## Modified graphene oxide as a support for rhodium nanoparticles active in olefin hydroformylation\*

Yu. V. Ioni,<sup>a\*</sup> S. E. Lyubimov,<sup>b</sup> V. A. Davankov,<sup>b</sup> and S. P. Gubin<sup>a</sup>

 <sup>a</sup>N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 954 1279. E-mail: Acidladj@mail.ru
 <sup>b</sup>A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (499) 135 6549

A new two-step procedure for modifying graphene oxide by the methylation of its surface with trimethyl-*o*-formate followed by the treatment with methyl iodide was developed. The methylation product was used as a support for the formation of rhodium nanoparticles. The obtained samples of graphene oxide containing rhodium nanoparticles were characterized by IR spectroscopy, X-ray fluorescence spectroscopy, and transmission electron microscopy. The Rh-containing nanocomposites were used as catalysts for the hydroformylation of olefins in supercritical carbon dioxide and organic solvents.

Key words: graphene oxide, rhodium nanoparticles, hydroformylation.

Graphene and related nanomaterials with a well developed specific surface have interesting mechanical, electrical, thermal, and optical properties. Therefore, they attract attention of researchers. $^{1-4}$  There are many methods for synthesis of graphene, but the most promising is the chemical or thermal reduction of graphene, since with these simple methods scaling techniques can be used.<sup>2,3</sup> Graphene oxide is a graphene layer with diverse surface functional oxygen-containing groups.<sup>5,6</sup> These groups can participate in various reactions to form a new product, socalled modified or functionalized graphene oxide. The introduction of surface functional groups can enhance dispersion and increase compatibility of graphene oxide or graphene with various objects. In addition, covalently functionalized graphene oxide can further be used for the preparation of new substances. For example, the possibility of functionalization of the graphene surface by amide groups was reported.<sup>7</sup> In several works modification of the graphene oxide surface by diverse organic substances was described.<sup>8–10</sup> To change the optical properties, graphene oxide was modified by porphyrin-containing primary amines and fullerene-containing secondary amines. In these reactions, porphyrin and fullerene molecules were grafted to the graphene oxide surface via the formation of amide bonds. The degree of functionalization of graphene and graphene oxide significantly affects these properties and, hence, new approaches to the chemical modification of graphene and its derivatives are aimed at searching for mild functionalization methods.

One of interesting examples for the modification of graphene structures is preparation of supported metal nanoparticles. Adsorption of  $Cu^{2+}$  ions on the graphene oxide aerogel used for the preparation of a new sorption material was described.<sup>11</sup> Graphene oxide can act as an efficient support for catalytically active surface nanoparticles on the surface. In some cases, metal nanoparticles immobilized on solid supports can manifest unique catalytic properties.<sup>12–14</sup> Catalytic activity of particles significantly depends on the surface area of metal accessible for reacting molecules and on the support nature. Earlier, <sup>15</sup> platinum and palladium nanoparticles immobilized on the graphene oxide surface were used in the Suzuki and Heck cross-couplings.

In this work, a novel method for graphene oxide modification by the two-step methylation of its surface is described. Modified graphene oxide was used as a support for rhodium surface nanoparticles, and the obtained nanocomposite was applied as a catalyst for alkene hydroformylation. Hydroformylation is widely used in industry to obtain solvents, detergents, biodegradable surfactants, lubricants, and plasticizers.<sup>16–18</sup> The development of an efficient heterogeneous catalyst would significantly improve commercial processes, which are currently in use.

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 2243-2249, October, 2014.

<sup>\*</sup> Dedicated to Academician of the Russian Academy of Sciences Yu. N. Bubnov on the occasion of his 80 birthday and to the 60th anniversary of the foundation A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

<sup>1066-5285/14/6310-2243 © 2014</sup> Springer Science+Business Media, Inc.

## **Results and Discussion**

Graphene oxide was prepared in several steps from natural graphite using the modified Hummers method<sup>19</sup> (see Experimental). The oxidation of natural graphite leads to a non-stoichiometric graphite oxide with surface oxygencontaining groups. As-synthesized graphite oxide was dispersed in water using a powerful ultrasound treatment to obtain a dispersion of graphene oxide (Fig. 1). Graphite oxide is hydrophilic, since after ultrasonication it forms stable dispersions in water and in other polar solvents. These dispersions undergo no agglomeration within a long time.

The X-ray diffraction analysis (XRD) (Fig. 2) shows that the structure of synthesized graphene oxide includes phases of graphite oxide  $(2\theta = 10-12^{\circ})$  and graphite (peaks at  $2\theta = 26.5$  and  $54.5^{\circ}$ ).<sup>20</sup>

It is known<sup>2</sup> that graphene oxide is a polyfunctional ligand having a number of different oxygen-containing groups (OH, C=O, COOH) on its surface. Upon the addition of metal salts to graphene oxide, metal ions form bonds with oxygen-containing surface groups. This interaction is visualized when the solution is bleached after the addition of salts to a dispersion of graphene oxide.<sup>21</sup> This property was used for the introduction of Rh<sup>3+</sup> ions onto the graphene oxide surface. After the system was reduced by NaBH<sub>4</sub>, rhodium nanoparticles stabilized by functional groups on the graphene oxide surface are formed (Scheme 1).

The obtained sample was studied using transmission electron microscopy (TEM) (Fig. 3). The TEM image shows that rhodium nanoparticles on the graphene oxide surface have a narrow particle-size distribution (the average diameter of the nanoparticles is 2.3 nm). The X-ray diffraction analysis (Fig. 4) showed that the maxima in the diffraction patterns corresponded to the phase of metallic Rh with the cubic face centered lattice (JCPDS cards



Fig. 1. TEM image of graphene oxide.

Scheme 1



(Rh) is Rh nanoparticle, GO is graphene oxide.

i. Reducing agent.

# 05–0685) and graphene oxide. The reflections corresponding to rhodium are broadened. This characterizes a small size of the nanoparticles, which correlates well



**Fig. 2.** Diffraction pattern of graphene oxide: GO is graphene oxide, and G is graphite.



Fig. 3. TEM image of the nanocomposite of Rh/GO nano-particles.



**Fig. 4.** Diffraction pattern of the nanocomposite of Rh/GO nanoparticles.

with the TEM data. Calculation of the average size of rhodium nanoparticles by the Scherrer equation gives a value of 3.7 nm.

The obtained rhodium nanoparticles on the graphene oxide surface (Rh/GO) were used as catalysts for the hydroformylation of styrene and other olefins (according to the X-ray fluorescence analysis data, the rhodium content was 4.1%). Hydroformylation is usually carried out in organic solvents in combination with fire hazardous and explosive agents. Therefore, it is interesting to use alternative media for the process, in particular, supercritical carbon dioxide (scCO<sub>2</sub>) since carbon dioxide is accessible and environmentally friedly and fire-safe.<sup>22</sup> The use of scCO<sub>2</sub> makes it possible to operate with lowly boiling reagents and products, isolation of which from organic solvents is difficult because it requires fractional distillation. Unlike this, carbon dioxide can readily be removed from the synthesis products. Hydroformylation of styrene and other olefins in organic solvents and in scCO<sub>2</sub>

at 50 °C under a pressure of 25 atm of syngas is shown in Scheme 2.



*i*. Rh nanoparticles/GO<sub>mod</sub> (GO<sub>mod</sub> is modified GO),  $H_2/CO$  (1:1), 25 atm, solvent, 4 h.

However, the primary experiments show that the use of rhodium nanoparticles on the unmodified graphene oxide surface as a catalyst did not reveal any conversion using toluene or  $scCO_2$  as solvents (Table 1).

It was assumed that the surface polar hydrophilic groups C=O and OH inhibit hydroformylation. It is most likely that the approach to the nanoparticle surface is hindered for hydrophobic styrene molecules. The two-step methylation of graphene oxide was carried out according to Scheme 3 in order to change polarity.

At the first step, the C=O groups on the graphene oxide surface (see Scheme 3, **A**) interact with trimethyl-*o*-formate (in the presence of catalytic amounts of *p*-tolue-nesulfonic acid) to form acetal groups (see Scheme 3, **B**). At the second step, the obtained intermediate reacted with MeI to methylate the hydroxo groups (see Scheme 3, **C**). To confirm the efficiency of the proposed reaction scheme, IR studies of graphene oxide graphene oxide surface (*a*), intermediate product (*b*), and completely methylated graphene oxide (*c*) have been performed (Fig. 5).

According to the obtained data, the reaction of the initial graphene oxide (see Fig. 5, *a*) with trimethyl-*o*-formate (see Fig. 5, *b*) results in the appearance of new bands in the spectrum. Among these are an intense band at 2900 cm<sup>-1</sup> corresponding to stretching vibrations of the C–H bonds in B the Me groups, a band at 2850 cm<sup>-1</sup> corresponding to stretching vibrations of the C–H bonds in the Me groups attached to the oxygen heteroatoms, and a medium-intensity band at 1458 cm<sup>-1</sup> corresponding to antisymmetric bending vibrations of the C–H bonds in the Me groups. The spectrum also exhibits bands at

 Table 1. Parameters of styrene hydroformylation using the Rh/GO nanoparticle as a catalyst

Solvent	Pressure/atm	τ/h	Conversion (%)
Toluene	25	5	0
scCO <sub>2</sub>	250	5	0





*i*. 36 h.



Fig. 5. IR spectra of the starting graphene oxide (a), intermediate methylation product (b), and modified graphene oxide (c).

1023–1155 cm<sup>-1</sup> assigned to stretching vibrations of the C-O-C bonds in the epoxy groups. The IR spectrum of the final methylation product is almost identical to the spectrum of the intermediate. However, a comparison of this spectrum with the spectra of the initial graphene oxide and the product of the first methylation step shows that the shape of the peak corresponding to stretching vibrations of the OH groups changes. A weak peak at  $3550 \text{ cm}^{-1}$ can be attributed to free OH groups, and a stronger peak at 3300 cm<sup>-1</sup> can be assigned to the residual bound hydroxy groups. A decrease in the band intensity indicates a nearly complete methylation of graphene oxide. According to the elemental analysis data (Table 2), the carbon content increases by 7.7% and the oxygen content decreases by 6.5% in the sample, being the intermediate methylation product. In the final product, the amount of carbon increases to 70% (an increase by 4.3% compared to the product of the first methylation step) and the amount of oxygen decreases to 26.5% (a decrease by 6% compared to the product of the first methylation step). These data provide the evidence of a chemical reaction between the graphene oxide and methylation agents.

The dispersion of modified graphene oxide in hexane was examined by TEM. The TEM image (Fig. 6) shows that the sample is characterized by a layered uniform structure, similarly to the initial graphene oxide, it is transparent and has a few layers.

Modified graphene oxide was also used as a support for the formation of surface rhodium nanoparticles (see Experimental). The sample of  $Rh/GO_{mod}$  nanocomposite was studied by TEM (Fig. 7). The obtained TEM image is shown in Fig. 7. The TEM image of the sample of  $Rh/GO_{mod}$  nanoparticles shows that spheroid rhodium nanoparticles tend to form "star-like" agglomerates. Individual rhodium nanoparticles have a narrow particle-size distribution with an average particle size of 2.4 nm.

The catalytic activity of the nanocomposite of  $Rh/GO_{mod}$  nanoparticles was also studied in the hydroformylation of unsaturated hydrocarbons (see Scheme 2).

The use of the  $Rh/GO_{mod}$  nanocomposite in toluene as a catalyst results in a high conversion; however, the regioselectivity of the obtained branched product with respect to unbranched aldehyde is 65% (Table 3, entry 1).

**Table 2.** Results of C,H,N analysis of the starting graphene oxide (**A**) and intermediate (**B**) and final (**C**) methylation products

Sample	Content of element (%)			
	С	Н	0	
Α	58.0	1.5	39.0	
В	65.7	1.5	32.5	
С	70.0	1.8	26.5	



Fig. 6. TEM image of modified graphene oxide.



Fig. 7. TEM image of the  $Rh/GO_{mod}$  nanocomposite (*a*) and the rhodium nanoparticle distribution in the nanocomposite (*b*).

The replacement of the solvent by benzene gives an insignificant increase in conversion, but the regioselectivity decreases (see Table 3, entry 2). Among the solvents used, THF is characterized by the lowest activity (see Table 3, entry 3).

The replacement of organic solvents by  $scCO_2$  made it possible to attain the complete conversion in the styrene hydroformylation and to increase regioselectivity (see Table 3, entry 4). The hydroformylation of 4-methylstyrene and 4-bromostyrene in  $scCO_2$  also proceeds quan-

**Table 3.** Parameters of the hydroformylation of olefins  $H_2C=CH-R$  in the presence of Rh/GO<sub>mod</sub> nanoparticles as a catalyst (65 °C)

Entry	R	Solvent	τ/h	Conver- sion (%)	Selectivity* (%)
1	Ph	Toluene	4	88	65/35
2	Ph	Benzene	4	90	56/44
3	Ph	THF	4	12	51/49
4	Ph	$scCO_2$	4	100	84/16
5	4-MePh	$scCO_2$	4	100	86/14
6	4-BrPh	$scCO_2$	4	100	87/13
7	Bu <sup>t</sup>	$scCO_2$	4	84	0/100
8	Bu <sup>t</sup>	$scCO_2$	5	100	0/100

\* Ratio of the branched to linear reaction products.

titatively with high regioselectivity (see Table 3, entries 5 and 6). The use of 3,3-dimethylbut-1-ene as a substrate resulted in the selective formation of 4,4-dimethylpentanal with 84% within 4 h (see Table 3, entry 7). The prolongation of the reaction to 5 h resulted in the complete conversion of olefin (see Table 3, entry 8).

Thus, a two-step modification procedure for graphene oxide was developed. The methylated graphene oxide was used as a support for the formation of rhodium nanoparticles (2–3 nm) on the surface. The prepared catalyst showed moderate and high substrate conversion as well as regioselectivity in the hydroformylation of various olefins in in the "green" medium of  $scCO_2$ . The results of this study can provide new prospects for the further investigation of the chemical properties of graphene oxide and its application as a support in other catalytic reactions.

## **Experimental**

IR absorption spectra were recorded on a Specord M-82 spectrometer (VEB Carl Zeiss Jena, Germany) in the range  $400-4000 \text{ cm}^{-1}$  with a scan increment of 4 cm<sup>-1</sup>. The sample was triturated in an agate mortar together with anhydrous KBr (0.1 mg of the studied powder per 100 mg of KBr) and then pressed in pellets on a hydraulic press (pressing effort 6 metric tons). The X-ray diffraction measurements were carried out on a Bruker D8 Advance spectrometer operating in the reflectance mode with Cu-Ka radiation (35 kV, 30 mA). Elemental analysis (C, N, H) was carried out on a VarioEL instrument by burning microweights of the samples of the determined substance. The content of rhodium nanoparticles on the graphene oxide surface was determined by X-ray fluorescence spectroscopy on a Zeiss Jena VRA-30 spectrometer. The size and morphology of Rh<sup>0</sup> nanoparticles were studied with a JEM-1011 transmission electron microscope at an accelerating voltage of 100 kV.

Synthesis of graphene oxide. Graphite oxide obtained by the modified Hummers method<sup>19</sup> was placed in the solvent and subjected to the powerful ultrasonication treatment for 30-60 min (parameters: frequency 20.4 kHz, specific power 0.1-1 W cm<sup>-3</sup>). The formed dispersion of graphene oxide was centrifuged

(6000 rpm, 12 min) to separate the solid product from the liquid phase, and the final product was dried for 6 h at 60  $^{\circ}$ C *in vacuo* and in air.

Methylation of graphene oxide. Graphene oxide (500 mg) was continuously stirred for 36 h in 6 mL of trimethyl-*o*-formate with the addition of a catalytic amount (4 mg) of *p*-toluene-sulfonic acid. An excess of trimethyl-*o*-formate was removed by heating *in vacuo*. Methyl iodide (4 mL),  $K_2CO_3$  (1 g), and aceto-nitrile (4 mL) was added to the dry residue after the first step of the reaction, and the mixture was continuously stirred for 36 h at ~20 °C. After the reaction, the solid residue was separated from the liquid phase by centrifugation (4000 rpm, 5 min), washed with water (5 mL) and acetone (2×5 mL), and dried *in vacuo* for 1 h.

Preparation of rhodium nanoparticles on the surface of graphene oxide and methylated graphene oxide. A solution of  $RhCl_3 \cdot 4H_2O$  (46.5 mg) in methanol (4 mL) was added to graphene oxide (330 mg) with continuous stirring. After 30 min, an excess of dry NaBH<sub>4</sub> (77 mg) was added by portions. The solid precipitate was washed with hot water (4×5 mL) and acetone (3×5 mL) and dried *in vacuo* for 6 h.

Catalytic hydroformylation of olefins. The catalyst 30 mg, 0.01 mmole of Rh) and the corresponding unsaturated substrate (1 mmol) were placed in a 10-mL stainless steel autoclave. The autoclave was filled with syngas (25 atm,  $P_{\rm H_2}/P_{\rm CO} = 1:1$ ) and then with carbon dioxide to a pressure of 200 atm with a High Pressure Equipment manual press. The reactor was heated to the corresponding temperature for 5 min, and the experiments were carried out with magnetic stirring. After a certain time, the autoclave was cooled to 5 °C for 20 min, reaction gases were slowly fed, and the reaction mixture was diluted in 1.5 mL of CDCl<sub>3</sub>, filtered through a thin silica gel layer to separate catalyst residues, and analyzed by the <sup>1</sup>H NMR method. The spectral characteristics of the hydroformylation products correspond to the literature data: 2-phenylpropanal and 3-phenylpropanal (R = Ph), 2-(4-methylphenyl)propanal and 3-(4-methylphenyl)propanal (R = 4-MePh), 2-(4-bromophenyl)propanal and 3-(4-bromophenyl) propanal (R = 4-BrPh), and 4,4-dimethylpropanal. Experiments in organic media were carried out similarly using 2 mL of the corresponding solvent.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 14-03-31813 mol\_a).

## References

- 1. A. K. Geim, K. S. Novoselov, Nat. Mater., 2007, 6, 183.
- 2. S. Park, R. S. Ruoff, Nat. Nanotechnol., 2009, 4, 217.
- 3. H. Bai, C. Li, C. Shi, Adv. Mater., 2011, 23, 1089.
- C. Soldano, A. Mahmood, E. Dujardin, *Carbon*, 2010, 48, 2127.
- 5. D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228.
- T. Szab, O. Berkesi, P. Forgo, K. Josepovits, Y. Sanakis, D. Petridis, I. Dekany, *Chem. Mater.*, 2006, 18, 2740.
- 7. S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, *J. Am. Chem. Soc.*, 2006, **128**, 7720.
- B. G. Choi, W. H. Hong, Y. M. Jung, H. S. Park, *Chem. Commun.*, 2011, 47, 10293.

- 9. M. Quintana, K. Spyrou, M. Grzelczak, W. R. Browne, P. Rudolf, M. Prato, *ACS Nano*, 2010, **4**, 3527.
- Z.-B. Liu, Y.-F. Xu, X.-Y. Zhang, X.-L. Zhang, Y. S. Chen, J. G. Tian, J. Phys. Chem. B, 2009, 113, 9681.
- 11. X. Mi, G. Huang, W. Xie, W. Wang, Y. Liu, J. Gao, *Carbon*, 2012, **50**, 4856.
- 12. H. W. Ha, I. Kim, S. J. Hwang, R. S. Ruoff, *Electrochem.* Solid State Lett., 2011, 14, B70.
- G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mulhaupt, J. Am. Chem. Soc., 2009, 131, 8262.
- 14. B. Xiong, Y. Zhou, Y. Zhao, J. Wang, X. Chen, R. O'Hayre, Z. Shao, *Carbon*, 2013, **52**, 181.
- Yu. V. Ioni, S. E. Lyubimov, A. A. Korlyukov, M. Yu. Antipin, V. A. Davankov, S. P. Gubin, *Russ. Chem. Bull.* (*Int. Ed.*), 2012, **61**, 1825 [*Izv. Akad. Nauk, Ser. Khim.*, 2012, 1810].
- 16. V. Agabekov, W. Seichea, B. Breit, Chem. Sci., 2013, 4, 2418-2422.

- 17. J. Klosin, C. R. Landis, Acc. Chem. Res., 2007, 40, 1251.
- 18. F. Ungvary, Coord. Chem. Rev., 2007, 251, 2087.
- W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339.
- 20. S. V. Tkachev, E. Yu. Buslaeva, A. V. Naumkin, S. L. Kotova, I. V. Laure, S. P. Gubin, *Inorg. Mater. (Engl. Transl.)*, 2012, **47**, 796 [*Neorg. Mater.*, 2012, **48**, 909].
- I. L. Laure, S. V. Tkachev, E. Yu. Buslaeva, E. V. Fatushina, S. P. Gubin, *Russ. J. Coord. Chem (Engl. Transl.)*, 2013, 39, 487 [Koord. Khim., 2013, 39, 387].
- S. E. Lyubimov, E. A. Rastorguev, K. I. Lubentsova, A. A. Korlyukov, V. A. Davankov, *Tetrahedron Lett.*, 2013, 54, 1116.

Received June 18, 2014; in revised form August 19, 2014