Efficient and environmentally friendly microwave-assisted synthesis of catalytically active magnetic metallic Ni nanoparticles

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ABSTRACT

Pure magnetic metallic nickel was synthesized by a simple and fast microwave-assisted method using a monomode microwave reactor. Nickel chloride was employed as metal precursor, while an environmental-friendly mixture of ethylene glycol and ethanol was simultaneously used as solvent and reducing agent. The parameters combination, for the occurrence of the reaction, of the mixture molar fraction and the metal precursor concentration was developed. The influence of the temperature and the time of the irradiation was investigated. The best performance (71% yield) was achieved at 250°C in 5 minutes of microwave irradiation. The phase and the morphology of the metal were analyzed by X-ray diffraction (XRD), scanning emission microscopy (SEM) and transmission electron microscopy (TEM) while the surface area was determined by nitrogen physisorption. The material exhibited a strong magnetic behavior. The metallic Nickel showed high catalytic activity for the hydrogenolysis of benzyl phenyl ether, a lignin model compound, in a microwave-assisted environmental-friendly reaction.

INTRODUCTION

Magnetic nanostructured materials have attracted significant interest due to their technical application in several fields including optoelectronics, magnetics, catalysis, biologic engineering, information storage and photovoltaic technology.[1-3] Nickel nanoparticles are particularly emerging for their unique characteristics such as high magnetism, high surface area, large surface energy, excellent chemical stability, low melting point, resource-richness, and low cost.[4,5] Several techniques for the synthesis of Nickel materials, including thermal decomposition, pulsed laser ablation, sputtering and metal vapor condensation have been extensively reported in literature.[6-9] However, only a few reports on the synthesis of pure Ni magnetic nanoparticles are available.[10-12] Microwave-assisted reactions emerged as alternative reaction media to conduct catalytic processes and importantly in nanomaterials synthesis due to associated advantages of the technique that include the possibility to obtain higher yields, different selectivities, as well as the potential to accomplish reactions/chemistries that generally do not take place under conventional heating conditions.[13-15]

Based on our experience in microwave chemistry for the design of nanomaterials and nanoparticle systems,[16-20] herein we disclose a simple, efficient and environmentally friendly unprecedented synthesis of magnetic metallic Nickel (denoted as MMN) under microwave-assisted conditions, employing a mixture of ethylene glycol (EG) and ethanol, and $NiCl_2$ as metal precursor. The so-produced Nickel nanoparticles were used as heterogeneous catalyst for the hydrogenolysis of benzyl phenyl ether (BPE), a commonly used lignin model compound.[21,22]

RESULTS AND DISCUSSION

PXRD pattern of MMN is shown in Figure 1. The peaks at 44,5°, 51,9° and 76,4° can be respectively indexed to the (111), (200) and (220) diffraction planes, from a face-centered cubic structure (Fm-3m) of pure metallic Nickel. No other distinctive diffraction peaks indicate high purity and crystallinity of the samples. The XRD pattern showed a strong diffraction peak at (111) and the ratio of intensity of the (111) to (200) peak is 3.068.

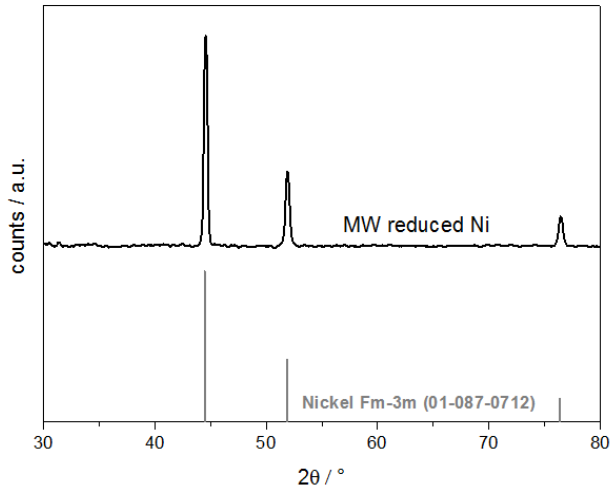


Figure 1. Powder X-ray diffraction of the MMN.

Figure 2 shows SEM and TEM images of the Nickel nanoparticles synthesized. No specific description of the shape and the size of the particles was possible to define; nevertheless, most of the particles were in the form of spheres of approximately 200-500 nm of diameter. EDS analysis showed no relevant material adsorbed on the surface (95,65%wt Ni, Table S1).

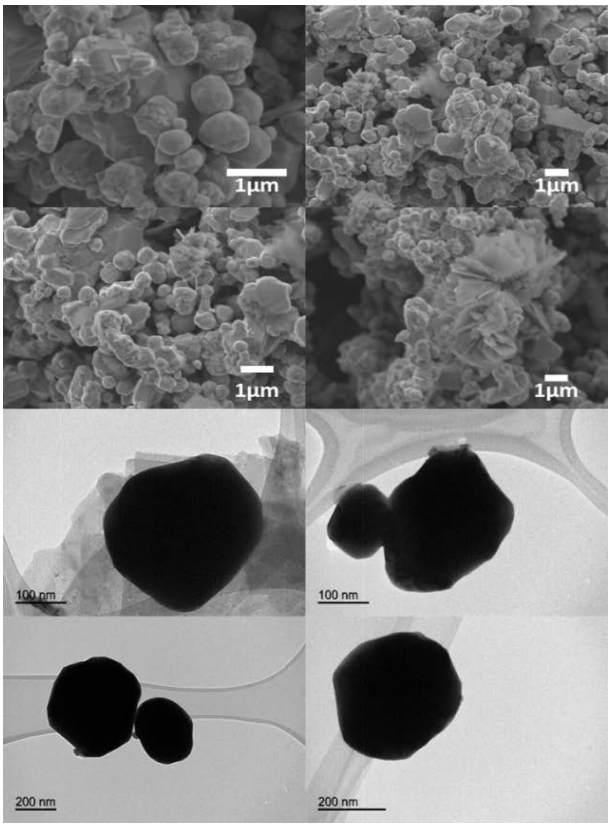


Figure 2. SEM and TEM images of the MMN.

The nitrogen absorption/desorption and pore size distribution revealed a non-porous material with a surface area of < 5 m^2/g. The magnetic mass susceptibility of the precipitate was determined to be $442 \cdot 10^{-6}$ m^3 Kg^{-1} at room temperature, close to that of pure maghemite (*ca.* $500 \cdot 10^{-6}$ m^3 Kg^{-1}).[23] These findings indicate that a strong magnetic phase (Figure S1) could be created for metallic nickel under the proposed microwave reaction conditions, truly unprecedented in previous literature work.

The formation of the MMN was found to be a process depending on different variables. Specifically, the concentration of $NiCl_2$ (therefore Ni^{2+} concentration), the molar fraction of the

ethylene glycol-ethanol solution, the irradiation time and the temperature were investigated. Table 1 summarizes the most relevant experiments (for a more detailed list of the experiments, see Table S2). The optimum yield (71%) was obtained with 0.031 molar concentration of $NiCl_2$, in a mixture of 2.5 mL of 0.904 molar fraction of EG-EtOH, at 250°C with an irradiation time of 5 minutes. The formation of the metallic precipitate was observed at a concentration of Ni^{2+} ions up to 0.182 mol L^{-1} and an EG molar fraction between 0.85 and 0.97.

Table 1 Most significant trials varying different reaction parameters

[Ni2+] (mol L-1)	Time (min)	T (°C)	EG (Xi)	Yield (%)
Increasing reaction time				
0.031	**20**	200	0.904	24
0.031	**30**	200	0.904	22
0.031	**60**	200	0.904	30
Varying mixture composition				
0.031	5	200	**0.846**	20
0.031	5	200	**0.865**	9
Increasing reaction temperature				
0.031	5	**220**	0.904	26
0.031	5	**230**	0.904	34
0.031	5	**240**	0.904	44
0.031	5	**250**	0.904	71
Increasing metal precursor concentration				
0.072	20	210	0.904	8
0.110	20	210	0.904	6
0.182	20	210	0.904	4

The yield of the reaction was strongly dependent on temperature, but less influenced by the reaction time. The minimum values of temperature and time for the formation of the metal precipitate were 180°C and 5 minutes irradiation, respectively.

As this work was aiming to a fast and simple reaction (with time found as low-influencing parameter), one-hour of irradiation was chosen as a limit. The upper limit of 250°C was forced by a safe pressure limit. Figure 3 represents the combination of the parameter of Ni^{2+} ion

concentration and solution composition for the formation of MMN. After extensive optimization, the MMN was obtained if the parameters matched a point inside the grey rectangle.

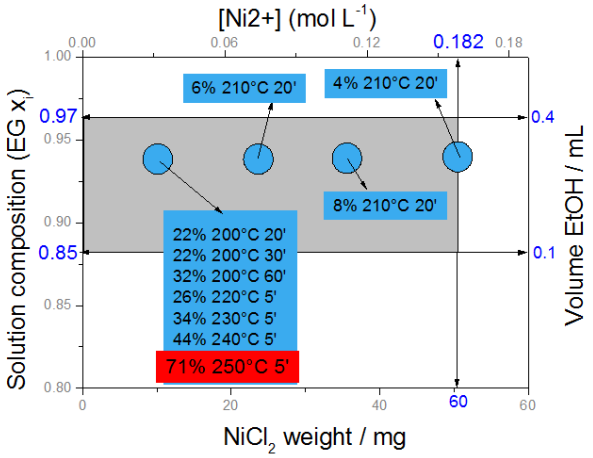
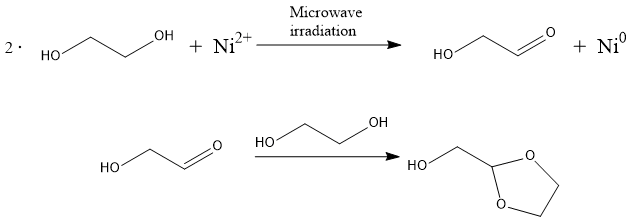


Figure 3. Schematic representation of the occurrence of the reaction depending on the nickel ion concentration and mixture composition. Best results are in the blue boxes where the yield, the reaction temperature and the time of reaction are reported.

The reduction of Ni^{2+} could be attributed to the action of EG as a reducing agent. Miller et al. purposed a reaction mechanism for the oxidation of different terminal diols employing an oxoammonium salt as oxidizing agent: the diol is oxidized to the corresponding aldehyde, which is immediately converted by protection of the aldehyde group with the same diol.[24] The overall reduction reaction is illustrated in Scheme 1.

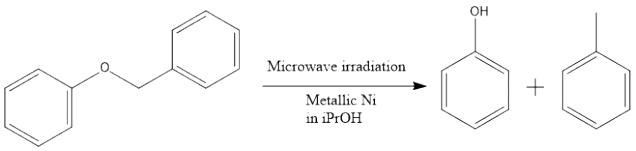
Scheme 1. Proposed reaction scheme of the reduction of Nickel via microwave-assisted synthesis.



GC-MS analysis of the solution after the production of MMN demonstrate the presence of 1,3-Dioxolane-2-methanol (Figure S2), confirming the purposed mechanism. As the reaction was found to be possible at specific temperature and pressure, ethanol was likely increasing the penetration depth of the MWs irradiation, and lowering the bubble point of the mixture, therefore increasing vapor pressure. A simulation made with PRO/II software (Invensys System Inc.) at 70 psi showed a decreasing of the bubble point down to 185-220°C considering the EG molar fraction between 0.85-0.97, instead of 260°C of the pure EG. Similar results were obtained substituting EtOH with water and isopropanol, where still the MMN was successfully produced. Without this condition, the production of MMN would have requested hardly condition to occur, primarily the addition of other chemicals and longer time.[25-27]

Catalytic test of the hydrogenolysis of BPE, described in Scheme 2, were performed under microwave irradiation at 230°C employing isopropanol as green solvent and H donor.

Scheme 2. Hydrogenolysis of Benzyl Phenyl Ether.



Blank runs, in the absence of catalyst, showed no BPE hydrogenolysis under the investigated conditions. Best results were obtained after 45 mins of irradiation, for which a conversion of BPE of 24%, compared to the conversion of 43% obtained with commercial 5% Pd/C. The nanoparticles were stable and reusable under the investigated conditions, allowing a conversion of BPE of 21% after 5 cycles of 45 mins of irradiation each one. Despite the palladium catalyst exhibiting higher catalytic activity, the MMN possess extremely competitive characteristic such as easy and rapid synthesis being cost competitive due to reduced reagents costs (Pd vs Ni). For a detailed list of the results, please see Table S3.

CONCLUSIONS

In conclusion, pure metallic Nickel was prepared under a simple microwave-assisted hydrothermal method using a specific combination of $NiCl_2$, ethylene glycol and ethanol. The ethylene glycol act as both solvent and reducing agent. The temperature was the most influencing factor for the yield of the reaction, while the reaction time was found to be less relevant under the investigated conditions.

Due to its simple, low-toxicity and efficient features, this new methodology could track ways to large-scale productions of Ni nanoparticles as possible alternative to maghemite/magnetite nanoparticles. In fact, despite γ-Fe_2O_3 is nowadays widely used in industry, its production is still long and quite toxic.[28]

Furthermore, this work is a first example of employing the metallic Nickel produced with the microwave-assisted technique in the hydrogenolysis of BPE. The observed results offer a potential in a large number of green and fast hydrogenolysis as well as hydrogenation reactions that will be reported in due course.

Supporting Information. Additional materials characterizations and detailed experimental section.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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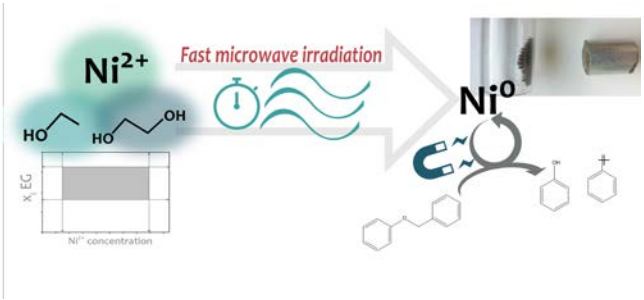

SYNOPSIS. Nickel nanoparticles were synthesized using a simple and environmentally friendly microwave-assisted method, exhibiting catalytic activity in the hydrogenation of a lignin model compound.