Pt supported on reduced graphite oxide catalysts for H₂ activation

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Platinum catalysts of H_2 activation with average size ≤ 2.0 nm were prepared in a base of reduction conversion of graphene oxide. A low few-layered carbon nanomaterial was prepared by thermoexpansion and annealing of graphene oxide. The uniformly dispersed Pt nanoparticles were supported on two-dimension graphene flat material by the use of pyridine or polyethyleneimine in alkaline (pH~10) media as chelating agent modificating both metal precursor H_2PtCl_6 and support. Vacancies in carbon material formed as a result of thermoexpansion and annealing of graphite oxide probablly serve as anchor groups in platinum supporting.

Keywords: Graphene Oxide, Thermoexpansion, Platinum, Nanoparticle, Chelating Agent, Complexation.

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Since the discovery by Geim and Novoselov in 2004, graphene, a flat monolayer of sp^2-bonded carbon atoms tightly packed into a two-dimensional honeycomb lattice has received considerable attention due to its high specific surface area (≈ 2600 m$^2 \cdot$g^{-1}), high chemical stability, and unique electronic, mechanical properties [1]. This unique nanostructure holds great promise for potential applications as support of catalyst or electrocatalyst and material for membranes of fuel cell. The first challenge for the practical applications of graphene is its processing of reduced graphene oxide (RGO) by an effective and scalable approach. Up to now, numerous techniques such as micromechanical exfoliation, chemical vapor deposition, chemical reduction of graphene oxide, and other special strategies, etc. have been successfully developed for synthesis of RGO. Among them, the chemical reduction of graphite oxide (GO) has been proved to be a promising method due to its intriguing features of low cost, bulk quantity production and suited for chemical modification and subsequent processing. Graphene stabilises colloidal particles of metal onto its surface and prevents their aggregation [2].

Only positive charged Pt^{4+} ions may be add to hydroxy- and epoxy- (1,2-ethers) groups in graphite oxide structure. Hydroxy- and epoxy- (1,2-ethers) groups are monodentate ligands whereas bidentate ligands as carboxyl groups few in graphite oxide structure need for addition to Pt^{4+}. Ion Pt^{4+} adds to epoxy- (1,2-ethers) group as trans-addition i.e. appears with inverse, concerning to hydroxyl group, the side.

Atoms of metals as platinum strongly contact with defects of graphene as single and double vacancies [3, 4]. Graphene vacancies i.e. closed polygons with number of carbon atoms dissimilar to 6, unlike defects, are not produced by action of chemical reducers on graphite oxide. These fragments in graphene structure are produced by removal of carbon atoms as its monoxide at thermal reduction of graphene oxide, for example. In Pt - graphene compositions as was shown by functional density theory the platinum electronic structure at every step of catalytic reaction is controlled by electron

transfer between □-orbitals of graphene and *d*-orbitals of metal atoms [5].

Retried changes of oxidation state of the active metal Pt during the catalytic reaction call its solution-state transfer, its migration on support surfaces and metal aggregation [6–9]. So, fixation of metals through anchoring functional groups is an important aspect of the problem of preparation supported on carbon nanomaterials catalysts [10–13].

In this work, we designed catalysts Pt/RGO, in which the two-dimensional RGO acted as support to disperse Pt metal nanoparticles. These catalysts were prepared via immobilizing Pt particles onto the RGO. RGO was produced by a) simultaneous reduction of GO in the presence pyridine and metal precursor H_2PtCl_6 in alkaline (pH~10) media by $NaBH_4$ or hydrazine called as Pt/aBRGO and Pt/aHRGO, or b) GO reduction by $NaBH_4$ or hydrazine, Pt^{4+} supporting in pyridine presence and subsequent composition reduction by $NaBH_4$ in alkaline (pH~10) media called as Pt/bBRGO and Pt/bHRGO, or c) GO thermoexpansion at 900ºC in N_2 flow, subsequent annealing at 1000ºC during 3 h in N_2 atmosphere and Pt^{4+} supporting in pyridine or polyethyleneimine presence, and subsequent reduction of platinum composition by $NaBH_4$ in alkaline (pH~10) media called as Pt/TRGO. The resultant materials were characterized by different techniques including elemental analysis, Raman spectroscopy, and X-ray diffraction (XRD). The catalytic performance of the Pt/RGO catalysts for liquid-phase hydrogenation of nitrobenzene (NB) and decene-1 in propanol-2 solution was investigated with focus on the influence of the support.

As a result of GO conversion on both a) and b) routes for conversion on c) route oxygen removal is observed. Oxygen content were decrease from 45 to ~19 % for products of reduction by $NaBH_4$ as bBRGO and Pt/aBRGO, and Pt/bBRGO and to ~7.5 % for products of hydrazine reduction as bHRGO and Pt/aHRGO, and Pt/bHRGO. GO thermoexpansion decreases oxygen content from 45 to ~19 % and subsequent annealing

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reduces it to ~4 %.

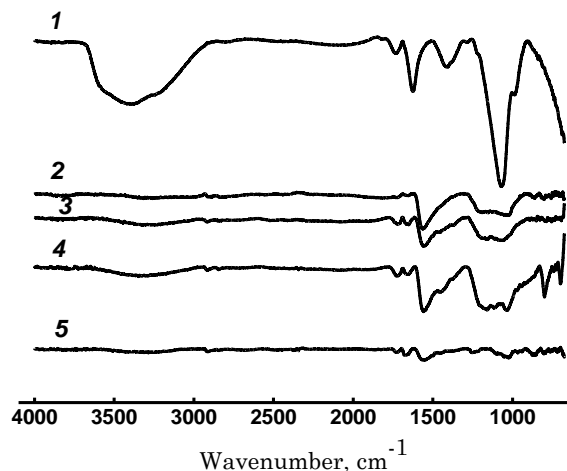These results correspond with FT-IR spectra (Fig. 1).

Fig. 1 – FT-IR spectra of (1) GO, (2) bHRGO, (3) Pt/aHRGO, (4) Pt/aBRGO, (5) TRGO.

Before the reduction, the vibration and deformation bands of the O−H groups on GO are at 3367 and 1363 cm⁻¹, respectively; the stretching vibration band of C=O is at 1722 cm⁻¹; the stretching vibration band of C=C is at 1620 cm⁻¹; and the stretching vibration bands of C−O in epoxy and alkoxy are at 1224 and 1045 cm⁻¹, respectively. It demonstrated that GO nanosheets have many oxygenous groups. After the reduction, the intensities of all FT-IR peaks that correlated to the oxygenous groups decreased dramatically.

The Raman spectrum of GO displays two prominent peaks at 1591 and 1352 cm⁻¹, which correspond to the well-documented G and D bands, respectively. Although the Raman spectrum of Pt/aBRGO, Pt/bBRGO, bHRGO and Pt/aHRGO, Pt/bHRGO, and TRGO samples also has D and G bands, the intensity ratio of D/G increases, compared to GO. The D/G ratio of GO is 0.964, and that of Pt/bHRGO is 1.106 whereas that of TRGO is 1.260. The D/G ratio identifies the sp^2/sp^3 ratio. This change in the intensity ratio of the D and G bands is attributed to the increased defect concentration in the structure of GO reduced in a variety of ways, indicating the successful deoxygenation in TRGO.

Only thermoexpansion and annealing lead to oxygen removal in a kind CO and to formation, thus, defects in the form of vacancies, the most suitable for anchoring of platinum [3, 4] and its functioning in several stages of catalytic reaction [5].

The specific surface area of carbon materials produced by chemical reduction of GO is less than that for TRGO. TRGO is characterized large specific surface area of 594 m²·g⁻¹. The performance of this "fluffy" material appreciably depends on preparation procedure and contains probably only a few (to 5) graphene layers (Fig. 2).
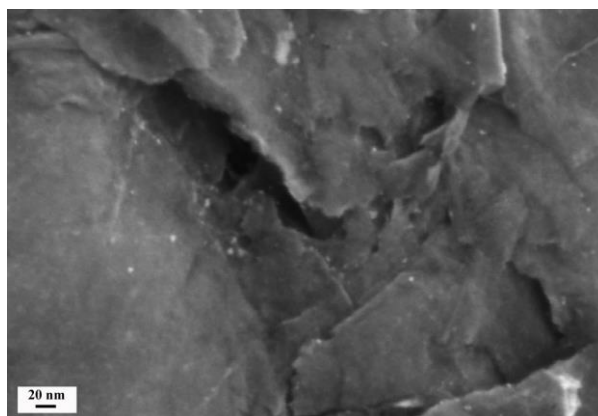

Fig. 2 – SEM image of Pt/TRGO.

The use of pyridine or polyethyleneimine in alkaline (pH~10) media leads to reconstruction of Pt precursor wherein platinum is in its cationic part. In other hand, pyridine or polyethyleneimine interacts with a surface of the carbon support and creates thus anchoring groups for platinum coordination mainly in a place of vacancies.

From compositions prepared by a) roure only Pt/aBRGO is characterized uniformly dispersed Pt nanoparticles with average size of 2.0 nm. Compositions prepared by b) roure are characterized uniformly dispersed Pt nanoparticles with average size of 1.9 nm (Fig. 3).
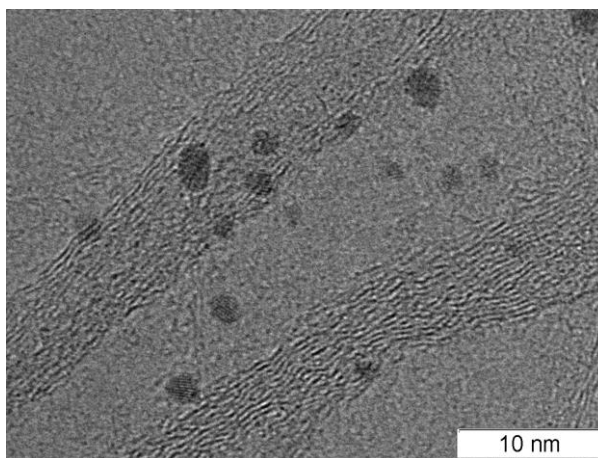

Fig. 3 – TEM image of Pt/bHRGO.

Compositions Pt/RGO catalyze NB hydrogenation and is found that its catalytic activities range as Pt/aRGO<Pt/bRGO<Pt/TRGO (Fig. 4). Platinum compositions inclusive GO reduced by NaBH₄ are more active than these reduced by hydrazine. NB hydrogenation is characterized by first reaction order with respect to NB i.e. NB hydrogenation is constant to ~90 % conversion (Fig. 4). NB hydrogenation with produced aniline accumulation (more than 15 mol % of aniline in media) is possible without activity loss.
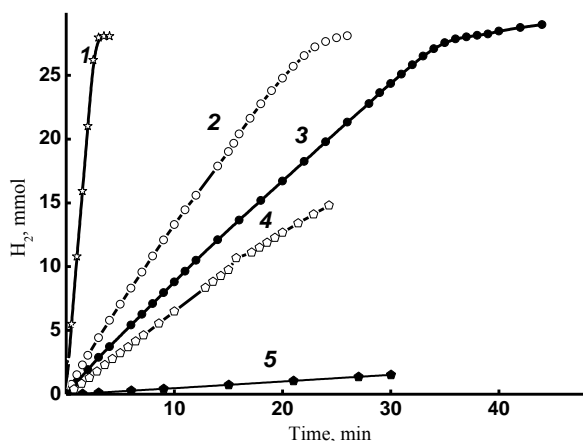
Fig. 4 – H₂ uptake kinetic profiles at NB hydrogenation in propanol-2 catalyzed by (1) Pt/TRGO, (2) Pt/bBRGO, (3) Pt/bHRGO, (4) Pt/aBRGO, (5) Pt/aHRGO.

Fig. 5 – H₂ uptake kinetic profiles at decene-1 hydrogenation in propanol-2 catalyzed by (1) Pt/TRGO, (2) Pt/bBRGO, (3) Pt/bHRGO, (4) Pt/aBRGO, (5) Pt/aHRGO.

Platinum does not migrate on support surface, is not washed away in a solution and the platinum loading in the catalyst does not decrease at its long use as have shown catalysts studies by PEM and SEM. The specific catalytic activity of Pt/TRGO in NB hydrogenation reaches a record value as 350 H₂ mole·(Pt mole·min)$^{-1}$ and exceeds literature data as we know.

Platinum composition catalyze decene-1 hydrogenation in propanol-2. Specific catalytic activity of compositions in decene-1 hydrogenation slightly more low than at NB hydrogenation however in this case specific catalytic activity range in the same order (Fig. 5).
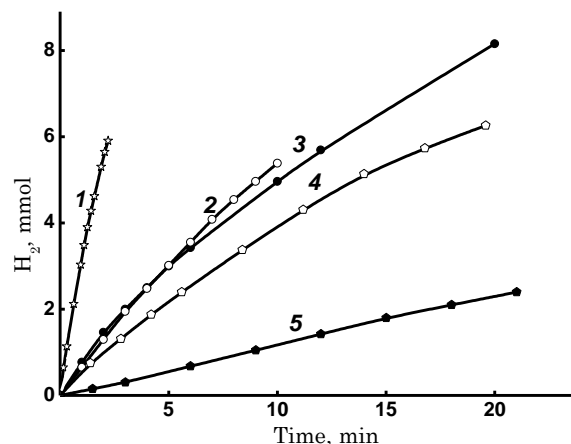
In conclusion, platinum catalyst of H₂ activation with average size ≤2.0 nm were prepared in a base of reduction conversion of graphene oxide. A low few-layered carbon nanomaterial was prepared by thermo-expansion and annealing of graphene oxide. The uniformly dispersed Pt nanoparticles were supported on two-dimension graphene flat material by the use of pyridine or polyethyleneimine in alkaline (pH~10) media as chelating agent modificating both metal precursor H₂PtCl₆ and support.

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