non-uniformly.

The reduction of composition by sodium borohydride produces platinum particles with average particle size ≈2.0 nm (Fig. 5). Nitrogen atomic content is in 2-4 times higher than platinum atomic content (Tabl. 1) that associated with our reasons on pyridine role [2-4, 8].

Pt - reduced graphite oxide compositions catalyze the hydrogenation of decene-1 in solution (Fig. 6). The hydrogenation rate in all instances is sufficiently low therefore in one of cases reaction has not been finished. Specific activity of the most preferable catalyst Pt/RGO$_B$ during reaction time 30 min decreases from 24 H$_2$ mole·(Pt mole·min)$^{-1}$ five times. Pt - reduced graphite oxide compositions catalyze the nitrobenzene hydrogenation in solution too.

The greatest catalytic activity is shown for the composition reduced by sodium borohydride with the particle size of 2.0 nm, however it is substantially lower than it for catalyst based on fullerene black (Fig. 6)[8].
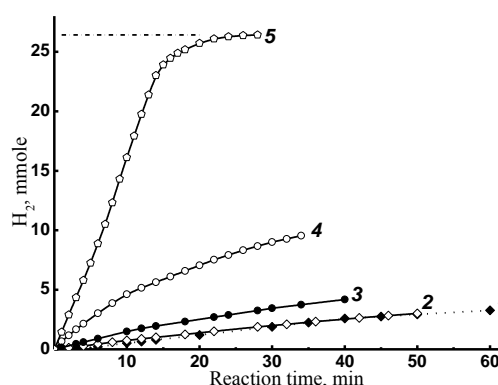

Fig. 6 - H$_2$ consumption profiles in decene-1 hydrogenation over (*1*) Pt/RGO$_F$, (*2*) Pt/RGO$_H$, (*3*) Pt/RGO$_{EG}$, (*4*) Pt/RGO$_B$, and (*5*) Pt/fullerene black

Decene-1 hydrogenation rate converted by the first reaction order, decreases disproportionately to decene-1 concentration loss (Fig. 1). These observations point to catalyst poisoning by reaction product as decane or to some inhibition of hydrogenation in presence incompletely reduced graphite oxide.

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