

# Ultra-fine Ni<sub>2</sub>P nanoparticles decorated r-GO: Novel Phosphidation approach and Dibenzothiophene Hydrodesulfurization

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**Abstract.** Nanostructured transition metal phosphides gathered last years an elevated scientific interest, due to their unique physical-chemical properties. Nickel phosphide nanoparticles, with the controllable crystal structure, from the metal rich tetragonal Ni<sub>12</sub>P<sub>5</sub> to the phosphorous rich hexagonal Ni<sub>2</sub>P, and *hcp* Ni<sub>2</sub>P decorated r-GO (reduced graphene oxide), nano-hybrid materials have been synthesized via a novel one step organometallic approach in primary-tertiary aliphatic amines mixture. The nanoparticles are monodispersed, with spherical shape and controllable size in the sub-10 nm regime and decorate uniformly the surface of the r-GO, leading to the formation of Ni<sub>2</sub>P/r-GO hybrid materials. The materials were characterized by powder XRD, TEM and Raman spectroscopy and catalytically evaluated for the dibenzothiophene hydrodesulphurization (HDS) reaction. The results show that the role of the tertiary amine is crucial for the phosphidation process and the r-GO is an ideal alternative, to the traditional inorganic ones, support for the immobilization of the catalytically active component, preventing significantly sintering effects.

**Keywords:** *Ni<sub>2</sub>P colloids, r-GO, composite nanomaterials, chemical synthesis, phosphidation reaction, hydrodesulphurization, dibenzothiophene*

## INTRODUCTION

During last decades the extensive study of matter in the nanosize regime ( $<100$  nm) have already gave an enormous boost in the materials science, introducing materials with improved or even novel physicochemical properties. Transition metal phosphides, although they discovered in the 18<sup>th</sup> century, in contrast with metallic, metal oxides and metal chalcogenide (quantum dots) nanoparticles, attract significant scientific interest in the last decades because of their potential applications, mainly in the fields of catalysis, replacing noble and precious metals, semiconductors and magnetic materials.<sup>1-5</sup>

With respect to catalysis, transition metal phosphides are being evaluated as hydro-treating catalysts for hydrodesulfurization (HDS)<sup>6-9</sup> hydrodenitrogenation (HDN)<sup>10</sup>, hydroprocessing (HPC)<sup>11</sup>, and hydrogen evolution reaction (HER)<sup>12-20</sup> processes and electrochemical energy storage.<sup>21, 22</sup> Among transition metal phosphides, nickel phosphides are attracting the greater interest because exhibits superior catalytic activities, especially in the HDS reactions, in comparison with other metal phosphides like Fe<sub>2</sub>P, MoP, WP, and Pd<sub>2</sub>P<sub>5</sub>.<sup>23-26</sup> Between nickel phosphides, the hexagonal one, Ni<sub>2</sub>P, is the most active as HDS catalyst in comparison with other nickel phosphides such as Ni<sub>12</sub>P<sub>5</sub>, Ni<sub>5</sub>P<sub>4</sub> and NiP<sub>2</sub>.<sup>27, 28</sup> Therefore becomes essential the development of methodologies for the selective synthesis of crystal structured control nickel phosphide catalysts. Up today various synthetic routes have been used for the synthesis of Ni<sub>2</sub>P nanoparticles in various morphologies, such as solid and hollow nanoparticles<sup>29, 30</sup> branched nanoparticles and nanorods<sup>31, 32</sup> and nanowires.<sup>33</sup> Solution phase approaches involves the direct reaction between a nickel and a phosphorous source at elevated temperature and produce particles with very narrow size distribution and discrete sizes. Mainly they are based on the use of inorganic metal salts, metal alkyls or metal carbonyls as metal sources, and alkyl or aryl phosphines<sup>34</sup> and phosphine oxides as phosphorous source.<sup>30, 32, 35-37</sup> These methods are based on the ability of the phosphine and phosphine oxide molecules to act as P atom donors, through their thermal decomposition at temperatures above 250 °C. Furthermore, the use of white phosphorous and, yellow molecular P<sub>4</sub>, as a phosphorous source for the synthesis of nickel phosphide nanoparticles has been also reported<sup>3, 38, 39</sup> and recently Ni<sub>2</sub>P nanoparticles in the sub-100 nm size regime were synthesized using a single molecular precursor.<sup>40</sup> Concerning the synthesis of Ni<sub>2</sub>P/graphene nanocomposites the last years a limited number of work appeared in the literature and the most of them focused on the electroactivity of the corresponded materials.<sup>41-52</sup>

Here we wish to report in the first section of our work an extensive study concerning the synthesis of nickel phosphide nanoparticle in discrete crystal structures introducing a modified phosphidation approach, following by the synthesis of Ni<sub>2</sub>P/r-GO nano-hybrids. Both nickel phosphide colloids and composites with r-GO were synthesized in liquid phase, using Ni(acac)<sub>2</sub>, as nickel precursor and tri-octylphosphine (TOP), as phosphorous source, in a mixture of aliphatic amines (oleyl amine, tri-octylamine) which seems that play a very important role on the phosphidation process, the size/morphology and the crystal structure of the produced nanoparticles. Finally, the Ni<sub>2</sub>P/r-GO hybrid materials were also evaluated as hydrotreating catalysts for the dibenzothiophene HDS in a batch, liquid phase reactor, and reveal a high activity at relatively low temperatures in comparison with similar materials from the literature or commercially available.

## EXPERIMENTAL

**Materials Synthesis.** The nickel phosphide nanoparticles were synthesized following an organometallic approach. In a typical experimental procedure 2 mmol Ni(acac)<sub>2</sub> are dissolved in 20 ml of an oleyl amine/tri-octylamine mixture that containing tri-octylphosphine (TOP), as a phosphorous source, varying the P/Ni<sup>2+</sup> molar ratio in the 1-18 range. The reaction mixture, after the formation of a clear solution, was heated, under nitrogen atmosphere, at 300 °C and kept at this temperature for 2 h. The colour of the reaction mixture changes from green to dark green and finally turned to black suggesting the nanoparticles formation. Following, the nanoparticles were precipitated, after the temperature solution was cooled down to room temperature, by the addition of ethanol and separated by centrifugation. This procedure was repeated many times to ensure the complete removal of any unreacted organic molecules and reaction by products.

The Ni<sub>2</sub>P/r-GO hybrids were synthesized following similar methodology, with sonochemical GO exfoliation before the Ni<sub>2</sub>P formation. In particular GO were first dispersed in the aliphatic amines (oleyl amine/tri-octylamine) mixture and probe sonicated in order to exfoliate them, following by the drop-wise addition of the Ni(acac)<sub>2</sub> solution in a similar aliphatic amines mixture which additional includes the phosphorous source, (TOP). Then the reaction mixture was removed from the sonication source and heated up to 300 °C for 2 h under a nitrogen blanket. The products separated first by centrifugation and washed couple of times with a 1/1 ethanol-hexane mixture in order to remove the excess of the organic solvents and reaction by-products, and finally stored in

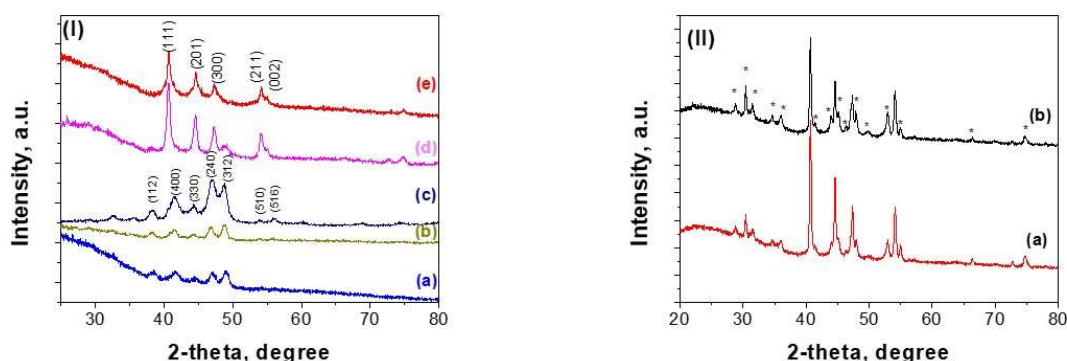
CHCl<sub>3</sub>.

**Materials Characterization.** All the materials were characterized with powder X-Ray diffraction, using a Siemens D500 diffractometer, with CuK $\alpha$  radiation ( $\lambda=1.5418$  Å), while TEM images were collected using a Philips CM20 operated at 200 kV microscope. Raman spectra were recorded with a Labram HR system by HORIBA Scientific, using a laser diode excitation line at 514.5 nm, in the frequency range of 100-3500 cm<sup>-1</sup>.

**Catalytic Evaluation.** The catalytic HDS experiments took place in liquid phase, using hexadecane as solvent, and 4,6-dibenzothiophene as sulphur contain molecule, in a batch Parr reactor under H<sub>2</sub>, (20 bar), at 300 °C for 4 h. In a typical procedure, 40 mg of the catalyst was dispersed in 50 ml of 1000 ppm dibenzothiophene in n-hexadecane solution. Following, the reactor was purged with He several times, to remove atmospheric air, and the temperature was raised to 300 °C under constant stirring. Then the sealed autoclave was charged with H<sub>2</sub> at the pressure of 20 bar. The overall sulphur content after the HDS reaction was analysed by a sulphur fluorescence analyser (KDS-300).

## RESULTS AND DISCUSSION

**Colloidal Nickel phosphides.** As mentioned, the synthesis of nickel phosphide nanoparticles took place following an organometallic approach which based on the phosphidation using a very common phosphorous source (TOP) in a mixture of aliphatic amines. The nature and the composition of the aliphatic amines mixture it seems that play a very crucial role on the crystal structure, the single-phase nature, the morphology, and the size of the synthesized phosphides nanoparticles. Oleyl amine were extensively studied in the literature as solvent and capping agent, and it is well known that favor the formation of the metal rich Ni<sub>12</sub>P<sub>5</sub> phase.<sup>32, 53</sup> The hexagonal Ni<sub>2</sub>P phase was observed only under quite high P/Ni<sup>2+</sup>, up to 15, molar ratio<sup>34</sup>, or under moderate, up to 11.2, P/Ni<sup>2+</sup> ratio but at higher reaction temperature (up to 350 °C), which enhance the phosphidation process, in order to formed the phosphorous rich phase.<sup>53, 54</sup>



**Figure 1.** Powder X-ray diffraction patterns of nickel phosphide nanoparticles synthesized in an oleyl amine mono-surfactant medium at 300 °C (I) and 350 °C (II) with different  $P/Ni^{2+}$  molar ratio varied from 1 (a), to 3 (b), 9 (c), 12 (d) and 18 (e), for the low temperature reaction, and 1 (a) and 18 (b) for the reaction at 350 °C.

The crystal structure and the phase purity of the nanoparticles were estimated using X-ray diffraction (XRD). In Figure 1, presented the XRD patterns of the as made nickel phosphide nanoparticles synthesized in commercial oleyl amine (80-90 % C18-content) using  $Ni(acac)_2$  and TOP as nickel and phosphorous source respectively. The reaction take place at 300 °C under Ar gas atmosphere for 2 h. The  $P/Ni^{2+}$  molecular ratio was varied from 1 to 18 in order to study its effect on the crystal structure of the synthesized nanoparticles.

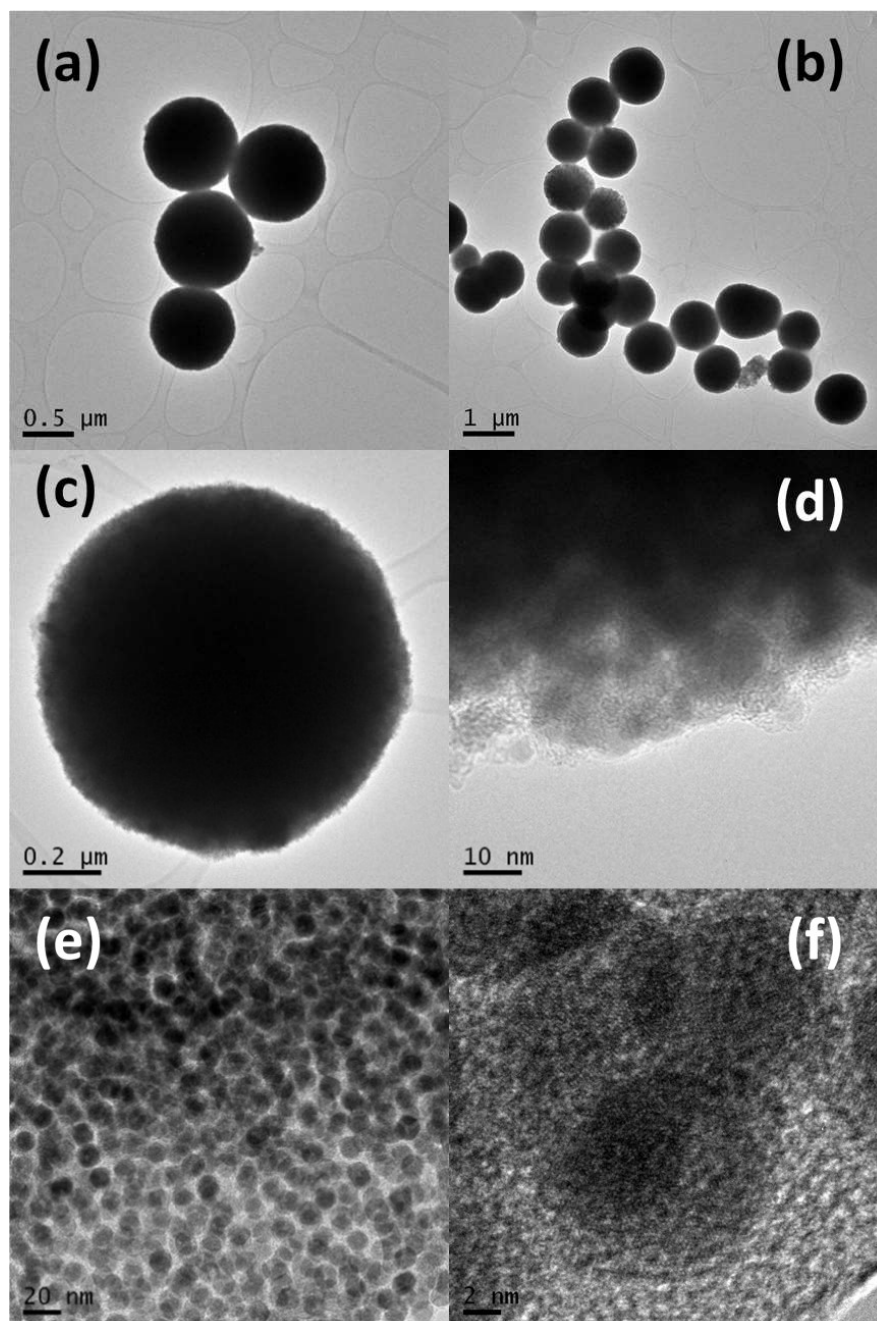
From the X-ray diffraction patterns it is clear that at very low  $P/Ni^{2+}$  molar ratio, in 1-3 range, and low reaction temperature, (300 °C), the nanoparticles have the metal rich tetragonal  $Ni_{12}P_5$  phase, while with the increasing drastically the  $P/Ni^{2+}$  molar ratio up to 18, the produced particles reveals the hexagonal phosphorous rich  $Ni_2P$  phase. The oleyl amine it was already observed that favours in general the formation of the metal rich phosphides phases<sup>32, 53</sup>, even under conditions that are more suitable for the formation of the phosphorous rich phases but the mechanism is still remains unknown. In the intermediate  $P/Ni^{2+}$  molar ratio values, (in the range 9 to 12), the XRD patterns shows clearly the co-existence of tetragonal and hexagonal crystal structures. More specific when the  $P/Ni^{2+}$  ratio is around 9 the dominant phase is the tetragonal one, while with the increasing  $P/Ni^{2+}$  molar ratio up to 12, the hexagonal phase became dominant. Finally, at very high, (up to 18),  $P/Ni^{2+}$  ratio, value which is among the highest in the literature, the nanoparticles crystallize into the hexagonal  $Ni_2P$  crystal structure without any obvious signs of secondary phases. On the

other hand, in the reactions that took place under reflux conditions, near to the oleyl amine boiling point, (348-350 °C), the nanoparticles do not reveal a single phase material, independently the P/Ni<sup>2+</sup> molar ration, but consist of multiple phosphorous rich phases and more specifically form the Ni<sub>2</sub>P and Ni<sub>5</sub>P<sub>4</sub>. In details, the diffractions at 38.3°, 41.7°, 44.5°, 47.1°, 48.9° 54.1°, 56.1°, 2 $\theta$ , (Fig.1a), are attributed respectively to the (112), (400), (330), (240), (312), (510) and (501) crystal planes of the tetragonal Ni<sub>12</sub>P<sub>5</sub> phase, (PDF 03-065-1623), while the diffractions at 40.8°, 44.7° 47.4°, 54.4° 2 $\theta$  belong to the hexagonal Ni<sub>2</sub>P phase (PDF # 74-1385). For the products of the reaction that took place at higher temperature (near to the oleyl amine boiling point), the diffraction peaks which indicated with an asterisk can attributed to the hexagonal Ni<sub>5</sub>P<sub>4</sub> phase, (PDF # 03-0652075), while the diffraction at 40.8°, 44.7° 47.4°, 54.4° 2 $\theta$  belongs to the hexagonal Ni<sub>2</sub>P phase (PDF # 74-1385). Consequently, at high reaction temperature the phosphidation process proceed much faster, and favor the formation of phosphorous rich phases, but with an uncontrollable manner which leads to the formation of mixed phase materials.

Oleyl amine it is a well-known in the literature coordination agent that bind quite strong on the surface of metallic nanoparticles.<sup>55-57</sup> On the other hand, tri-octyl phosphine molecules, mainly because of steric effects originated from the presence of three aliphatic groups, binding weaker with the metallic Ni surface and thus resulting in the need for higher TOP concentration or higher reaction temperature and time, in order to compete the oleyl amine molecules and thus to accelerate the phosphidation procedure for the formation of the phosphide materials. Additionally, when the reaction conditions, and mainly the temperature, favour the phosphidation process, this is happening with a manner that leading to multi-phase phosphorus rich particles.

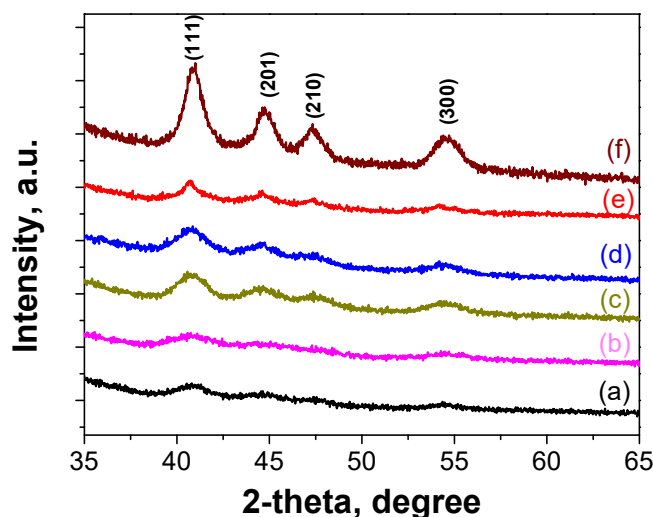
In terms of morphology it is observableness that the materials were synthesized with high phosphorous concentration, in order to enhance the formation of the hexagonal Ni<sub>2</sub>P phase, organized in spherical microparticles, while the particles that synthesized with lower phosphorous concentration and possess the tetragonal Ni<sub>12</sub>P<sub>5</sub> structure are dense and isolated as evidenced by the TEM images, (presented in Figure 2e), with excellent uniformity, 7.7 nm mean diameter and narrow size distribution (Fig. S1a). Although this organization in larger structures is a common phenomenon for metal nanoparticles,<sup>58-60</sup> and oxides nanostructures,<sup>61</sup> it is rarely in phosphides. These hierarchical three-dimensional structures were grown symmetrically in spherical shapes with a narrow size distribution in the sub-micro size regime. The fact that this morphology was not observed in the lower tri-octyl phosphine concentration, shows that the driving force does not

connected with the concentration of the inorganic precursor effect but probably originate from the nature and composition of the organic molecules. The aggregate formation may also be due to van der Waals interactions and needs further investigation but is not in the purpose of the current study.



**Figure 2.** TEM images from the phosphide nanoparticles which were synthesized in oleyl amine with P/Ni<sup>2+</sup> ratio 18 (a-d) and 1 (e, f).

Aiming to overcome all the above mentioned issues and synthesize the hexagonal structured, phosphorus rich,  $\text{Ni}_2\text{P}$  phase in a controllable way, using as low as possible  $\text{P}/\text{Ni}^{2+}$  ratio, and avoiding high temperatures, we are introducing here an organometallic reaction protocol based on the partial replacement in the reaction mixture of the primary amine, (oleyl amine), which is bind strongly on the metallic surfaces, with a tertiary amine, (tri-octyl amine), which because of the high steric effect, originated form the presence of three alkyl groups, bind on the nanoparticles surface weaker, but “working” similar with oleyl amine as a coordination solvent through the electron pair donor properties.



**Figure 3.** X-ray diffraction patterns of nickel phosphide nanoparticles synthesized in a tri-octylamine/oleyl amine mixture with different v/v ratio, varied from 4/6 (a), 6/4 (b), 7/3 (c), 8/2 (d), to 9/1 (e), and only TOA (f), while the  $\text{P}/\text{Ni}^{2+}$  atomic ratio is 2.8.

Therefore, part of the primary amine (oleyl amine) replaced by an also high boiling point (365 °C) and very stable tertiary amine (tri-octyl amine, TOA), and studied the nickel phosphide synthesis following the same reaction protocol keeping constant the reaction temperature, the reaction volume, and the phosphorous source concentration, ( $\text{P}/\text{Ni}^{2+}=2.8$ ), varying the TOA/oleyl amine volume ratio. The XRD patterns of the corresponded materials (presented in Figure 3), shows that in all cases the synthesized materials possess the hexagonal phosphorus rich  $\text{Ni}_2\text{P}$  phase. In details the diffraction peaks at 40.7°, 44.7° 47.4°, and 54.4°  $2\theta$  can be attributed respectively to the

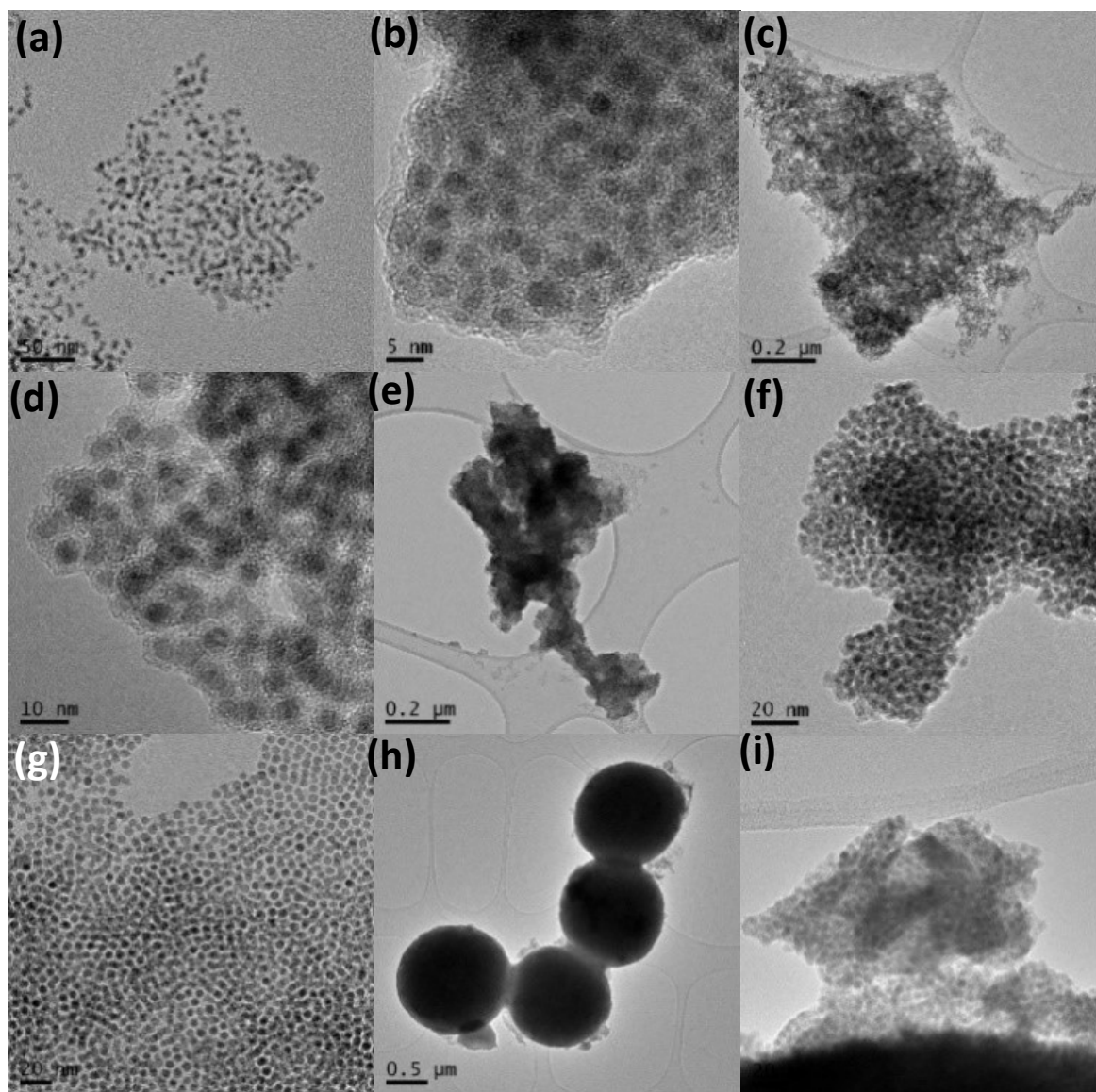


(111), (201), (210), (300) lattice planes of the hexagonal  $\text{Ni}_2\text{P}$  phase (PDF # 74-1385), while the absence of any other diffraction peaks confirms the single phase nature of the nanoparticles. Concerning the size of the particles it is obvious from the broad width of the diffraction peaks that the particles are quite small and actually in the range of the sub-10 nm in diameter (estimated using Scherrer equation), in contrast with another work, in which the  $\text{Ni}_2\text{P}$  synthesis took place in a low oleyl amine concentration solution in n-octadecene as reaction solvent, the nanoparticles have mean diameter in the range of 10-20 nm and hollow morphology.<sup>19</sup>

The nanoparticles size and the morphology were precisely estimated using TEM studies. As the reaction mixture consist form TOA-Oleyl amine with 4/6 v/v ratio the nanoparticles have an elongate morphology with few nanometer thickness (Fig. 4a), while increasing the TOA/oleyl amine volume ratio the nanoparticles becoming uniform, with near spherical shape, and mean diameter which is slightly increase with the increasing of the TOA concentration, but in all the cases remain in the 3-5 nm regime (Fig. 4b-g). There is a noticeable difference when the reaction take place only in TOA. In this case the produced particles were grown in spherical hierarchical three-dimensional structures which consist from 5 nm individual nanoparticles (Fig. 4h-i). Conclusively in the oleyl amine rich environment favor the irregular rod-like nanocrystal formation, while in the tri-octyl amine rich medium, with TOA/oleyl amine v/v ratio 7/3, 8/2 and 9/1, favor the formation of dense, monodispered, with narrow size distribution, spherical nanocrystals with mean diameter in the 4.3 to 5.1 nm size regime. (Fig. S1 b, c, and d). It is obvious that a moderate oleyl amine concentration it is necessary in order to keep the nanoparticles size at low dimensions.

The above findings show distinctly that ultra-small, monodispersed, single phase, *hcp*  $\text{Ni}_2\text{P}$  nanoparticles in the dense solid morphology, can be successfully synthesized in a TOA-Oleyl amine mixture using TOP, as phosphorous source, at relatively low temperatures (300 °C), in the sub-5 nm size regime. Additionally, it is worth to mention that in our approach the solid morphology  $\text{Ni}_2\text{P}$  nanoparticles are synthesized in a relatively low  $\text{P}/\text{Ni}^{2+}$  ratio (2.8), in contrast with the reaction in oleyl amine ( $\text{P}/\text{Ni}^{2+}=18$ ), and other reported works in which a  $\text{P}/\text{Ni}^{2+}$  molar ratio up to 5.6 is needed in order to synthesize  $\text{Ni}_2\text{P}$  nanoparticles in the solid morphology.<sup>53</sup> Thus, the presence of a weaker binding molecule on the surface of the nanoparticles, is very crucial for the phosphidation procedure allowing the crystallization of the nanoparticles into the hexagonal P rich phase. From the mechanistic point of view, the competitive adsorption on the nanoparticles

surface between the tri-octyl amine and tri-octyl phosphine, due to the lower steric inhibition in the tri-octyl phosphine molecule compared to the tri-octyl amine, (P atoms are much bigger than N), favor the phosphine adsorption and thus accelerate the phosphidation process.



**Figure 4.** TEM images of  $\text{Ni}_2\text{P}$  nanoparticles synthesized in TOA/Oleyl amine mixture with 4/6 (a), 6/4 (b), 7/3 (c, d), 8/2 (e, f), 9/1 (g) and 10/0 (h, i) v/v ratio.

**$\text{Ni}_2\text{P}$  decorated r-GO.** As we already mentioned in the introduction section  $\text{Ni}_2\text{P}$ /graphene nanocomposites have been attracted scientific interest in the last years and the majority of the

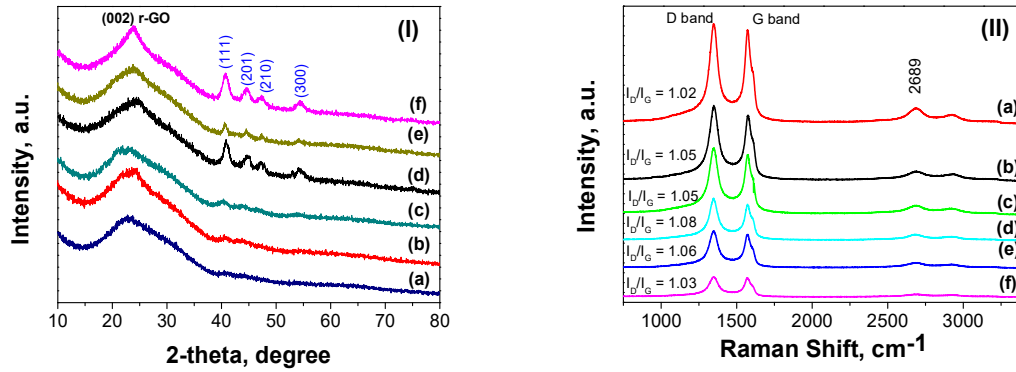
research works focused on the electroactivity of the materials either for electrocatalytic or energy storage applications. Following a quite similar synthetic protocol, Lu et al. reported the synthesis of hollow Ni<sub>2</sub>P nanoparticles covered by a graphitic layer that coming from the oleyl amine pyrolytic decomposition.<sup>62</sup> In a recent work the transition metal phosphide/r-GO composites synthesized starting from a metal hydroxide/GO composite material following by a solid state phosphidation at 300 °C and tested for hydrogen evolution reactions (HER).<sup>41</sup> Yolk-shell like Ni<sub>2</sub>P/Graphene were synthesized using a solid state procedure and tested for Li and Na ions storage.<sup>50</sup> The Ni<sub>2</sub>P nanoparticles are in the size range of few decades of nanometers with quite broad size distribution.

Utilizing the previously reported findings Ni<sub>2</sub>P decorated r-GO were synthesized in liquid phase and tested as catalysts for the dibenzothiophene HSD reaction. In this case the chemical nature of the reaction mixture plays a more complex role. TOA/oleyl amine favor the low temperature phosphidation process and the selective formation of the hexagonal Ni<sub>2</sub>P phase, and at the same time both the amine molecules participate into the chemical exfoliation and reduction of the GO<sup>63-65</sup>, while the TOP molecules were also contribute to the GO reduction<sup>65</sup> and serve as P source.

The crystal structure and the morphology of the Ni<sub>2</sub>P/r-GO nano-hybrids, were determined by XRD, Raman spectroscopy, and TEM studies. As shown in the powder XRD, in Figure 5(I), all the diffraction peaks correspond to the hexagonal Ni<sub>2</sub>P phase, (PDF # 074-1385), while the broad diffraction at 23.9° 2 $\theta$ , corresponds to the (002) short range order in stacked r-GO sheets. The Raman spectra of Ni<sub>2</sub>P/r-GO nano-hybrids exhibits both the characteristic G and D-bands at 1579 and 1347 cm<sup>-1</sup> respectively. The G-band at 1579 cm<sup>-1</sup>, which is associated with *sp*<sup>2</sup> hybridized carbon atoms, is asymmetric and shifted near the relevant peak of graphite which is positioned at ~1580 cm<sup>-1</sup>, indicating the successful removal of the most oxygen-containing groups and the aromatic ring restoration. The asymmetric nature of the G-band peak is due to the presence of a small amount of pristine GO (which reveals the G-band at 1600 cm<sup>-1</sup>) or less reduced GO. In our case it is clear that the dominant peak is shifted at the lower wavenumbers (around 1579 cm<sup>-1</sup>) and combined with the *I*<sub>D</sub>/*I*<sub>G</sub> ratio, which is varied from 1.02 to 1.08, we are able to support the successful GO reduction.

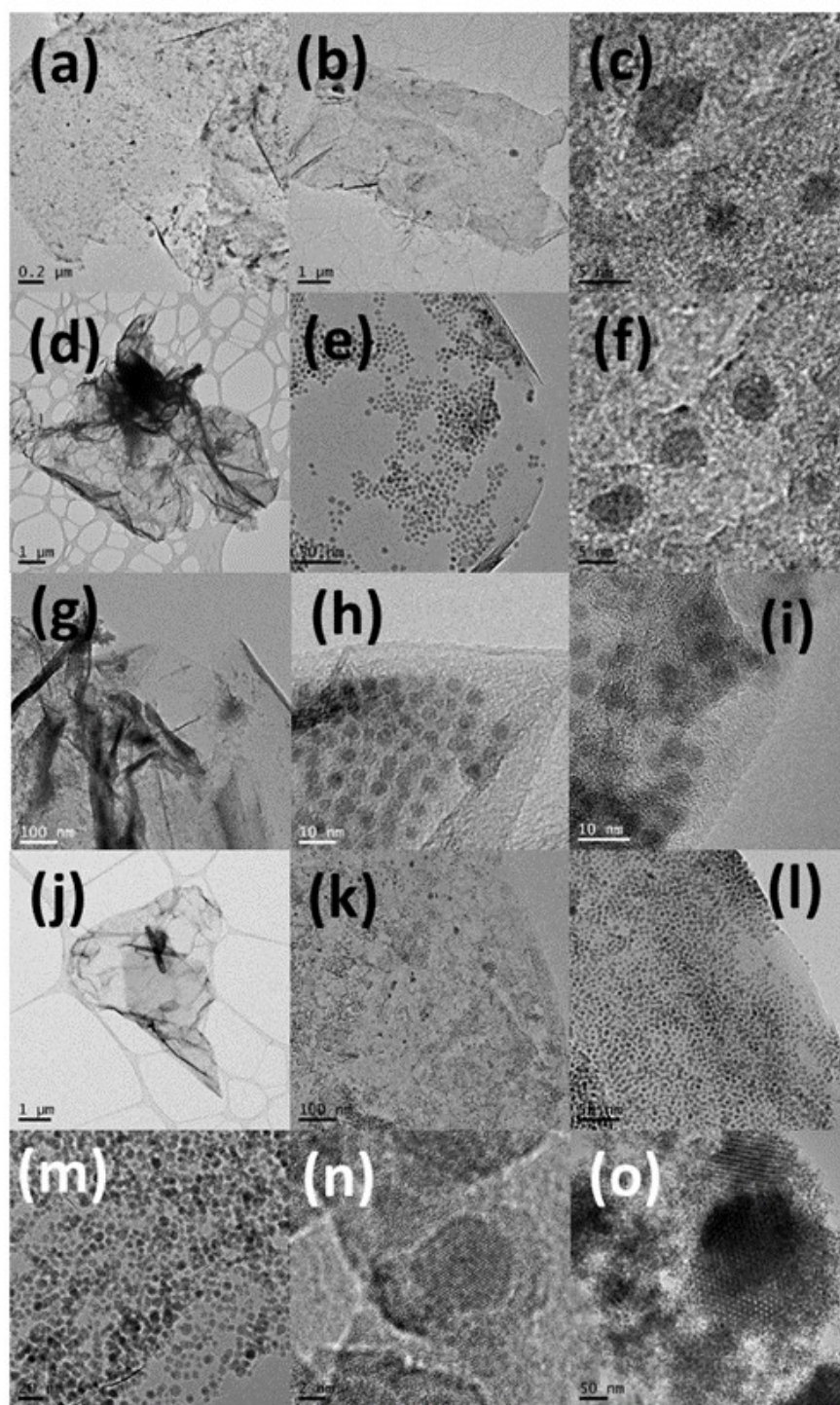
The increase of the *I*<sub>D</sub>/*I*<sub>G</sub> was originated by the increase of the *sp*<sup>2</sup> domains, upon reduction, within the initial GO sheets and as a decrease in the average size.<sup>66, 67</sup> Furthermore, while GO does not have significant peaks in the 2D region,<sup>68, 69</sup> a broad peak arises at 2689 cm<sup>-1</sup> in the Raman spectra.

This is ascribed to the 2D vibrational mode (overtone of the D peak).<sup>70, 71</sup> According to the literature, the red shift of G-band, the intensity of the 2D peak as well as its shift below 2700  $\text{cm}^{-1}$ <sup>1</sup> are clear evidence of the r-GO presence with a few layers formation.<sup>70</sup>



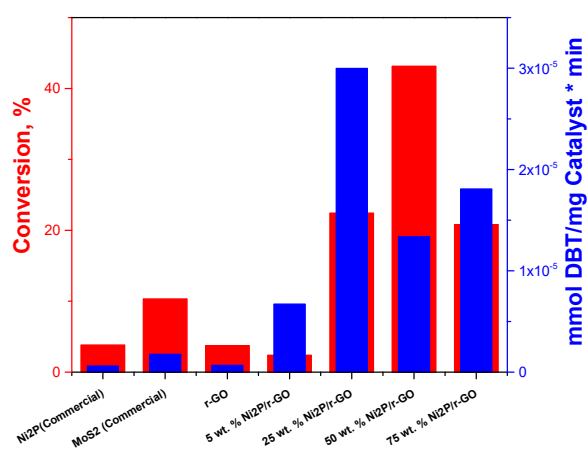
**Figure 5.** X-ray diffraction patterns (I) and Raman spectra (II) of  $\text{Ni}_2\text{P}/\text{r-GO}$  nano-hybrids with 5 (a), 10 (b), 25 (c), 40 (d), 50 (e), and 75 (f) wt. %  $\text{Ni}_2\text{P}$  nominal loading.

The TEM images of  $\text{Ni}_2\text{P}/\text{r-GO}$  nano-hybrids, with different  $\text{Ni}_2\text{P}$  loadings, were presented in Figure 6. In most of the cases uniform, monodispersed  $\text{Ni}_2\text{P}$  nanoparticles anchored on the r-GO surface leading to the formation of a more or less dense monolayer of  $\text{Ni}_2\text{P}$  without the presence of isolated nanoparticles which doesn't connected with the r-GO surface. The only exception is the case of the higher metal phosphide loading, in which we can clear observe the presence of a monolayer covering of the r-GO surface with nanoparticles and the presence of not anchored nanoparticles that forms self-assembly superlattices by themselves. At low magnification images is revealed the micron-sized nature of the r-GO sheets. The phosphide nanoparticles are spherical with an average diameter in the sub 5 nm size regime independently the nominal loading. The only difference is the r-GO surface coverage. Concluding, from the TEM observations it seems that our methodology working similarly in a wide range of metal phosphide loading, producing uniformly anchored  $\text{Ni}_2\text{P}$  nanoparticles on the r-GO surface.



**Figure 6.** TEM images of  $\text{Ni}_2\text{P}/\text{r-GO}$  nano-hybrids with 10 (a-c), 25 (d-f), 40 (g-i), 50 (j-l) and 75 (m-o) wt. % nominal metal phosphide loading.

The  $\text{Ni}_2\text{P}/\text{r-GO}$  nanocatalysts were evaluated for the hydrodesulfurization (HDS) of dibenzothiophene (DBT). The HDS reaction took place in a liquid phase batch reactor at 300 °C, using hexadecane as solvent, under 20 bar  $\text{H}_2$  pressure, using DBT as sulfur source molecule with 1000 ppm concentration, for 2 h reaction time. For comparison commercially available  $\text{Ni}_2\text{P}$  (Sigma-Aldrich) and  $\text{MoS}_2$ , (Sigma-Aldrich), which is the most studied and the industrial HDS catalyst, were also tested under the same reaction conditions. The DBT conversion and reaction rates, over different catalytic systems are presented in Figure 7. The DBT conversion is in the range of 10 % for the commercial bulk  $\text{MoS}_2$  and almost negligible over commercial  $\text{Ni}_2\text{P}$  (Nickel phosphide, -100 mesh, 98%, Sigma Aldrich) and r-GO, while concerning the  $\text{Ni}_2\text{P}/\text{r-GO}$  nanocatalysts the DBT conversion increasing with the increasing of the  $\text{Ni}_2\text{P}$  loading and reach 44 % over  $\text{Ni}_2\text{P}/\text{r-GO}$  nanocatalysts with 50 wt. % metal phosphide loading, while for the high dense  $\text{Ni}_2\text{P}/\text{r-GO}$  sample decreasing down to 20 %. This behavior can be attributed to the presence of a large nanoparticles population which are not anchoring on the r-GO surface and suffer from sintering and agglomeration effects. From the stability point of view the reaction rate is constant after 2 cycles of HDS for the low  $\text{Ni}_2\text{P}$  loading, while remain in the same level for the 25 and 50 %  $\text{Ni}_2\text{P}$  loading. In the case of 75 %  $\text{Ni}_2\text{P}$  loading the reaction rate decreased dramatically between first, second and third cycle (see ESI section Fig.S2). TEM studies for the materials after the HDS cycles showing that the nanoparticles remain isolated on the r-GO surface, without sintering signs even for the 50 %  $\text{Ni}_2\text{P}/\text{r-GO}$  material (see ESI section Figure S3).



**Figure 7.** Dibenzothiophene HDS conversion and reaction rate over different catalyst type.

In comparison with the literature the DBT conversion over 10 wt. % supported Ni<sub>2</sub>P/SiO<sub>2</sub> is less than 10% for 5, 10 and 15 nm Ni<sub>2</sub>P nanoparticles, while for 10 nm Ni<sub>2</sub>P<sup>24</sup> and Pd<sub>5</sub>P<sub>2</sub><sup>26</sup> nanoparticles in a core/shell morphology with SiO<sub>2</sub> the DBT conversion at 300 °C is in the range of 5 and 10 % respectively. At 310 °C the DBT conversion can reach 80 % over 20 wt. % Ni<sub>2</sub>P on MCM-41 while at 350 °C the conversion is almost 100 %, <sup>8</sup> while over Ni<sub>2</sub>P/TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> the DBT conversion is around 60 % at 310 °C for 3h time on stream.<sup>72, 73</sup> In all the above studies the reaction take place in a fixed bed continues flow reactor in the gas phase under 30 bar pressure, in contrast with our case that the HDS reaction took place in the liquid phase under batch conditions and 20 bar hydrogen pressure. Independently of the loading and the Ni<sub>2</sub>P nanoparticles size it is clear from the data that the DBT conversion is quite high (in the range of 50 %) for reaction temperatures and H<sub>2</sub> pressure higher than 300 °C and 20 bars respectively. In our case, in accordance with our Health, Safety and Environment (HSE) regulations we weren't able to exceed 300 °C and 20 bar H<sub>2</sub> pressure. In general, although the reaction rate constant, according to the Langmuir-Hinshelwood kinetic model, is independent of the reaction solvent the DBT/solvent adsorption constants decrease in the order heptane (gas phase reaction) to hexadecane (liquid phase reaction) due to the competitive adsorption between the DBT and the solvent for the catalytic active sites.<sup>74</sup> Additionally, the produced H<sub>2</sub>S in a batch reactions may also inhibit the dibenzothiophene HDS. Taking into account all the above remarks, including diffusion limitations and competitive adsorption in liquid phase in contrast with the gas phase, we can assume that the presented in the current work Ni<sub>2</sub>P/r-GO hybrids are excellent hydro-treating catalyst. Work is on progress for the effect of partial Ni substitution with Co and/or Fe and the formation of a bimetallic or ternary metal phosphide/r-GO composite materials. Preliminary results, presented in Figure S4 in the supplementary section, shows that the developed here phosphidation approach works sufficient for the synthesis of bimetallic Ni-Co phosphides.

## CONCLUSIONS

Summarizing we have developed a facile organic phase methodology for the synthesis of ultra-fine Ni<sub>2</sub>P nanoparticles by partial replacement of one the most commonly used organic capping agents, oleyl amine, by a tertiary organic amine, tri-octyl amine. The partial primary amine replacement accelerates the phosphidation process due to their steric effect differences, allowing



the formation of the phosphorus rich hexagonal phase Ni<sub>2</sub>P nanoparticles at lower temperature, in dense form, and ultra-small sizes with narrow size distribution. Furthermore, the methodology allows the in-situ reduction of graphene oxide (GO) and Ni<sub>2</sub>P nanoparticles formation, leading to the formation of Ni<sub>2</sub>P/r-GO nano-hybrids. The Ni<sub>2</sub>P/r-GO, nano-hybrid materials, were tested as hydrotreating catalysts for the dibenzothiophene hydrodesulfurization and appear, (taking into account that the reaction took place in liquid phase, where competitive adsorptions and diffusion phenomena are quite determinant), to be very active and stable, under the investigated conditions and it turns out that the r-GO can be an excellent alternative, to the inorganic ones, catalysts support for hydrotreating reactions.

## **ASSOCIATED CONTENT**

### **Supporting Information**

In the Supporting Information section were presented the size distribution histograms, additional TEM images of the materials after the HDS reaction, the catalytic activity after the first cycle and preliminary results for the synthesis of bimetallic NiCo phosphides following the presented here chemical methodology.

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## Graphic for the Table of Content

