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Palladium supported on graphene-like carbon: preparation and catalytic properties

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Graphene-like carbon, graphene shells, has been treated with $Pd_2(dba)_3$ to afford the supported palladium/carbon material that provided moderate catalytic activity in the Suzuki and Heck reactions.

In the modern heterogeneous catalysis, catalysts immobilized on various supports are widely applied. Among these supports are carbon nanomaterials such as active carbons, carbon molecular sieves, fullerenes, carbon nanotubes and nanofibres. Recently, graphenes were added to this list, materials built of the planar one-atom carbon layer, one or few, having interesting electrical, magnetic, optical and mechanical properties.^{1,2} One-layer graphenes are characterized by high specific surface (up to 2630 m² g⁻¹) that can be increased on oxidation³ to graphene oxides which can show some catalytic activity without any metal.⁴

In this work, the novel kind of graphene nanomaterials, graphene shells, are studied as support for catalytically active nanopalladium suitable for the Heck and Suzuki reactions.

The concept of nanocarbon⁵ unites different carbon forms including fullerenes (the only molecular form), nanotubes, nanodiamonds and, finally, graphenes. All of them were applied as supports for the catalytically active metal, e.g., palladium (see, for example, ref. 6). In part, earlier we have shown them to be effective catalysts in the hydrogenation of unsaturated hydrocarbons and C-C cross-coupling reactions.7-10 The feature of these catalysts is that no additional ligands are required, they are reusable and able to process in air and water meeting the conditions of 'green chemistry'. In this work which continues the series, palladium catalyst is composed on the basis of the novel graphene nanomaterial whose synthesis was firstly described elsewhere.¹¹ We wish to stress that our goal was the investigation of the novel catalyst, not the development of the catalyst of high efficiency. Therefore, we used few substrates in order to evaluate its activity. Graphene itself is a purely carbon support whereas graphene oxides studied by a majority of other authors contain a lot of oxygen atoms which are probably the sites of metal bonding.

This material, the graphene shells, was obtained through pyrolysis of methane at 800 °C on 1–2 μ m hexagonal plates of MgO. Such polycrystalline plates are substitutional pseudomorphs of the plate-like single crystal Mg(OH)₂, they retain the form of the starting particles and, in the case under study, have the greater specific surface. The same hexagonal form was retained in the pyrolysis products, which had even greater specific surface (see below). After MgO was dissolved in hydrochloric acid, the separate particles composing an aggregate consisted of the planar shells, with several graphene layers (two in average) sized about 15–20 nm. This material had in average a specific surface 1524 m² g⁻¹ (in some experiments up to 2000 m² g⁻¹), bulk weight 0.25 g cm⁻³ and electroconductivity 0.032 Ω cm⁻².

Microscopic investigations were made using the scanning (JEOL JSM 6490 LV) and transmissing (JEOL JEM 2100 F-Cs) electron microscopes. Specific surface was determined by BET method (AU-TISORB-1C/MS/TPR Quantachrome), and specific electric resistance by 4-point method using microohmmeter MH-10. The preparation of the catalyst was made following our original direct method.^{7,8} For introducing palladium we are using the stable Pd⁰ complex Pd₂(dba)₃ with a loosely bonded and easily leaving ligand dibenzylideneacetone (dba). This method is very simple, it does not require other ligands and additional treatment of the catalyst besides washing with a non-aqueous solvent unlike the convential procedure based on the reduction of Pd^{II} salts in water. The successive addition of Pd atoms results in the formation of metal nanoclusters fixed on the carbon support clearly seen in Figures 1 and 2. These nanoclusters are the true catalytic centers.

This graphene material is rather like nanodiamond than nanotubes because of functional groups in the shell that are probably responsible for binding palladium atoms whereas reactivity of nanotubes has its origin, like fullerenes, in the strained double bonds.

Analysis of microphotos showed that after introducing palladium, material changed its morphology and formed large aggregates of size up to 200 μ m (the major part of the particles was much smaller). Palladium particles were roundish and regularly spread over the support having size within the range 1.5–5.5 nm (more than 70% were within 2.0–3.0 nm) as it is shown in Figure 1. Crystalline structure of Pd nanoparticles corresponds to the tabular data. From the photos of some particles (Figure 2) it was possible to analyze reflections of the second order and to evaluate the interplanar spacing as 0.19–0.20 nm that corresponds to the period



Figure 1 High resolution TEM image of Pd particles on the graphene shells (general view).



Figure 2 Two representative high resolution TEM images of Pd particles on the graphene shells that have been used for estimation of interplanar spacing.

of Pd crystalline lattice (0.389 nm). Electroconductivity of the samples did not change after adding palladium.

The fact that the average size of Pd nanoparticles was about 2.5 nm seems to be very important. It was found earlier¹² that for Pd the maximum catalytic activity is observed for size within 3–4 nm. Note that size of Pd nanoparticles fixed on the oxidized graphene with a different method was also 2 nm in average.¹³ The size effect in catalysis was observed for nanoparticles of other metals as well. So, for Pt the maximum specific activity was found at size 2.2 nm¹⁴, for Au ~2.0 nm.¹⁵ Interestingly, the character of catalytic reactions may differ (oxidation, reduction, electrosynthesis, *etc.*), and the nature of size effect is supposed to be connected with maximum fraction of the catalytically active crystallographic faces in the particles of the definite size.

As follows from the experiments, the activity of the novel Pd catalyst supported on graphene shells is moderate in the Heck reaction (Scheme 1) and relatively high in the Suzuki reaction (Scheme 2).[†] Recycling the Pd/graphene catalyst in the Heck reaction is shown in Table 1.

Preparation of Pd/graphene catalyst. Complex $Pd_2(dba)_3$ (43.5 mg) was dissolved in toluene (20 ml). The red-wine coloured solution was filtered through a paper filter to remove insoluble particles and was magnetically stirred for 30 min under argon at 50 °C in the presence of graphene (160 mg). Solution turned to light yellow colour. Then the reaction mixture was cooled to room temperature, the black precipitate was separated, washed with toluene (4×20 ml), pentane (4×20 ml), and dried *in vacuo* to afford 169 mg of the catalyst. Found (%): C, 89.26; H, 2.04; Pd, 5.2.

Heck reaction. The mixture of aryl halide (3 mmol), ethyl acrylate (7.5 mmol), triethylamine (7.5 mmol) and 10 mg of the Pd/graphene catalyst was stirred in DMF (12 mmol) at 120–125 °C. In the case of iodobenzene reaction was complete in 2 h, whereas conversion of bromobenzene was only 16% in 20 h. The mixture was treated with water, the product was extracted with ethyl acetate (2×50 ml), dried over Na₂SO₄ and evaporated. The product was identified by ¹H NMR spectra.

Ethyl (2E)-3-*phenylacrylate.* ¹H NMR (CDCl₃) δ: 1.35 (t, 3H, Me), 4.28 (q, 2 H, CH₂), 6.46 (d, 1H, CH=CH, *J* 16.0 Hz), 7.39 (m, 3 H, Ph), 7.52 (m, 2 H, Ph), 7.71 (d, 1H, CH=CH, *J* 16.0 Hz).

Suzuki reaction. The mixture of bromobenzene (2 mmol), *m*-tolylboronic acid (3 mmol), K_2CO_3 (4 mmol) was stirred in MeOH (12 ml) and H_2O (4 ml) for 5 min. Then catalyst Pd/graphene (7 mg) was added and stirring was continued at 55 °C for 30 min. The mixture was diluted with water, the product was extracted with ethyl acetate (2×50 ml), dried over Na₂SO₄, evaporated. Product was taken into hexane, passed through the thin layer of SiO₂, once more evaporated and identified by ¹H NMR spectrum.

3-Methylbiphenyl: yield 90%. ¹H NMR (CDCl₃) δ: 2.55 (s, 3 H, Me), 7.29 (m, 1H, Ph), 7.48 (m, 2 H, Ph), 7.55 (m, 4 H, Ph), 7.70 (m, 2 H, Ph).



Scheme 1



Table 1 Conversion of aryl halides in the Heck reaction with ethyl acrylate.

Entry	ArHal	Time/h (cycle)	Yield (%)	
1	PhI	2(1)	100	
2	PhI	2 (2)	100	
3	PhI	4 (3)	80	
4	PhBr	20 (1)	16	

High activity was recently demonstrated¹⁶ for the palladium supported on the oxidized graphene. On the whole, Pd immobilized on carbon nanotubes^{7,8} is more active in the Heck and Suzuki reactions. Catalytic activity of Pd/nanodiamond in these reactions was not studied but in hydrogenation it was found to be very high.¹⁰

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[†] Starting graphene material, graphene shells, prepared as described, contained according to combustion analysis 94.32% of carbon. Method of carbon combustion for the determination of the percentage of non-volatile admixtures in carbon materials was standard. It consisted in the heating the samples in air at 800 °C when carbon is burnt off followed by weighing residue.