

Supplementary Information

Diaquabis(*L*-phenylalaninato)nickel(II) Encapsulated in Zeolite: An Efficient Heterogeneous Catalyst System for the Oxidation of Cyclohexene, Toluene and Ethyl Benzene

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Comparison of the Fourier transform infrared (FTIR) spectra of the free ligand and its Ni²⁺ complex (Figure S1a and S1b, respectively), offers the evidence for the coordination mode of the ligand.

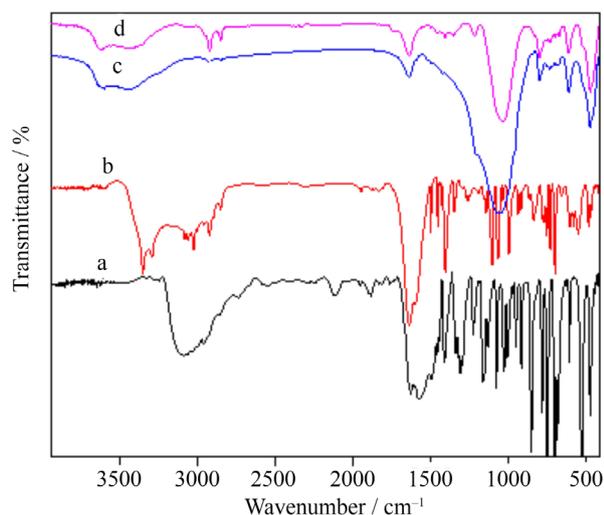


Figure S1. FTIR spectra of (a) phenylalanine, (b) [Ni(Phe)₂(H₂O)₂], (c) Na/Y, (d) [Ni(Phe)₂(H₂O)₂]/Y

The coordination mode of the carboxylate group can be determined according to the correlation reported,¹ where the value of the relation $\Delta\nu(\text{COO}) = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$, following the order: $\Delta\nu$ monodentate (much longer than $50 \text{ cm}^{-1} \approx 250$) > $\Delta\nu$ ionic $\approx \Delta\nu$ bridging > $\Delta\nu$ chelate (less than 50 cm^{-1}). The band assigned to the ν_{as} COO group vibrations is found at 1635 cm^{-1} for phenylalanine and at 1645 cm^{-1} for the complex. The $\nu_{\text{s}}(\text{COO})$ vibration frequency equals 1505 cm^{-1} for *L*-phenylalanine, while for the complex the ν_{s} vibration is found as a doublet with components centered at 1454 and 1404 cm^{-1} . The

magnitude of separation $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$ for the complex is 191 cm^{-1} . Hence, $\Delta\nu(\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO}))$ is $191\text{--}225 \text{ cm}^{-1}$, characteristic of monodentate coordination of the carboxylate group.¹

Also, strong to medium bands at ca. 467 and ca. 550 cm^{-1} are attributed to $\nu(\text{M-N})$ and $\nu(\text{M-O})$, respectively, for the complex.¹

FTIR spectroscopy provides information on the integrity of the encapsulated complexes, in addition to the crystallinity of the host zeolite. The IR bands of encapsulated complexes are weak owing to their low concentration in the zeolite, and hence can only be observed in the regions where the zeolite matrix does not absorb, i.e., from 1200 to 1640 cm^{-1} . Also it can be seen that considerable bands at about $2858\text{--}2928$, 3090 and 3370 cm^{-1} in the [Ni(phe)₂(H₂O)₂]/Y spectra are assigned to aliphatic C-H, aromatic C-H and N-H vibrations of the ligand. In contrast, these bands were lacking in the case of the Na/Y sample. In addition, the observed band at 1634 cm^{-1} is related to the bending vibration of H₂O molecules in the zeolite lattice in all spectra. As shown in Figures S1c, S1d, and S2A and S2C, the wavenumber shifts and relative intensity changes of the vibration bands show significant guest/host interactions. Actually, some changes in band intensities can be observed in the region of the N-H stretching vibration (at 3370 cm^{-1}). These observations not only verify the presence of the nickel(II) complex in the zeolite, but are also attributed to interactions with the zeolite matrix.

The X-ray powder diffraction (XRD) analysis of Na/Y and the [Ni(phe)₂(H₂O)₂]/Y encapsulated compounds were recorded at 2θ values between 5 and 50° to study the crystallinity and to confirm encapsulation (Figure S3).

The encapsulated complex exhibits similar peaks to those of zeolite Y; excepting a slight change in the intensity of the peaks, no new crystalline pattern emerges.

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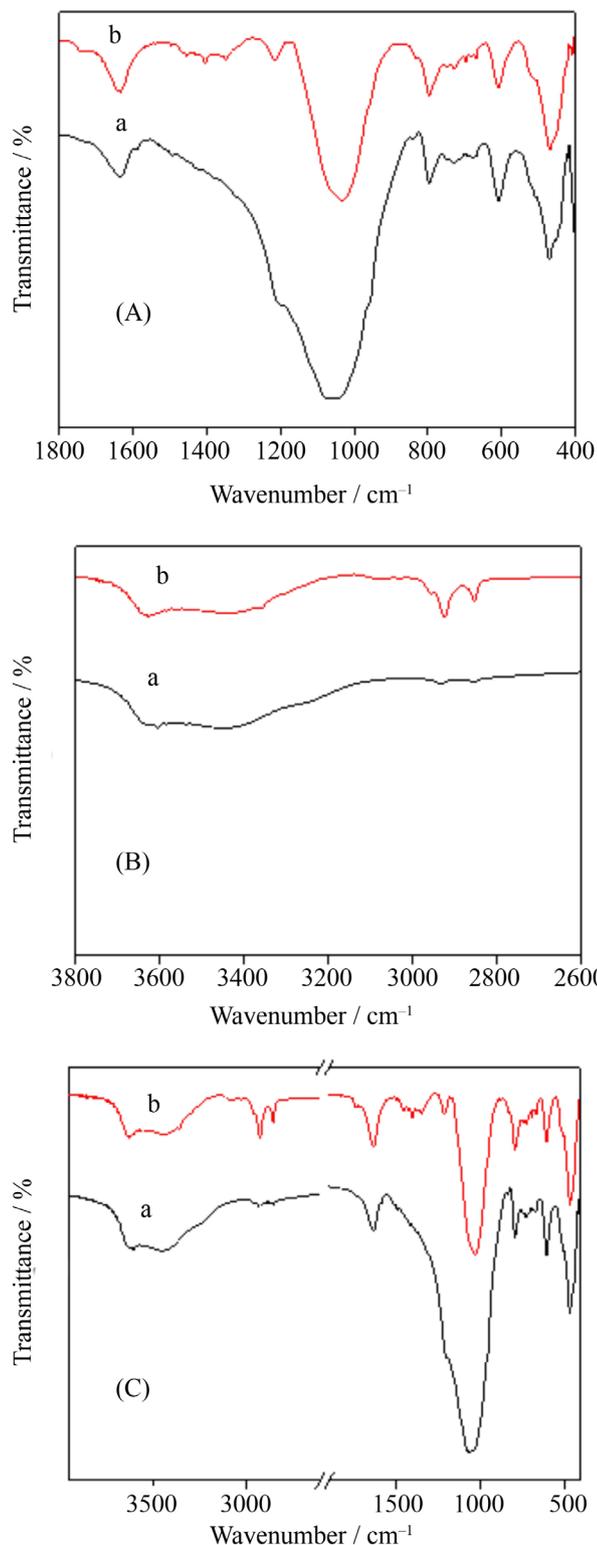


Figure S2. FTIR spectra of a) Na-Y, b) [Ni(Phen)₂(H₂O)₂]/Y at (A) 1800-400 cm⁻¹; (B) at 3800-2600 cm⁻¹; and (C) at 4000-500 cm⁻¹ with a break from 2600-1800 cm⁻¹.

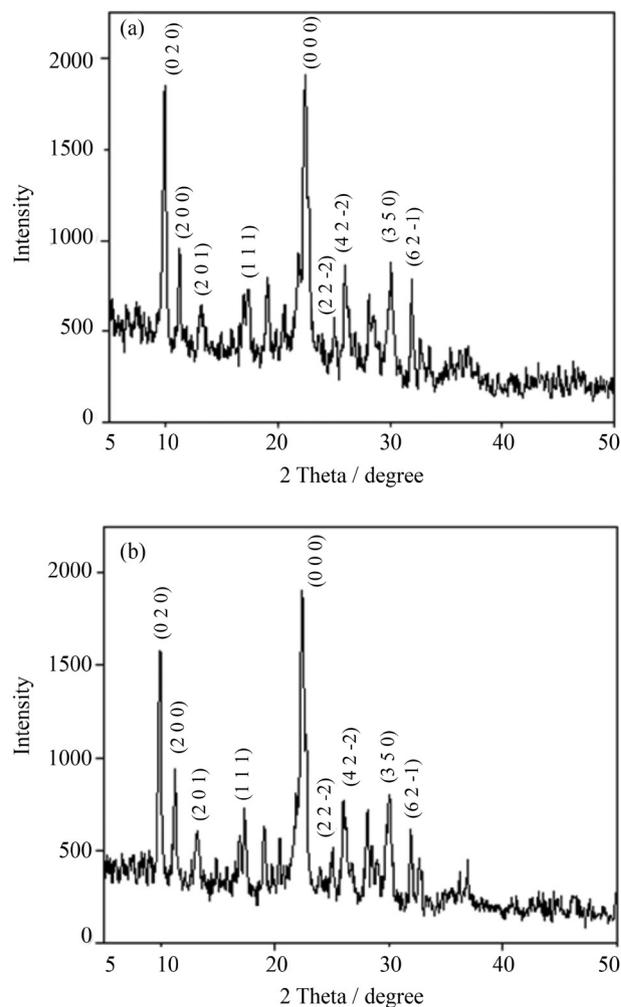


Figure S3. XRD spectra of (a) zeolite, (b) [Ni(Phen)₂(H₂O)₂]/Y.

The relative peak intensities of the (0 2 0), (2 0 0) and (2 0 1) reflections have been thought to be correlated to the locations of cations. Upon exchanging the metal or after, the encapsulation process affects the relative peak intensities of the (2 0 0) and (0 2 0) peaks.

Because of low percentage loading of metal complex, any new phases and peaks in diffractograms were not detected.

Reference

1. Nakamoto, K.; *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1986.