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PLATINUM ON REDUCED GRAPHENE OXIDE NANOSHEETS OBTAINED UNDER MICROWAVE IRRADIATION, USING REDUCING AGENTS

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Abstract:

Hydrophobic catalysts used in catalytic detritiation process of heavy water consist of platinum impregnated on charcoal (commercial material) and PTFE. For this type of material, Pt is found as agglomerates leading to an increase of hydrophilicity in the final catalyst and also, to a low number of functional groups for isotopic exchange. Therefore, in order to avoid these drawbacks, another type of platinum-based material was considered, with a higher platinum dispersion which would lead to an increase number of functional groups for the isotopic exchange process. There are different methods to synthesize Pt on graphene composites, but using microwaves involves advantages like fewer stages and shorter time to produce. The obtaining method uses reduction of H_2PtCl_6 in the presence of ethylene glycol and other reducing agents ($NaBH_4$ and KOH) and graphene oxide suspension. Samples were then microstructurally investigated using SEM, BET, X-ray diffraction, RAMAN and TGA.

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1. INTRODUCTION

Graphene is a material with a high potential for a wide range of applications. It has excellent physical and chemical properties including mechanical strength and strain, high thermal conductivity, electron mobility and chemical inertness (Chen, 2010). It is an ideal support material for noble metal. Also, carbon-based supports with Pd, Au, Ag or Pt

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nanoparticles have already been demonstrated to exhibit high efficiencies for different processes (hydrogen storage, CO oxidation, oxygen reduction or in fuel cell applications, hydrogen peroxide detection, lithium-ion batteries) (Kundu et al., 2011; Kundu et al., 2014; Sun et al., 2015).

The microwave-assisted techniques have been demonstrated as a rapid and high effective strategy for preparation of graphene-based materials. The microwave heating has been used for exfoliation of graphite, reduction of graphene oxide (GO) and preparation of graphene-based hybrid materials (Kundu et al., 2014). Microwave-assisted techniques ensures a high local temperature and pressure and the energy is transferred directly into the graphene oxide. The heat and the pressure are produced by the interaction of the irradiation with the polar bonding of the functional groups containing oxygen from the surface and from the edge of the graphene oxide sheets, (Sun et al., 2015)

The hydrophobic catalyst is considered an essential element for increasing the tritium separation performances and in minimizing Liquid Phase Catalytic Exchange (LPCE) column sizes, facilitating tritium transfer from tritiated vapor water to deuterium. Worldwide were prepared and tested more than 100 catalysts at laboratory scale, (Ionita et al., 2015). National Research and Development Institute for Cryogenic and Isotopic Technologies - ICSI Rm. Valcea developed his own catalyst for removing tritium from heavy water. Until now, the catalytic efficiency of the catalyst has been satisfactory, but there are possibilities to improve the characteristics, with improving the catalytic efficiency. The catalyst uses platinum-like active metal placed on charcoal, and PTFE for hydrophobicity. For this type of material, Pt is found as agglomerates that leading to an increase of hydrophilicity in the final catalyst and also, to a low number of functional groups for isotopic exchange, (Bornea et al., 2019). In order to avoid these drawbacks, another type of platinum-based material was considered, with a higher platinum dispersion on the surface which would lead to an increase number of functional groups for the isotopic exchange process. Platinum on graphene was considered in order to improve platinum distribution on the catalyst. The paper presents the effect of the reducing agents on the morphological and structural properties of the platinated graphene oxide. $NaBH_4$ and KOH were used as both reductive and dispersing agents for deposition of Pt nanoparticles on sheets of graphene oxide, sample prepared with ethylene glycol being used like reference. The aim of the research is to obtain a platinum concentration in graphene higher than 10% (this is the concentration of platinated charcoal), using a faster method (microwave irradiation) than the classical one (Hummers method).

2. SAMPLES PREPARATION AND METHOD OF ANALYSIS

Materials used were: GO partially reduced, from Magna Vision, Alfa Aesar H_2PtCl_6 premion 99,9999% (metals basis) crystalline, ethylene glycol, 99+% spectrophotometric grade and$NaBH_4$ 98% and KOH 99,995% from Sigma Aldrich, purified water (through a Millipore system).

Samples of Pt on GO were prepared by microwave-assisted reduction of GO partially reduced and H_2PtCl_6. The 3 samples were prepared under the same conditions (platinum precursor concentration, microwave power, temperature, etc.) with ethylene glycol as polar solvent. First sample was considered the reference and was prepared with ethylene glycol only, the other two were prepared using $NaBH_4$ and KOH. These chemical compounds are considered dispersing agents for platinum in graphene when classical method is used, (Qiu et al., 2011). First, the solutions of GO, ethylene glycol and water were sonicated for 30 minutes and after that was added H_2PtCl_6 (0,04M) and, in case of samples 2 and 3, adding $NaBH_4$or KOH (10%). The solutions were sonicated for another 30 minutes and then placed in the microwave reactor (MARS 6 One touch, CEM Corporation, USA) in iWave PTFE cylinders. The mixtures are heated rapidly at

elevated pressure, obtaining the reaction. The following reaction conditions were used: 30 minutes - reaction time, 180°C - reaction temperature; 800 W - microwave power. The pressure increased to 16 bar during the microwave process. The dispersions of Pt on graphene were obtained after being sonicated for 30 minutes. At first, samples were filtered and washed with a mixture of ethanol plus distilled water and then washed again with distilled water for reducing acidity and removing of chlorine. They were dried in the oven overnight, at 50°C in air. A diagram of the preparation process is presented in figure 1.

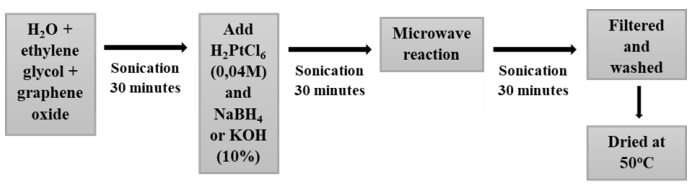

Figure 1. Diagram of obtaining Pt/reduced graphene oxide nanosheets

Samples were named as follows: sample 1 prepared with ethylene glycol only; sample 2 prepared with ethylene glycol and $NaBH_4$; sample 3 prepared with ethylene glycol and KOH.

The samples were analysed for specific surface using Brunauer, Emmett and Telle (BET) theory, performing nitrogen sorption measurements using Quantachrome Autosorb IQ equipment. The adsorption and desorption analysis were done at 77K after initial pre-treatment of the samples by degassing at 115°C for 4 h.

The determination of the amount of platinum in graphene samples was carried out by Analytik Jena AG - contrAA 700 - High-Resolution Continuum Source Atomic Absorption Spectrometer.

The samples were microstructurally investigated using a Field Emission Gun Scanning Electron Microscope (FESEM). Powders were placed directly on a double-sided sticky carbon tape and then blown away with compressed air. The remaining powder was enough and the right size to be measured. Information about the topography of the sample was given by secondary electrons (SE) whereas the different phases were revealed using back scattered electrons (BS) – white areas correspond to phases with high Z (strong signal) and black areas correspond to low Z phases (weak signal). To highlight the distribution of Pt throughout the sample, the BS (back scattered) mode was used.

The XRD studies were carried out with a MiniFlex 600 Rigaku, Japan with 40 kV and 15 mA in the 2-theta range set between 10° and 90°.

Raman spectroscopy is carried out by using alpha 300 RAS+ Witec from Ulm, Germany. The system comprises an inverted microscope with 100X magnification objective connected to a 75 mW Ar laser (~532 nm line) with variable aperture and a grating spectrometer with 600 grooves/mm which is coupled to an ultra-fast CCD camera that makes it possible to acquire one spectrum in 5 ms over the spectral range between 100 cm^{-1} and 3800 cm^{-1} with a resolution better than 5 cm^{-1}. All spectra are recorded over 10s integration time to optimize for signal-to-noise ratio. The background is subtracted by using the same parametric function, between 500 cm^{-1} and 3600 cm^{-1}.

The thermogravimetric analysis (TGA) measurement of the samples was carried out using Netzsch STA 449 F Jupiter Simultaneous Thermal Analyzer. The thermal analysis was carried out in the temperature range of 25÷800°C at a heating rate of 10° C/min under nitrogen flow, (Vasut et al., 2019).

3. RESULTS AND DISCUSSION

Specific surface of GO that was used for producing platinate samples was presented in an earlier paper (Vasut et al., 2019). Table 1 presents specific surfaces of the prepared samples and the platinum concentrations obtained by atomic sorption. The specific surface areas are quite similar for all 3 samples and shows that including metal atoms through the graphene sheets partially maintains the layer-to-layer stacking of initial porous area of the precursor (GO), (Vasut et al., 2019). The platinum concentration is reduced by half in the case of sample 2, the use of $NaBH_4$ leading to a product with the similar specific surface area but with lower platinum content. This can be explained by the reduction of graphene oxide by $NaBH_4$ before platinum has reacted with the functional groups, thus allowing a smaller amount of platinum to be deposited on graphene oxide.

Table 1. Specific surface and platinum concentration

Sample	S_{BET} (m^2/g)	Pt (%, weight)
1 –with ethylene glycol only	190.26	11.4 %
2 –with $NaBH_4$	191.37	5.8 %
3 – with KOH	186.30	13.5 %

The adsorption–desorption isotherms are presented in figure 2. The shape was similar for all 3 prepared samples. For exemplification, is presented the sample that was considered the reference one, prepared with ethylene glycol only. The isotherms have a type IV shape with hysteresis loop in the range of 0.45-0.95P/P_0. This type of hysteresis indicates the presence of a large number of mesopores and some micropores and confirms that a hierarchical porous structure was achieved by microwave treatment with preservation of the mesoporous structure after the microwave-assisted process. The pore volume function of radius distribution was estimated based on desorption process, using Barrett-Joyner-Halenda method (BJH).

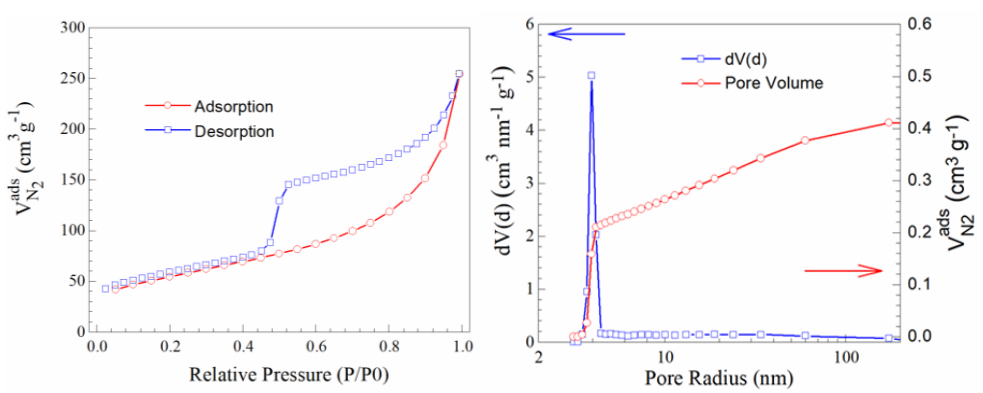

Figure 2. BET isotherms and pore size distribution calculated by Barrett-Joyner-Halenda (BJH) method for Pt on GO (sample 1)

Figure 3 presents SEM analysis for prepared samples. For sample 1 (A images), SEM micrographs show the flake-like single layer morphology. BS image very clearly indicates the presence of Pt nanoparticles uniformly dispersed throughout the sample (the bright spots). In case of sample 2 (B images), SE image of the sample indicates the flake-like morphology; BS image of micrograph shows the agglomerates of Pt distributed in rather non-homogeneous manner throughout the sample. For sample 3 (C images) SEM micrographs show a more compact morphology when compared to the other two flake-like samples; BS image shows a uniform distribution of Pt.

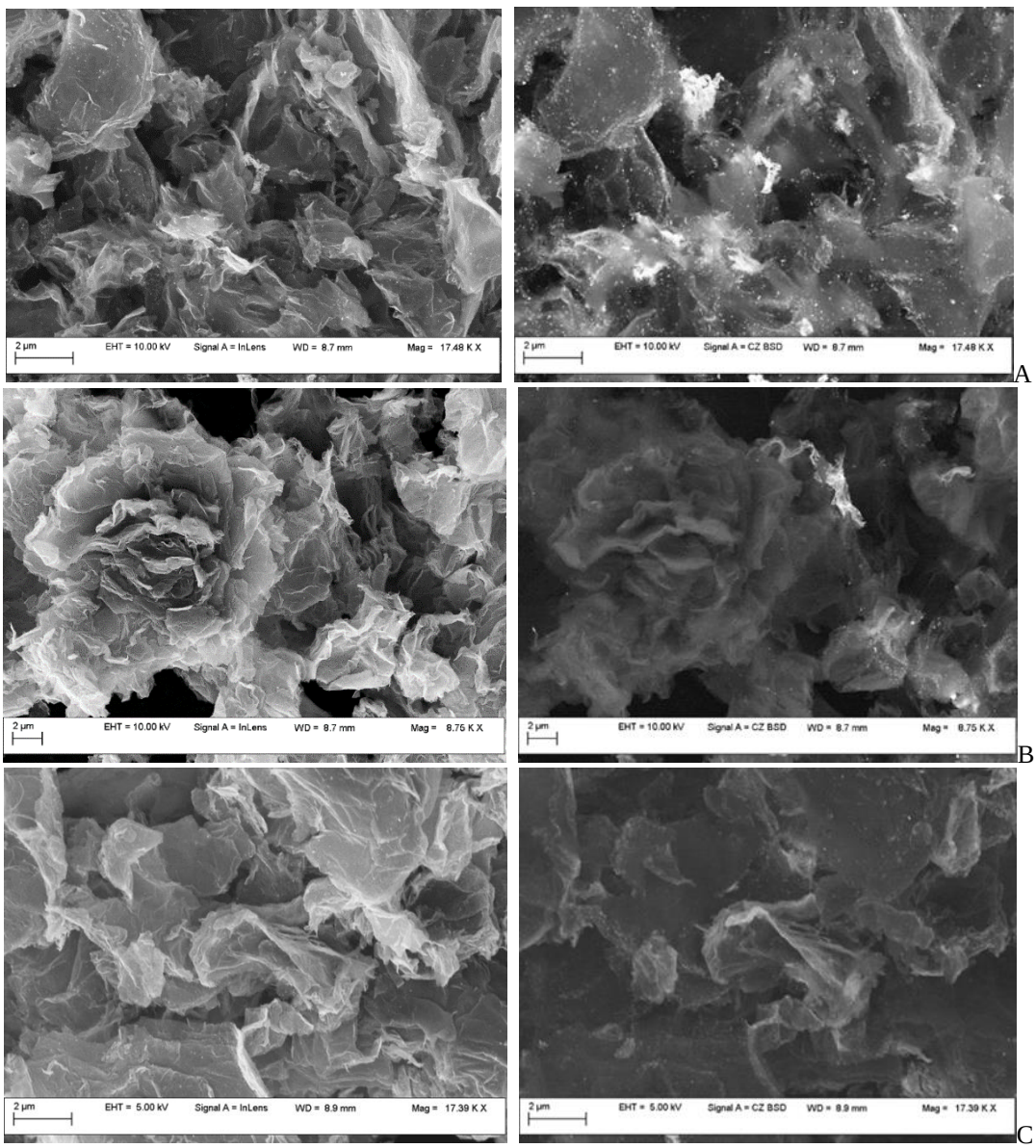

Figure 3. SEM analysis for Pt on graphene oxide (A-sample 1, B-sample 2, C-sample 3)

Figure 4 shows the broad peak at about 23.5° attributed to the typical C (002) planes of graphene, highlighted in case of graphene oxide (Kurt et al., 2016). All other peaks are indexed to the cubic phase of Pt with 111, 200, 220 and 311 reflection planes consistent with the XRD pattern of DB card 01-087-0646 with 2-theta = 39.73°, 46.53°, 67.38°, 81.41°.

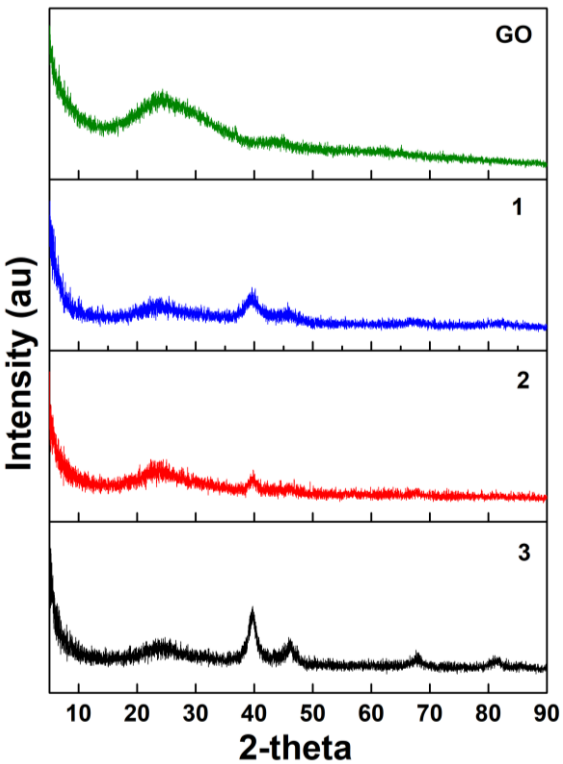

Figure 4. X-Ray diffraction analysis for GO and Pt on GO

In figure 5, the Raman spectrum of GO contains two characteristic bands. The intense peak at 1359 cm^{-1} is attributed to D band, which corresponds to sp^3 hybridized carbon. This is associated with the presence of defects and disordered carbon. The broad band observed at 1599 cm^{-1} is ascribed to G band. This band is related to the vibration of ordered sp^2 hybridized carbon. The position of these bands is essentially similar to those reported for GO (i.e., 1350 cm^{-1} for the D band and 1590 cm^{-1} for the G one, (Lopez-Diaz et al., 2017)). However, the intensity ratio of D band and G (i.e., I_D/I_G) indicates whether defects are created and the level of disorder in oxide graphene layers is introduced upon the preparation route. In figure 5, the intensity ratio I_D/I_G of graphene oxide precursor is 0.905. The corresponding intensity ratio values of samples 1, 2 and 3 are 0.949, 0.904 and 0.879, respectively. These values are essentially similar within 5% (i.e., the largest difference of 4.86% corresponds to sample 1). These features indicate that the preparation route and the loading level with Pt does not influence drastically the composition of the GO support. This is emphasized in the inset of figure 5, in which all spectra are superimposed on top of each other by multiplying the corresponding intensities with an arbitrary factor.

In addition to that, the weak and broad peaks observed above 2500 cm^{-1} (i.e., in figure 5, 2D at 2680 cm^{-1} and (D+G) at 2901 cm^{-1}) are associated with the overtone of the D band and the combination of the D and G bands, respectively. The 2D band is related to the number of layers of graphene sheets and their relative orientation, (Johra et al., 2014). Its intensity is very small compared to the D and G peaks, although it may be enhanced by

reducing the number of graphene oxide layers. The (D+G) combination peak supports strongly the presence of a higher disorder structure for GO.

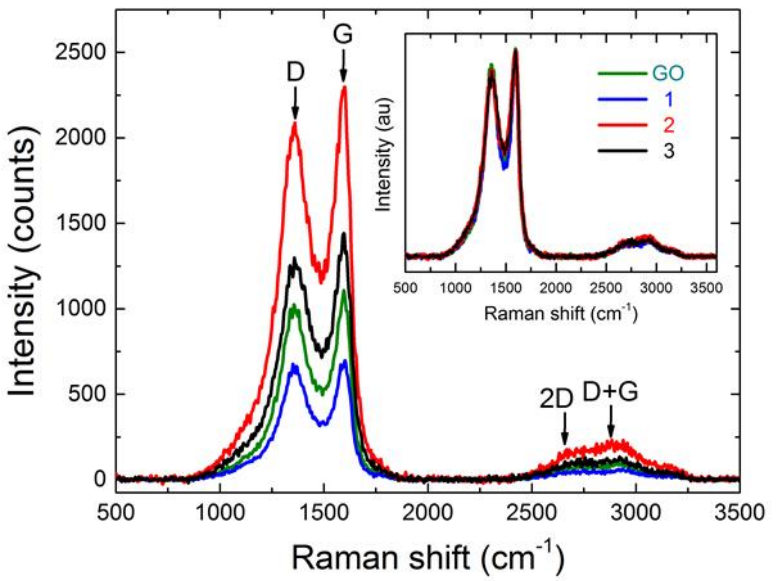

Figure 5. Raman spectra measured on GO and samples 1, 2 and 3, respectively.

Figure 6 shows the TGA spectrum for the prepared samples. The curve for sample 1 shows a mass loss with four stages. The first loss of 4.5% is due to the release of water at about 120°C, the second loss of 4.1% is attributed to the loss of volatile products from ethylene glycol, and the third step of 59.5% is due to the ethylene glycol decomposition. The last step is starting around at 490°C and is due to the gradual mass loss (21.4%) of the graphene. The presence of KOH in the sample 3 influences the thermal stability in the sense of decreasing the mass loss, both in the second and third steps due to the interaction between KOH and ethylene glycol, as well as in the fourth step that is much lower (11.7%) in comparison with the sample without KOH treatment.

The introduction of $NaBH_4$ during the graphene treatment is noticed also in the TGA curve of sample 2. The ethylene glycol reacts with $NaBH_4$ and this process is noticed in the presence of an additional mass loss step between 240°C and 410°C of 33.6% that may be attributed to the release of one polyethylene glycol per 3-to4borate. This step is followed by a 22.8% weight loss that ends at 420°C and may be due to the decomposition of borates with sp^2 and sp^3 boron atoms (Ould-Amara et al., 2018). From the analysis of the three overloaded curves, it can be noticed that the presence of KOH improves the thermal stability of the samples, and the less stable is the one which is treated with $NaBH_4$.

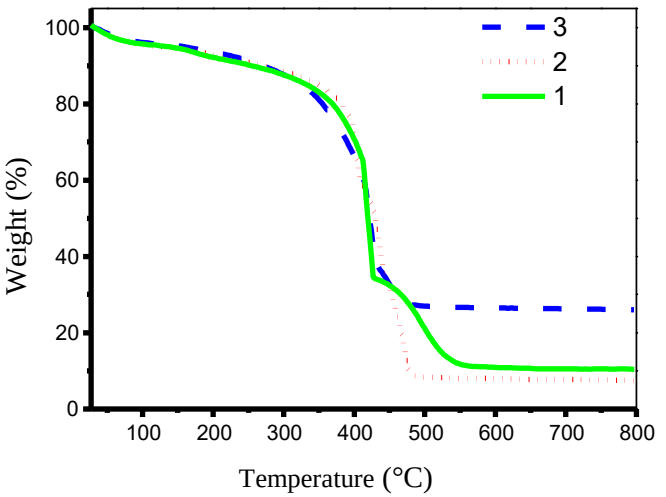

Figure 6. TGA curves of platinated GO

4. CONCLUSIONS

Three samples of platinum graphene were prepared and physico-structurally characterized, using the same polar solvent and in the case of two of them using $NaBH_4$ and KOH as reducing and dispersing agents. The sample prepared with ethylene glycol only, was considered the reference sample.

The surface area values for platinum on GO indicates a decrease of specific surface area from initial GO. The specific surface values are quite similar for all samples. The obtained surface areas show that the introducing of metal atom through the graphene sheets maintain partially the initial porous area of the solid precursor.

It was observed that in the case of using $NaBH_4$, the obtained platinum concentration is lower than in the case of the KOH. The reason that concentration of platinum is lower in the sample that used $NaBH_4$ could be that $NaBH_4$ reduces oxygen-containing functional groups before platinum is added on it, while KOH reduces platinum.

In order to prepare the catalyst for isotopic exchange process, it is desirable that the structure of graphene to be preserved, also a homogeneous distribution of platinum crystals is required. From the microstructural point of view, samples 1 and 3 show a uniform distribution of platinum on the surface but in case of sample 3, the structure is more compact. In case of using $NaBH_4$, platinum is not distributed homogenous on the graphene surface.

The XRD analysis confirmed that platinated compound was reduced to the metal for all samples.

Raman analysis of the samples shows that the preparation route and the loading level with Pt does not influence drastically the composition of the graphene oxide support.

From the thermal analysis of the three overloaded curves, it can be noticed that the presence of KOH improves the thermal stability of the samples, and the less stable is the one which is treated with $NaBH_4$.

Sample 3 indicates great thermal stability, a uniform distribution of platinum and the highest concentration of platinum on surface. This sample and the one prepared with ethylene glycol only will be prepared for reproducibility and will be tested for obtaining a catalyst for isotopic exchange process.

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Author Contributions: Felicia Vasut prepared the samples and contributed to the analysis of the results and wrote the paper with input from all authors; Anisoara Oubraham prepared the samples and contributed to the analysis of the results; Amalia Maria Soare performed SEM analysis and interpretation; Adriana Marinoiu performed BET analysis; Daniela Ion-Ebrasu performed TGA measurements and interpretation; Mirela Dragan XRD analysis; Stanica Enache performed RAMAN measurements; Ramona Ionela Zgavarogea determined platinum concentration of the samples.

Conflict of Interest Statement: The authors declare no conflicts of interest associated with this manuscript.

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