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Understanding the Catalytic Site Structure in Metal Poly(Heptazine Imide) – Crystalline Carbon Nitride

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Metal Poly(Heptazine Imide), Carbon Nitride, Single Atom Catalysis, DFT, Molecular Dynamics, CO-DRIFTS.

ABSTRACT

Metal poly(heptazine imide) (M-PHI), a crystalline carbon nitride, has emerged as a highly promising platform for surface and single-atom catalysis (SAC). However, the precise structure and coordination environment of its catalytically active sites remain unresolved. In this work, we elucidate the structure of a representative M-PHI catalytic site, nickel poly(heptazine imide) (Ni-PHI), through a synergistic experimental–computational approach integrating synthesis,



characterization, and CO probe-assisted diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) with DFT-based static and molecular dynamics simulations combined with vibrational density-of-states analysis of CO bond stretching (CO-VDOS). By systematically assessing different nickel loadings, examining the formation of nickel single atoms and nickel-based nanoparticles, comparing static and dynamic DFT energetics, and correlating the experimentally measured CO-DRIFTS spectra with the simulated CO-VDOS features, we identify highly probable Ni-PHI catalytic site structures that account for nickel single-atom and nickel-based nanoparticle cases. This work provides a general and efficient experimental–computational strategy for molecularly understanding the catalytic sites in metal poly(heptazine imide) - crystalline carbon nitrides.

1 INTRODUCTION

Over the past two decades, extensive research has focused on two-dimensional (2D) carbon nitride-based materials ($g\text{-C}_3\text{N}_4$) for artificial photosynthesis, aiming at the sustainable production of solar fuels (*e.g.*, H_2 , H_2O_2) and high-energy carbon compounds (*e.g.*, CH_3OH , CO , CH_4), starting from abundant raw sources such as H_2O , CO_2 , and N_2 .^{1,2} As recently outlined by Pelicano and Antonietti, the structure of the layered polymeric semiconductor $g\text{-C}_3\text{N}_4$, usually categorized on its triazine or heptazine units, can also be classified based on its covalent or ionic structure.³ Both types of carbon nitride have risen as excellent candidates to achieve an efficient single-atom catalysis (SAC) hosting single metal atoms coordinated into the carbon-nitrogen framework.³ Focusing on heptazine-based carbon nitride structures as highly favorable for holding SAC, the covalent type displays an sp^2 -hybridization, with sporadic charge and hole delocalized in the C-N framework, and with the heptazine units connected via amine bridges.^{3,4} The ionic-type heptazine-based $g\text{-C}_3\text{N}_4$ material, also defined as 2D crystalline ionic carbon nitride, was first reported in



2015 by Dontsova et al. with the synthesis of a metal poly(heptazine imide) (M-PHI) based on potassium ions (K-PHI).⁵ Specifically, for the PHI, the large pores in the C-N framework allow for the accommodation of metal ions coordinated to the negatively charged N atoms on the imide bridges, providing unique photophysical properties, such as time-delayed catalytic function.⁶ The accurate investigation of the PHI structure was found crucial for correlating the (photo)catalytic performance with specific structural features.³ While K-PHI's initial models were giving heptazine units in an AAA stacking, later studies have reported different interlayer stackings, with potassium atoms positioned nearer the central region of the channels and between the layers.⁷ Pioneered by the work of Savateev et al.,⁸ further and recent research demonstrated that K⁺ ions, intercalated in the PHI framework, display mobility, thus allowing for their exchange with other cations among alkali metals, alkaline-earth metals, organic cations, and, of particular catalytic interest, transition metals.^{8–17} Initially, noble metals such as platinum played the most prominent role as cocatalysts within PHI for SAC, but at impractical costs due to their low natural abundance.¹⁸ Recently, among the non-noble transition metals,^{19,20} nickel has emerged as a highly promising candidate within the PHI framework (Ni-PHI) for sustainable and efficient photo- and electro-SAC applications, including H₂ evolution, H₂O₂ generation, synthesis of organic compounds, and potential CO₂ reduction.^{21–26} On the covalent carbon nitride side, Allasia *et al.* reported an elegant first study of the nickel catalytic sites, identifying a melon-type g-C₃N₄ structure as the most favorable for potential SAC.²⁷ In parallel, the recent advancements in ionic carbon nitride research highlight PHI as an efficient, highly versatile, and stable framework for metal-based and, specifically, nickel-based SAC.^{12,23} At the beginning of 2026, Guimarães Noletto *et al.* reported a novel example of the Ni-PHI catalytic potential for the photocatalytic hydrogenation of alkynes using water as a hydrogen source, noting a variation in the catalytic turnover frequency (TOF) with Ni content.²⁶



Similarly, Silva *et al.* have demonstrated that Ni-PHI with low Ni loadings display higher TOFs for the selective nitrobenzene coupling into azo/azoxy compounds, also indicating that single-atom species are more active than cluster/nanoparticles.²³ This calls for an urgent and accurate understanding of the M-PHI catalytic site structure and its local coordination environment.

In this study, we present a general integrated experimental and computational strategy to investigate the catalytic site structure in M-PHI, focusing on the Ni-PHI case. We monitored the CO molecular probing of the nickel catalytic sites both experimentally and theoretically using spectroscopic probe-assisted techniques combined with multiscale computational approaches. Crystalline Ni-PHI with varying nickel concentrations was experimentally synthesized and characterized using X-ray diffraction (XRD), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), elemental mapping using energy dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). Following CO adsorption probing, the CO frequencies at the catalytic sites were evaluated via diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) for the different nickel loadings. Density functional theory (DFT)-based static calculations were employed to gain energetic, electronic, and conformational insights into the Ni-PHI catalytic site structure. We performed DFT-based ab initio molecular dynamics (DFT-MD) simulations to investigate the dynamics of Ni-PHI at room temperature and the vibrational modes of the CO molecular probe, with correlated CO frequencies analyzed across different Ni-PHI configurations. By combining experimental characterization and spectroscopic analysis with DFT-based static and DFT-MD simulations, we identified the formation of either a linear Ni-CO σ -bond or a π -backdonation Ni-CO-Ni bridge interaction depending on the nickel amount and localization, as well as the formation of nickel-based nanoparticles, thus revealing favorable Ni-PHI configurations for the catalytic site. Overall, this



study establishes a combined computational–experimental protocol for accurately resolving the M-PHI catalytic site structure and provides insight for the potential rational design of M-PHI toward highly efficient surface and single-atom catalysis.

2 RESULTS AND DISCUSSION

2.1 Ni-PHI Synthesis and Characterization

Experimentally, Ni-PHI was prepared following the protocol reported in the work by da Silva *et al.*, as detailed in the Experimental Methods section.²³ Successively, the Na-PHI and the Ni-PHI systems with increasing nickel loadings (0.5–4 wt%) were characterized with XRD patterns, as shown in Figure 1a. The reflections at 8.3° and 14.2° are indicative of the 2D ordering of heptazine units, while the peaks at 25° and 29° correspond to interlayer stacking, which diminishes with increasing nickel concentration. This change in the intensity is also in line with the XRD patterns estimated from the DFT simulations (Figure S1 and DFT-based static simulations section). This reduction in crystallinity is attributed to nickel coordination (cation exchange), which alters the diffraction pattern through electrostatic interactions and loss of hydration water from the sodium coordination shell.^{23,28} High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images further reveal the nickel distribution. For the low-loading sample (0.5 wt.%, Figure 1b), only atomically dispersed Ni species are observed as bright spots, which are highlighted by circles in the image. In contrast, the higher-loading sample (4 wt.%, Figure 1c) shows both isolated single atoms and predominantly nickel-based clusters and nanoparticles, indicating aggregation at elevated nickel concentrations (highlighted by circles). The lattice distances of these nanoparticles were measured to be 0.245 nm and 0.205 nm, attributed to the (111) and (200) planes of NiO, respectively, as shown in Figure 1d.^{29,30} Furthermore, a region



predominantly containing nanoparticles was selected (Figure 1e), and the particle sizes displayed a median of 1.97 nm, as calculated from the particle size distribution histogram in Figure 1f.

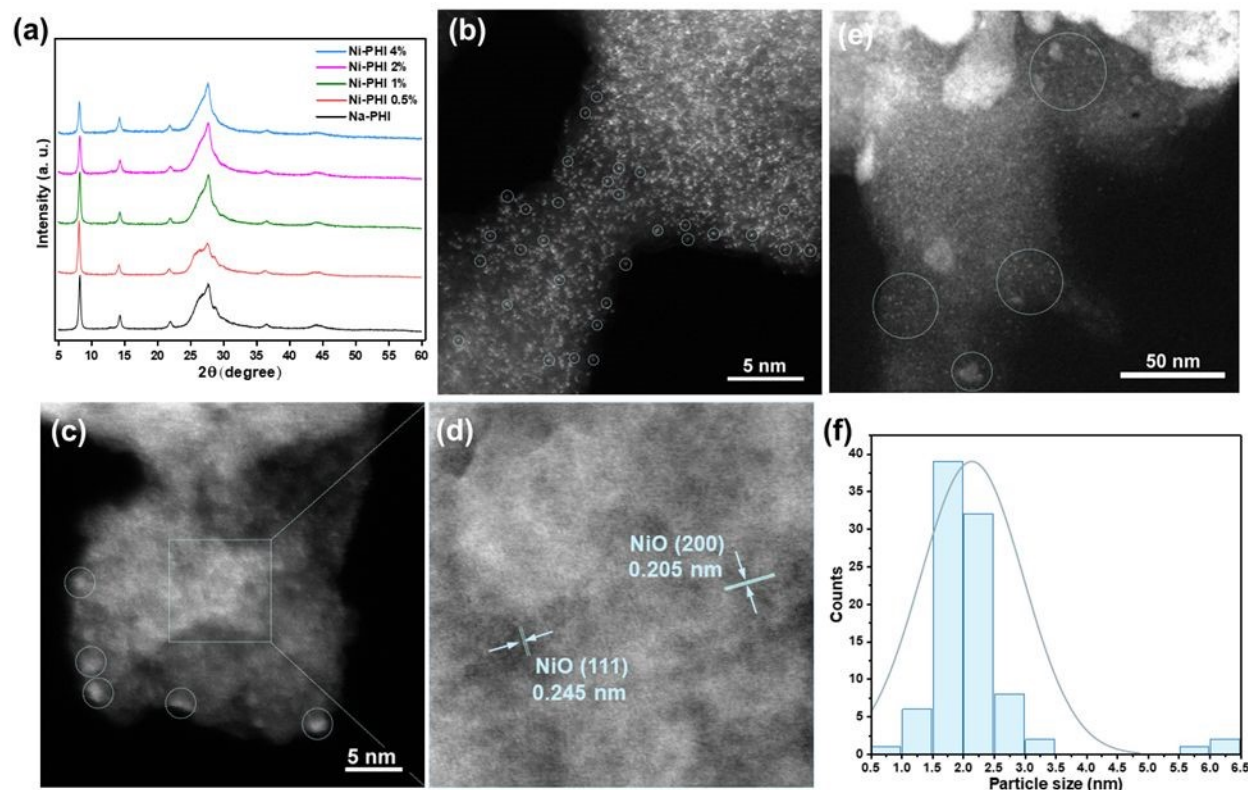


Figure 1. a, X-ray diffraction (XRD) of Na-PHI and Ni-PHI with different nickel loadings (0.5 wt %, 1 wt%, 2 wt%, 3 wt%, and 4 wt%). b, HAADF-STEM image of Ni-PHI 0.5 wt% showing atomically dispersed Ni species. c, HAADF-STEM image of Ni-PHI 4 wt% showing Ni-based clusters and nanoparticles, likely such as NiO and/or Ni(OH)₂. d, Lattice fringes corresponding to the (111) and (200) planes of NiO. e–f, Representative region containing clusters and nanoparticles, and particle size distribution diagram for Ni-PHI 4 wt.%.

To evaluate the elemental distribution and confirm the successful incorporation of nickel, EDS mapping was performed on the Ni-PHI 0.5 wt% sample. Figure 2 shows a HAADF-STEM image and corresponding EDS elemental mapping, illustrating the spatial distribution of nitrogen (N) and nickel (Ni). The EDS spectrum of the Na-PHI sample is shown in Figure S2. The uniform dispersion of both elements throughout the sample indicates the successful incorporation of nickel



into the PHI framework and suggests good interaction between the metal species and the support. The quantification of nickel loading was performed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and reported in Table S1.

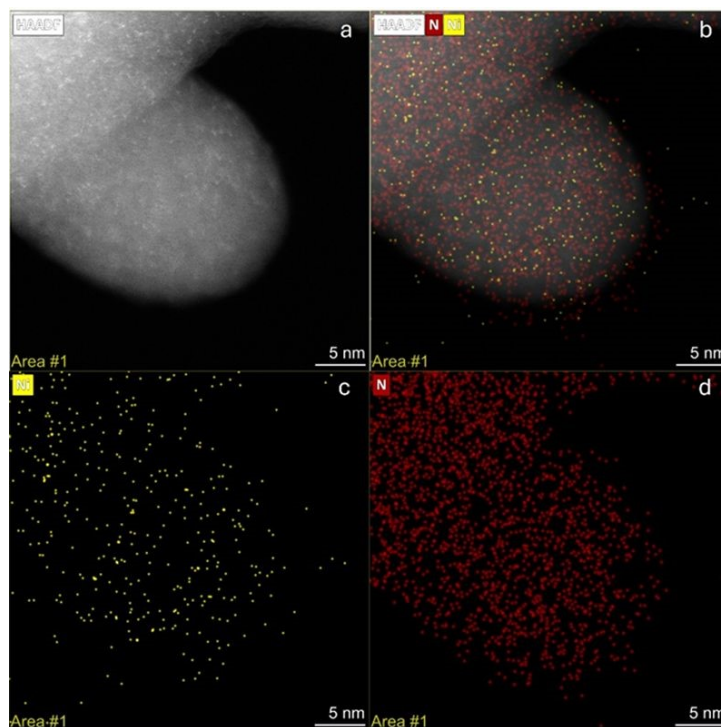


Figure 2. Elemental analysis of the Ni-PHI 0.5 wt% sample. **a**, HAADF-STEM image; **b**, EDS elemental mapping showing the distribution of Ni and N; **c**, mapping of Ni; **d**, mapping of N.

To further clarify the chemical composition and oxidation state of surface elements in Ni-PHI materials, X-ray photoelectron spectroscopy (XPS) analyses were performed. High-resolution spectra in the N 1s region, reported in Figure 3 a, show the presence of four typical signals after peak fitting, which can be assigned to pyridinic nitrogen (398.7 eV), amino groups (399.9 eV), graphitic nitrogen (401.2 eV), and π - π^* interactions (404.2 eV). This spectral pattern remains unchanged with varying nickel loadings, indicating that the increasing of Ni loading does not significantly affect the nitrogen chemical environment of the PHI framework. In the O 1s XPS region, an important trend can be observed as a function of nickel loading (Figure 3 b). With



increasing Ni content, the intensity of the signal associated with hydroxyl species increases accordingly. More importantly, a clear change in the peak profile and a systematic shift in binding energy are observed when comparing Ni-PHI 0.5 wt% with Ni-PHI 1 wt%, 2 wt%, and 4 wt%. This behavior indicates the presence of distinct hydroxyl environments among the samples. The progressive increase of the OH-related signal with higher metal loading strongly suggests the formation of Ni(OH)₂ species within the PHI surface. This assignment is supported by the emergence of a component around 531.2 eV, which is characteristic of nickel hydroxide.^{31,32} In contrast, for Ni-PHI 0.5 wt%, the OH-related contribution appears at a higher binding energy (531.8 eV), which is more consistent with surface-adsorbed hydroxyl species and/or C-O functionalities.^{33–35} Overall, these results indicate that the incorporation of higher amounts of nickel into the PHI structure promotes the formation of nickel hydroxide species within the surface. The remaining components in the O 1s region can be attributed to adsorbed water (533.0 eV) and to the Na KLL Auger signal arising from sodium cations present in the PHI structure.

In the Ni 2p XPS region, no significant differences are observed among the samples (Figure 3 c), indicating that the overall oxidation state of nickel does not vary with metal loading. The main Ni 2p_{3/2} peak is located at 855.8 eV, which is consistent with the presence of Ni²⁺ species in all samples. For the Ni-PHI 4 wt% sample, we attempted to fit the Ni 2p spectrum using the Ni(OH)₂ reference parameters reported by Biesinger *et al.*³¹ However, a noticeable mismatch in the fitting was observed (Figure S3). This discrepancy suggests that the nickel species in Ni-PHI are not exclusively present as Ni(OH)₂. A reliable peak fitting is difficult to attempt since we probably



have a mixture of isolated nickel sites and clusters of nickel hydroxide in the Ni-PHI 4 wt%.

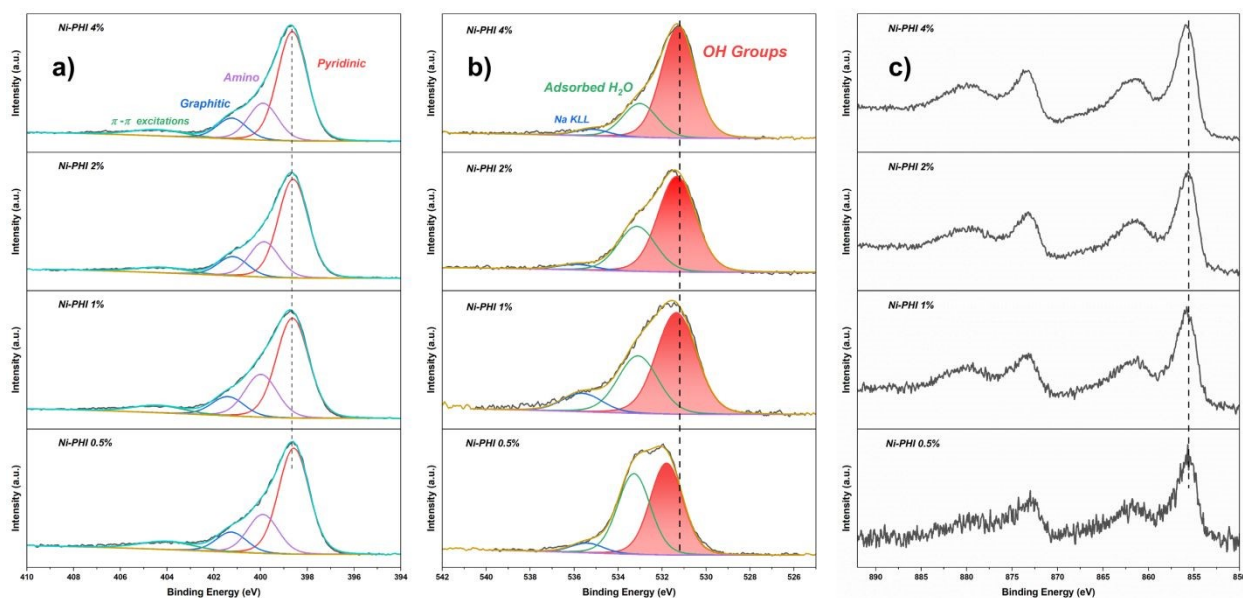


Figure 3. High-resolution XPS **a**, N 1s, **b**, O 1s, and **c**, Ni 2p spectra of Ni-PHI 4 wt%, 2 wt%, 1 wt% and 0.5 wt%.

2.2 CO Adsorption Probing via Diffuse Reflectance Infrared Fourier Transform Spectroscopy (CO-DRIFTS)

The CO-DRIFTS spectroscopy analysis was performed on Ni-PHI samples for each Ni concentration (0.5 wt%, 1 wt%, 2 wt%, and 4 wt%). The samples were pretreated at 300 °C and analyzed as detailed in the Experimental Methods section. In Figure 4, we report the CO-DRIFTS spectra of Ni-PHI materials. For the Ni-PHI 0.5 wt% and 1 wt% samples, bands at 2188 and 2190 cm^{-1} , respectively, are assigned to linearly σ -bond chemisorbed CO on Ni^{2+} sites, while the band at 2135 cm^{-1} corresponds to physisorbed CO, reflecting weak and reversible interactions with the surface.^{27,36,37} At nickel concentrations of 2 wt% and above, the CO bands red-shift to lower frequencies than the 0.5-1 wt% cases, consistent with the possible presence of π -backdonation and decreased polarization of the CO molecule. The bands observed at 2075–2080 cm^{-1} and 2006 cm^{-1} in the Ni-PHI 2 wt% and 4 wt% samples are likely associated with bridge-bonded CO (Ni-CO-



Ni), indicating the presence of sites where the molecule is simultaneously coordinated to two metal atoms.^{38,39} In this concentration range, the intensity of bands associated with linear CO adsorption decreases significantly, suggesting the formation of nickel clusters or nanoparticles, most likely composed of Ni(OH)₂, and/or NiO species, since the samples are being pretreated at 300 °C and the hydroxyl groups might dissociate.^{40–42} The predominance of bridge-bonded CO bands reinforces this hypothesis. To investigate the possible formation of NiO particles after the thermal treatment performed prior to the CO-DRIFTS analysis, XPS measurements were carried out on the Ni-PHI 4% sample after treatment (Figures S4-S5). The high-resolution O 1s spectrum can be fitted into four components. The peak at higher binding energy is attributed to the Na KLL Auger feature, while the contributions at 533.0 eV and 531.5 eV are assigned to adsorbed water and hydroxyl groups, respectively, consistent with the observations for the untreated sample. Notably, a new feature emerges at lower binding energy (530.4 eV), which is characteristic of NiO and confirms the formation of NiO clusters upon thermal treatment.^{43,44} In contrast, the high-resolution Ni 2p region does not show significant changes and does not resemble the profile of NiO.³¹ This suggests the coexistence of different Ni species in the material, including isolated Ni single atoms and NiO clusters.

Considering that CO-DRIFTS peak intensity is proportional to the available metal surface area, the results indicate that higher nickel concentrations promote the formation of aggregated metallic structures such as Ni(OH)₂ and/or NiO nanoparticles, which favor bridge CO adsorption due to the presence of multiple adjacent metal centers. To comprehensively understand the structure of the catalytic sites in Ni-PHI, and correlate the experimental analysis to a molecular description, we performed DFT static and DFT-MD simulations on an extensive series of possible Ni-PHI models and a NiO-PHI representative one. The theoretical models used in the present study are



grounded in realistic coordination environments based on X-ray absorption fine structure (XAFS) analysis of the da Silva *et al.* and recent Guimarães Noleto *et al.* works.^{20,26}

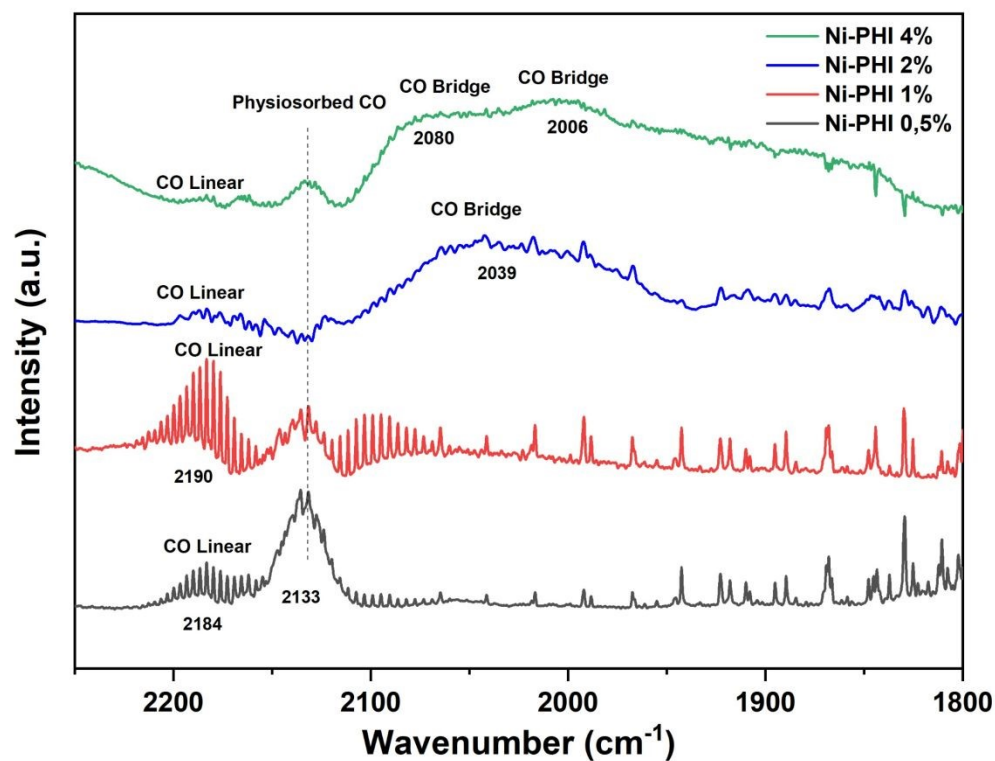


Figure 4. Kubelka–Munk plots of CO desorption from Ni-PHI measured by CO-DRIFTS. Intensities are in arbitrary units (a.u.) and frequencies in cm^{-1} . Ni-PHI samples with 0.5 wt%, 1 wt%, 2 wt%, and 4 wt% nickel concentration are shown in black, red, blue, and green, respectively.

2.3 DFT-based Static Simulations: One Ni^{2+} Ion within PHI Layers (Ni-2(PHI)) and with Adsorbed Carbon Monoxide Molecular Probe ((Ni-CO)-2(PHI))

Initially, we investigated the optimal configuration of one Ni^{2+} ion in a double-layer PHI (Ni-2(PHI)), considering both in-plane and out-of-plane starting arrangements, as represented in Figure 5 a and b, respectively (see Computational Methods section for details). To study these systems in



a periodic 2D computational fashion and thus achieve a comprehensive description of the nickel ion(s) embedded within a multilayer PHI catalytic site,^{13,14,20} we provided for the entire system a total net charge equal to zero by removing two of the six Na⁺ ions from an ideal Na-saturated PHI active site, thus depicting a local cation exchange with Ni²⁺ (Figure 5, orange triangle areas, and Figure S6).²³ We performed DFT-based, both DFT and DFT+*U* (Hubbard correction), static simulations at the GGA level throughout this work to investigate the systems and also obtain a comparison between standard and Hubbard corrected DFT methods (see Computational Methods section for details). The DFT+*U* method served as our primary approach because it is cost-effective and highly reliable at the GGA level for transition-metal complexes in SAC.^{45,46} We performed geometry optimizations of the initial structures shown in Figure 5. In both relaxed structures, the Ni²⁺ ion adopts an out-of-plane configuration, with a negligible total energy difference of 0.013 eV between them with respect to thermal energy ($k_B T_{300\text{ K}} \approx 0.027\text{ eV}$). The Ni²⁺ coordinates to three nitrogen atoms of the PHI layers with Ni-N distances within the range of $\approx 1.9\text{-}2.1\text{ \AA}$, indicative of strong metal–nitrogen binding (Figure S7), and with a triplet electronic state for both DFT+*U* and DFT approaches.^{27,45–47}

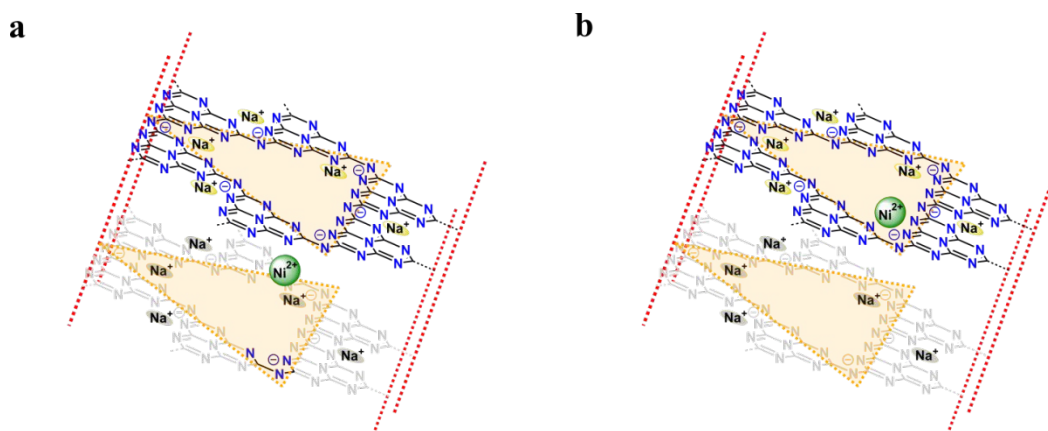


Figure 5. Idealized 2PHI layers with starting configurations **a**, out-of-plane, and **b**, in-plane, Ni²⁺ ion: Ni-2(PHI). The orange area describes the catalytically active site with the Ni²⁺ ion. The atoms are sketched in ball-and-stick



representation, with nickel in green, carbon in black, nitrogen in blue, and sodium in yellow. In color and grey, the upper and bottom, respectively, are PHI layers and sodium cations. The interacting part of the bottom PHI layer with the Ni^{2+} ion is kept colored.

Successively, on the energetically most stable optimized configuration, a CO molecule was added in the proximity of the Ni^{2+} ion at a distance of $d(\text{Ni}-\text{C}_{\text{CO}}) \approx 2 \text{ \AA}$ in two different starting positions (see Figure S8 and Computational Methods section). As we also reported in the CO-DRIFTS section, the use of the CO probe molecule is experimentally justified since it is sensitive to the oxidation state and location of metal sites.²⁷ We geometry optimized the (Ni-CO)-2(PHI) system and identified a singlet electronic state for both DFT+*U* and DFT approaches. We estimated the Ni-CO binding energy (ΔE_{B}) to be approximately 1.05 eV (1.76 eV for the DFT), as detailed in the Computational Methods section. We explored the structural configurations to assess the potential π -backdonation (also named π -backbonding) from the Ni to the CO, such as $\text{Ni}^{2+} \rightarrow \text{C}\equiv\text{O}^+$, outlining the Ni_1-N_n , $\text{Ni}_1-\text{C}_{\text{CO}}$, and $\text{C}_{\text{CO}}-\text{O}_{\text{CO}}$ distances depicted in Figure 6 a, b (Figure S9 a), and the charge density difference (Figure 6 c and Figure S9 b).⁴⁸ After CO adsorption, we found the nickel ion still coordinating with three nitrogens in the PHI's catalytic site with an average of Ni_1-N_n bond lengths of 2.002 Å (1.955 Å for DFT) within the strong metal-nitrogen interaction range of $\approx 1.9\text{-}2.0 \text{ \AA}$.^{27,45,46} According to the classical concept of π -backdonation, the $\text{C}\equiv\text{O}$ bond length ($d(\text{C}_{\text{CO}}-\text{O}_{\text{CO}})$) of the isolated free CO molecule increases upon interaction with the Ni^{2+} ion. The free CO bond length, $d(\text{C}_{\text{free-CO}}-\text{O}_{\text{free-CO}})$, is experimentally estimated to be $d(\text{C}_{\text{free-CO}}-\text{O}_{\text{free-CO}})_{\text{exp}} = 1.128 \text{ \AA}$ (via X-ray crystallography).⁴⁹ However, in DFT simulations, the $d(\text{C}_{\text{CO}}-\text{O}_{\text{CO}})$ can vary depending on the level of theory employed, which also shifts the reference value for the free CO bond length. In this work, we used as a reference value the $d(\text{C}_{\text{free-CO}}-\text{O}_{\text{free-CO}})_{\text{DFT}} = 1.144 \text{ \AA}$, obtained from the same level of DFT applied throughout all static DFT calculations (see Computational Methods section), and consistent with previous literature.⁵⁰



For the (Ni-CO)-2(PHI) system, $d(C_{CO}-O_{CO})$ shows only a slight elongation to 1.146 Å (1.151 Å for DFT), as reported in Figure 6 b (Figure S9 a), indicating no significant π -backdonation interaction between nickel and CO.^{48,51} The charge density difference reported in Figure 6 c (Figure S9 b) reveals localized negative and positive isosurfaces on the oxygen atom of the CO molecular probe, suggesting a slightly less polarized CO bond, compared to the isolated CO fully polarized case.⁴⁸ We performed Bader charge analysis on the optimized structures to specifically verify whether nickel retains a positive charge within the periodic framework, as shown in Table S2.⁵² In both cases, Ni-2(PHI) and (Ni-CO)-2(PHI), the Bader charge on the nickel was found to be positive, +1.11 |e| and +0.96 |e|, respectively. Finally, to further ensure an accurate description of the nickel ion within this periodic scheme, we performed geometry optimizations, followed by frequency and Bader charge analyses on the molecular complexes $[Ni-(melem)_2]^{2+}$ and $[(Ni-CO)-(melem)_2]^{2+}$ in both singlet and triplet states, and the free isolated CO molecule (see Figure S10, Table S3, and Computational Methods section). The obtained spin-state energetic trend was consistent with the periodic calculations, having the $[Ni-(melem)_2]^{2+}$ and $[(Ni-CO)-(melem)_2]^{2+}$ complexes preferably in triplet and singlet spin states, respectively. The trend of the Bader charges on nickel was also in line with the periodic systems, showing values of +1.32 |e| for the $[Ni-(melem)_2]^{2+}$ triplet state complex and +1.11 |e| for $[(Ni-CO)-(melem)_2]^{2+}$ singlet state complex.



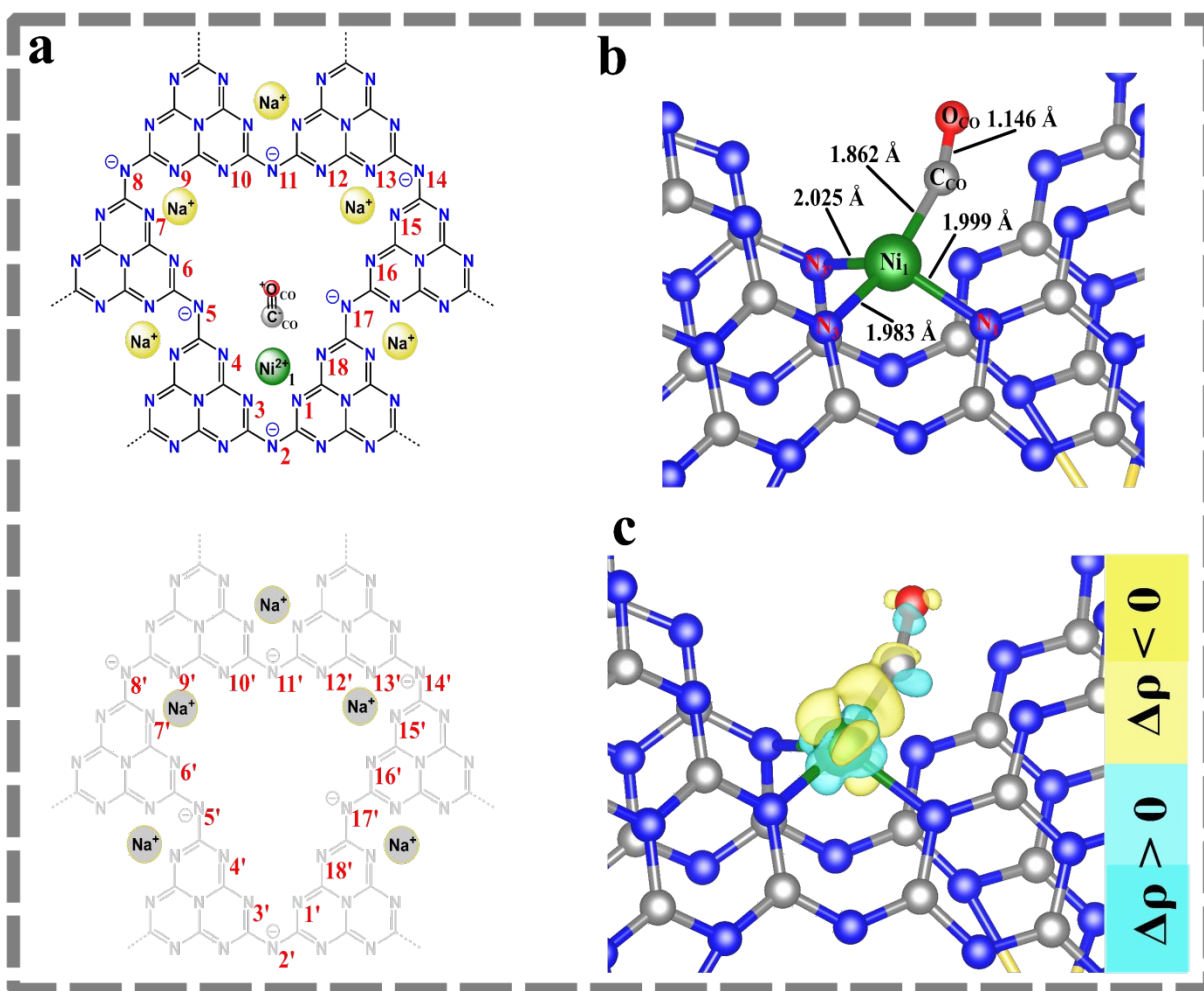


Figure 6. **a**, Idealized (Ni-CO)-2(PHI) with numbering of the Ni²⁺ ion (Ni₁), and CO atoms (C_{CO} and O_{CO}) in black, and N_{*n*} atoms (1 ≥ *n* ≥ 18) in red, without and with the single quote symbol (') for the top and the bottom PHI layers, respectively. The atoms are sketched in ball-and-stick representation, with nickel in green, carbon in black, nitrogen in blue, oxygen in red, and sodium in yellow. In color and grey, the upper and bottom, respectively, are PHI layers and sodium cations. **b**, Zoom on the DFT+*U* geometry optimized (Ni-CO)-2(PHI) system to highlight the Ni₁-C_{CO}, C_{CO}-O_{CO}, and Ni-N₁ (Ni₁-N₁, Ni₁-N₃, and Ni₁-N₃) distances. **c**, DFT+*U* charge density difference (Δρ) for the (Ni-CO)-2(PHI) system. Yellow and cyan colors are used to represent the negative and positive charge density differences, respectively, with an isosurface value of 0.01. The atoms are depicted as ball-and-stick models, with nickel in green, carbon in grey, nitrogen in blue, oxygen in red, and sodium in yellow.



2.4 DFT-based Static Simulations: Two Out-of-plane Ni²⁺ Ions within PHI Layers (Ni₂-2(PHI)) and with Adsorbed Carbon Monoxide Molecular Probe ((Ni₂-CO)-2(PHI))

To preliminarily understand an increase in the amount of Ni²⁺ ions in the active pocket of the PHI layer, we investigated two nickel ions, such as Ni₂-2(PHI) systems. The total net charge of the entire system in our periodic 2D computational model was set equal to zero by removing four of the six Na⁺ ions from an ideal Na-saturated PHI active site, thus describing a local cation exchange with two Ni²⁺ ions (Figure S11, orange triangle areas). The initial configurations of the two Ni²⁺ ions are taken out-of-plane, as this was found to be the most stable arrangement for a single Ni²⁺ ion. To explore different nickel positions within the catalytic pocket, we performed geometry optimizations on three system types, varying the position of one Ni²⁺ ion relative to the other Ni²⁺ within the catalytic pocket. The two Na⁺ ions in the catalytic site were considered in two possible swapped arrangements, resulting in a total of six configurations (Figure S11). For each of the two permutations of Na⁺ corresponding to the same Ni²⁺ ion positions in the catalytic pocket, we identified the most stable configurations. For both DFT and DFT+*U* methods, the Ni₂-2(PHI) optimized structures display the Ni²⁺ ions in a sandwich out-of-plane configuration between two PHI layers (Figure S12). Of these three optimized structures, two adopt configurations in which both Ni²⁺ ions are tri- and tetra-coordinated to the nitrogen atoms of the PHI's catalytic pocket (Figure S12 c, d, e, and f). In contrast, in one configuration where the two Ni²⁺ ions are constrained to mirror each other within a limited volume, each nickel interacts with the catalytic pocket via only Ni-N di-coordination (Figure S12 a, and b). The reduced Ni-N coordination for the Ni²⁺ ions mirror system (Figure S12 a, and b) may explain why the di-coordinated system is less stable in total energy by ≈ 1 -2 eV compared to the other two configurations shown in Figure S12 c, d, and e, f, respectively. For these three most stable Ni₂-2(PHI) optimized structures, a CO molecule was



placed near each nickel atom at $d(\text{Ni}_n\text{-C}_{\text{CO}}) \approx 2 \text{ \AA}$, in two different initial positions, as described for the single Ni^{2+} in Figure S8, for a total of twelve initial configurations (four for each system). This setup allows evaluation of the Ni-CO interaction and possible π -backdonation $\text{Ni}^{2+} \rightarrow \text{C}\equiv\text{O}^+$. After geometry optimization, we identified the three most stable geometries for each of the three Ni^{2+} arrangements in the catalytic pocket, labeled **1**, **2**, and **3** (Figure 7, Figure S13, and Figure S14).

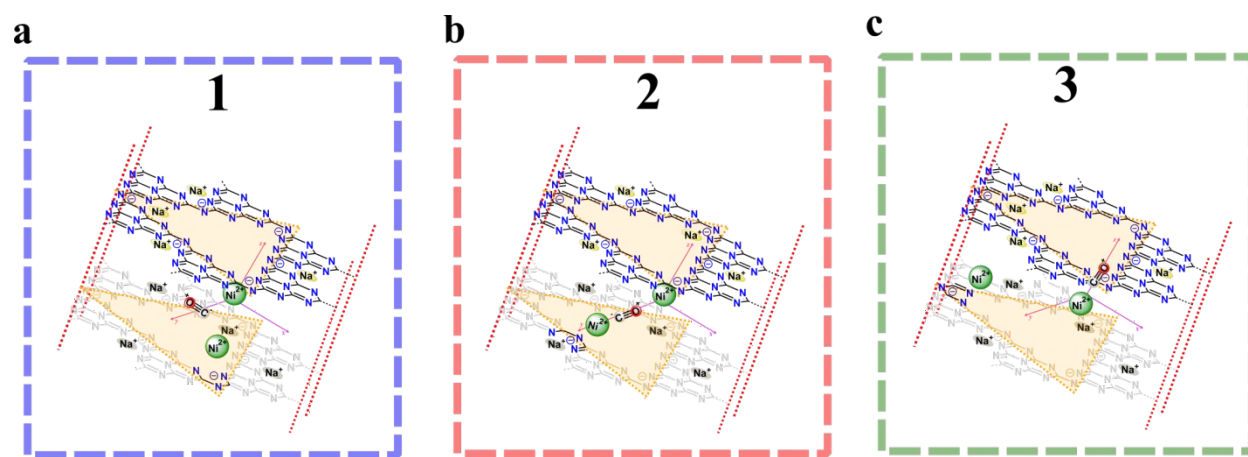


Figure 7. DFT+*U* case: representative initial idealized three configurations of two out-of-plane Ni^{2+} ions within 2PHI layers with adsorbed carbon monoxide molecular probe, $(\text{Ni}_2\text{-CO})\text{-2(PHI)}$: **a**, (system **1**), **b**, (system **2**), and **c**, (system **3**), respectively. The orange area describes the catalytically active site with Ni^{2+} ions. The atoms are depicted as ball-and-stick models, with nickel in green, carbon in black, nitrogen in blue, oxygen in red, and sodium in yellow. In color and grey, the upper and bottom, respectively, are PHI layers and sodium cations. The interacting part of the bottom PHI layer with the Ni^{2+} ion is kept colored. The reference *x*, *y*, and *z* axes to mark the initial CO orientation are shown in pink.

The CO strongly binds to the Ni^{2+} species, with the Ni-CO binding energies (ΔE_{B}) reported in Table 1 (see Computational Methods for details). For the $(\text{Ni}_2\text{-CO})\text{-2(PHI)}$ system **1**, the binding energy increases by approximately 1.06 eV and 0.75 eV (0.45 eV and 0.10 eV for standard DFT, respectively, Table S4) compared to systems **2** and **3**, respectively. The configuration with the two nickel ions mirrored along the *z*-axis exhibits the strongest Ni-CO binding among those analyzed.



Table 1. DFT+*U* (PBE-D3+*U*) results: binding energy (ΔE_B) in eV of Ni-CO interaction, and distances (d) in Å for the systems (Ni₂-CO)-2(PHI), **1**, **2**, and **3**, respectively. Distances include $\langle d(\text{Ni}_n\text{-N}_n) \rangle$ (averaged value), Ni_{1,2}-C_{CO}, and C_{CO}-O_{CO}, where the N_{*n*} atoms ($1 \geq n \geq 18$), without and with the single quote symbol (') correspond to the top and the bottom PHI layers (Figure 5 a), respectively. The binding energy is calculated as $\Delta E_B = E_{(\text{Ni}_2\text{-CO})\text{-2(PHI)}} - E_{\text{Ni}_2\text{-2(PHI)}} - E_{\text{CO}}$, using single-point calculations on (Ni₂-CO)-2(PHI), and its components Ni₂-2(PHI) and CO, respectively.

System	ΔE_B (eV)	$\langle d(\text{Ni}_n\text{-N}_n) \rangle$ (Å)	$d(\text{Ni}_n\text{-C}_{\text{CO}})$ (Å)	$d(\text{C}_{\text{CO}}\text{-O}_{\text{CO}})$ (Å)
(Ni₂-CO)-2(PHI) system 1	-2.25	1.965 (Ni ₁)	1.852 (Ni ₁)	1.154
		1.917 (Ni ₂)	2.366 (Ni ₂)	
(Ni₂-CO)-2(PHI) system 2	-1.19	2.261 (Ni ₁)	1.934 (Ni ₁)	1.140
		2.075 (Ni ₂)		
(Ni₂-CO)-2(PHI) system 3	-1.50	2.006 (Ni ₁)	1.1964 (Ni ₁)	1.143
		2.075 (Ni ₂)		

The structural configurations and charge density difference distributions were then analyzed. The results show that the optimized CO adopts a tilted orientation relative to its initial Ni-CO interacting position (Figure 8, Figure S14, and Figure S15). The highest binding energy observed for system **1** can be attributed to the catalytic site structure and Ni-N di-coordination, which may enhance the interaction with the CO probe. From the optimized geometries, we outline the Ni_{1,2}-C_{CO}, C_{CO}-O_{CO}, and Ni_{1,2}-N_{*n*} distances (Figure 8a, c, and e, Figure S15 a, c, and e). The averages of Ni_{1,2}-N_{*n*} bond lengths reported in Table 1 (Table S4) indicate strong metal-nitrogen interactions ($\approx 1.9\text{-}2.0$ Å) for system **1**, and mild ($\approx 2.1\text{-}2.2$ Å) metal-nitrogen interactions for systems **2** and **3**.^{27,45,46} Notably, in the (Ni₂-CO)-2(PHI) system **1**, the two mirrored Ni²⁺ ions are both within interacting distance with the CO molecular probe, Ni₁-C_{CO} and Ni₂-C_{CO}, respectively (Table 1 and Table S4). This configuration can be described as a semi-bridge Ni-CO-Ni interaction, due to an



asymmetry in the Ni-C_{CO} bond lengths: 1.852 Å and 2.366 Å (Table 1 and Table S4), respectively. This particular semi-bridge interaction likely accounts for the stronger Ni-CO binding energy, compared to the linear Ni-CO interaction in systems **2** and **3**, as reported in Table 1 (Table S4). As a consequence of this firm Ni-CO binding, the C_{CO}-O_{CO} bond length increases to 1.154 Å (Table 1 and Table S4) in system **1**, compared to the free isolated CO molecule ($d(C_{\text{free-CO}}-O_{\text{free-CO}})_{\text{DFT}} = 1.144 \text{ \AA}$) and the systems **2** (1.140 Å) and **3** (1.143 Å), as detailed in Table 1 (Table S4). This elongation indicates an enhanced metal-CO interaction due to a Ni²⁺ → ⁻C≡O⁺ π-backdonation in system **1**.^{48,51} On the other hand, for systems **2** and **3**, the CO bond length results shorter than the isolated CO molecule, suggesting the formation of a linear Ni-CO σ-bond accompanied by a decrease of the electron density of the weakly antibonding 5σ orbital of CO or electrostatically physisorbed CO, thus resulting in a shorter CO bond than free CO. Furthermore, the charge density difference analysis shown in Figure 8 (Figure S15) reveals a more localized negative isosurface on both the C_{CO} and O_{CO} atoms in system **1** than systems **2** and **3**, suggesting a less polarized CO molecule (C=O) for the former, whereas the latter systems exhibit a persistently polarized CO (⁻C≡O⁺). This is consistent with a longer CO bond in system **1** than in systems **2** and **3**. We performed Bader charge analysis on the Ni₂-2(PHI) and corresponding (Ni₂-CO)-2(PHI) optimized structures to verify whether nickel preserves a positive charge within the periodic framework.⁵² As reported in Table S2, the Bader charges on nickel atoms were found to be positive in all cases, supporting the reliability of our periodic approach. Interestingly, a higher positive charge was observed for both the nickel atoms in the (Ni₂-CO)-2(PHI) system **1** compared to the ones in (Ni₂)-2(PHI) system **1**, indicating the Ni²⁺ → ⁻C≡O⁺ π-backdonation upon CO interaction. Conversely, for the other systems, the presence of CO leads to a decrease in the positive charge on the nickel bound to the CO (Table S2), consistent with a predominantly linear



σ -type interaction between the Ni^{2+} and CO. Moreover, in the $(\text{Ni}_2\text{-CO})\text{-2(PHI)}$ system **1**, the sum of the Bader charges on the CO probe molecule results in a negative value compared to $(\text{Ni-CO})\text{-2(PHI)}$ and $(\text{Ni}_2\text{-CO})\text{-2(PHI)}$ systems **2** and **3**, where the sums persist in being positive (Table S2), further evidencing the π -backdonation only in system **1**. Overall, these findings feature a Ni-CO π -backdonation in the $(\text{Ni}_2\text{-CO})\text{-2(PHI)}$ system **1**, in line with the higher binding energy ΔE_B compared to systems **2** and **3**, where the Ni interacts linearly to CO or electrostatically via physisorption.

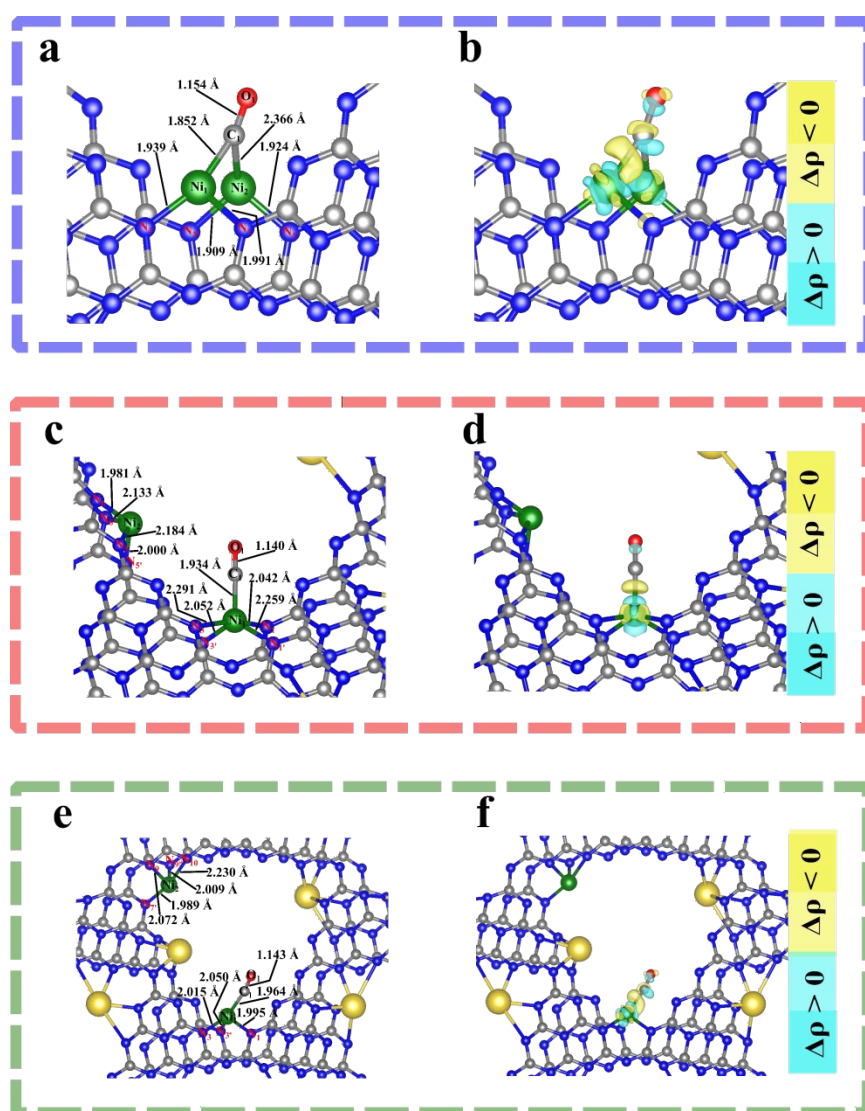


Figure 8. DFT+*U* geometry-optimized three configurations of two out-of-plane Ni²⁺ ions within 2PHI layers with adsorbed carbon monoxide molecular probe, (Ni₂-CO)-2(PHI): **a**, (system **1**), **c**, (system **2**), and **e**, (system **3**), inside the blue, red, and green dashed line boxes, respectively. Highlighted Ni_{1,2}-C_{CO}, C_{CO}-O_{CO}, and Ni_{1,2}-N_{*n*} distances, with N_{*n*} atoms (1 ≥ *n* ≥ 18), without and with the single quote symbol (') for the top and the bottom PHI layers, respectively. DFT+*U* charge density difference (Δρ) for the (Ni₂-CO)-2(PHI) system: **b**, (system **1**), **d**, (system **2**), and **f**, (system **3**), inside the blue, red, and green dashed line boxes, respectively. Yellow and cyan colors are used to represent the negative and positive charge density differences, respectively, with an isosurface value of 0.01. The atoms are depicted as ball-and-stick models, with nickel in green, carbon in grey, nitrogen in blue, oxygen in red, and sodium in yellow.

Notably, at standard DFT, the calculated spin states among the three (Ni₂-CO)-2(PHI) systems are different: quintet for system **1**, and triplet for systems **2** and **3**. This discrepancy can arise because standard DFT tends to over-delocalize the nickel 3*d* electrons. As a result, Ni²⁺ ions in different positions may artificially stabilize different spin states due to varying degrees of hybridization with the surrounding carbon nitride framework. In contrast, the DFT+*U* calculations yield a quintet spin state for these three systems. The Hubbard correction localizes the nickel 3*d* electrons more effectively, enforcing a more consistent *d*⁸ electronic configuration across all nickel sites. The DFT+*U* approach leads to a uniform high-spin state and provides a more reliable and physically consistent description of the nickel electronic structure in the PHI catalytic pocket than standard DFT. Di Liberto *et al.* reported that for a single nickel atom tetracoordinated to nitrogens in a pyridinic N-doped graphene-like (Gr) system (Ni(4N-Gr)), the spin polarization was almost unaffected by the Hubbard correction compared to other transition metals.⁴⁵ On the other hand, our (Ni₂-CO)-2(PHI) systems, containing two Ni²⁺ ions in the same catalytic pocket, different positions, and a sandwich configuration between two PHI layers, represent a case where the Hubbard correction to GGA-based DFT features as decisive in ensuring the reliability of the electronic structure description. This behavior may be related to the diverse coordination modes



of Ni²⁺ ions toward the periodic multilayer PHI, deviating from the conventional Ni(4N-Gr)-type tetra-coordination interaction.

2.5 DFT-based Static Simulations: Representative NiO-Nanoparticle Model with Adsorbed Carbon Monoxide Molecular Probe ((Ni₁₀O₈-CO)-2(PHI))

To understand the effect of the likely presence of a nickel oxide (NiO) nanoparticle within the PHI catalytic system, after the pretreatment at 300 °C highlighted from the experiments, we generated a representative (Ni₁₀O₈)-2(PHI) model. This model was chosen to have a typical cubic NiO crystal structure fitting the PHI pore volume,⁵³ and providing a site for CO probe interaction. The total net charge of the entire system in our 2D periodic framework was set equal to zero by removing four of the six Na⁺ ions from an ideal Na-saturated PHI active site, thus describing a charged (Ni₁₀O₈)⁴⁺ cluster (Figure 9 a). The configuration of (Ni₁₀O₈)⁴⁺ is chosen so that the distances between the nickel and oxygen atoms at the edges of the simulation box are consistent with a periodic NiO cluster under periodic boundary conditions (PBC). First, we performed a DFT+*U* geometry optimization of the (Ni₁₀O₈)-2(PHI) system (Figure 9 a, c top, and d). Then, on the optimized (Ni₁₀O₈)-2(PHI) system, we added a CO molecular probe in the vicinity of two nickel atoms $d(\text{Ni}_n\text{-C}_{\text{CO}}) \approx 2 \text{ \AA}$, and performed another DFT+*U* geometry optimization on the (Ni₁₀O₈-CO)-2(PHI) (Figure 9 b, c bottom, and e). The protocol used for the DFT-based static calculations follows the Computational Methods section. The CO bond elongates to 1.194 Å when the CO molecule interacts with two Ni atoms of the NiO cluster in a symmetric bridge binding (Figure 9 e). The Ni₂-C_{CO} and Ni₅-C_{CO} bond lengths are nearly equivalent, at 1.976 Å and 2.000 Å, respectively (Figure 9 e). The charge density difference analysis (Figure 9 f) shows an inverted localization of a negative and a positive isosurface on the O_{CO} and C_{CO} atoms (⁺C=O⁻), respectively, compared to the free CO (⁻C≡O⁺). The CO strongly binds to two Ni in a Ni-CO-Ni



bridge configuration with the binding energy (ΔE_B) approximately 1.57 eV, which is lower than that of the semi-bridge interaction observed in the $(\text{Ni}_2\text{-CO})\text{-2(PHI)}$ system **1**. We performed Bader charge analysis on the $(\text{Ni}_{10}\text{O}_8)\text{-2(PHI)}$ and corresponding $(\text{Ni}_{10}\text{O}_8\text{-CO})\text{-2(PHI)}$ optimized structures to verify whether nickel oxide preserves a positive charge within the periodic framework.⁵² As reported in Table S5, the sums of the Bader charges of nickel and oxygen atoms belonging to the $(\text{Ni}_{10}\text{O}_8)^{4+}$ in the $(\text{Ni}_{10}\text{O}_8)\text{-2(PHI)}$ and $(\text{Ni}_{10}\text{O}_8\text{-CO})\text{-2(PHI)}$ systems were found to be positive, +1.86 $|e|$ and +2.15 $|e|$, respectively, supporting the reliability of our periodic approach. A higher positive charge was observed for both the nickel atoms interacting with CO in the $(\text{Ni}_{10}\text{O}_8\text{-CO})\text{-2(PHI)}$ compared to the same nickel atoms in $(\text{Ni}_{10}\text{O}_8)\text{-2(PHI)}$. The sum of the Bader charges in the CO probe molecule results in being negative, further suggesting $\text{Ni}^{2+} \rightarrow \text{C}\equiv\text{O}^+$ π -backdonation. Overall, these findings indicate a π -backdonation from Ni atoms interacting with the CO molecular probe in a bridge configuration. Additionally, to address the possible residual presence of Ni(OH)_2 nanoparticles, we produced a representative $(\text{Ni}_9\text{(OH)}_{14})\text{-2(PHI)}$ model, selected to have the stable hexagonal β -phase Ni(OH)_2 crystal structure, fitting the PHI pore volume,⁵⁴ and providing a site for CO probe interaction. On this system, we performed DFT+ U simulations to understand the static properties, as reported in the Supporting Information (Figure S16).



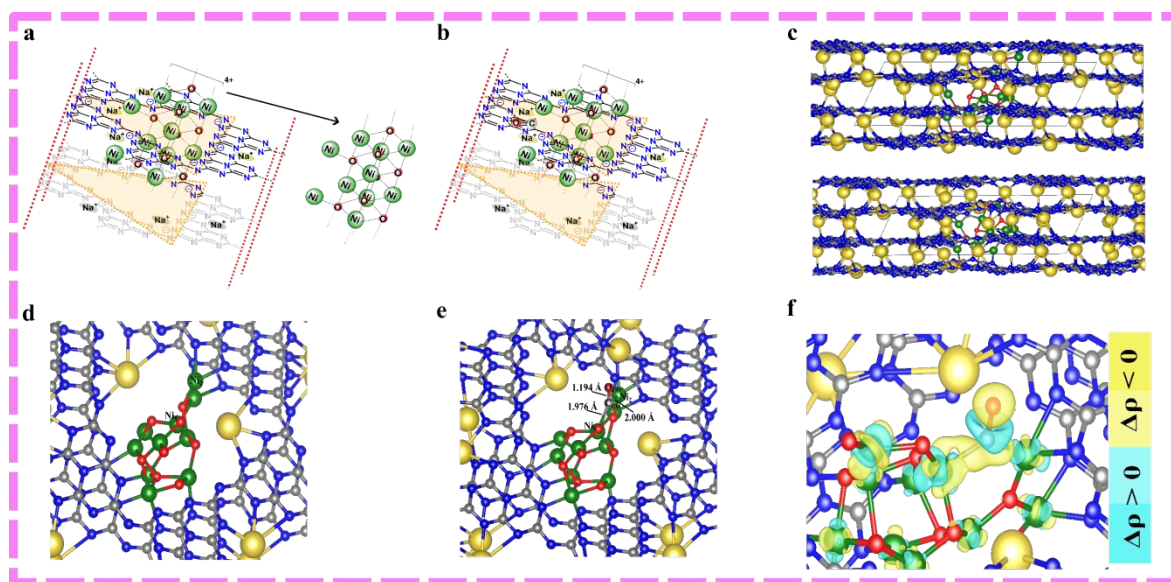


Figure 9. Representative initial idealized 2PHI layers with **a**, a nickel oxide cluster $(\text{Ni}_{10}\text{O}_8)^{4+}$, $(\text{Ni}_{10}\text{O}_8)\text{-}2(\text{PHI})$, and **b**, a nickel oxide cluster $(\text{Ni}_{10}\text{O}_8)^{4+}$ interacting with a carbon monoxide molecular probe, $(\text{Ni}_{10}\text{O}_8\text{-CO})\text{-}2(\text{PHI})$. The orange area describes the catalytically active site with a nickel oxide cluster $(\text{Ni}_{10}\text{O}_8)^{4+}$. The atoms are depicted as ball-and-stick models, with nickel in green, carbon in black, nitrogen in blue, oxygen in red, and sodium in yellow. In color and grey, the upper and bottom, respectively, are PHI layers and sodium cations. The interacting part of the bottom PHI layer with a nickel oxide cluster $(\text{Ni}_{10}\text{O}_8)^{4+}$ is kept colored. **c**, Side views of DFT+ U geometry-optimized $(\text{Ni}_{10}\text{O}_8)\text{-}2(\text{PHI})$, and $(\text{Ni}_{10}\text{O}_8\text{-CO})\text{-}2(\text{PHI})$ systems, top and bottom, respectively. DFT+ U geometry-optimized configurations of **d**, $(\text{Ni}_{10}\text{O}_8)\text{-}2(\text{PHI})$, **e**, $(\text{Ni}_{10}\text{O}_8\text{-CO})\text{-}2(\text{PHI})$, respectively. Highlighted $\text{Ni}_{2.5}\text{-C}_{\text{CO}}$, and $\text{C}_{\text{CO}}\text{-O}_{\text{CO}}$. **f**, DFT+ U charge density difference ($\Delta\rho$) for the $(\text{Ni}_{10}\text{O}_8\text{-CO})\text{-}2(\text{PHI})$ system. Yellow and cyan colors are used to represent the negative and positive charge density differences, respectively, with an isosurface value of 0.01. The atoms are depicted as ball-and-stick models, with nickel in green, carbon in grey, nitrogen in blue, oxygen in red, and sodium in yellow.

2.6 DFT-based Molecular Dynamics Simulations

To further understand the CO-DRIFTS findings shown in Figure 4 and bridge them to a molecular interpretation, DFT-MD serves as an ideal approach for analyzing dynamical effects of the CO interaction with the $(\text{Ni})\text{-}2(\text{PHI})$, $(\text{Ni}_2)\text{-}2(\text{PHI})$ **1**, **2**, and **3**, and $(\text{Ni}_{10}\text{O}_8)\text{-}2(\text{PHI})$ systems as well as following the structural rearrangements of PHI at room temperature. Therefore, five separate



1.25 ps NVT DFT-MD simulations were performed on the previously DFT+*U* optimized isolated CO molecular probe, (Ni-CO)-2(PHI) system, (Ni₂-CO)-2(PHI) systems **1**, **2**, and **3**, and (Ni₁₀O₈)-2(PHI) system (see Computational Methods for details). After an initial 0.25 ps of thermal equilibration, both the temperature and the Kohn-Sham (KS) potential energies stabilized (Figure S17 and Figure S18). The remaining 1.0 ps of each trajectory were used to perform vibrational density of states (VDOS) analysis of the time evolution of the CO bond length stretching (Figure S19), from which the frequency trends were compared with the experimental CO-DRIFTS spectra.⁵⁵ A Gaussian window function with a sigma value of 15 was chosen for each VDOS analysis. The CO stretching frequencies obtained from VDOS, named CO-VDOS, are systematically shifted by $\approx 70\text{--}80\text{ cm}^{-1}$ to higher values compared with the experimental CO-DRIFTS spectra. This baseline shift is inherent to the PBE0-D3 functional, which typically overestimates CO stretching frequencies (Table S3).⁵⁶ Nevertheless, PBE0-D3 reduces delocalization error compared with GGA functionals, such as PBE, providing insightful results.⁵⁷ The CO-VDOS analysis serves as a compass to understand the trend in the CO stretching frequencies observed in the CO-DRIFTS results and to interpret it at the molecular level, rather than to provide simulated CO frequencies for direct comparison with the CO-DRIFTS ones. We analyzed the CO-VDOS of the free CO, which peaks at 2213 cm^{-1} (Figure 10 grey line), consistent with the $\approx 70\text{ cm}^{-1}$ PBE0 shift with respect to the experimental gas-phase frequency of 2143 cm^{-1} .⁵⁶ The (Ni-CO)-2(PHI) system, and the (Ni₂-CO)-2(PHI) systems **2** and **3** exhibit CO-VDOS blue-shifted to higher frequencies around 2260 cm^{-1} (Figure 10 black, red, and green lines) compared to the free CO, indicating that the CO bond remains strongly polarized, oscillating at shorter values than the free CO (Figure S19). These CO-VDOS frequencies, after accounting for the systematic PBE0 overestimation of $\approx 70\text{--}80\text{ cm}^{-1}$, agree well with the CO-DRIFTS peaks at 2190 cm^{-1} for



low nickel concentrations (0.5 wt% and 1 wt%), as shown in Figure 4, where Ni-CO linear σ -bond interaction is suggested. In contrast, the CO-VDOS for (Ni₂-CO)-2(PHI) system **1** is red-shifted compared to the free CO (Figure 10 blue line). This CO-VDOS frequency, ranging around 2150 cm⁻¹, shows close agreement with the CO-DRIFTS results in the range of 2000-2080 cm⁻¹ for high nickel loadings (2 wt% and 4 wt%) displayed in Figure 4, once the intrinsic PBE0 frequency shift (≈ 70 –80 cm⁻¹) is taken into account. The CO bond length fluctuates to larger values than the free CO (Figure S19), pointing out a less polarized bond in line with the shift to lower frequencies. Interestingly, during the DFT-MD of (Ni₂-CO)-2(PHI) system **1**, the PHI layers exhibited a larger stacking shift relative to (Ni)-2(PHI) system, and (Ni₂-CO)-2(PHI) systems **2** and **3** (Figure S20). This stacking movement in (Ni₂-CO)-2(PHI) system **1** at 1.25 ps introduces a third nitrogen atom from the PHI framework into interaction with Ni²⁺ positioned farthest from the CO (Figure S21 b), thereby stabilizing the configuration energetically compared to systems **2** and **3** (Figure S18). In this arrangement, the CO bond length in (Ni₂-CO)-2(PHI) system **1** continues to oscillate at larger values compared to (Ni)-2(PHI) system, and (Ni₂-CO)-2(PHI) systems **2** and **3** (Figure S19). For system **1**, the semi-bridge Ni-CO-Ni bond lengths fluctuate during the DFT-MD trajectory from 2.01 Å and 3.88 Å at 0.25 ps, 1.86 Å and 3.14 Å at 0.5 ps, 1.94 Å and 2.44 Å at 0.75 ps, 1.86 Å and 3.94 Å at 1.0 ps, and 1.87 Å and 3.53 Å at 1.25 ps (Figure S21 b and Figure S22). In the NiO-nanoparticle representative model with the CO molecular probe, (Ni₁₀O₈-CO)-2(PHI), the CO-VDOS results in a broad and bimodal curve with two peaks around 2150 cm⁻¹ and 2000 cm⁻¹ (Figure 10 pink line), respectively, red-shifted with respect to the free CO. This broad CO-VDOS, considering the PBE0-based offset of ≈ 70 -80 cm⁻¹, is found in agreement with the CO-DRIFTS ones within the range of 2080-2000 cm⁻¹ at high nickel loading (2 wt% and 4 wt%) reported in Figure 4. This CO-VDOS curve behaviour arises from the dynamic movement of the CO molecular



probe, changing the type of interactions within the NiO-nanoparticle surface, from a Ni-CO-Ni bridge to a semi-bridge configuration (Figure S21 and Figure S22). The Ni-CO-Ni bond lengths oscillate during the DFT-MD trajectory from 2.01 Å and 2.12 Å at 0.25 ps, 2.00 Å and 2.01 Å at 0.5 ps, 2.00 Å and 2.39 Å at 0.75 ps, 1.77 Å and 3.96 Å at 1.0 ps, and 1.71 Å and 3.82 Å at 1.25 ps (Figure S21 and Figure S22). The presence of NiO-nanoparticles can provide stable Ni-CO-Ni interactions, alternating from a bridge to a semi-bridge type, while in both the π -backdonation $\text{Ni}^{2+} \rightarrow \text{C}\equiv\text{O}^+$ is likely retained with different magnitudes. The employment of DFT-MD simulations offers valuable insight to understand the dynamic interactions of Ni^{2+} and NiO within the PHI layers and with the CO molecular probe at room temperature, where thermal fluctuations play a decisive role in sampling different stable configurations along the potential energy surface.

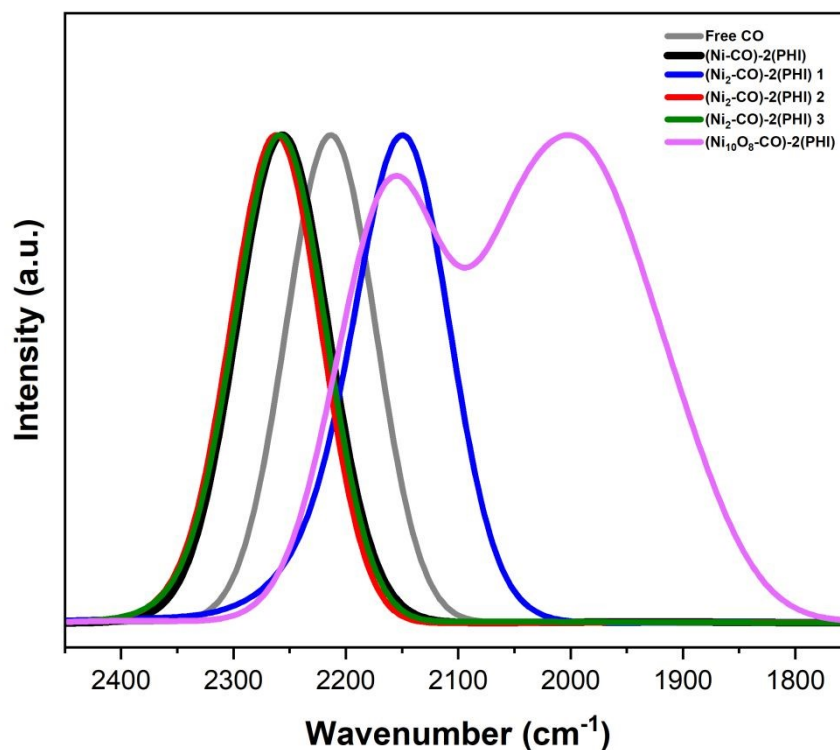


Figure 10. Computational CO-VDOS analysis, with intensity in arbitrary units (a.u.) and frequencies (in cm^{-1}). The computational CO-VDOS are extracted from the CO molecular probe distance in the last 1.0 ps of each separate NVT DFT-MD for the free CO molecular probe, (Ni-CO)-2(PHI) system, (Ni₂-CO)-2(PHI) systems **1**, **2**, and **3**, and (Ni₁₀O₈-CO)-2(PHI) in grey, black, blue, red, green, and pink solid lines, respectively.

3 CONCLUSIONS

In this study, we effectively integrated experimental and multiscale computational investigations to resolve the structure of the Ni-based poly(heptazine imide) crystalline carbon nitride (Ni-PHI). The CO-DRIFTS measurements reveal that, at low nickel loadings (0.5-1 wt%), CO preferentially binds linearly to isolated Ni²⁺ single sites, whereas increasing nickel content (2–4 wt%) promotes the formation of nickel aggregates such as Ni(OH)₂/NiO nanoparticles, leading to the emergence of bridge-bonded Ni-CO-Ni species and a progressive red shift of the CO-DRIFTS stretching frequencies. DFT-based static and DFT-MD simulations consistently reproduce the CO-DRIFTS spectroscopic trends via CO-VDOS frequency analysis and provide molecular-level understanding of the evolution of CO bonding. The simulations demonstrate that increased nickel aggregation enhances π -backdonation from Ni to CO, weakening the C-O bond and stabilizing bridge and semi-bridge Ni-CO-Ni interaction-like configurations. Thermal fluctuations captured by DFT-MD further highlight the dynamic nature of Ni coordination and PHI layer rearrangements at room temperature. Notably, recent research on M-PHI has reported enhanced catalytic activity arising from the synergy between single-atom centers and nanoparticles.^{58,59} Overall, this combined experimental–computational approach establishes a coherent structural picture linking nickel loading to the transition from isolated Ni²⁺ single-atom sites to nanoparticle-like catalytic environments in Ni-PHI. This work provides important molecular insight into the catalytic site structure of Ni-PHI and introduces a transferable experimental–computational strategy for



investigating the catalytic sites in various M-PHIs, thereby supporting the rational design of M-PHIs for surface and single-atom catalysis.

4 EXPERIMENTAL and COMPUTATIONAL METHODS

4.1 Experimental Methods: Ni-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. Cation exchange was conducted by dispersing PHI into aqueous nickel solutions at varying concentrations. The suspension was subjected to ultrasonic treatment for 30 minutes, followed by centrifugation to separate the solid. The recovered material was then dried at 80 °C overnight.

4.2 Experimental Methods: Ni-PHI Characterization: X-Ray Diffraction (XRD)

The Na-PHI precursor and the Ni-PHI materials were characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer equipped with a Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$).

4.3 Experimental Methods: Ni-PHI Characterization: High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) Imaging

HAADF-STEM images were acquired using a Thermo Fisher Scientific Titan Cubed Themis (TEM-Titan) equipped with a cold-field emission gun and double Cs aberration correction, operated at 300 kV, with a probe convergence semi-angle of 25 mrad. For sample preparation, the catalyst was suspended in 2-propanol, dispersed using ultrasonication for 10 min, and then deposited onto a Cu holey carbon TEM grid.



4.4 Experimental Methods: CO Adsorption Probing via Diffuse Reflectance Infrared Fourier Transform Spectroscopy (CO-DRIFTS)

The CO-DRIFTS analysis was performed using a Nicolet iS50 FTIR spectrometer equipped with a Praying Mantis accessory and a Harrick reaction cell. The sample was pretreated at 300 °C under a He flow (20 mL min⁻¹) for 10 min. After cooling to room temperature, a reference spectrum (baseline) was recorded under He prior to CO exposure. CO was then introduced for 10 min (with the He flow temporarily stopped), followed by a He purge for 15 min to remove physisorbed species, after which a post-desorption spectrum was collected. All spectra presented in this work correspond to difference spectra (Δ DRIFTS), obtained by subtracting the baseline spectrum from the post-desorption spectrum (Figure S23). This baseline subtraction allows isolating the vibrational features specifically associated with CO adsorption and its interaction with Ni sites. Spectra were recorded with a resolution of 1 cm⁻¹ and averaged over 256 scans.

4.5 Computational Methods: DFT and DFT+U Static Simulations

Spin-polarized DFT and DFT+*U* were carried out by using the Vienna Ab initio Simulation Package (VASP).⁶⁰ The projector-augmented wave (PAW) pseudopotential and the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional with generalized gradient approximation (GGA) were considered to describe the interactions between valence electrons and ionic cores and the exchange–correlation effects, respectively.^{61,62} The kinetic cutoff energy was set to 400 eV for the wave function calculation. The lattice parameters *a*, *b*, *c*, and α , β , γ of the simulation cell are 26.081 Å, 26.081 Å, 8.504 Å, and 98.1°, 112.1°, 119.8°, respectively, as represented in Figure S6. The vacuum gap of ~1.80 Å was chosen to account for interactions between the system and its mirror images, based on the crystal structure.²⁰ The bulk model takes into consideration the multilayered disorder nature of the PHI framework,⁶³ also during the CO molecular probe



interaction. The van der Waals interaction was described by the Grimme *et al.* D3 dispersion correction.⁶⁴ The convergence criteria were set to be 1×10^{-5} eV for energy change and 0.05 eV \AA^{-1} for force change during the geometrical optimization. To accurately describe and compare the Ni properties, we performed DFT+*U* calculations. The Hubbard correction was applied to the Ni element, with a *U*-value of 3.40 eV, in agreement with previous literature and benchmarks.^{27,45,46} The charge density difference analysis was performed using the VASPKIT code.⁶⁵ The benchmark of the periodic system calculations with total net charge zero was carried out using molecular complexes such as $[\text{Ni}-(\text{melem})_2]^{2+}$ and $[(\text{Ni-CO})-(\text{melem})_2]^{2+}$ through spin-polarized (unrestricted) DFT calculations with the Gaussian 16 code.⁶⁶ We employed the PBE0-D3 hybrid functional,^{67,68} for the optimization and frequency calculations, using the 6-31++G(d, p) basis set with diffuse functions for all atoms.^{69,70} For the $(\text{Ni}_{1\text{or}2}\text{-CO})\text{-}2(\text{PHI})$ geometry optimizations, the CO molecular probe was placed in proximity of each nickel atom, at $\text{Ni}_{1\text{or}2}\text{-C}_{\text{CO}}$ distance $d(\text{Ni}_{1\text{or}2}\text{-C}_{\text{CO}}) \approx 2 \text{\AA}$, and in the two positions with respect to the nickel atoms, along the x-y and z planes, respectively (Figure S8). On these structures, we performed DFT and DFT+*U* geometry optimizations at the GGA level described above. Successively, the Ni-CO binding energies (ΔE_{B}) were estimated for each $\text{Ni}_{1\text{or}2}$ and NiO-nanoparticle systems ($\text{Ni}_{\text{system}}$) as the difference: $\Delta E_{\text{B}} = E_{(\text{Ni}_{\text{system}}\text{-CO})\text{-}2(\text{PHI})} - E_{\text{Ni}_{\text{system}}\text{-}2(\text{PHI})} - E_{\text{CO}}$, performing on each optimized $(\text{Ni}_{\text{system}}\text{-CO})\text{-}2(\text{PHI})$ system separate single-point calculations on $(\text{Ni}_{\text{system}}\text{-CO})\text{-}2(\text{PHI})$, and its components $\text{Ni}_{\text{system}}\text{-}2(\text{PHI})$ and CO, respectively.

4.6 Computational Methods: DFT-based Molecular Dynamics Simulations

The spin-polarized (unrestricted) DFT-MD NVT simulations were carried out using periodic boundary conditions (PBC) and with the hybrid Gaussian and plane wave approach,⁷¹ as implemented in the CP2K/Quickstep code.⁷² The spin multiplicity employed is singlet for (Ni)-



2(PHI) system, and quintet for (Ni₂-CO)-2(PHI) systems **1**, **2**, and **3**, and also for the (Ni₁₀O₈)-2(PHI) system, noting that for the latter the multiplicity is an imposed constraint to maintain consistency with the two-Ni reference systems, since at room temperature a small NiO-nanoparticle surface is likely highly paramagnetic.⁷³ The Kohn-Sham (KS) orbitals were described by an accurate molecularly optimized double-zeta basis set with one additional set of polarization functions (DZVP-MOLOPT-GTH), while the charge density was represented by plane waves with a density cutoff of 600 Ry.⁷⁴ Separable norm-conserving pseudopotentials were used to mimic the interactions between the valence electrons and the ionic cores.^{75,76} The PBE0 hybrid functional was employed because it has been shown to be highly accurate in describing transition-metal complexes and is suggested for describing CO vibrations when CO interacts with Ni²⁺ ion(s).^{27,67,68} The damped D3 atom-pairwise Grimme *et al.* dispersion correction was added to account for long-range van der Waals interactions.⁶⁴ A Nosé-Hoover chain (NHC) thermostat was used, with a length of the Nose-Hoover chain, time constant of the thermostat chain of 7 and 10 fs, respectively, and the time step and temperature were 0.5 fs and 300 K, respectively.

AUTHOR CONTRIBUTIONS

D.C., I.F.T., A.K., and T.D.K. conceived the idea to study computationally and experimentally the Ni-PHI catalytic site structures. D.C. performed the DFT-based static and MD simulations and analyzed and interpreted all the simulations. D.C. coordinated the project. D.C. wrote the manuscript with the help of all authors. I.G.F. and D.N.B. performed the synthesis, XRD and EDS characterization, and CO-DRIFTS analysis. L.F.G.N. collected and analyzed the HAADF-STEM data. M.A.R.d.S. performed and interpreted the XPS characterization. T.D.K. and A.K. supervised the computational work. I.F.T. supervised the experimental work.

SUPPORTING INFORMATION



The Supporting Information includes additional computational and experimental analysis: S1. Characterization of Ni-PHI; S2. Computational Results on Ni_{1or2}-2(PHI) and (Ni_{1or2}-CO)-2(PHI): DFT-based Static Simulations; S3. Computational Results on a NiO/Ni(OH)₂-Nanoparticle Representative Models: DFT-based Static Simulations; S4. Computational Results: DFT-based Molecular Dynamics Simulations.

DATA AVAILABILITY

The computational metadata, including DFT-based static and DFT-MD data, and the plots' raw data are provided as supporting material, openly available in the ZENODO EU Open Research Repository at <https://doi.org/10.5281/zenodo.19814862>. All the rest of the data will be available upon a reasonable request.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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