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Title: Synthesis and catalytic application of Pt and Pt-Bi nanoparticles in graphite oxide
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The bi-metallic catalysts based on Pt-Bi are widely used in catalysed organic reactions, where the catalyst has a solid nature and is dispersed into the solution. Catalysts based on noble-metals (e.g. Pt or Pd) are structured in NPs and are used for the selective oxidation of alcohols, ketones and diols [1,2]. When Pt operates in strong oxidative environment, it undergoes substantial poisoning with a consequently reduction of its activity. This behaviour justified the presence of Bi used to prevent this problem. The Pt-Bi coupled system is one of the common catalyst proposed and studied in literature [3,4], where the two metals have to work as "coupled system". Only on this way, indeed, Bi exploits its protective action and for this reason the nature of NPs must be verified before catalyst's exploitation.
Moreover a fundamental parameter dealing with NPs based catalysts is the NPs distribution on the support that should be homogeneous as much as possible. With the aim to reduce the noble metal loading, a good NPs distribution on the support, indeed, is able to reduce the metals loading also improving the activity of the catalyst. Anyway, when operating with bi-metallic catalysts like Pt-Bi based ones, during NPs deposition particles tend to aggregate each other increasing the medium size of the particles: it is well-known that smaller is the particle higher is its activity. Summarizing dimension and distribution are two strictly correlated parameters that must be taken into account synthesizing catalysts based on NPs.
In this work we want to present an alternative way to synthesize catalysts based on Pt-Bi. As a support graphite oxide (GO) was used and its choice was guided starting from work of A. Mastalira and co-workers that used GO as support for Pd NPs, showing an improved catalytic activity of Pd for alcohols oxidation [5]. Graphite oxide (GO) is an oxygen-rich carbonaceous material, synthesized by the controlled oxidation of graphite [6]. It is a non-stoichiometric compound, in which the lamellar structure of graphite is preserved, but its polyaromatic character is lost, as related to the presence of oxygen-containing functional groups [6-9]. Moreover GO is a hydrophilic material, which readily undergoes intra-crystalline swelling and disaggregation. Thanks to its hydrophilic nature, indeed, GO resulted to be a good support for a catalyst operating in polar solvents (e.g. water). For all these reasons and properties, GO was regarded as a good catalyst support material and a promising host for the intercalation of catalytically active noble metal NPs using functional groups on the surface of support as anchoring points.
The GO was synthesized starting from commercial graphite powder, using Hummer method for the functionalization and subsequently modifying it [7,8]. Modifying the original method was possible to synthesize different levels of functionalization useful to test the best conditions for metal NPs loading. The modification mainly involved time reaction and molar ratio (support to reagents).
At the end of the work the graphite oxide functionalization grade has been recognized playing an important role on the NPs deposition. A slightly oxidation of the graphite, indeed, has permitted to reach the better results, and one of the reasons has been founded on the method followed for the synthesis.
Once synthesized the GO was directly used as support and subsequently after characterization the best one catalyst was tested in a tri-phase laboratory reactor for the selective oxidation of the glycerol.
Chloroplatinic metal precursor (H_2PtCl_6), sodium borohydride ($NaBH_4$ granular 99.99% metal basis), Bismuth Nitrate ($Bi(NO)_3$), Potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4) and phosphoric acid (HPO_3) were purchased from Sigma-Aldrich, Steinheim, Germany.
The GO was synthesized starting from graphite powder (Sigma-Aldrich) mixing it with H_2SO_4, $KMnO_4$, $NaNO_3$ and adapting original Hummers method to the quantity [7,10,11]. A slight functionalization (GO I and GO II, figure 1) was obtained reducing in ratio 1 to 10 each reagent from the original Hummers. GO III has been obtained following the original procedure proposed by Hummers. Finally GO IV was synthesized reducing the stirring time after the water addition while for the GO V synthesis phosphoric acid instead of H_2SO_4 was used. Once synthesized the GO was grinded and the powder was directly used as support for the synthesis.
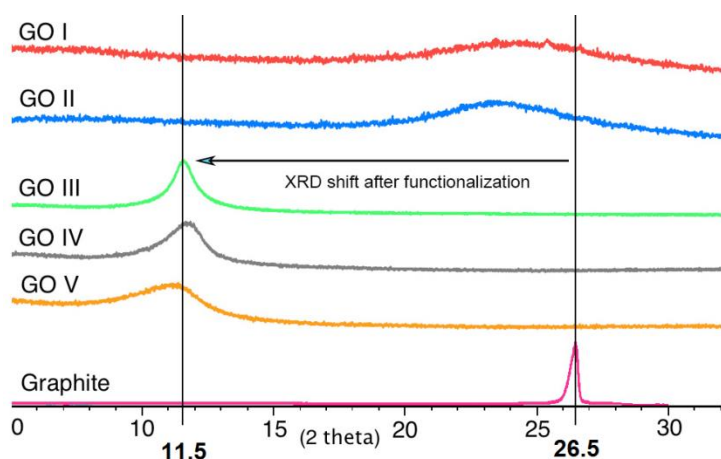
Figure 1. The XRD analysis on the GO samples with different functionalization compared with graphite (by Sigma-Aldrich) used as starting material. The characteristic peak of graphite disappears and shift on left after strong functionalization.

The synthesis of the catalysts was conducted in a flask with three necks. A magnetic stirrer was used to mix the solution during the impregnation of the support [12,13] and a Liebig refrigerant ensured the reflux. Every step was conducted in an inert atmosphere in order to avoid (reducing) the Bi oxidation during synthesis.

Before the impregnation an amount of the support was dried in the oven at 110°C for 1 h. The $Bi(NO)_3$ precursor was dissolved in a 0.012 M of HNO_3 and the amount of support was added. While stirring a solution of $NaBH_4$ was added drop by drop (molar ratio $NaBH_4$:$Bi(NO)_3$ equal to 10:1) performing the reduction of metal precursors by an excess of $NaBH_4$ [14, 15].

After the $NaBH_4$'s addition the solution was leaved under stirring overnight. The day after a solution with H_2PtCl_6 was added drop by drop. After 5 h the solution was centrifuged and the solid was collected and dried into the oven at 105-110°C for 2 h. The dried solid was washed several times with demineralized (DM) water to remove the unreacted species.

Field Emission Scanning Electron Microscopy (FE-SEM) analysis was performed by means of a Zeiss Merlin microscope (equipped with GEMINI II column and an EDS detector) in order to study the size, shape and NPs distributions. The electron microscope operated at an accelerating voltage of 500 kV. The samples were dispersed in ethanol and mounted on a coated copper-grid, followed by solvent evaporation. The EDX detector was used to verify the presence of Pt-Bi as coupled system.

X-ray diffraction (XRD) measurements were performed by means of an Analytical X'Pert Pro diffractometer. The nature of the NPs and the support were investigated with the X-ray photoelectron spectroscopy (XPS) technique. In particular X-ray photoelectron spectroscopy was carried out by means of a PHI 5000 Versa Probe (USA), with a scanning ESCA microscope fitted with an Al monochromatic X-ray source (1486.6 eV, 25.6 W). The acquired spectra were charge corrected to give the adventitious C_{1s} spectral component a binding energy of 284.6 eV. Curve-fits were performed using Casa-XPS software (version 2.3.16).

Finally the HPLC analysis was carried out on a HP liquid chromatograph equipped with binary pump delivery system. In order to identify the two first by-products, GLYA and dihydroxyacetone (DHA), from glycerol oxidation two methods have been developed.

Observed changes in the XRD diffraction pattern (figure 1) was the direct evidence about the shift of the characteristic peak of graphite after the functionalization, with its translation from 26° (2θ) to 11°-12° (2θ) [14]. Even the functionalization grade has been qualitatively evaluated from XRD diffraction pattern, analysing the peaks intensity (count per seconds) at 11°-12° (2θ). Combining XRD and XPS analysis has been confirmed the effective functionalization with the formation of functional group on the support (-C-OH, -C=O, -COOH) [6].

The GOI and GOII XRD diffraction pattern shows neither the graphite peak nor the peak normally associate to GO, proving a intermediate condition, a not complete functionalization. This condition was interpreted as a light functionalization of the support also confirmed by the XPS analysis (figure 2 A and B) [6,16,17]. On the other hand, the absence of graphite's peak suggested a significant modification on the typical lamellar structure of the graphite itself [11,14].
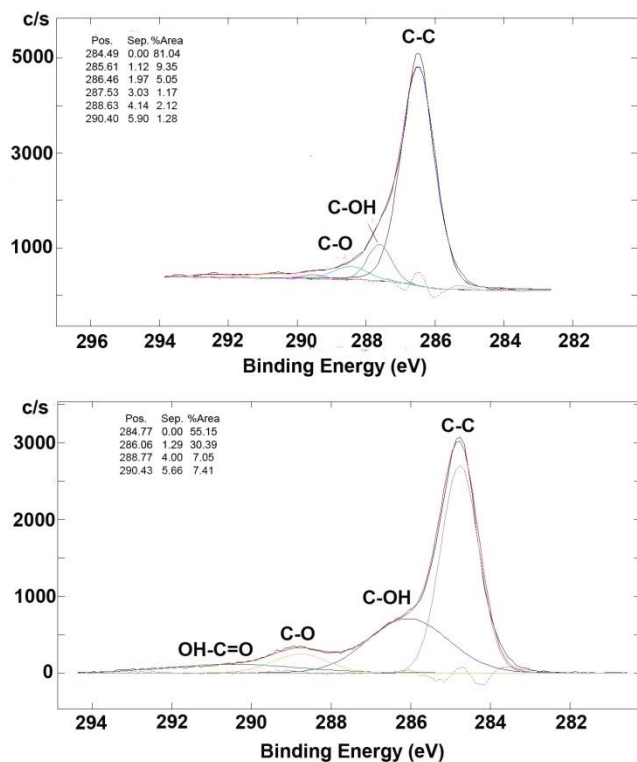
Figure 2. The XPS analysis on GO samples (GOII here represented) shows the presence of new functional group on the support surface after the functionalization with a subsequent C-C percentage Area reduction. The functional groups have been designed as helping anchorage points for the NPs deposition.

After impregnation the microscopy analysis performed by FE-SEM permitted to take evidence on the NPs distribution on the support. In figure 3 we reported the best results in terms of particles distribution and dimension, obtained using GOI and GOII as supports. The results seemed to confirm how the functionalization represents a good way to obtain a uniform NPs distribution having homogeneous dimensions.
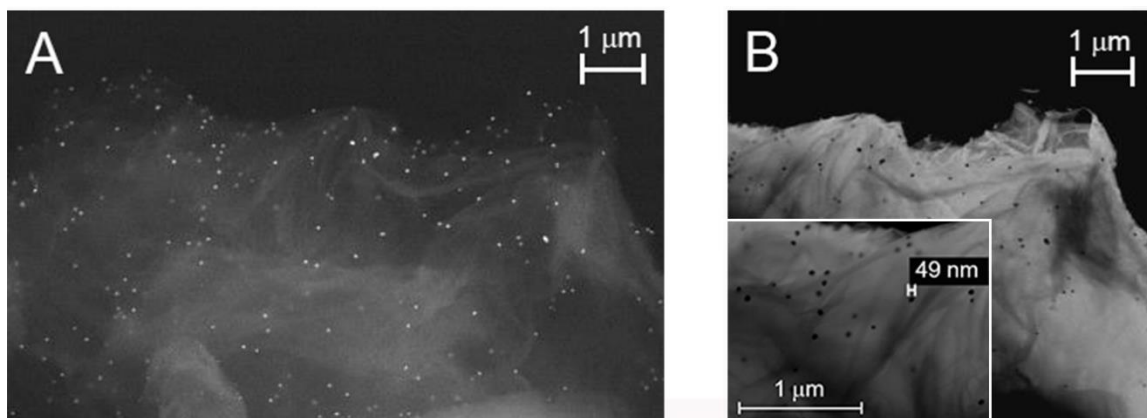

Figure 3. FE-SEM analysis on Pt/BI on GOII; (A) back-scattering analysis gave an image about the NPs distribution on the GOII (graphite low-functionalized) flakes; (B) inlens setting permitted to evaluate NPs medium-size of the particles (49 nm)

The presence of Pt and Bi NPs was evaluated by XPS and EDX (added material) analysis. The XPS spectrum (figure 4) obtained from the GOII samples showed a peak at 159.8 eV, associated to the presence of a bi-metallic Pt/Bi coupled system [18].
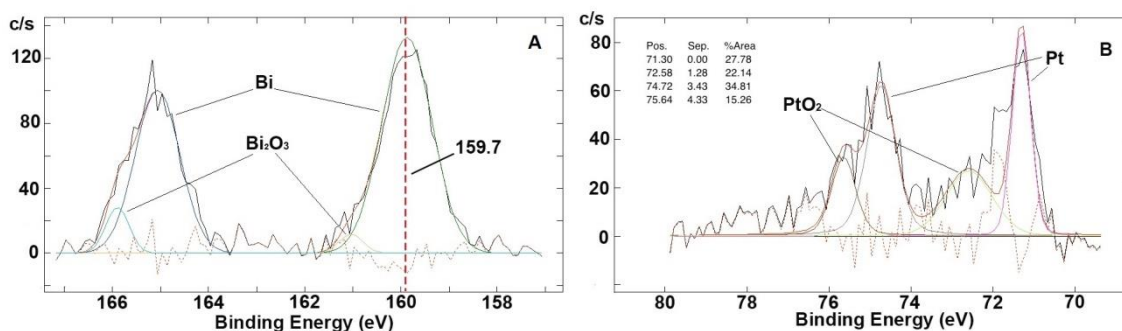
Figure 4. XPS analysis of the coupled system Pt/BI on GOII. (A) Bi spectrum shows a peak at 159.7 eV associated to the presence of Pt/Bi coupled system. (B) Pt appears in its metallic form, a good purpose to indicate the potential high catalytic activity.

Once obtained the required specifications, in order to test the catalytic activity, a laboratory reaction in a stirred tank tri-phase batch reactor was performed using glycerol as substrate [13]. The results showed a high activity, selectivity to glyceraldehyde (GLYA) with a low Pt loading (1 to 10) if compared to commercial catalysts, tested at the same conditions, obtaining the same conversion level. A comparison with other catalysts became necessary to estimate the improvement granted by the catalyst (table 1). The catalysts used for the comparison were based on graphite, synthesized in laboratory with the same method here proposed, carbon and Al_2O_3. Even mono-metallic Pt based catalyst was tested in order to confirm the important role played by Bi as co-catalyst.

All tests were performed at 30 bar of oxygen, a high oxidative environment, at 60°C for 300 min and results are listed in table 1.

Catalyst	Conditions		Time	ζ [glycerol]	Selectivity	
	[°C]	[bar]	[min]	[%]	GLYA	DHA
$Pt_{5wt\%}$ on Al_2O_3	60	30	300	26,62		x
$Pt_{5wt\%}$ $Bi_{1-1,2wt\%}$ on Al_2O_3	60	30	300	46,7		x
$Pt_{5wt\%}$ on C *	60	30	300	44,3		x
$Pt_{0,5-1,0wt\%}Bi_{0,65-1,10wt\%}$ on GOI-II	60	30	300	44,34	X	
$Pt_{0,5-1,0wt\%}Bi_{0,65-1,10wt\%}$ on graphite	60	30	300	≈ 0	-	-
$Pt_{0,5-1,0wt\%}$ on GOI-II	60	30	300	23,66	X	

Tab. 1 Glycerol oxidation (60°C and 30 bar of O_2) comparing commercial catalysts (the first three ones) and Pt and Pt/Bi catalysts based on GOI, GOII and graphite. In the last column was reported in qualitative way the selectivity. *starting material was the commercial $Pt_{5wt\%}$ on C to which Bi was added by impregnation technique.

If compared with the commercial catalysts, the Pt and Pt-Bi based on GOI (or GO II) showed a good selectivity for the oxidation of the primary carbons. Moreover, if compared with the commercial catalysts, the Pt-Bi on GO permitted to obtain the same conversion percentage using a lower amount of Pt, passing from 5wt% to 0.5-1.0wt% (1 to 10 of Pt loading). However it is important to underline the well-known activity exploited from graphite oxide in the oxidation of alcohols [16,17,19,20]. For this reasons in order to verify how much the support could influence the results some tests using only GO were performed. With the same metal free amount of GO I and II the same experiments were performed into the reactor. These tests showed a predictable activity on glycerol conversion in accord with literature's results. Anyway the conversion grade obtained from these tests was estimated smaller than 4% of the total substrate conversion due to the bi-metallic catalyst based on Pt-Bi. On the other hand simply using the graphite no conversion was achieved. Referring to the results obtained, it was clear how the Pt-Bi based on GO catalysts activity mainly comes from the presence of Pt particles and to a minor extent to the support.

In this work was developed a new procedure in order to synthesize a bi-metallic Pt-Bi catalyst based. The aim has been based upon to find a good support for a heterogeneous catalyst, reducing Pt and Bi loading but maintaining a high activity if compared with "traditional" and commercial catalysts. Starting from the literature know how and work of A. Mastalira and co-workers, GO has been chosen as support for noble metal NPs, but we tested how the functionalization grade of GO could improve the catalyst's activity reducing the metals loading. The weakly GOI and GOII have guaranteed a homogeneous dispersion and size of NPs at nanometre scale. Moreover, despite of hydrophobic nature of graphite, it was possible to exploit the natural GO hydrophilic behaviour, fundamental when operating with a polar solvent like water. We observed this behaviour even with the weakly functionalized GO. Finally, the method here presented permits to obtain easily a coupled Pt/Bi catalytic system, whose presence was demonstrated by XPS analysis

and EDX (see added material). This can be considered a good result, not trivial at all, because aggregation problems seemed to be avoided.

The tests conducted on glycerol oxidation have permitted to obtain the same level of conversion but using a lower metals amount. It is still open the question about the selectivity because nowadays the analytical method can only give a qualitative response about the nature of the by-products.

It is important to underline how the method works mainly if applied to a low functionalized support because the $NaBH_4$, used for the chemical reduction of metal precursor, reacts easily with the functional groups on the GO. The reaction between $NaBH_4$ and functional groups did not permit the chemical reduction of metal precursor, obstructing the NPs synthesis and deposition. For this reason a high oxidation level of graphite should be avoided to reach an optimum. In this work we have showed how the low functionalized graphite could be one of the bet support exploiting a high alcohols conversion grade reducing drastically the metal loading.

Acknowledgements

[1] S. E. Davis, M. S. Ide, R. J. Davis, Selective oxidation of alchols and aldehyde over supported metal nanoparticles, Green Chemistry Review, 2013

[2] S. Hirasawa, H. Watanabe, T. Kizuka, Y. Nagagawa, K. Tomishige, Performance, structure and mechanism of Pd-Ag alloy catalyst for selective oxidation of glycerol to dihydroxyacetone, vol. 300, 205-216, 2013

[3] W. Hu, D. Knight, B.Lowry and A. Varma; Selective Oxidation of Glycerol to Dihydroxyacetone over Pt-Bi/C catalysts:optimization of catalyst and reaction conditions – Ind. Eng. Chem. Res., 10876-10883, 2010

[4] M. Wenkin, P. Ruiz, B. Delmonb and M. Devillers; The role of bismuth as promoter in Pd–Bi catalysts for the selective oxidation of glucose to gluconate; Journal of Molecular Catalysis A: Chemical 2002, 180 (1-2), 141–159, 2002

[5] A. Mastalira, Z. Kiraly, A. Patzko, I. Dékany, P. L'Argentiere, Synthesis and Catalytic application of Pd nanoparticles on graphite oxide, Carbon, 46, 1631-1637, 2008

[6] D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, The chemistry of graphene oxide, Chemical Society Review, 39 (1), 228-240, 2009

[7] S. Jr. W. Hummers and R. E. Offerman, Preparation of Graphitic Oxide, Journal of the American Chemical Society, 80 (6), 1339, 19585

[8] L. Shahriary and A. A. Athawale, Graphene Oxide Synthesized by using Modified Hummers Approach, Int. Journal of Renewable Energy and EnvironmentalEngineering, 2 (1), 2348-0157, 2014

[9] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, Improved Synthesis of Graphene Oxide, ACS Nano,4 (8), 4806–4814,2010

[10] L. Shahriary and A. A. Athawale, Graphene Oxide Synthesized by using Modified Hummers Approach, Int. Journal of Renewable Energy and EnvironmentalEngineering, 2 (1), 2348-0157, 2014

[11] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, Improved Synthesis of Graphene Oxide, ACS Nano,4 (8), 4806–4814,2010

[12] E.G. Rodrigues, S.A.C. Carabineiro, J.J. Delgado, Gold supported on carbon nanotubes for the selective oxidation of glycerol, Journal of Catalysis, 285 (1), 83-91, 2011

[13] E.G. Rodrigues, M.F.R. Pereira, J.J. Delgado, X. Chen, J.J.M. Orfao, Enhancement of the selectivity to dihydroxyacetone in the glycerol oxidation using gold nanoparticles supported on the carbon nanotubes, vol. 16, 64-69, 2011

[14] H.J. Shin, K. K. Kim, A. Benayad, S.Yoon, H. K. Park, I. Jung, M. H. Jin, H. K. Jeong, J. M. Kim, J. Choi and Y. H. Lee, Efficient Reduction of Graphite Oxide by Sodium Borohydride and Its Effect on Electrical Conductance, 19 (12), 1987-1992, 2009

[15] Y. Zhu, M. D. Stoller, W. Cai, A. Velamakanni, R. D. Piner, D. Chen and R. S. Ruoff, Exfoliation of Graphite Oxide in Propylene Carbonate and Thermal Reduction of the Resulting Graphene Oxide Platelets, ACS Nano, 4(2), 1227-1233, 2010

[16] D. R. Dreyer, H. P. Jia, C. W. Bielawski, Graphene oxide: a convenient carbocatalyst for facilitating oxidation and hydration reactions, Angew Chem Int Ed Engl., 49(38), 6813-6, 2010

[17] D. R. Dreyer, A. D. Todd, C. W. Bielawski , Harnessing the chemistry of graphene oxide, Chem. Soc. Rev.,43, 5288-5301, 2014

[18] A.V. Naumkin, A.K. Vass, S.W. Gaarenstroom and C.J. Powell, NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database 20, Version 4.1,

[19] D. R. Dreyer, C. W. Bielawski, Carbocatalysis: Heterogeneous carbons finding utility in synthetic chemistry, Chem. Sci., 2, 1233-1240, 2011

[20] H. P. Jia, D. R. Dreyer, C. W. Bielawski, Graphite Oxide as an Auto-Tandem Oxidation–Hydration–Aldol Coupling Catalyst, Advanced Synthesis & Catalysis, Volume 353, Issue 4, pages 528–532, March 7, 2011