

Probing Single Ni Sites in Crystalline Carbon Nitride via CO Adsorption and DRIFT-FTIR Spectroscopy

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Resumo/Abstract

RESUMO - O nitreto de carbono cristalino, especificamente a poli(heptazina imida) (PHI), tem se destacado como um suporte catalítico promissor devido à sua estrutura robusta e propriedades eletrônicas favoráveis, especialmente para a estabilização de átomos metálicos isolados. No entanto, identificar e caracterizar esses sítios isolados de forma confiável continua sendo um desafio significativo. Neste estudo, a adsorção de CO foi empregada como molécula sonda em combinação com a espectroscopia DRIFT-FTIR para investigar espécies de níquel dopadas em PHI. Em baixas cargas de níquel (0,5% e 1%), o CO se liga predominantemente de forma linear a sítios isolados de Ni²⁺, como indicado por bandas características em torno de 2190 cm⁻¹. À medida que o teor de níquel aumenta (2% e 4%), as bandas de CO se deslocam para menores números de onda, e sinais associados ao CO ligado em ponte tornam-se dominantes. Essa evolução espectral reflete um aumento na π -retrodoação e a formação progressiva de agregados de níquel, como clusters ou nanopartículas. A diminuição simultânea na intensidade das bandas lineares de CO reforça essa transição de espécies de Ni dispersas atômica para espécies agregadas. Cálculos de Teoria do Funcional da Densidade (DFT) e DFT+U corroboram os resultados experimentais, fornecendo insights sobre os fatores estruturais e eletrônicos que impulsionam a π -retrodoação e a evolução da especiação do Ni em PHI. *Palavras-chave: DRIFT-FTIR, Átomos individuais, Caracterização, Adsorção.*

ABSTRACT – Crystalline carbon nitride, specifically poly(heptazine imide) (PHI), has emerged as a promising catalyst support due to its robust structure and favorable electronic properties, particularly for stabilizing isolated metal atoms. However, reliably identifying and characterizing these isolated sites remains a significant challenge. In this study, CO adsorption was employed as a probe molecule in combination with DRIFT-FTIR spectroscopy to investigate nickel species doped into PHI. At low nickel loadings (0.5% and 1%), CO binds predominantly in a linear fashion to isolated Ni²⁺ sites, as indicated by characteristic bands around 2190 cm⁻¹. As the Ni content increases (2% and 4%), the CO bands shift to lower wavenumbers, and signals associated with bridge-bonded CO become dominant. This spectral evolution reflects enhanced π -backdonation and the progressive formation of Ni aggregates, such as clusters or nanoparticles. The concurrent decrease in the intensity of linear CO bands further supports this transition from atomically dispersed Ni to aggregated species. Density Functional Theory (DFT) and DFT+U calculations corroborate the experimental results, providing insights into the structural and electronic factors driving π -backdonation and the evolution of Ni speciation on PHI.

Keywords: DRIFT-FTIR, Single-atoms, Characterization, Adsorption

Introduce

Crystalline carbon nitride (PHI) is a material with great potential for catalytic applications, especially in photocatalysis, due to its crystalline structure and excellent electronic properties. Furthermore, PHI serves as a suitable support for anchoring different active species, broadening its range of applications(1).

Single metal atoms, in turn, can significantly enhance catalytic activity compared to nanoparticles or clusters, while also presenting lower costs. Despite these advantages, the identification of single atoms remains challenging, requiring advanced techniques and complementary methods for confirmation(2).

Therefore, this study proposes the use of CO adsorption as a probe molecule, in combination with the DRIFT-FTIR technique, to identify single nickel atoms that doped into carbon nitride. The vibrational frequency of adsorbed CO is commonly employed to probe the charge state of metal centers in single-atom catalysts, an approach supported by a wealth of experimental and computational data on CO interactions with metal surfaces and nanoparticles(3).

Experimental

PHI synthesis

PHI was prepared by ball-milling 1 g of melamine with 10 g of NaCl, followed by thermal treatment at 600 °C for 4 hours under a nitrogen flow (5 L min⁻¹) with a heating rate

of 2.3 °C min⁻¹. After cooling, the material was washed with deionized water to remove residual salt(4).

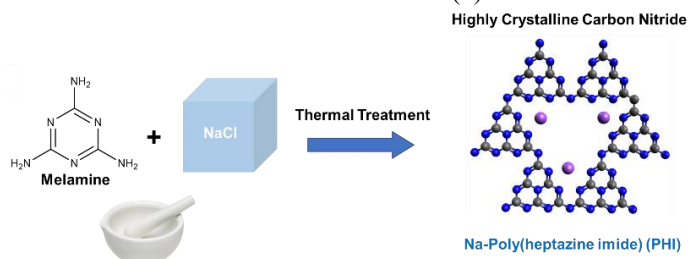


Figure 1. Synthesis of carbon nitride (PHI).

PHI/single-atom synthesis

Cation exchange was performed by dispersing PHI in aqueous nickel solutions with varying concentrations. For the synthesis of Ni-PHI with 0.5% nickel, 200 mg of Na-PHI were added to a solution containing 0.02 mmol of NiCl₂·6H₂O and sonicated for 30 minutes. Catalysts with different metal loadings (0.5%, 1%, 2%, and 4%) were prepared by proportionally adjusting the nickel concentration. After sonication, the suspension was centrifuged to recover the solid, which was then dried overnight at 80 °C.



Figure 2. Cation exchange for the formation of Ni²⁺-PHI.

CO-DRIFTS experiment

CO-DRIFTS analysis was carried out using a Nicolet iS50 FTIR spectrometer equipped with a Praying Mantis accessory and a Harrick cell. The sample was pretreated at 300 °C under a He flow (20 mL min⁻¹) for 10 minutes. After cooling to room temperature, the He flow was stopped and CO pulsing was initiated for 10 minutes. Physiosorbed CO was then removed by Helium purging for 15 minutes. Spectra were collected at a resolution of 1 cm⁻¹ and averaged over 256 scans.

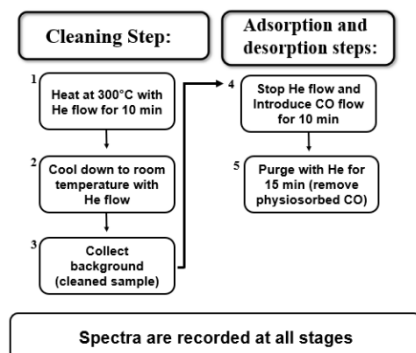


Figure 3. Process for obtaining the spectra of CO adsorption in the material.

Theoretical Calculations

Spin-polarized DFT and DFT+U calculations were performed using the VASP code(5) with the PBE functional under the GGA framework(6, 7), and a plane-wave cutoff energy of 400 eV. The DFT-D3 method accounted for van der Waals interactions, and convergence criteria were set to 1×10^{-5} eV for energy and 0.05 eV·Å⁻¹ for forces(8). A Hubbard U correction of 3.40 eV was applied to better describe the Ni electronic properties(9-11). Charge density difference analyses were carried out using VASPKIT(12).

Results and discussion

Characterizations

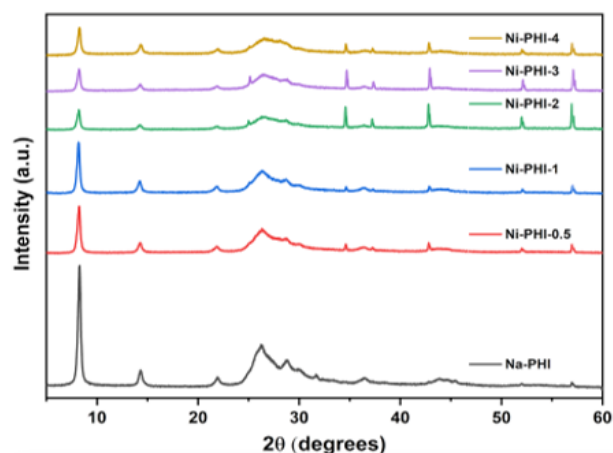


Figure 4. X-ray diffraction (XRD) of Na-PHI and Ni-PHI with different concentrations (0.5, 1.0, 2.0, 3.0 and 4.0 %).

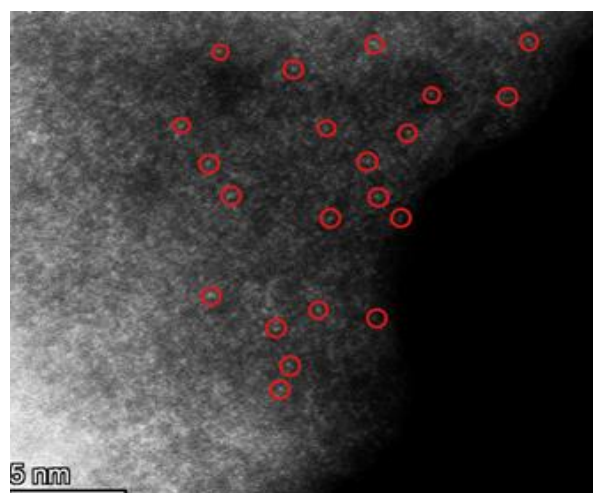


Figure 5. HAADF-STEM image of Ni-PHI 0.5%

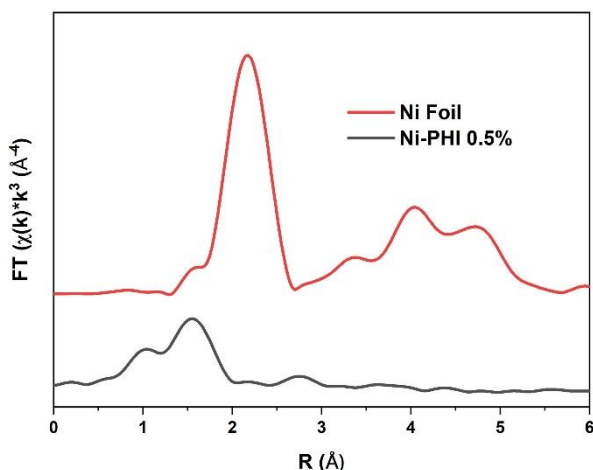


Figure 6: Fourier transform of the EXAFS spectra of Ni^{2+} -PHI 0.5% and Ni foil.

The crystal structure of Na-PHI and Ni-PHI was analysed using X-ray powder diffraction (XRD). Figure 4 shows the XRD patterns of Na-PHI and Ni-PHI with increasing nickel loadings (0.5–4%). The reflections at 8.3° and 14.2° indicate the 2D ordering of heptazine units, while those between 25° and 29° correspond to interlayer stacking. Upon nickel coordination, these reflections are altered due to electrostatic interactions between Ni^{2+} and the PHI framework, leading to a gradual reduction in crystallinity(13).

The dispersion and atomic distribution of nickel were investigated using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). As shown in Figure 5, the HAADF-STEM image reveals individual nickel atoms (observed as bright spots) uniformly dispersed on the PHI support, with no significant evidence of cluster or nanoparticle formation.

The local coordination environment of nickel in the Ni-PHI catalysts was investigated using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. Figure 6 shows the Fourier transform of the EXAFS spectra for Ni^{2+} -PHI 0.5% and metallic Ni foil. While the Ni foil exhibits characteristic peaks corresponding to Ni–Ni metallic bonding, the Ni^{2+} -PHI 0.5% sample displays a distinct peak at shorter radial distances, associated with Ni–N or Ni–C coordination. These results confirm that nickel atoms are atomically dispersed within the PHI framework, without the formation of metallic nickel.

CO-DRIFTS results

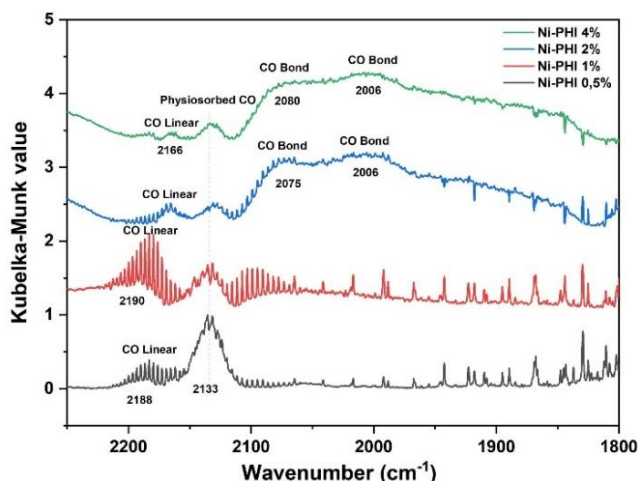


Figure 6. Kubelka-Munk plots of CO desorption in DRIFT-FTIR for (a) Ni^{2+} -PHI 0.5%, 1%, 2% and 4%.

In the Ni-PHI 0.5% and 1% materials, the bands observed at 2188 and 2190 cm^{-1} , respectively, is attributed to linear chemisorbed CO on Ni^{2+} sites, while the band at 2135 cm^{-1} corresponds to physisorbed CO, characterized by weak and reversible interactions with the surface(14).

Starting from a nickel concentration of 2%, a shift of the CO bands to lower frequencies is observed, which is consistent with an increase in π -backdonation and a decrease in the polarization of the CO molecule. The bands at 2075–2080 cm^{-1} and 2006 cm^{-1} , detected in the Ni-PHI 2% and 4% materials, are likely associated with bridge-bonded CO, indicating the presence of sites where the molecule is simultaneously coordinated to two metal atoms

In this same concentration range, a significant reduction in the intensity of the bands attributed to linear CO adsorption is observed, suggesting the onset of cluster or nanoparticle formation(15). The predominance of bridge-bonded CO bands reinforces this hypothesis. Considering that DRIFTS peak intensity is proportional to the available metal or metal oxide surface area, the results indicate that higher nickel concentrations promote the formation of aggregated metallic structures, which favor bridge CO adsorption due to the presence of multiple adjacent metal centers.

Theoretical Calculations

Initially, a single PHI layer was modelled with a single atom of Nickel (II) (Ni^{2+}) substituted at intralayer sites (Ni@PHI). To ensure charge neutrality in the periodic 2D computational model, two Na^+ ions were removed from the PHI active sites where Ni^{2+} was inserted. A CO molecule was then positioned at approximately 2 Å from the Ni site to act as a catalytic probe, enabling investigation of the

surface properties of the catalyst, since CO is experimentally known to be sensitive to the oxidation state and coordination environment of metal sites.

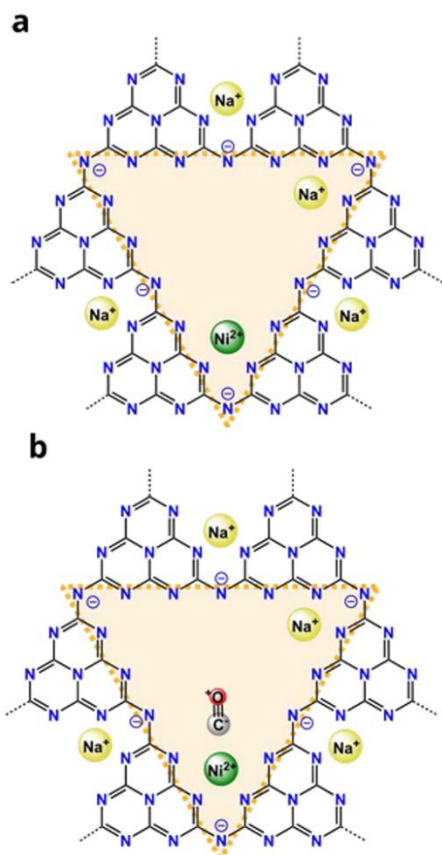


Figure 7. Idealized structure of poly (heptazine imide) (PHI) single layer: (a) Ni@PHI, (b) Ni-CO@PHI. The orange area describes the catalytic active site with Ni^{2+} . The structural configurations of the optimized systems and the charge density difference in the presence of CO were investigated to assess the potential π -backdonation effects in Ni^{2+} .

The study analyses the optimized structure and charge density difference in the presence of CO, revealing that Ni^{2+} promotes strong π -backdonation to the CO molecule, as indicated by the localized electron density on the carbon atom.

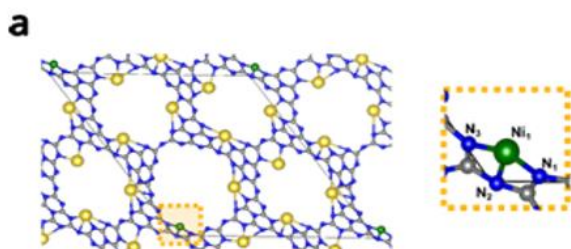


Figure 8. DFT geometry-optimized configurations for a single PHI layer in the following systems: (a) Ni@PHI; and (b) Ni-CO@PHI. Zoom on the charge density difference ($\Delta\rho$) is shown for: (c) Ni-CO@PHI.

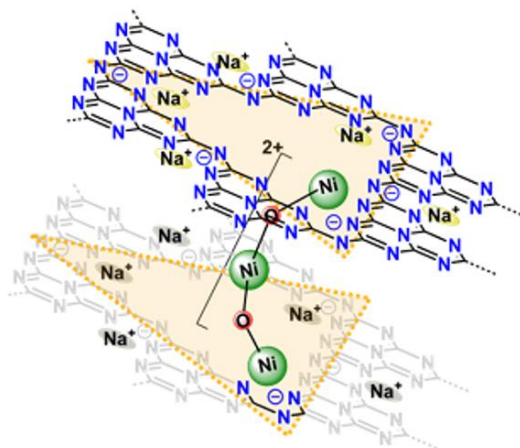


Figure 9. Idealized structure of poly (heptazine imide) (PHI) double layer (2-PHI): interlayer Ni@2PHI.

DFT and DFT+U optimizations were performed to explore the optimal configuration of a nickel-containing PHI system in 2-PHI layers. After optimizing the intralayer and interlayer structures without CO, a CO molecule was introduced near the nickel site, and further geometry optimizations were conducted.

Conclusions

This study demonstrated that the combination of CO adsorption and DRIFT-FTIR is effective for identifying and characterizing isolated Ni^{2+} atoms in PHI. Changes in the spectral bands with increasing nickel concentration, indicating enhanced π -backdonation, caused by the formation of clusters or nanoparticles. These findings were

supported by DFT calculations, which confirmed the correlation between electronic structure and adsorption behavior, highlighting the value of this approach for investigating metal-doped catalytic materials.

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