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Fe_2O_3/NGr@C- and Co-Co_3O_4/NGr@C-catalysed hydrogenation of nitroarenes under mild conditions

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AN IMPROVED HYDROGENATION OF NITROARENES USING NANO-STRUCTURED IRON- AND COBALT-BASED CATALYSTS IS PRESENTED. MODIFICATIONS OF THE HETEROGENEOUS CATALYSTS BY N-DOPED GRAPHENE-FLAKES ARE CRUCIAL FOR THE SUCCESS OF SELECTIVE REDUCTIONS. THE USE OF POLAR SOLVENTS AND BASIC ADDITIVES HAS A SIGNIFICANT POSITIVE INFLUENCE ON THE RATE OF REDUCTION OF NITROARENES. THIS ALLOWS PERFORMING NON-NOBLE METAL-CATALYSED HYDROGENATIONS UNDER VERY MILD REACTION CONDITIONS (E.G. 70 °C AND 20 BAR). ON THE BASIS OF THE OBTAINED CATALYTIC RESULTS A HETEROLYTIC MECHANISM FOR THE HYDROGENATION PROCESS IS POSTULATED, TOO.

Catalytic systems based on non-precious, bio-relevant and abundant metals are the base of a virtuous development of cost-effective and sustainable chemical processes.[1] In the last decades many efforts have been made to discover and to improve efficient and competitive catalysts based on non-noble metals.[2] In addition to well-defined organometallic complexes, the combination of cheap metals with suitable supports allows producing robust heterogeneous catalysts which are recyclable, thus enhancing the global efficiency of the chemical transformation.[3] In this context, the replacement of expensive noble metal-based hydrogenation systems for more economic versions is still a great challenge. In the last three years, we reported versatile novel catalytic applications with different nanoscale heterogeneous carbon supported catalysts based on Co and Fe.[4] These catalysts are prepared by pyrolysis of *in situ* generated complexes of Co and Fe acetate with 1,10-phenanthroline (Phen) using Vulcan® XC 72R as carbon support.[5] These nanocomposites exhibit a core-shell architecture which constitutes the structural prerequisite for catalytic activity. In the case of the Co-based catalyst (Co-Co_3O_4/NGr@C), an inner metallic core is surrounded by a Co_3O_4 layer, whereas in the Fe-congener (Fe_2O_3/NGr@C) almost only an oxidic phase composed of Fe_2O_3 is present. In both cases, the oxidic shell is decorated with layers ("flakes") of nitrogen-doped graphene (NGr) derived from the thermal decomposition of the ligated Phen (see ESI). These two catalytic materials were successfully applied in many reactions ranging from reductions,[4,6] reductive amination[6] and oxidative transformations.[7b,8] Concerning hydrogenations, both catalysts showed excellent chemoselectivities towards the reduction of a variety nitroarenes bearing reducible and/or poisoning-capable functional groups. Nevertheless the original reaction conditions were quite harsh (>120°C, 50 bar H_2).

Here, we demonstrate for the first time that the use of polar solvents and the addition of bases allow to perform such hydrogenations under considerably milder reaction conditions. We commenced our study with testing various solvents in the hydrogenation of nitrobenzene. As shown in Figure 1, the use of polar solvent mixtures results in an increasing of the conversions compared to apolar or low-polar ones. In particular, alcoholic solvents such as ethanol or methanol give higher conversions. Furthermore, addition of water leads to improvements in almost every case (see Figures S5 and S6 for overall results). Merely, with MeOH as solvent, addition of water does not affect conversion or selectivity (Figures 1(b) and S7). Thus, EtOH-H_2O and MeOH were chosen as solvents, which are in accordance with guidelines as green and sustainable choice for chemical transformations.[9]

As shown in Table S3 and S4, the catalysts prepared without Phen (Co_xO_y@C and Fe_xO_y@C) do not exhibit any catalytic activity. Thus, the basicity provided by the NGr is crucial for the activity. This evidence is in agreement with a heterolytic cleavage of the dihydrogen molecule in which the N present in the graphitic matrix can act as proton acceptor. As a consequence, an additional base present in the liquid phase

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should enhance the catalytic activity. In order to confirm this assumption, we tested the model reaction in the presence of a variety of inorganic and organic bases (1 equiv. with respect to $PhNO_2$). For both catalysts, although high conversions were achieved, poor aniline selectivities were observed when inorganic bases (except NH_3) were added to the reaction mixture. In this case, azobenzene as well as azoxybenzene were identified as major side products (see Figure S8 and S9 for further details).

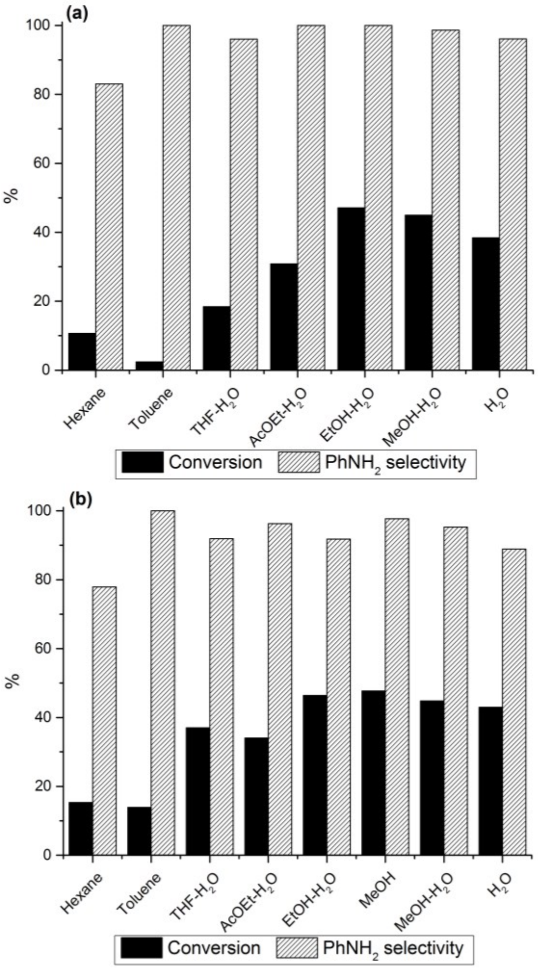

Figure 1. Influence of the solvent on conversion and selectivity for Co-Co_3O_4/NGr@C (a) and Fe_2O_3/NGr@C (b). Reaction conditions are based on previous optimizations: 0.5 mol % Co (5 mg), 70 °C, 20 bar H_2, 13 h or 4.5 mol % Fe (42 mg), 120 °C, 50 bar H_2, 4 h.

In fact it is known that alcohols in combination with strong inorganic bases act as reducing agents towards nitro compounds, giving rise to undesired coupling products.[10] On the contrary, when the catalytic transformation was conducted in the presence of an organic base, higher conversions were achieved compared to the reaction that was carried out without additives. Noteworthy, unwanted by-products did not form and the selectivity towards aniline remained very good (>95 %), (Figures 2(a) and (b)). Among the tested bases triethylamine (Et_3N) and 4-dimethylaminopyridine (DMAP) were found to be the best additives for Co-Co_3O_4/NGr@C and Fe_2O_3/NGr@C, respectively. However, DMAP is a toxic and corrosive solid,[11] which makes the use of chromatographic separation methods for its removal from the reaction mixture indispensable. Therefore, aqueous ammonia was chosen instead of DMAP since it is less toxic and possesses a negligible environmental impact.[11] Advantageously, ammonia is gaseous and thus readily removed from the reaction mixture. Since bases and alcoholic solvents are known to act as transfer hydrogenation agents, control experiments were carried out in order to rule out this reaction pathway (Table S3 and S4). As expected, no substrate conversion was detected in each case. Following our initial hypothesis, acidic additives were also examined (Figure S10 and S11).

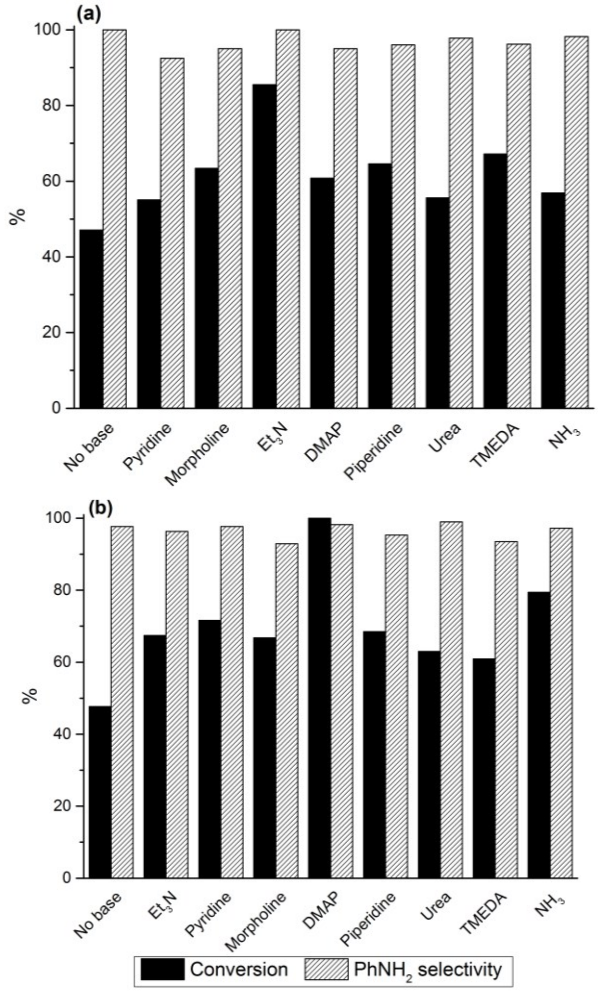

Figure 2. Influence of added organic base on conversion and selectivity for Co-Co_3O_4/NGr@C (a) and Fe_2O_3/NGr@C (b). Reaction conditions are based on previous optimizations: 0.5 mol % Co (5 mg), 70 °C, 20 bar H_2, 13 h or 4.5 mol % Fe (42 mg), 120 °C, 50 bar H_2, 4 h.

The results clearly indicate that addition of Lewis acids has a detrimental effect for the reaction outcome. For both heterogeneous materials the addition of metal triflates led to a marked decrease of catalyst performance. This behaviour is attributed to the interaction of acidic additives with the basic N-sites in the NGr that inhibit the catalytic activity. Next, we proceeded to evaluate the optimum amount of base. We conducted the reactions applying different equivalents of Et_3N

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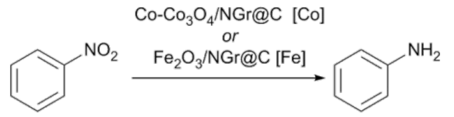
and NH_3 for Co-Co_3O_4/NGr@C and Fe_2O_3/NGr@C, respectively. The results are summarised in Figures S12 and S13. Even a small amount of base (0.05 and 0.1 equiv. of Et_3N and NH_3 for Co-Co_3O_4/NGr@C and Fe_2O_3/NGr@C, respectively) is able to accelerate the reaction significantly. However, best conversions were achieved with 1 equiv. of base with respect to the substrate. Using amount of bases higher than 1 equiv. (Co-Co_3O_4/NGr@C) or 1.5 equiv. (Fe_2O_3/NGr@C), resulted in a slight decrease of both conversion and selectivity. In the presence of an optimal base amount, catalytic hydrogenations were performed under milder conditions (Table 1). In case of Co-Co_3O_4/NGr@C a prolonged reaction time allowed for complete conversion at 70 °C and 20 bar (Table 1, entry 3), while with Fe_2O_3/NGr@C 90 °C and 30 bar hydrogen pressure are required (Table 1, entry 7). Nevertheless, to the best of our knowledge this latter example represents the first Fe-catalyzed hydrogenation of nitroarenes at such low temperature and pressure.

Then, the recyclability of the catalysts was explored (Figure 3). In the case of the Co catalyst, a slight decreasing of the conversion was detected in the third run while for Fe after an initial decrease after the first run, the activity stayed almost constant. ICP analysis of the liquid phase after each run reveals no metal leaching for both the catalysts (detection limit < 0.5 ppm).

Table 1. Hydrogenation of nitrobenzene to aniline: reaching mild conditions.[a)]



Entry	Catalyst	T [°C]	P [bar]	t [h]	Conv. [%][b)]	Sel. [%][b)]
1	[Co]	70	20	13	85	>99
2	[Co]	70	20	18	95	>99
3	**[Co]**	**70**	**20**	**20**	**>99**	**>99**
4	[Fe]	120	50	4	79	99
5	[Fe]	90	30	20	65	>99
6	[Fe]	90	30	24	86	>99
7	**[Fe]**	**90**	**30**	**28**	**>99**	**>99**

a) Reaction conditions for [Co]: 0.5 mmol $PhNO_2$, 0.5 mol % [Co] (5 mg), 2 mL EtOH + 100 μL H_2O, 1 equiv. of Et_3N; reaction conditions for [Fe]: 0.5 mmol $PhNO_2$, 4.5 mol % [Fe] (42 mg), 3 mL MeOH, 1 equiv. of NH_3; b) GC conversions and selectivities using *n*-hexadecane as internal standard.

In addition, Maitlis' hot filtration test ruled out any catalytic activity provided by soluble Co or Fe metal species (Table S5). Elemental analyses of both materials after the fifth run are within the experimental error the same of the pristine ones. In addition, the found values are very similar to those reported in the two original papers.[4a,b] These findings, coupled with ICP analyses, clearly demonstrates that the catalysts maintained their original composition even after the recycles.

To evaluate the scope of the new catalytic protocol, we tested various substituted aromatic nitro compounds bearing reducing-labile functional groups (Scheme 1). Substrates decorated with halogen atoms are smoothly converted to the corresponding anilines (**2a** and **2b**) without any hydrodehalogenation. Furthermore, both catalysts tolerate C=C double bonds (**2c**), nitriles (**2d**), carbonyl (**2e**), esters (**2n**) and amides (**2i**). In no case any further undesired reduction product was detected. In the case of **2n**, a reaction carried out with addition of Et_3N produced mono- and di-ethyl esters from the methyl congener by transesterification (see Figure S14 and S15) after 20 h (conversion >99 %). The ratio between the two compounds was around 2:1 in favour of the di-ethylated product. In order to avoid this side-reaction, Co-catalysed hydrogenation of **2n** was run in the absence of any base. As expected, no transesterification product was detected and thus an excellent yield of the desired aniline derivative was achieved. Sterically demanding substrates such as 2-nitrobiphenyl (**1j**) and 2,4,6-tri-t-butylnitrobenzene (**1m**) were hydrogenated upon applying a prolonged reaction time without affecting the selectivity and hence the corresponding yield.

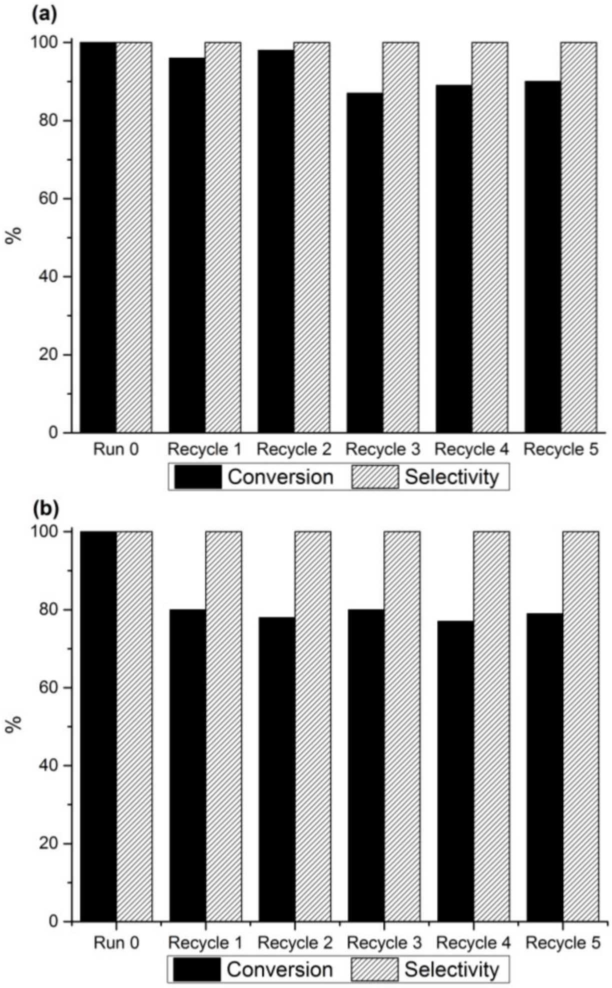
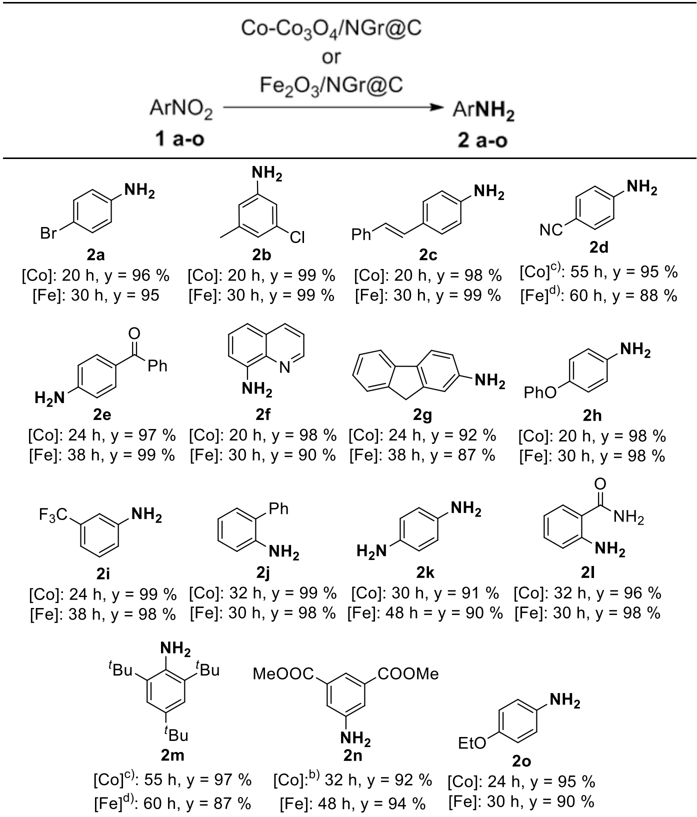


Figure 3. Recycling experiments for Co-Co_3O_4/NGr@C (a) and Fe_2O_3/NGr@C (b). Reaction conditions for [Co] and [Fe] are reported in Table 1, entries 3 and 7 respectively.

Based on the presented results we conclude that: (1) a correlation between higher solvent polarity and higher conversion is present, (2) basic additives increase the catalyst activity (even at low concentration) whereas (3) acid additives are detrimental for the conversion. On the base of these outcomes it is clear that the reaction needs a basic and polar environment. These observations support our working hypothesis that the dihydrogen molecule is activated by heterolytic cleavage. This assumption is in agreement with observations by Sánchez-Delgado and co-workers for Ru and Rh NPs supported on MgO.[12]

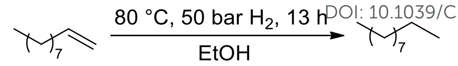
Scheme 1. Co- and Fe-catalyzed hydrogenation of nitroarenes: Substrate scope.a)



a) Reaction conditions for [Co]: 0.5 mol % Co (5 mg), 0.5 mmol $ArNO_2$, 70 °C, 20 bar H_2, 1 equiv. Et_3N, 2 mL EtOH + 100 µL H_2O. Reaction conditions for [Fe]: 4.5 mol % Fe (42 mg), 0.5 mmol $ArNO_2$, 90 °C, 30 bar H_2, 1 equiv. aqueous NH_3, 3 mL MeOH. Yields were calculated by GC analysis (calibration curve, *n*-hexadecane as internal standard) using commercially available anilines. In all cases, complete conversions were observed. b) Reaction carried out without Et_3N. c) 1 mol % Co was used. d) 6 mol % Fe was used.

In this process the dihydrogen molecule is formally cleaved into a hydride and a proton.[13] The hydride atom is bound to the metal-based nanoparticle whereas the proton is attached to the basic N atoms in close proximity to the nanoparticle or by the basic additive present in the liquid phase. In order to further understand this heterolytic activation mechanism, we decided to hydrogenate non-polar 1-decene. In principle, this terminal olefin is less prone to heterolytic hydrogenations compared to nitrobenzene.[14] Accordingly, Co-based catalysts prepared with and without Phen, do not show any difference in the hydrogenation of 1-decene (Table 2, entries 1 and 2).

Table 2. Hydrogenation of 1-decene.a)



Entry	Catalyst	Additive	Conv. [%]a)
1	Co_xO_y@C	-	9
2	Co-Co_3O_4/NGr@C	-	9
3	Co_xO_y@C	Et_3N (1 equiv.)	11
4	Co-Co_3O_4/NGr@C	Et_3N (1 equiv.)	11
5	Fe_xO_y@C	-	11
6	Fe_2O_3/NGr@C	-	16
7	Fe_xO_y@C	NH_3 (1 equiv.)	12
8	Fe_2O_3/NGr@C	NH_3 (1 equiv.)	19

a) Reaction conditions: 0.5 mmol 1-decene, 0.5 mol % Co (5 mg) or 4.5 mol % Fe (42 mg). b) GC conversions using *n*-hexadecane as internal standard.

Moreover, addition of basic promoters does not change the rate of the reaction (Table 2, entries 3 and 4). Applying Fe-based catalysts a similar trend is observed. Carbonyl and cyano groups and quinolines were completely unreactive with these catalysts (Scheme 1). This is not surprising because these substrates are generally activated by Lewis acids and the catalysts herein presented are composed by a carbonaceous support that completely lacks any acidic sites. In keeping with this, some of us recently reported that Co-based catalysts similarly prepared using ceria[15] or α-alumina[16] as supports instead of carbon were active in the hydrogenation of ketones to alcohols and quinolines to 1,2,3,4-tetrahydroquinolines, respectively. In comparison, the materials prepared with Vulcan® carbon were much less active in the same transformations. On the contrary, nitroarenes are unlikely to require a Lewis acid as an activator, since they are among the weakest nucleophiles known. This results in a very high selectivity towards the reduction of the nitro functionality with respect to other reducible groups when the carbonaceous support is employed.

Conclusions

In conclusion, we presented the hydrogenation of nitroarenes catalysed by N-doped graphene coated Co- and Fe-nanocomposites under improved mild conditions. Crucial for success were the use of polar solvents and/or the addition of base to the reaction mixture. Under optimal conditions demanding substrates gave excellent yields and selectivities. Furthermore, recyclability of the heterogeneous catalysts was explored and maintained even in the presence of additives. On the basis of the obtained results, an ionic hydrogenation mechanism involving heterolytic activation of H_2 is likely to be involved.

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Notes and references

‡ Standard catalytic reaction: An 8 mL reaction vial was charged with the substrate, internal standard (*n*-hexadecane), catalyst, additive (if stated) and solvent. Then, the vial was closed with a screw cap equipped with septum and needle. The reaction vessels (up to 7) were placed into a 300 mL Parr autoclave. The latter was flushed with hydrogen twice at 10 bar and the loaded with the desired pressure. After that it was placed into a pre-heated aluminium block. At the end of the reaction, the autoclave was quickly cooled down using an ice bath and vented. Finally, the samples were removed, diluted with a suitable solvent, filtered using a Pasteur pipette filled with celite and analysed by GC. For catalysts preparation, recycling experiments and Maitlis' test procedures see ESI.

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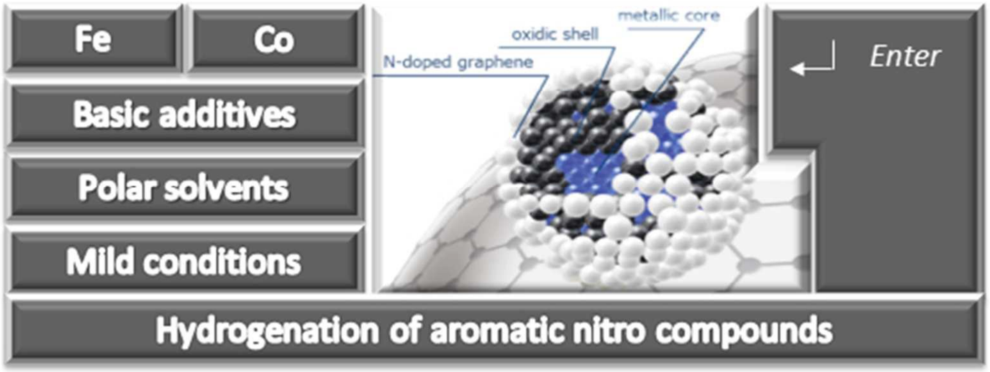

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