

Supplementary Material

Porous Hexacyanometallate(III) Complexes as Catalysts in the Ring-Opening Copolymerization of CO₂ and Propylene Oxide

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Abstract: In this work, six porous hexacyanometallate complexes (Ni₃[Co(CN)₆]₂, Co₃[Co(CN)₆]₂, Fe₃[Co(CN)₆]₂, Ni₃[Fe(CN)₆]₂, Co₃[Fe(CN)₆]₂, Fe₄[Fe(CN)₆]₂) were synthesized by a complexing agent assisted coprecipitation method and thoroughly characterized via X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), in situ high-temperature X-ray diffraction (HT-XRD), elemental analysis (EA), X-ray fluorescence (XRF), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂ physisorption, and gas–solid phase titration with NH₃. The thermal stability, chemical composition, pore size and volume, crystallite size and density of surface acid sites were strongly sensitive to both the transition metal and the cyanometallate anion employed. On that basis, transition metal hexacyanometallates must be perceived as an adaptable class of zeolite-like microporous materials. The catalytic properties of these compounds were tested by copolymerization of propylene oxide and CO₂, a green route to obtain biodegradable aliphatic polycarbonates. All compounds under study showed moderate activity in the target reaction. The obtained copolymers were characterized by modest CO₂ content (carbonate units ranging from 16 to 33%), random structure (R_{PEC} ≈ 70%), and moderate molecular weight (M_w = 6000–85,400 g/mol) with broad dispersity values (Đ_M = 4.1–15.8).

Keywords: microporous materials; zeolite-like materials; transition metal hexacyanometallates; CO₂ utilization; copolymerization; biodegradable polymers

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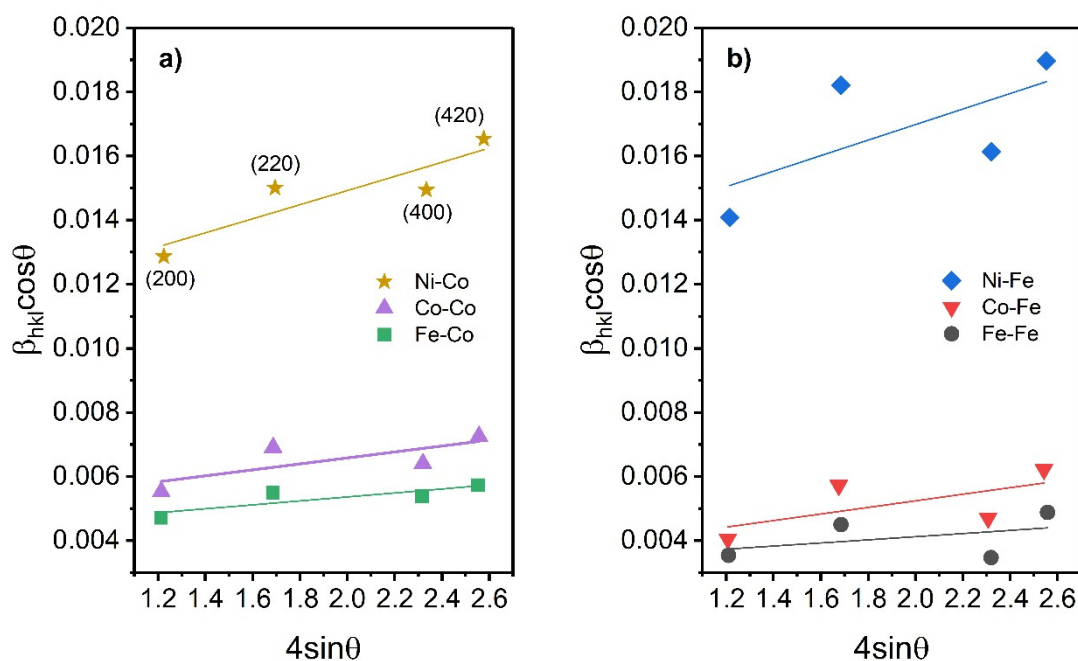


Figure S1. Williamson-Hall plot for (a) T-Co and (b) T-Fe compounds. Continuous lines represent the straight line fit to the data.

The Williamson-Hall (W-H) method was employed to estimate the crystallite size of the porous hexacyanometallates(III). The W-H method takes into consideration peak broadening due to lattice strain, so it is especially useful in inherently disordered and nanosized materials like the hexacyanometallates(III) here considered. The W-H equation adopts the form [80]:

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad (\text{S1})$$

where β_{hkl} : instrumental broadening, K : shape factor (0.9), λ : wavelength of $\text{CuK}\alpha$, D : effective particle size, and ε effective strain. The W-H plot is a plot of $\beta_{hkl} \cos \theta$ vs. $4 \sin \theta$. Data is fit to a straight line. While the effective strain value is determined from the slope of the straight line, the crystallite size is calculated from the y-intercept.

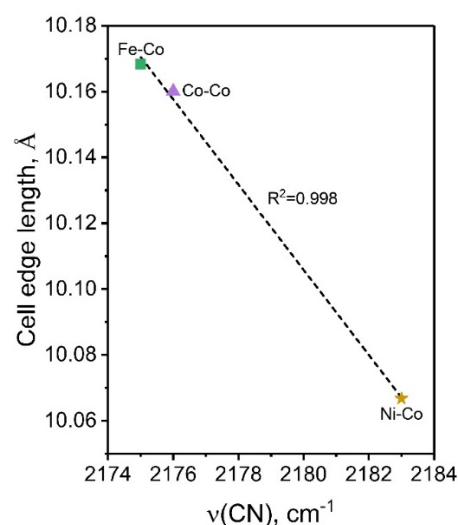


Figure S2. Relationship between unit cell edge length and $\nu(\text{CN})$ band in cyanocobaltates.

The linear relationship that exists for the hexacyanocobaltate(III) complexes ($T_3[Co(CN)_6]_2$) between cell edge length and the frequency of the $\nu(CN)$ band indicates that the length of the $T-N\equiv C-Co$ chain is determined by the strength of the interaction between the CN^- group and the transition-metal cations. These results implicate that the pore width of cubic hexacyanocobaltates can be easily tuned by selecting the appropriate outer transition-metal cation (T). Outer transition-metal cations with higher electronegativity will lead to lower cell edge length, that is to say, to lower pore width.

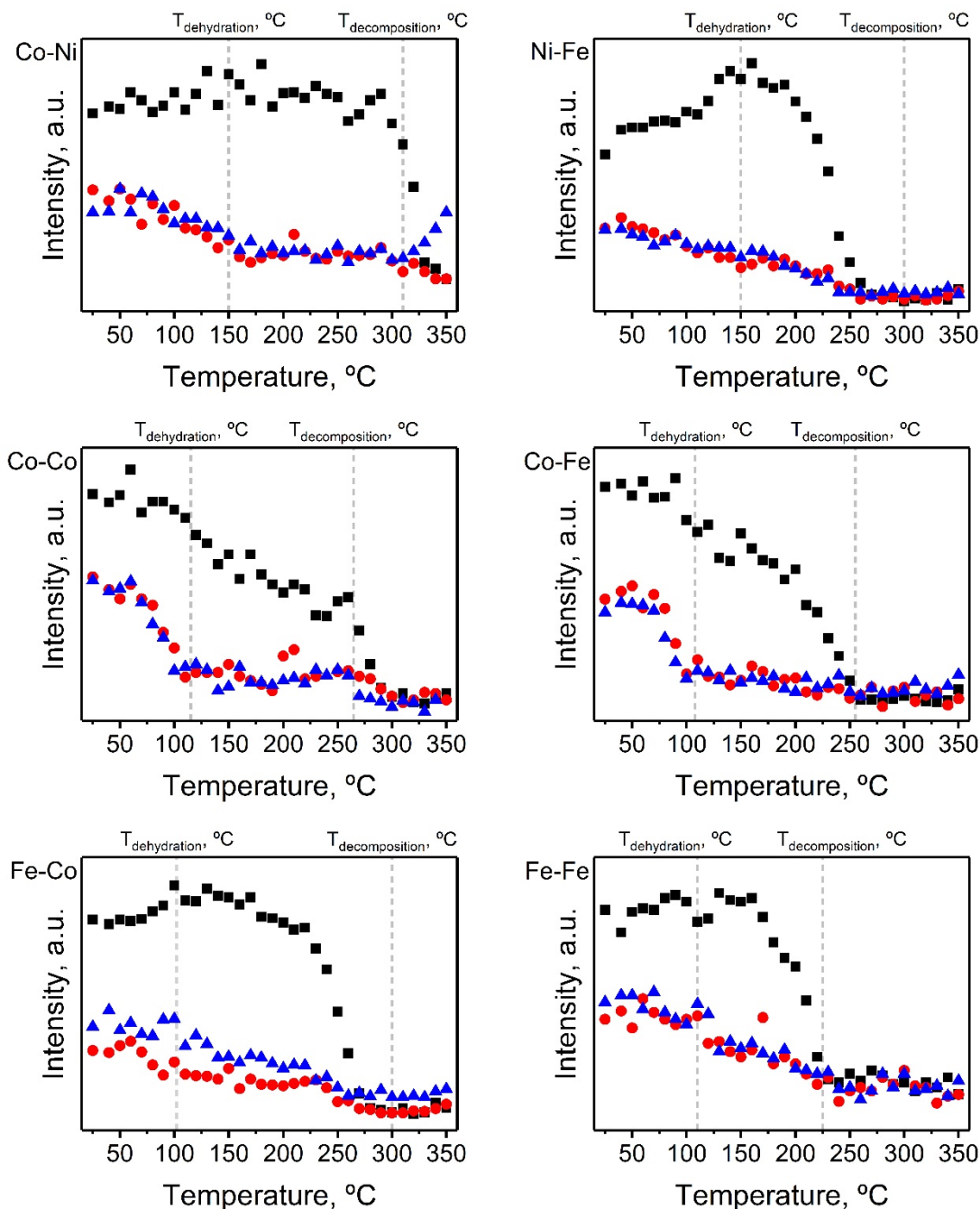


Figure S3. Evolution of main hexacyanometallates(III) XRD peaks intensity with temperature. (■ $2\theta \approx 17.5^\circ$ (200), ● $2\theta \approx 24.9^\circ$ (220), ▲ $2\theta \approx 35.4^\circ$ (400)).

XRD peaks intensity decreases rapidly upon heating, which evidences a partial collapse of the hexacyanometallates(III) framework due to the loss of structural water. The peak at $2\theta = 17.5^\circ$, corresponding to the crystallographic plane (200), can be observed with

appreciable intensity until the decomposition, which indicates that the structure maintains part of its cubic identity.

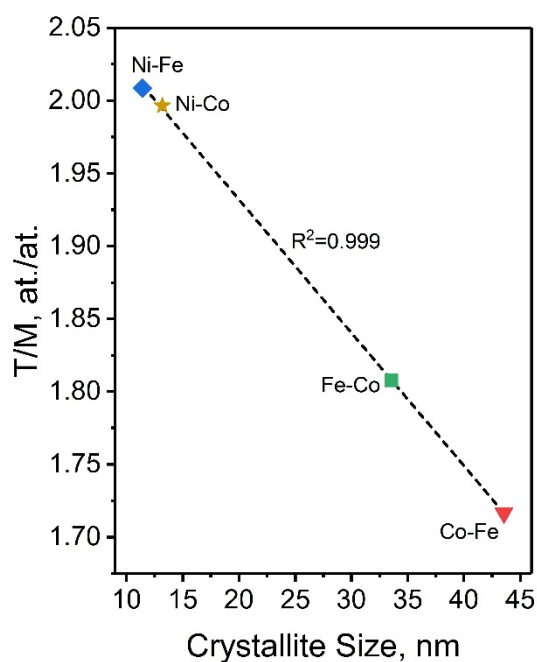


Figure S4. Relationship between T/M atomic ratio and crystallite size in the studied porous hexacyanometallates(III).

For the studied porous hexacyanometallates(III), the atomic ratio between the outer (T) and the inner (M) transition-metal cations follows a linear increase with decreasing crystal size. This proves the increase in the number of exposed surface T atom with increasing the surface to volume ratio and shows the ability to modulate the density of active sites by controlling the crystallite size of the complexes.

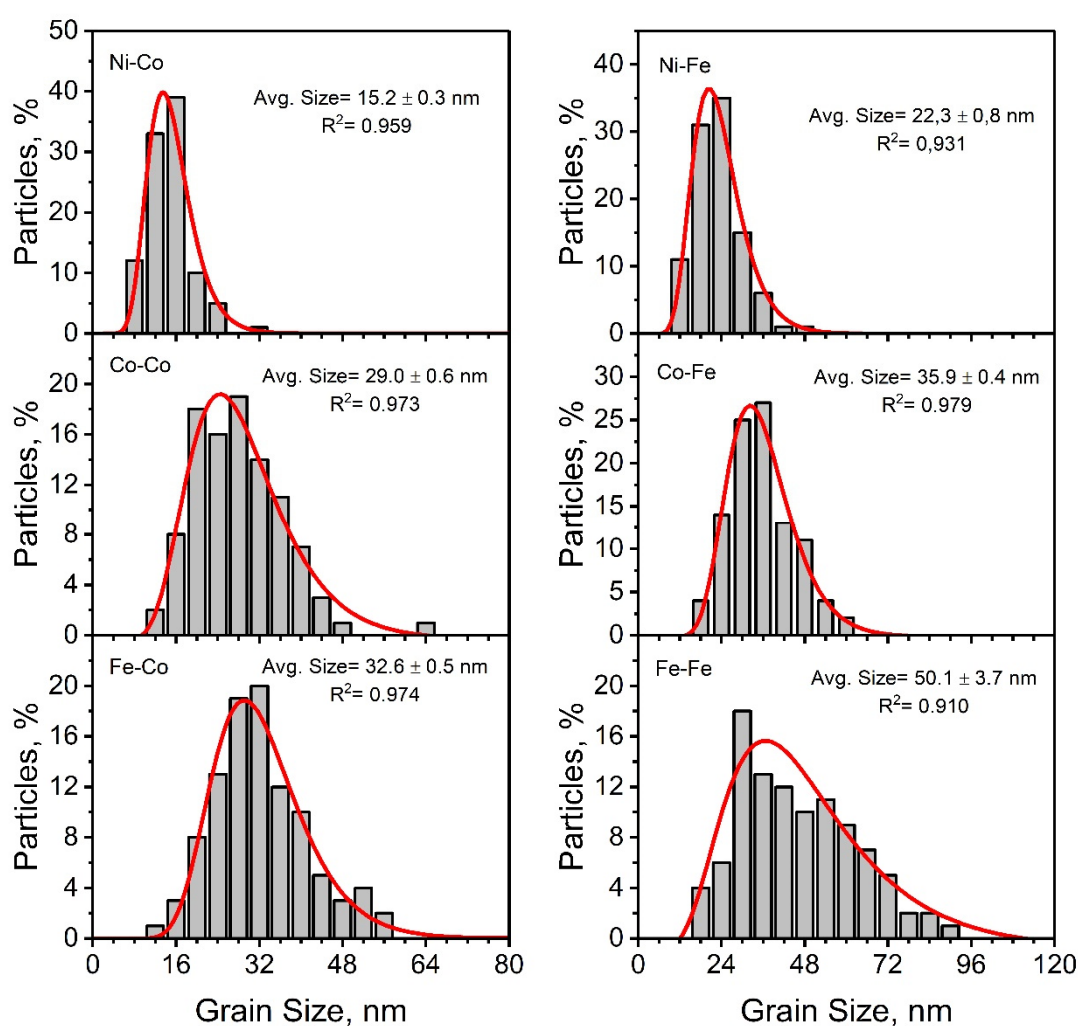


Figure S5. PSD of the studied porous hexacyanometallates(III).

Primary particle size distribution (PSD) was determined from TEM micrographs using the software ImageJ. More than 100 particles were counted. Samples show narrow distributions with grain sizes in the nano-range. The crystallite size is also influenced by the combination of the outer ($\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+}$) and inner ($\text{Co}^{3+} < \text{Fe}^{3+}$) transition-metal cations.

Table S1. Parameters for the Dubinin-Asthakov equation.

Compound	$S_{D-A}^a, \text{m}^2/\text{g}$	$E_0, \text{kJ/mol}$	$V_p, \text{cm}^3/\text{g}$	n	$n_p, \text{cm}^3/\text{g STP}$
Ni-Co	410	34.9	0.146	1.91	94.3
Co-Co	914	27.8	0.325	1.58	210.0
Fe-Co	868	24.0	0.309	1.51	199.5
Ni-Fe	182	37.5	0.065	1.45	41.8
Co-Fe	751	26.1	0.267	1.35	172.6
Fe-Fe	274	17.8	0.097	1.27	63.0

a: Apparent surface area quantified from the amount of N_2 required to fill the micropores.

The Dubinin-Asthakov (D-A) method is a recurrently used procedure for the evaluation of the adsorption capacity in microporous materials. It has been employed in the study of zeolites, carbons, cyanometallates and related materials. N_2 adsorption data were fitted to the D-A equation [86]:

$$n_{ads} = n_p \cdot \exp \left\{ - \left[\frac{R \cdot T}{E_0} \ln \left(\frac{P}{P_0} \right) \right]^n \right\} \quad (S2)$$

where n_{ads} : amount adsorbed at relative pressure P/P_0 and temperature T , n_p : the limiting micropore volume, E_0 : the characteristic energy of adsorption, n : the heterogeneity parameter, R : the universal gas constant; and T is the absolute temperature. The model was adjusted to the experimental data using a non-linear least squares fitting. For calculations, n_p and E_0 values were first estimated using the Dubinin-Radushkevich (D-R) method ($n=1$).

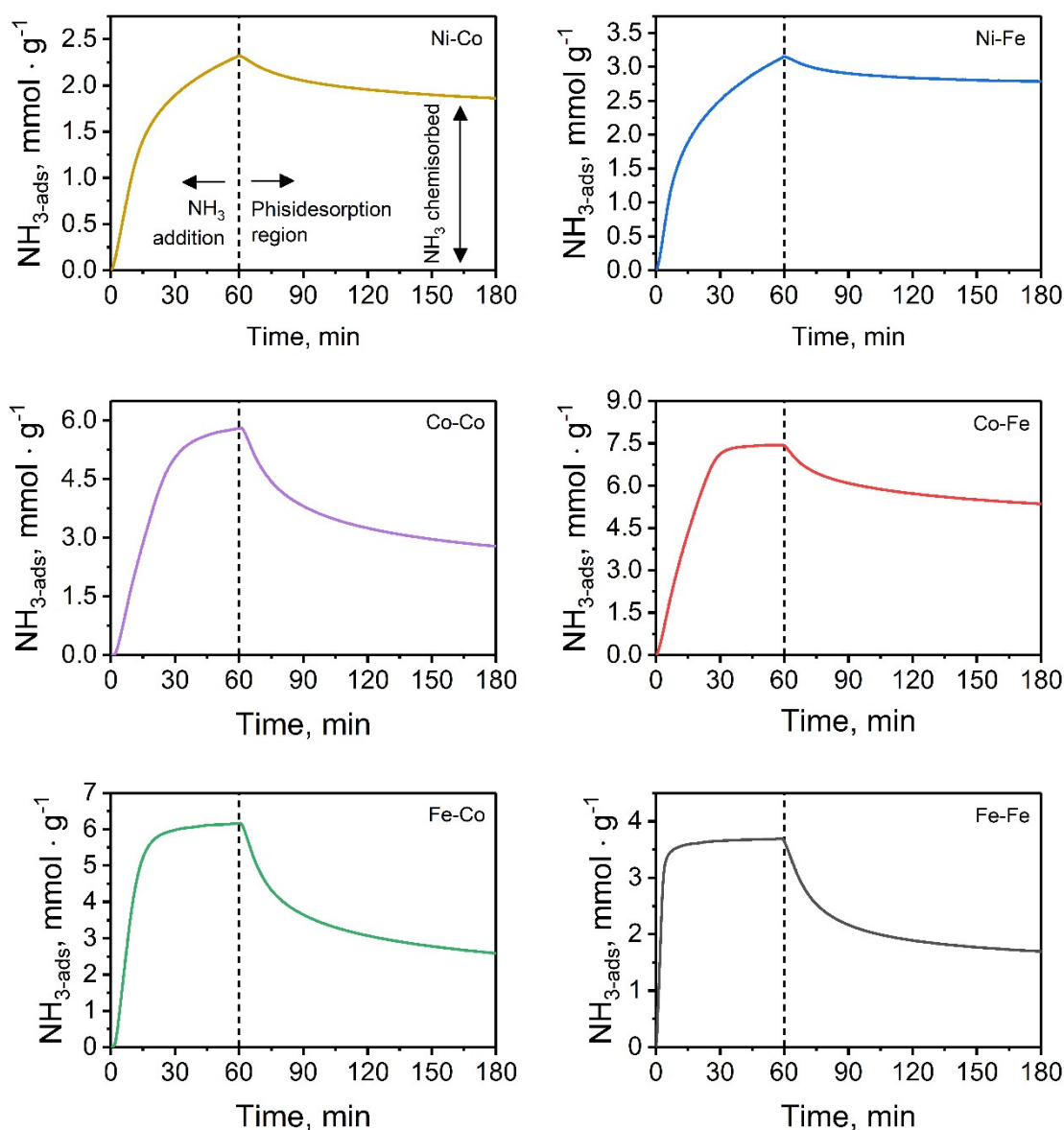


Figure S6. NH_3 -saturation curves of the different porous hexacyanometallates(III) studied.

The density of coordinatively unsaturated metal sites (CUMSs) or Lewis acid sites (LASs) was measured by gas-solid titration with NH_3 . Experiments were carried out in a TG equipment. Initially, a stream containing NH_3 was fed to the furnace and a weight gain was observed as NH_3 was adsorbed. After an hour, the furnace feed was switched to an inert atmosphere (He) so that the physisorbed NH_3 could be released. The total amount

of NH_3 chemisorbed was measured gravimetrically from the weight gain of the sample at the end of the physidesorption step.

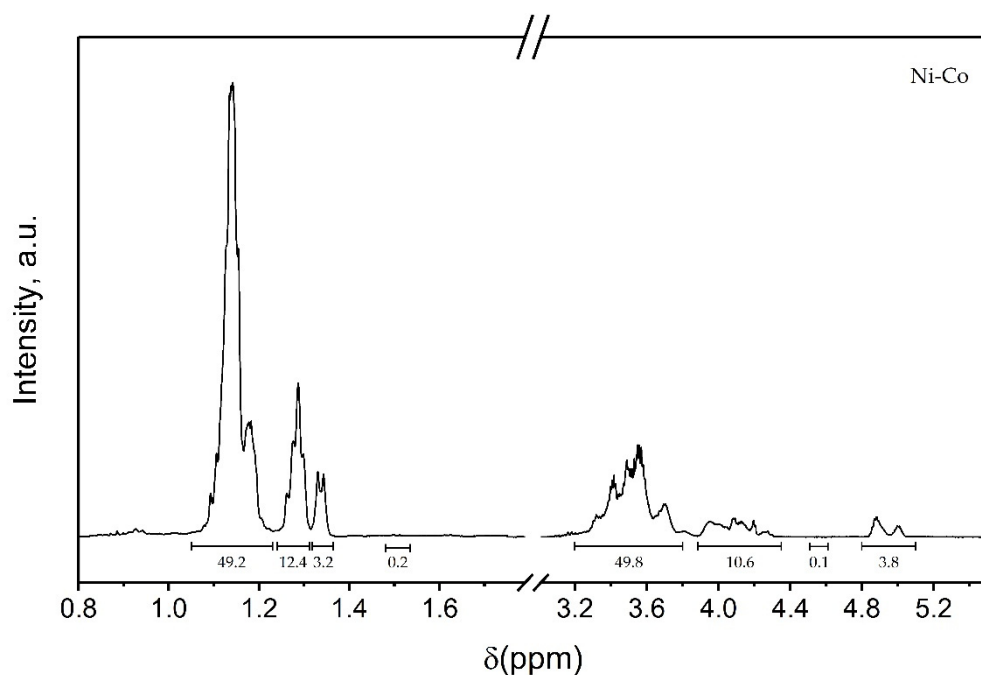


Figure S7. Detailed ^1H -NMR spectrum for the product obtained employing the Ni-Co complex.

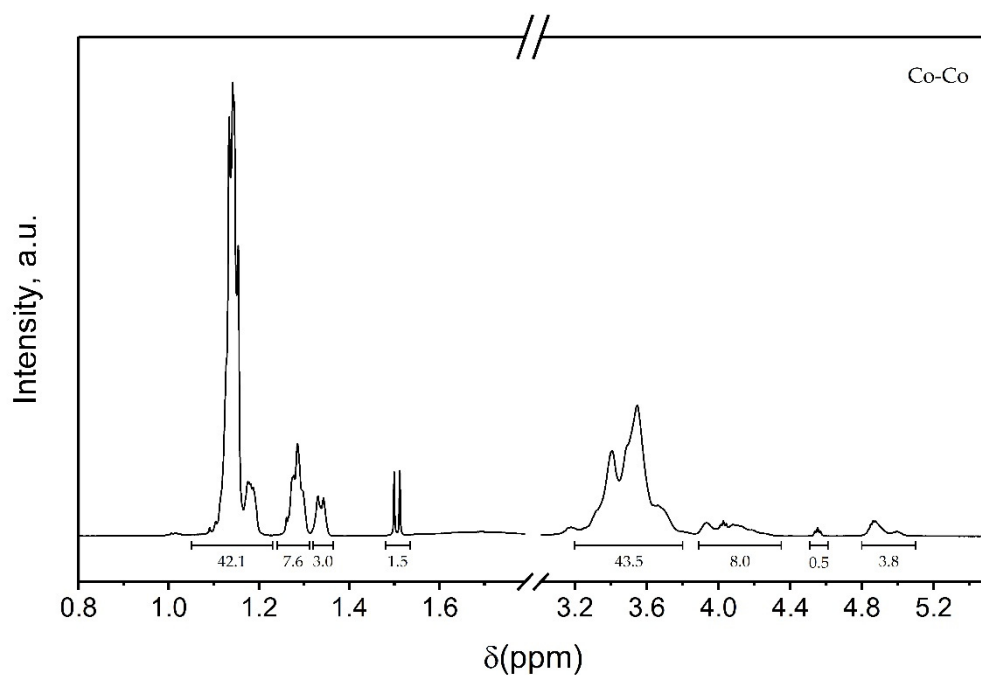


Figure S8. Detailed ^1H -NMR spectrum for the product obtained employing the Co-Co complex.

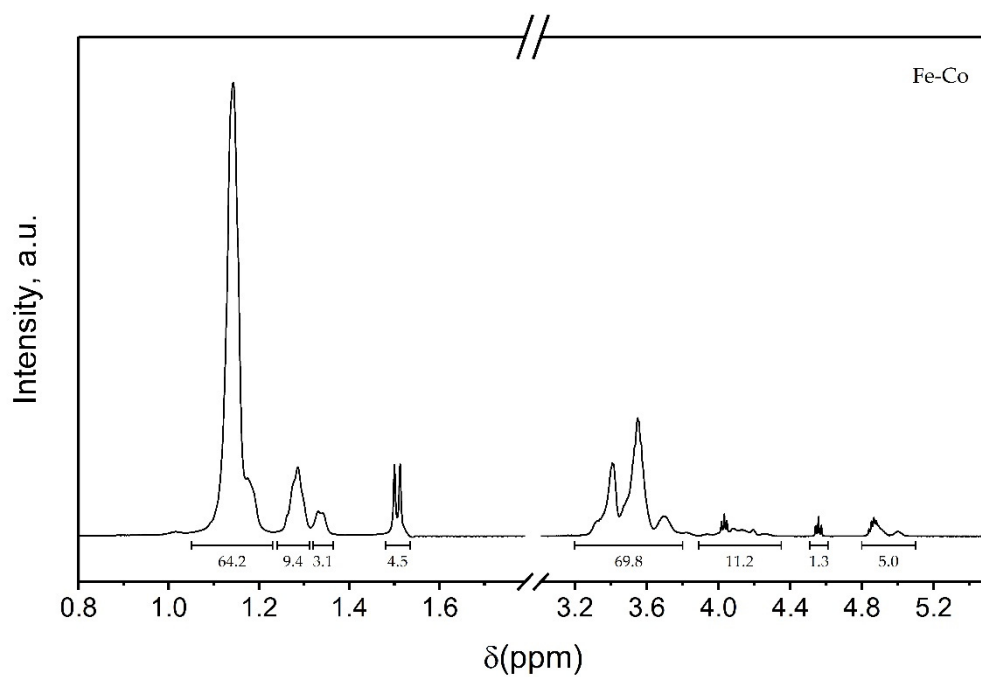


Figure S9. Detailed ¹H-NMR spectrum for the product obtained employing the Fe-Co complex.

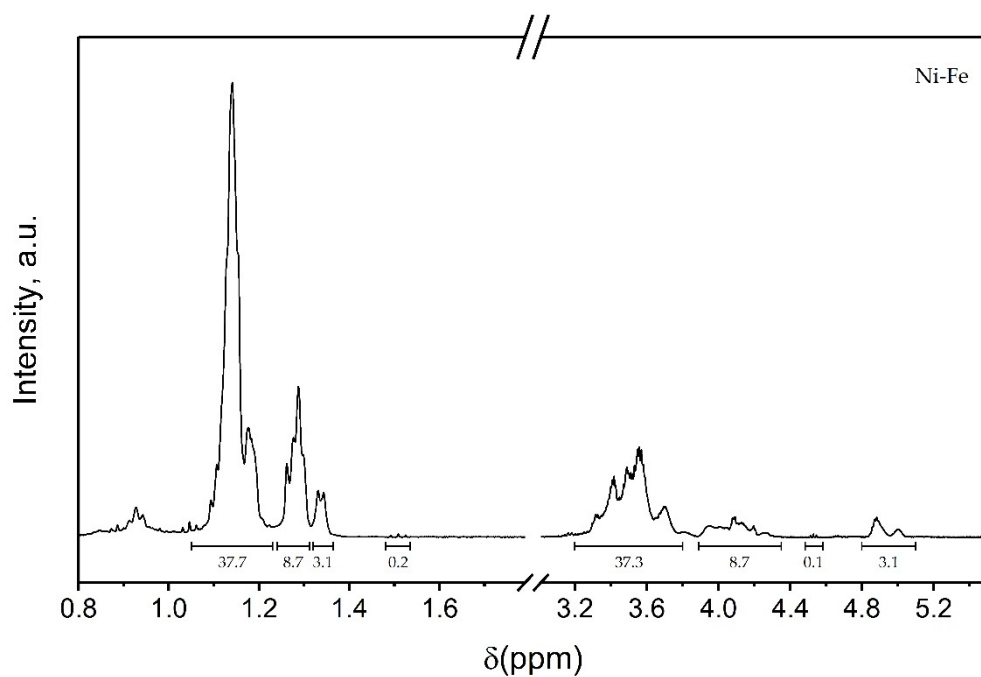


Figure S10. Detailed ¹H-NMR spectrum for the product obtained employing the Ni-Fe complex.

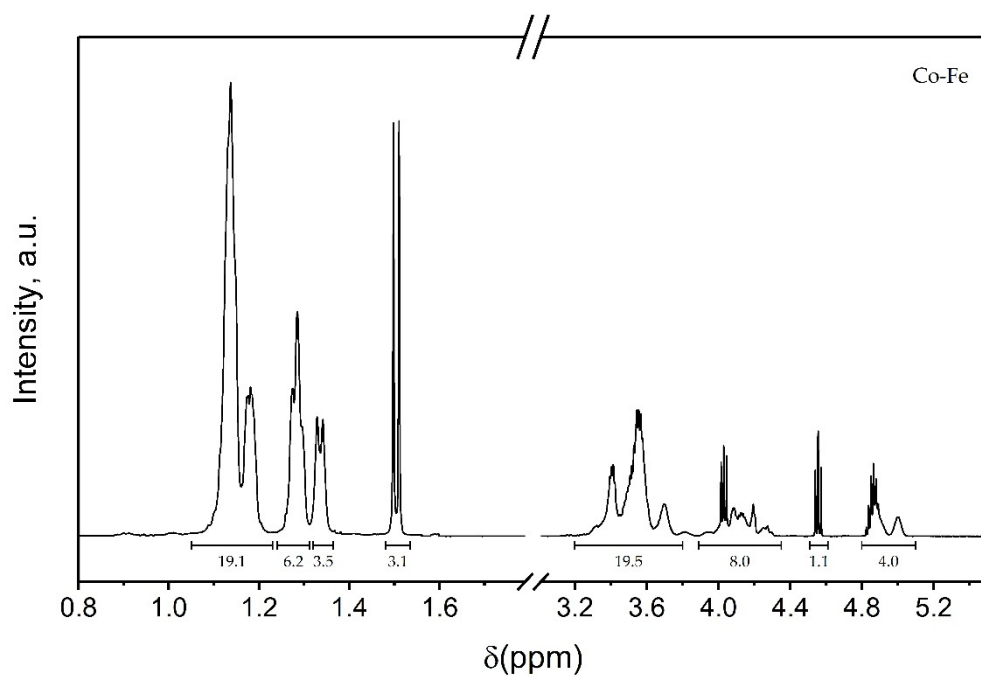


Figure S11. Detailed ¹H-NMR spectrum for the product obtained employing the Co-Fe complex.

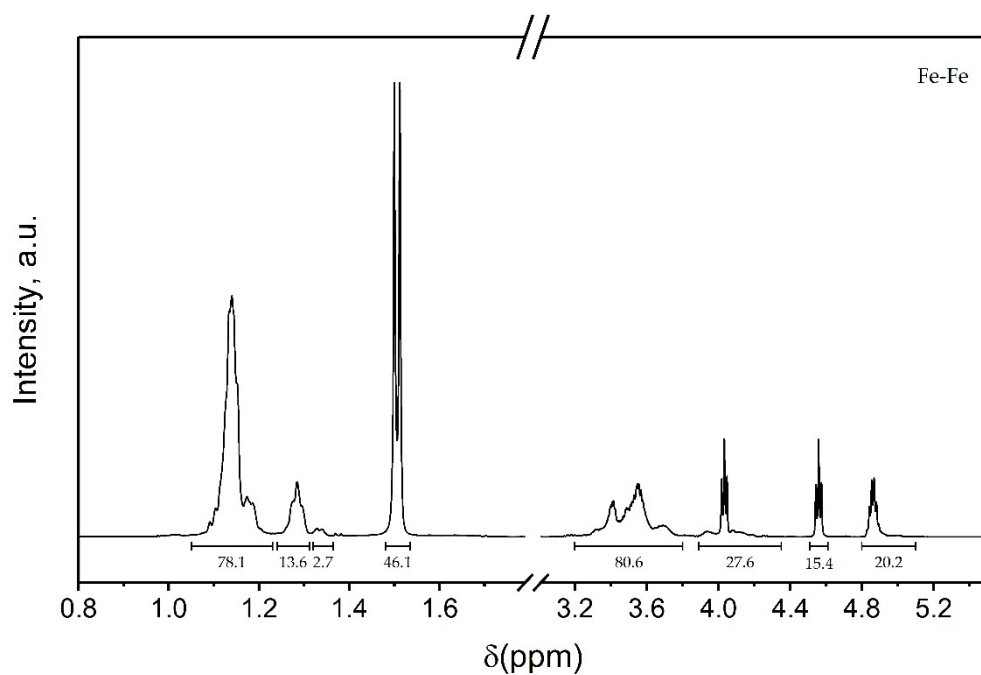


Figure S12. Detailed ¹H-NMR spectrum for the product obtained employing the Fe-Fe complex.

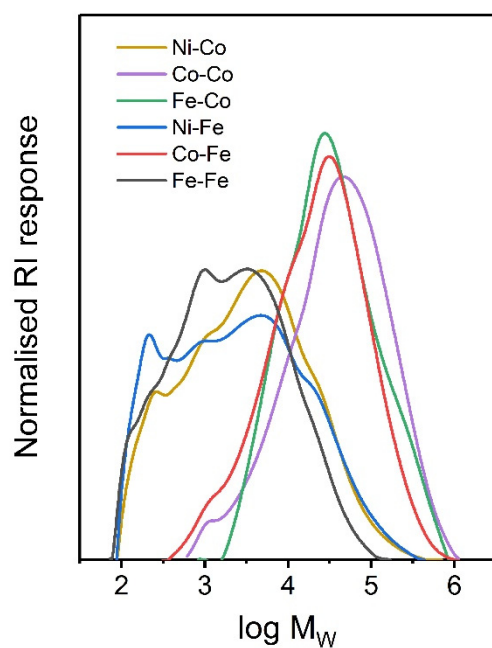


Figure S13. SEC plots ($\log M_w$) of the polyethercarbonates (PECs) formed using the studied porous hexacyanometallates(III).

The obtained polyethercarbonates (PECs) show moderate molecular weight values and broad dispersity, which is characteristic of heterogeneous polymerization catalysts.