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NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

Technical Progress Report for the Period
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with

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SUMMARY OF TECHNICAL PROGRESS

During this quarter, the studies with Co(II) ion exchanged erionite were continued. Last quarter, it was shown that diffuse reflectance spectroscopy (DRS) studies indicated that the Co(II) cations can occupy three different sites in the erionite structure. The occupancy depended upon the Co(II) content of the erionite and upon the temperature of dehydration. Semi-quantitative occupancy numbers have now been derived and are presented here. Adsorption studies have been continued using CO and ethylene to probe whether the Co(II) cations in all of these sites are accessible to ligands such as CO and ethylene. It is shown that Co(II) cations that are designated as Species 1 and 3, with optical bands centered at $\approx$17,000 cm^{-1} and $\approx$24,000-25,000 cm^{-1}, respectively, are located in sites that are accessible to guest molecules. In contrast, Co(II) cations designated as Species 2, characterized by an optical band centered at $\approx$19,000 cm^{-1}, are not accessible to guest molecules.

TECHNICAL PROGRESS

As pointed out in our previous report [1], our recent research has been centered on Co(II) ion exchanged erionite because it was previously demonstrated that these zeolites are fairly active at 400°C for the selective reduction of NO by methane in an oxidative atmosphere [2]. The Co(II) erionite samples were described previously [1], and they consisted of 0.002, 0.12, 0.15, 0.30, 1.3, 1.5, 3.2, 7.9, and 8.2 wt% Co(II) erionite prepared by aqueous ion exchange.

After dehydration to 350°C or 525°C, CO (99.0^{+}% from Aldrich Chem. Co.) and ethylene (CP Grade from Linde) were adsorbed at ambient temperature. The CO was dried by the freeze/thaw technique using a trap of liquid nitrogen. The amount of gas adsorbed was controlled by adsorption at various pressures (0.5 to 700 Torr) from volumes of 40, 180, or 1400 ml. Pressures of gases before and after adsorption were measured using a Pirani vacuum gauge. Adsorption was complete when no decrease in the pressure of the adsorbing gas was observed during a time interval of 15 min.

Diffuse reflectance spectra of the zeolites were obtained at ambeint temperature using a computer-controlled Varian 2300 spectrophotometer having a MgO-coated integrating sphere. Data were collected and analyzed using a Zenith 386 computer with Spectracalc software. The silica sample cell contained 0.6-1.0 g of zeolite and contained an Infrasil window (5 mm thick with a 24 mm diameter). The absorption intensities were evaluated by the Schuster-Kubelka-Munk theory [$F(R_\infty) = (1-R)^2/2R$] using the Spectracalc software, with final data processing and plotting carried out with Origin software.

Adsorption of CO and Ethylene on Co(II) Erionite Dehydrated at 350°C

After dehydration of 0.15 wt% and 3.2 wt% Co(II) erionites at 350°C under dynamic vacuum in diffuse reflectance (DRS) cells, the zeolites were equilibrated with carbon monoxide at ambient temperature. The resultant spectra are shown in Figure 1 (solid lines), and they are compared with the spectra obtained for the dehydrated samples (dashed line). The initial spectrum of the 0.15 wt% Co(II) erionite consisted of a band centered at ≈17,000 cm^{-1}, which is characteristic of Co(II) in low exchanged samples, and this was assigned to Co(II) Species 1 [1]. The spectrum of the dehydrated 3.2 wt% Co(II) erionite (Figure 1b) clearly shows a second band at ≈19,000 cm^{-1}, and this was assigned to Co(II) Species 2 [1]. The spectra show that the CO interacted with the Species 1 Co(II) cations. Upon deconvolution of the spectra in Figure 1b, little change in intensity of the 19,000 cm^{-1} occurred upon adsorption of CO. Therefore, it appears that Co(II) Species 2 did not interacted strongly with CO.

After dehydration of 0.15 and 8.2 wt% Co(II) erionite samples at 350°C, equilibration with ethylene was carried out. The resultant spectra are shown in Figure 2 and are compared with those obtained for the initial dehydrated samples. The bands at 16,300 and 17,000 cm^{-1} were significantly reduced in intensity. It is clear that the ethylene interacted with the Co(II) Species 1 and that a new fairly strong band at 14,700 cm^{-1} was observed for both zeolites. Again, it appeared that the gas phase ligand did not interact with the Species 2 Co(II).

Previously, 3.2 and 1.5 wt% Co(II) samples were dehydrated at 525°C and CO and ethylene, respectively, were adsorbed onto the samples, and the resultant visible spectra were shown as Figures 2 and 3 in Reference[3]. In both case, the optical band at ≈24,000 cm^{-1}

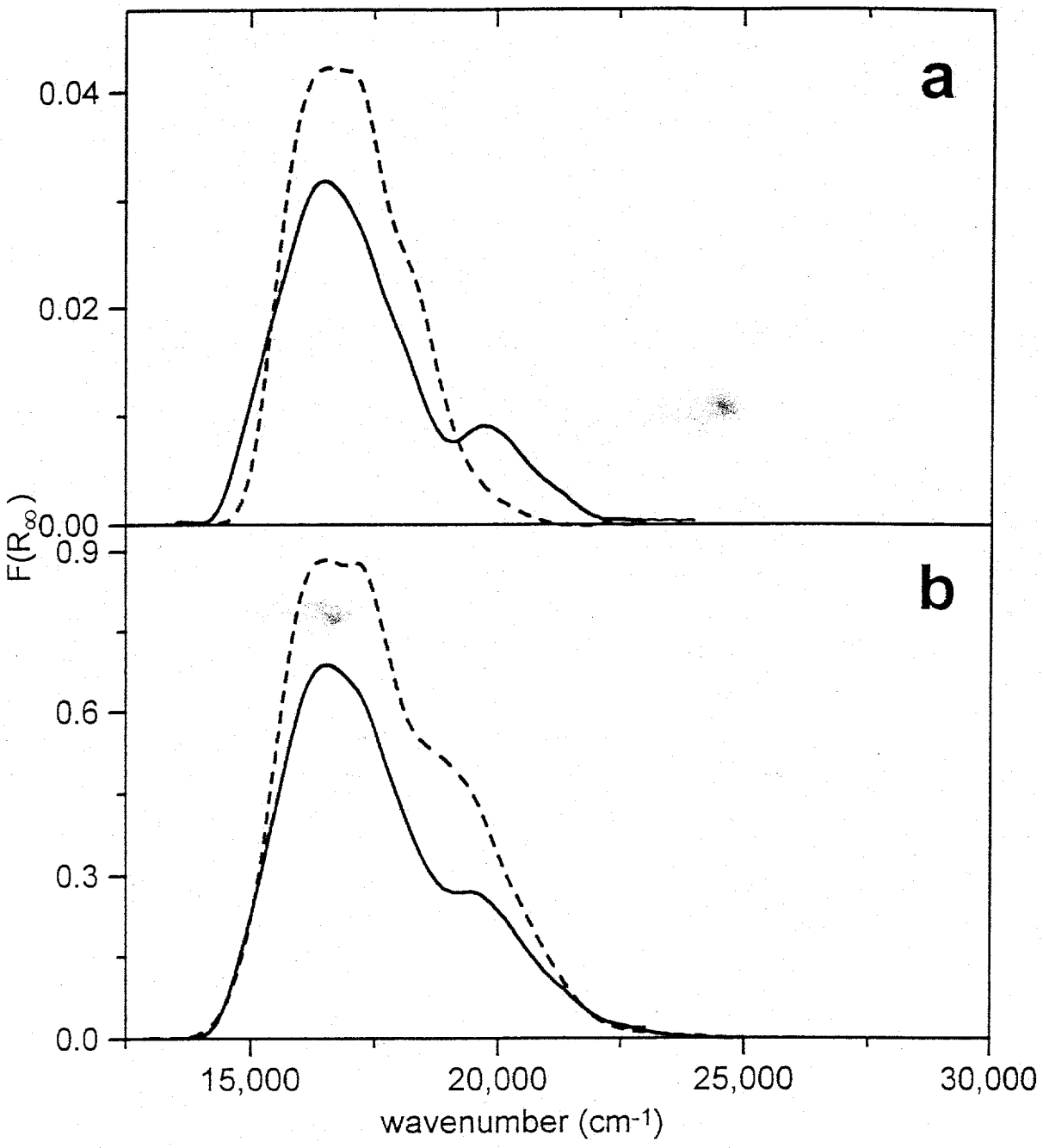

FIGURE 1. The DRS visible spectra of Co(II) erionite samples containing **(a)** 0.15 and **(b)** 3.2 wt% Co(II) after dehydration at 350°C (- - - -) and after adsorption of CO (——). The spectrum of the parent zeolite that did not contain Co(II) was subtracted to obtain the spectra shown.

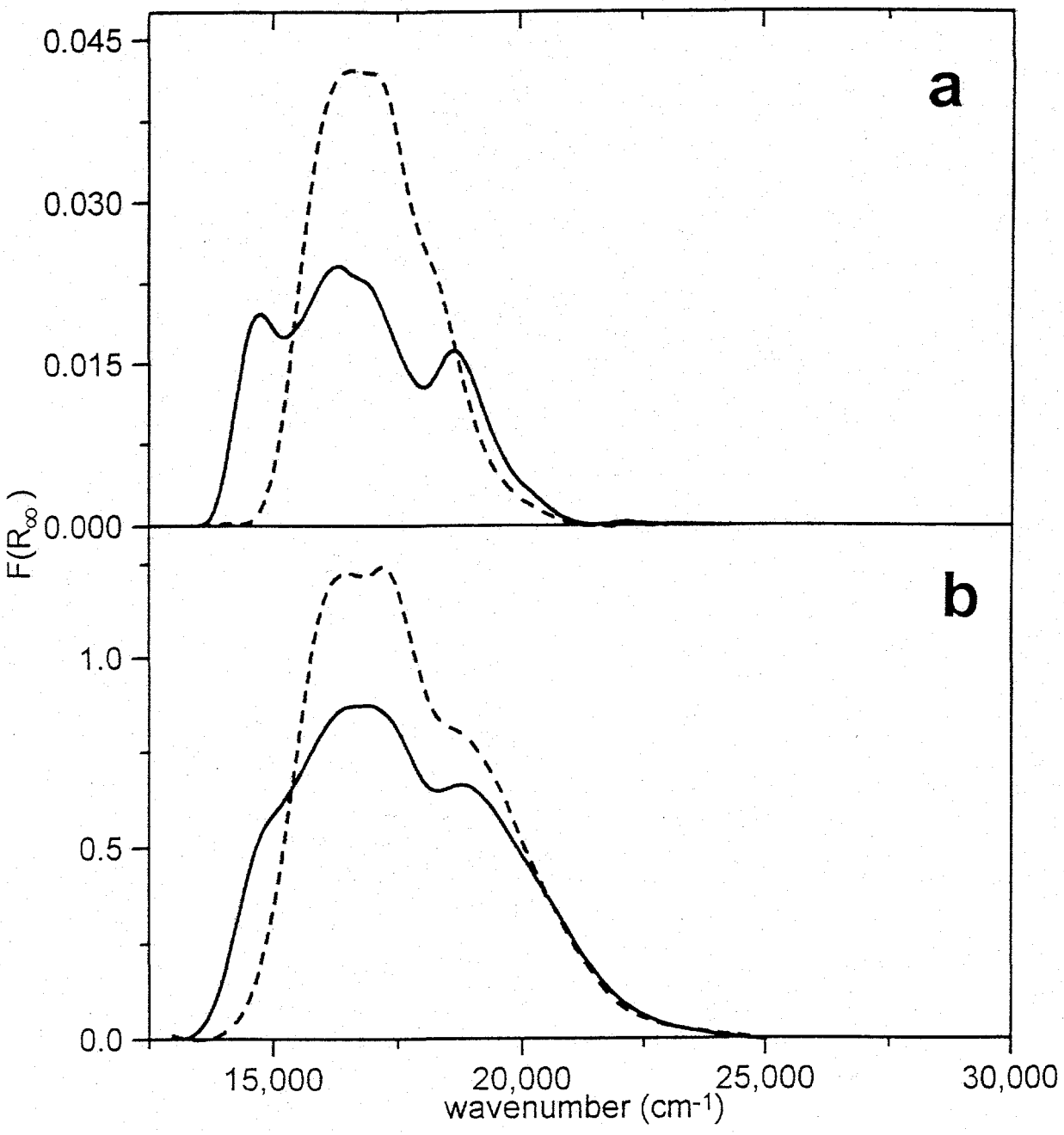

FIGURE 2. The DRS visible spectra of Co(II) erionite samples containing **(a)** 0.15 and **(b)** 8.2 wt% Co(II) after dehydration at 350°C (- - - -) and after adsorption of ethylene (——). The spectrum of the parent zeolite that did not contain Co(II) was subtracted to obtain the spectra shown.

attributed to Species 3 disappeared upon adsorption of these ligands. This indicated that Co(II) Species 3 in these zeolites were accessible and interacted with these ligands.

Quantification of the Spectroscopically Distinct Species

Using data in this report and in our previous reports [1-3], estimates of the occupancy of individual sites corresponding to spectroscopic species *via* comparison of the visible spectral bands can be made. Assuming that the area of Species 1 is proportional to the content of Co(II) ions located in the site characterized by this species, the concentration of Co(II) ions corresponding to Species 1 and 2 can be estimated.

For Co(II) erionite samples dehydrated at 350°C and having low Co(II) concentrations, spectral Component 1 (located at ≈17,000 cm^{-1}) corresponding to Species 1 was the dominant feature in the spectra, and the areas of the bands corresponding to this species exhibited a linear dependence on the Co(II) concentration in erionite. This is shown in Figure 3. At high Co(II) concentrations, Component 2 (located at ≈19,000 cm^{-1}), having a different optical sensitivity and corresponding to Species 2, became a more important feature of the spectra (see Figure 1 in Reference [1]), and again a linear dependence was observed. In this case, it appeared to cover the complete range of Co(II) concentrations utilized in this research.

Similarly, the spectral area of Component 3 (located at ≈24,000-25,000 cm^{-1}) that was observed with Co(II) erionite samples that were calcined at 525°C was plotted as a function of the Co(II) content, as shown in Figure 4. At very low Co(II) concentrations, this optical band was the only band present, and a linear dependence was obtained, as extrapolated in

Figure 4. At higher Co(II) concentrations, a non-linear trend was observed. Using the data shown in Figures 3 and 4 and extrapolating from the spectral areas observed at very low Co(II) ion exchange levels, estimates of the occupancies of the three cation sites were made. The estimates obtained here are shown in Table 1. These sites are now being correlated with the possible cation sites in the erionite

TABLE 6. Estimated relative populations of Co(II) in individual ion sites in erionite containing different Co(II) contents and calcined at 350°C and at 525°C under dynamic vacuum.

Co(II) in Erionite (wt%)	Relative Population of Co(II) in Sites (wt% of all Co(II) ion exchanged into the zeolite)				
	Dehydration at 350°C		Dehydration at 525°C		
	Site 1	Site 2	Site 1	Site 2	Site 3
< 1.5	100	0	0	0	100
3.2	95	5	30	5	65
7.9	85-95	5-15	30-40	5-15	55
8.2	85-95	5-15	35-45	5-15	50

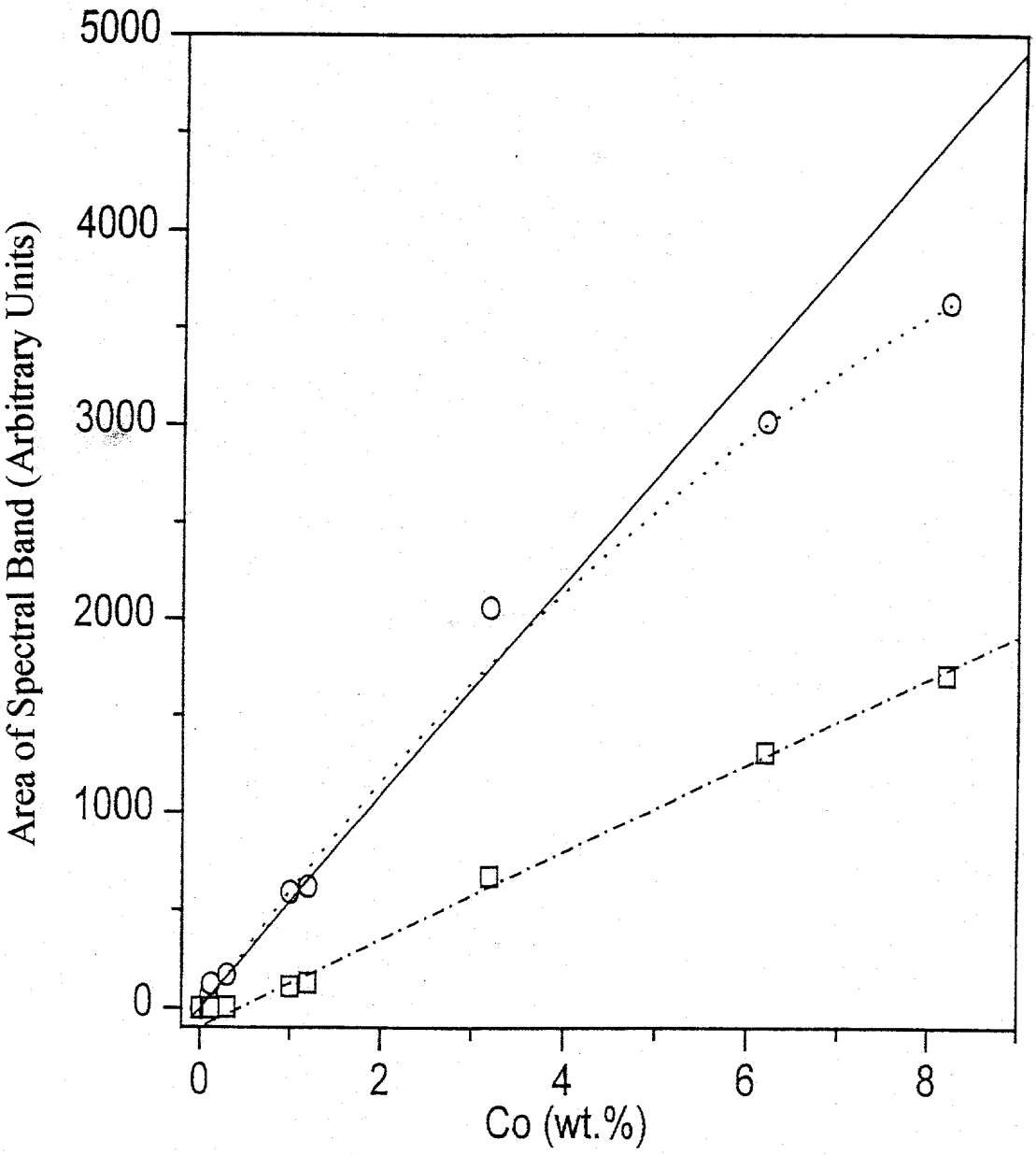

FIGURE 3. Dependence on the visible spectral band areas of Component 1 centered at ≈17,000 cm^{-1} corresponding to Co(II) Species 1 (○) and of Component 2 centered at ≈19,000 cm^{-1} corresponding to Co(II) Species 2 (□), obtained upon calcination of Co(II) erionite samples at 350°C.

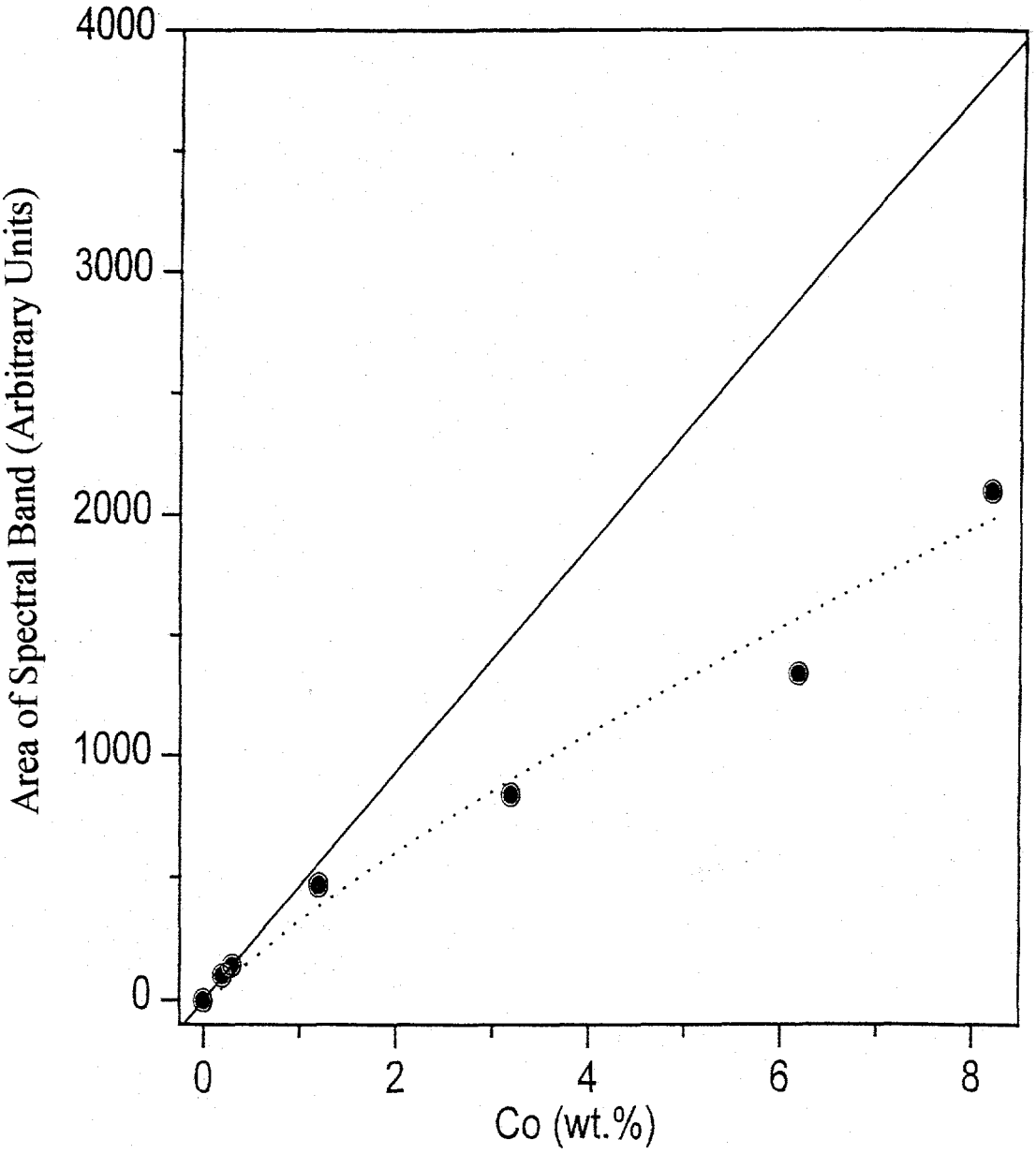

FIGURE 4. Dependence of the spectral areas of Component 3, observed at ≈24,000-25,000 cm^{-1} upon calcination of Co(II) erionite samples at 525°C, corresponding to Co(II) Species 3 (●).

REFERENCES

1. Klier, K., Herman, R.G., and Dědeček, J., Quarterly Technical Progress Report DOE/PC/93222-13, 17 pp (February 1997).
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