

**A COORDINATION POLYMER BASED ON NICKEL(II)-CYAMELURATE : A
ROBUST CATALYST WITH HIGHLY DISPERSED NICKEL SITES FOR
NITROFENOL REDUCTION UNDER AMBIENT CONDITIONS**

**Taís dos Santos da Cruz^a, Eduarda Ferreira de Oliveira^a, Wanessa Lima de
Oliveira^a, Walker Vinícius Ferreira do Carmo Batista^a, *Dilton Martins Pimentel^a*,
Gabriel Ali Atta Diab^c, Ivo Freitas Teixeira^c, Marcio Cesar Pereira^d, and João
Paulo de Mesquita^{a,c*}**

^aDepartment of Chemistry – Federal University of Jequitinhonha and Mucuri Valleys, Rodovia MGT 367 - Km 583, n° 5000, Alto da Jacuba, Diamantina-MG, Brazil, CEP 39100-000.

^bInstituto de Física de São Carlos, Universidade de São Paulo, Avenida Trabalhador São-carlense, 400, 13566-590, São Carlos, SP, Brazil.

^cDepartment of Chemistry – Federal University of São Carlos. Rod. Washington Luís km 235 - SP-310 - São Carlos – SP, Brazil, CEP 13565-905

^d Instituto de Ciência, Engenharia e Tecnologia – Federal University of Jequitinhonha and Mucuri Valleys, Rua do Cruzeiro, n° 01-Bairro Jardim São Paulo-Teófilo Otoni, MG, Brazil, CEP 39803-371

E-mail: joaopm2000@yahoo.com.br and joao.mesquita@ufvjm.edu.br

Abstract

Cyamelurate anions obtained from the hydrolysis of polymeric graphitic carbon nitride were used for the preparation of a water-stable and crystalline coordination polymer based on nickel(II)-cyamelurate. It was prepared and applied as a catalyst for the reduction of 4-nitrophenol to 4-aminophenol in the presence of borohydride under ambient conditions. The catalyst was prepared by a simple and environmentally friendly method in an aqueous medium and it was completely characterized by a variety of techniques including, FTIR, UV-Vis, XRD, TGA, TEM, and STEM. The obtained catalyst was able to catalyze the reaction of 4-nitrophenol to 4-aminophenol with a good kinetic constant. In addition, the catalyst proved to be significantly robust, maintaining a conversion greater than 80% after five minutes of reaction for eight consecutive catalytic cycles. In addition, the catalytic activity of the coordination polymer was much higher than that observed for a homogeneous catalyst based on aqueous Ni²⁺ ions, suggesting the importance of the structure of the coordination sphere formed by the cyamelurate anions. The results presented here can contribute to the application of other coordination polymers anchored with cyamelurate-like ligands and derivatives, as well as to new catalyst designs based on this coordination site formed by oxygen and nitrogen donor atoms.

Keywords: coordination polymer, cyamelurate, nickel, 4-nitrophenol.

Table S1. Elemental composition obtained for nickel(II)-cyamelurate CP and MOP-3 reported by Mohan et al.

Element	Weight / %	
	Nickel(II)- cyamelurate CP	MOP-3* (Ni ₂ C ₁₂ H ₂₂ N ₁₄ O ₁₆)[1]
	Ni _{0.24} C _{1.3} N _{1.9} O _{2.6}	
Carbon	15.6	19.6
Nitrogen	27.0	26.6
Oxygen	42.7	34.8
Potassium	0.17	---
Nickel	14.5	15.9

*Results obtained by Mohan et al.

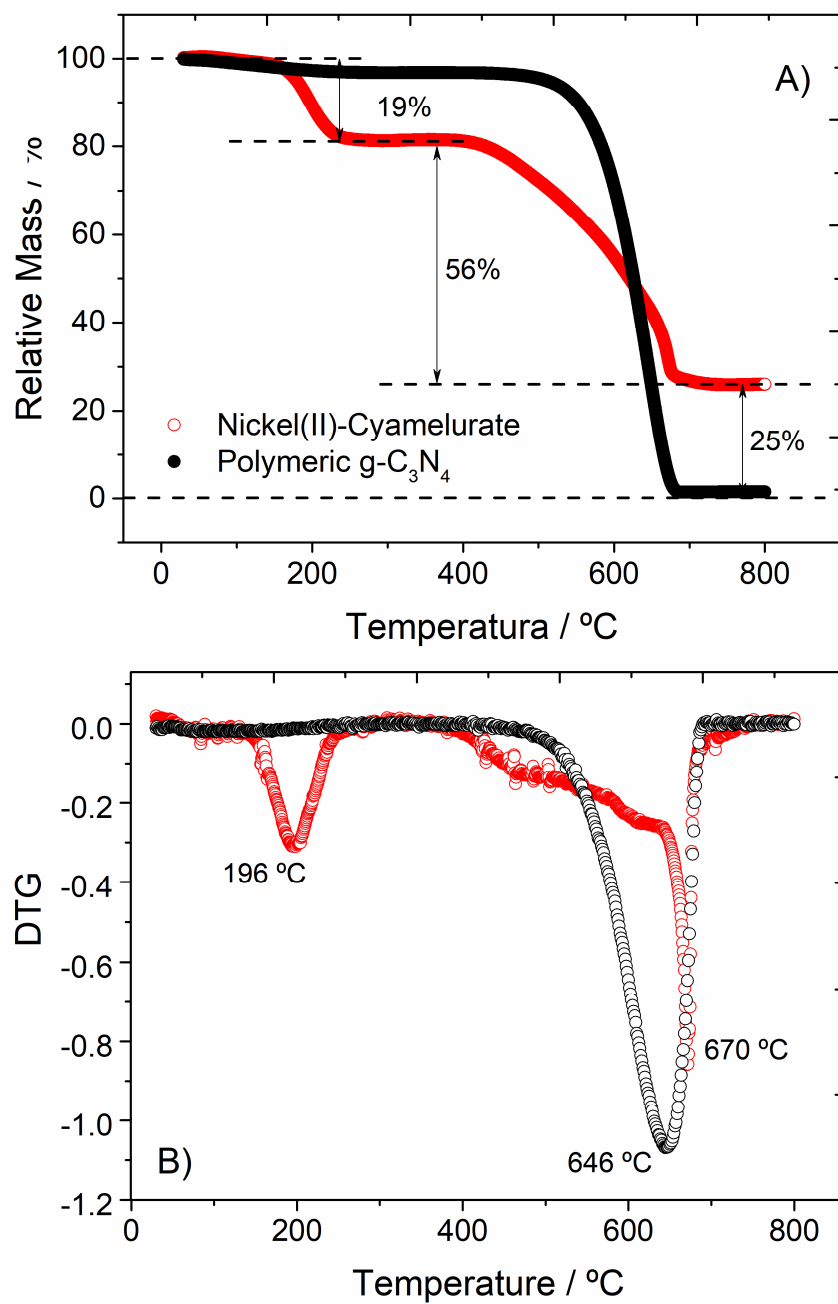


Figure S1. Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) obtained for polymeric $g\text{-C}_3\text{N}_4$ and nickel(II) cyamelurate CP.

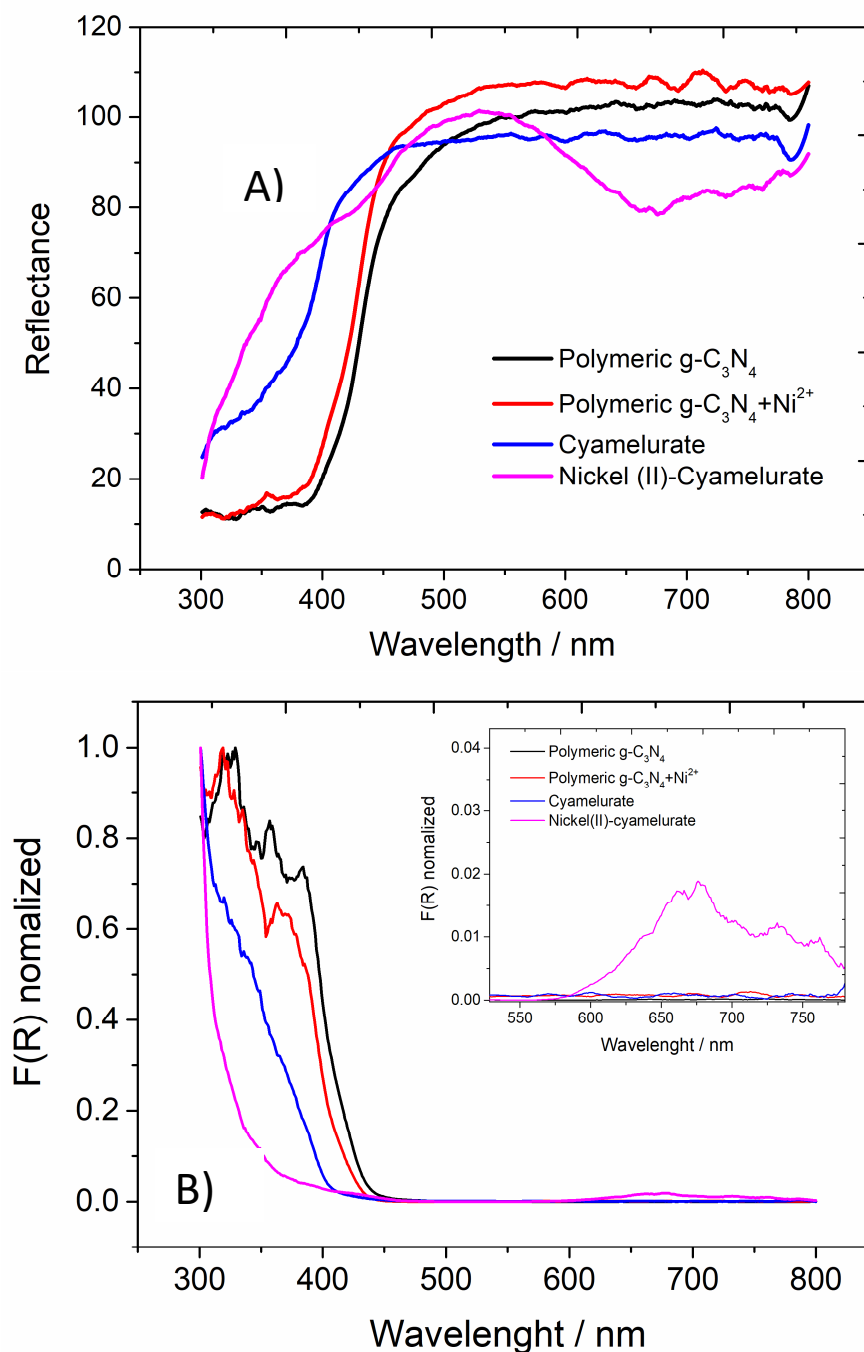


Figure S2. DRS spectra (A) and Kubelka-Munk absorbance (B) obtained from polymeric $g\text{-C}_3\text{N}_4$, polymeric $g\text{-C}_3\text{N}_4 + \text{Ni}^{2+}$, cyamelurate and nickel(II)-cyamelurate CP. Inset in B): amplification of the absorbance of the region located between 600 and 800 nm.

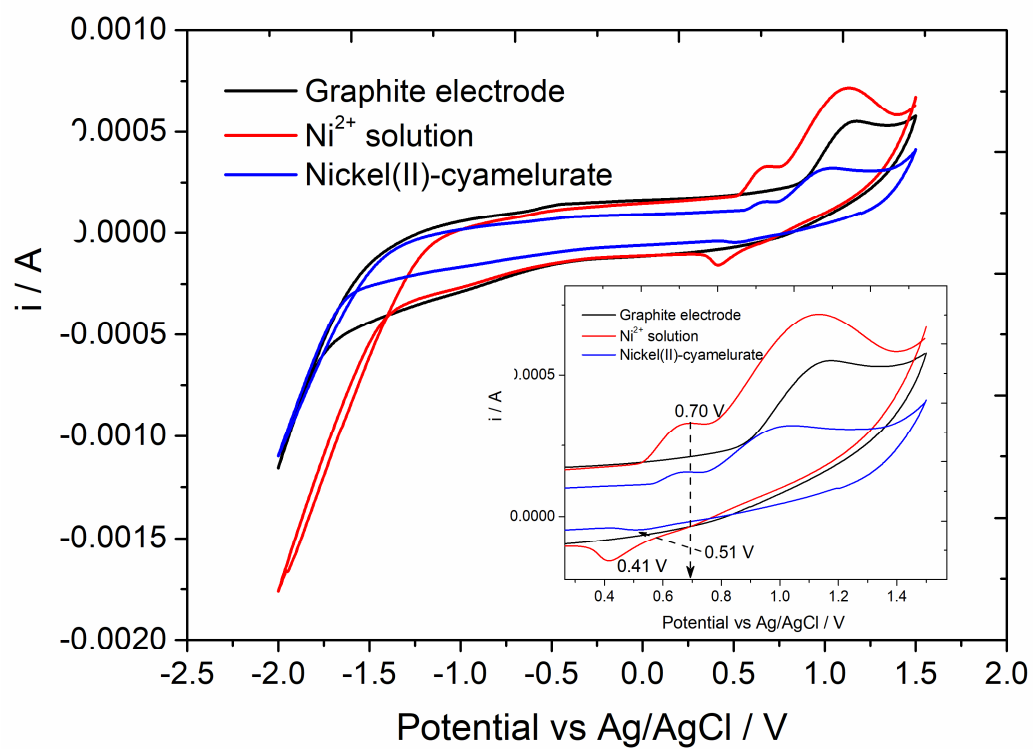


Figure S3. Cyclic voltammograms obtained for nickel(II)-cyamelurate CP and aqueous NiCl_2 solution.

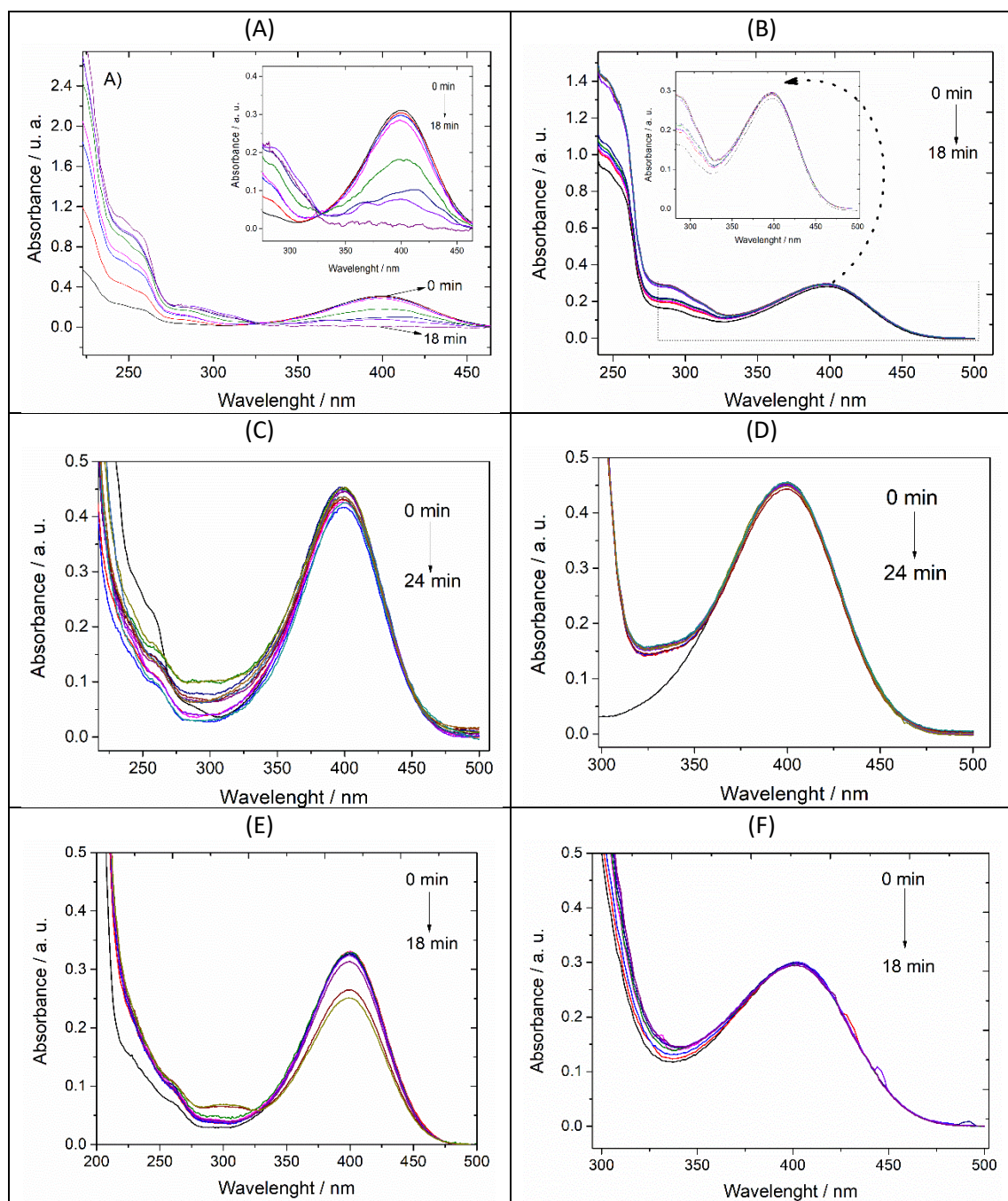


Figure S4. Time-dependent UV-Vis spectra obtained for 4-NP solution in the presence of the nickel(II)-cyamelurate CP and borohydride (A), in the presence of only the nickel(II)-cyamelurate CP catalyst (B). In (B) the initial pH of the solution was adjusted to 10. 4-NP solution in the presence of the borohydride and C) polymeric $g\text{-C}_3\text{N}_4$ and D) cyamelurate. In (D), the high absorption from 325 nm is caused by cyamelurate. (E) 4-NP solution in the presence of the NiCl_2 and borohydride. (F) 4-NP solution in the presence of the nickel(II)-cyamelurate CP, borohydride and dimethylglyoxime (DMG).

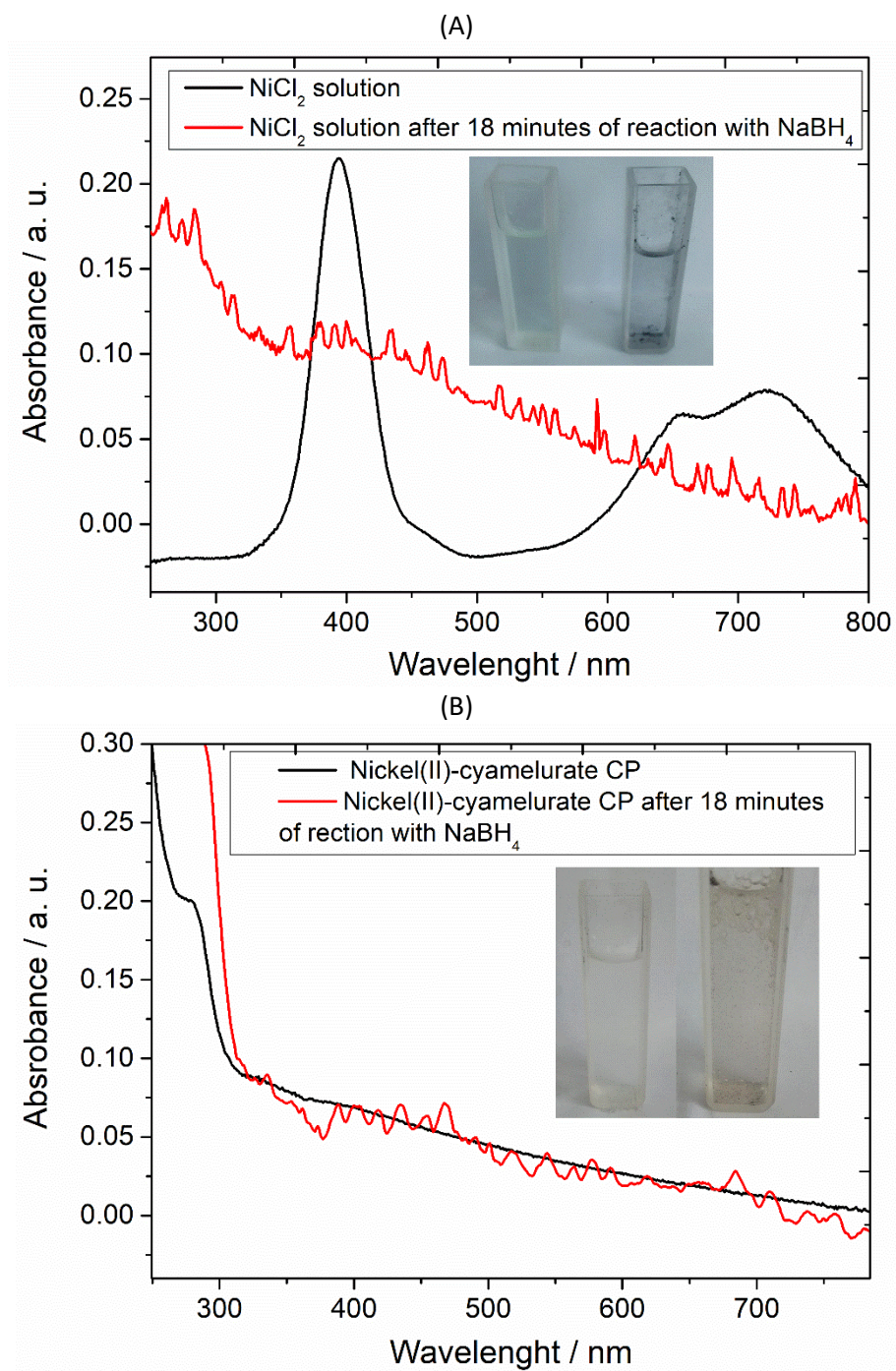


Figure S5. UV-Vis spectra obtained for NiCl_2 solution (A) and nickel(II) cyamelurate CP dispersion (B) before and after 18 minutes of reaction with NaBH_4 .

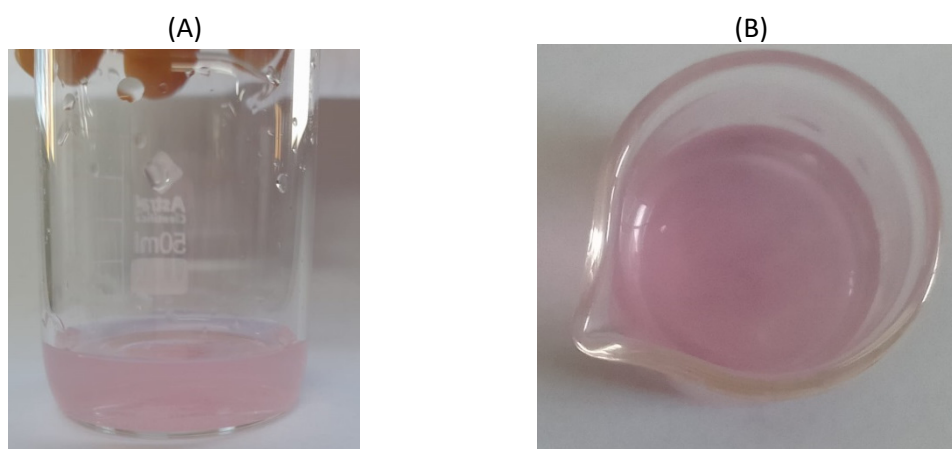
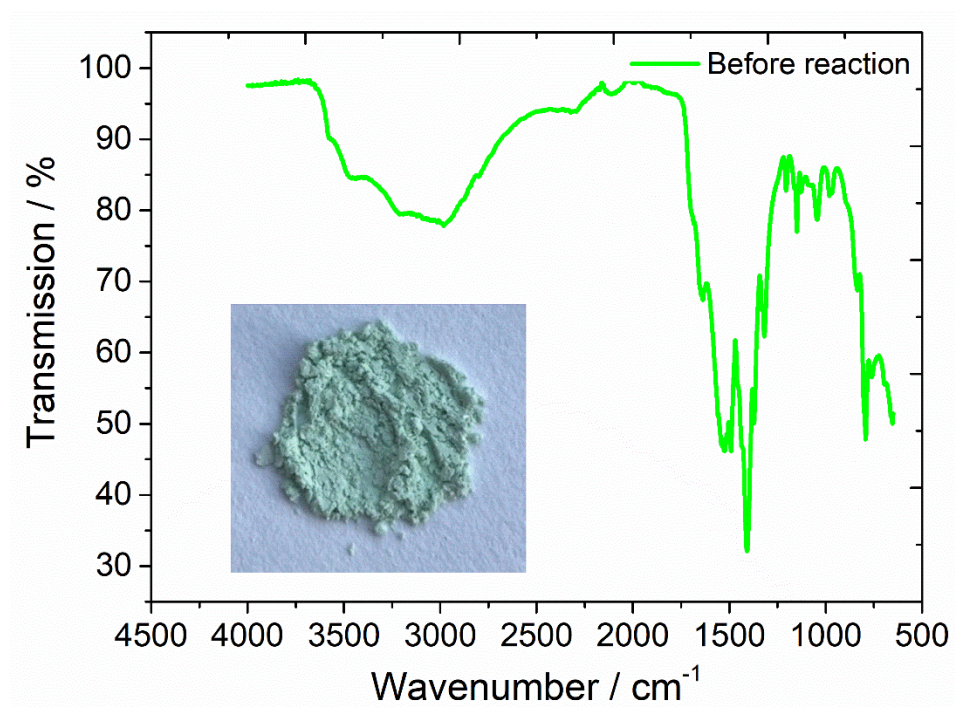


Figure S6. Digital images of suspensions containing nickel (II)-cyamelurate CP before (A) and after (B) reduction reaction of 4-nitrofenol.



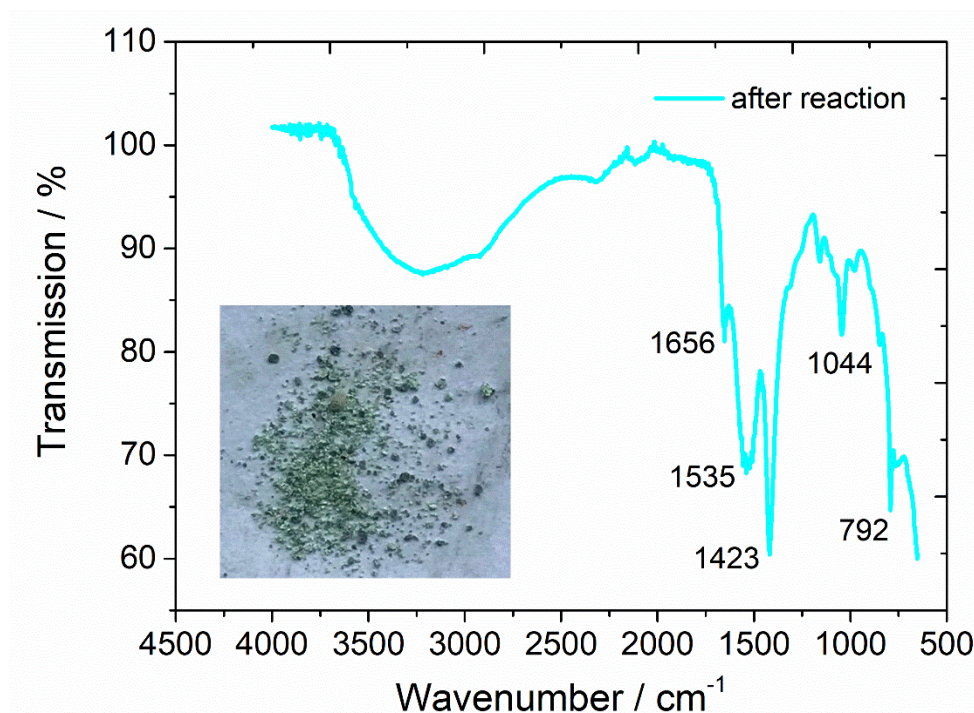


Figure S7. FTIR Spectra obtained for the catalyst before and after the catalytic tests in the presence of sodium borohydride. The spectra were obtained in IRSPIRIT equipment (Shimadzu) using the Single Reflection ATR measurement accessory (QATR-S).

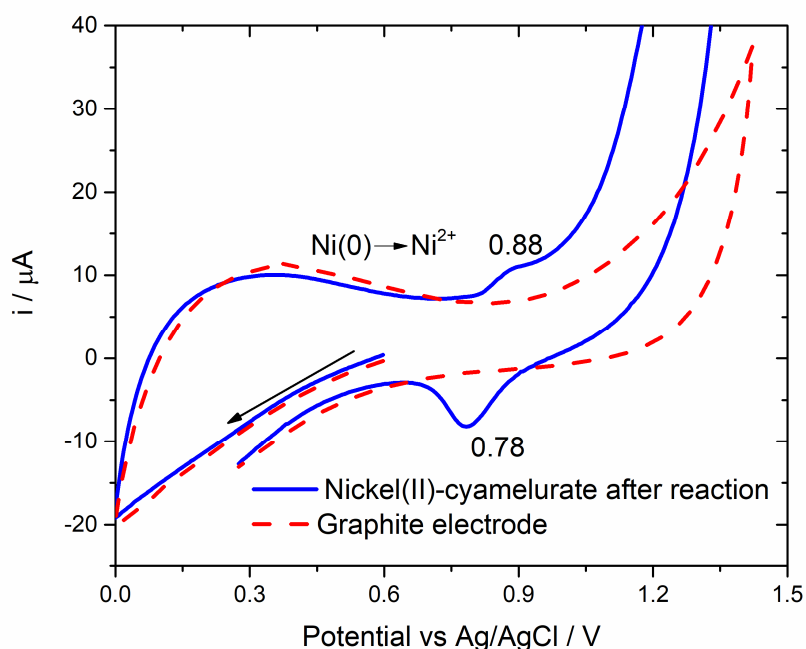


Figure S8. Cyclic voltammograms obtained for the nickel(II)-cyamelurate CP catalyst after use in the 4-NP reduction reaction in the presence of NaBH₄. The traditional three-electrode system was used in the experiment using as reference an Ag/AgCl electrode saturated with KCl and a platinum wire counter electrode. The working electrode was prepared by depositing 10μL of a suspension (1mg/ml) of the material on the surface of a glassy carbon electrode. 0.1M NaClO₄

was used as supporting electrolyte. The arrow indicates the scanning direction. The results shown refer to the first scan within the potential window from 0 to 1.4V.

[1] M. Mohan, S. Rajak, A.A. Tremblay, T. Maris, A. Duong, Syntheses of mono and bimetallic cyamelurate polymers with reversible chromic behaviour, Dalton Transactions 48(20) (2019) 7006-7014.