

NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

Technical Progress Report for the Period
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SUMMARY OF TECHNICAL PROGRESS

During this quarter, four additional samples of Co(II) ion exchanged erionite were prepared and shown to contain 0.002, 0.12, 0.30, and 1.3 wt% Co(II). These samples, as well as the five previously prepared and studied, were investigated by diffuse reflectance spectroscopy (DRS) studies to probe the state of the Co(II) cation in erionite zeolites and whether the zeolites were completely dehydrated at 350°C and 525°C. By comparing spectra as a function of Co(II) content and temperature of dehydration and by using second derivative mode analysis, it was shown that the Co(II) cations occupy three different sites in the erionite structure. DRS studies are underway to determine if Co(II) cations in all of these sites are accessible to ligands such as CO and ethylene.

TECHNICAL PROGRESS

The research during this quarter was centered on the Co(II) erionite zeolite that was previously found to be fairly active at 400°C for the selective reduction of NO by methane in an oxidative atmosphere [1]. As pointed out in a previous report [2], under the reaction conditions employed, the Co(II) erionite catalyst exhibited approximately the same activity (8.7×10^{-6} mol of NO converted /g of zeolite/sec) as the Co(II) ZSM-5 zeolite and double that of the Co(II) A zeolite [1].

Preparation of Additional Co(II) Erionite Samples

Studies were previously carried out with five Co(II) erionite samples indicated as being exchanged with 0.2, 1.7, 3.2, 6-8, and >8 wt% Co(II) [2,3]. The first four samples were prepared by single equilibrations with aqueous Co(II) solutions, usually the acetate salt, of various molarities. The most highly exchanged sample was prepared using a three-step exchange process. Upon analysis, these samples were more accurately shown to contain 0.15, 1.5, 3.2, 7.9, and 8.2 wt% Co(II). Four additional samples have now been prepared, and these contained 0.002, 0.12, 0.30, and 1.3 wt% Co(II). After equilibration in aqueous solution, the solids were filtered, washed three times with hot distilled water, and air dried.

Diffuse Reflectance Studies of Co(II) Erionite Dehydrated at 350°C

To clarify the location and accessibility of the Co(II) cations in erionite, further adsorption studies with CO and ethylene have been initiated. These studies, centered on changes in the electronic spectra of the zeolites upon formation of Co(II) complexes, are

being carried out with the Co(II) erionite dehydrated only to 350°C and to the higher temperature of 525°C. After dehydration, 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 ambient 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.

The DRS spectra in the visible spectral region are shown in Figure 1 for the nine Co(II) erionite samples after dehydration at 350°C. Five of these were previously shown (Figure 1 in Reference 2). The characteristic asymmetric absorption band for Co(II) cations centered at 16,000-18,000 cm^{-1} , designated here as Component 1, is evident for each sample. As the Co(II) content of the erionite was progressively increased, a band centered at about 19,000 cm^{-1} , designated here as Component 2, increased in intensity. The spectra indicate that both bands are complex.

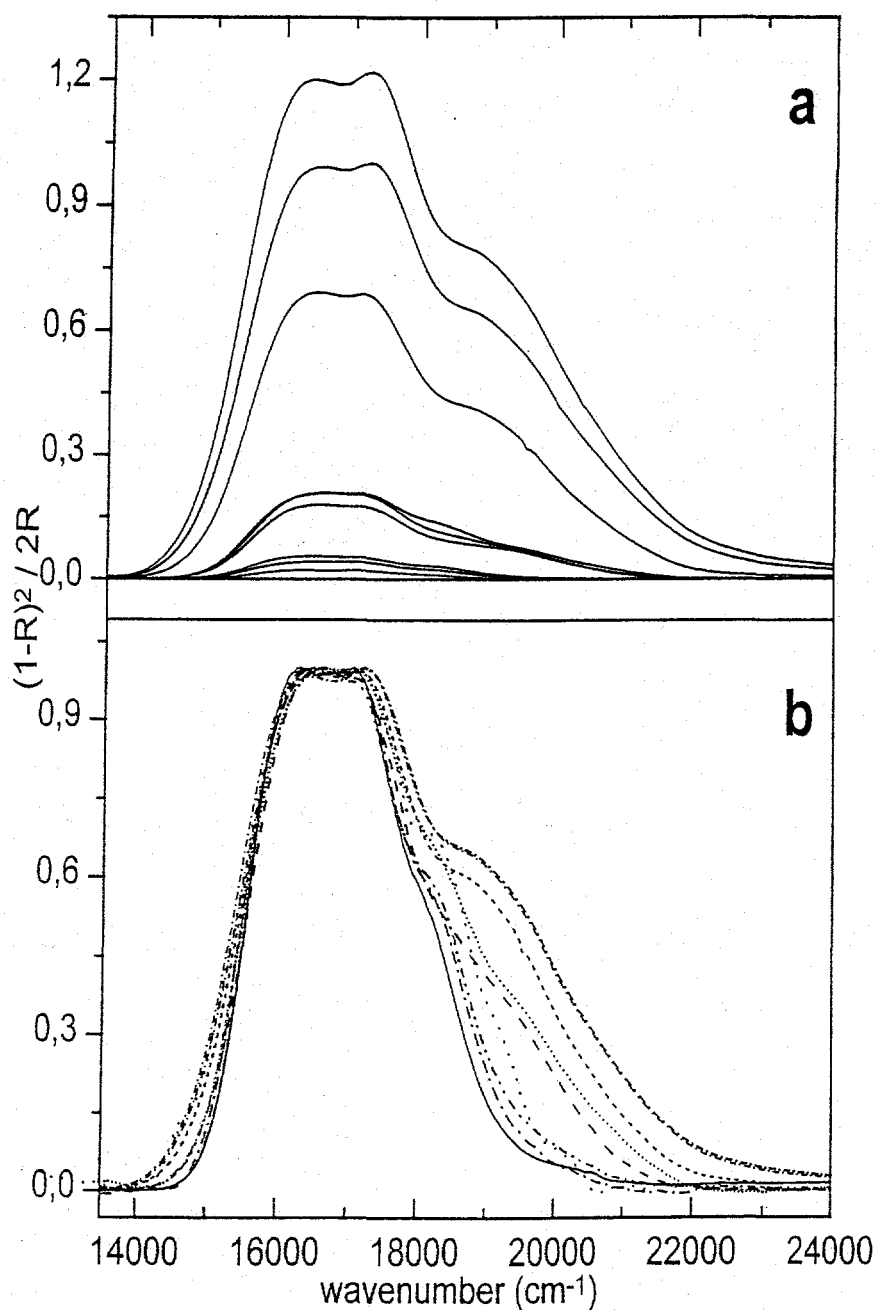


FIGURE 1. The effect of Co(II) concentration on the visible spectrum of Co(II) erionite samples dehydrated at 350°C. The spectrum of the parent zeolite that did not contain Co(II) was subtracted to obtain the spectra shown. In (a), the spectral intensity increases with increasing Co(II) concentration for samples containing 0.002, 0.12, 0.15, 0.30, 1.3, 1.5, 3.2, 7.9, and 8.2 wt% Co(II). In (b), the visible spectra have been normalized with respect to Co(II) concentration and Component 1 to emphasize the effect of Co(II) concentration on Component 2.

The fine structure for Components 1 and 2 was further analyzed using second derivative mode analysis of the spectra for low Co(II)-containing erionite samples (Figure 2) and for high Co(II)-containing erionite samples (Figure 3). It is noted that the minimum in the second derivative mode is localized close to the maximum of the absorption band. Wavenumbers corresponding to the optical transitions were taken as maxima of Gaussian curves to which each spectrum was deconvoluted. Component 1 is composed of three bands with maxima located at 16,050, 17,080, and 18,040 cm^{-1} , while Component 2 is composed of two bands with maxima at 19,250 and 20,600 cm^{-1} . The areas of the bands at 16,050, 17,080, and 18,040 cm^{-1} were in the ratio of 1.9/1.0/1.5 for the whole concentration range studied. The areas of the bands at 19,250 and 20,600 cm^{-1} were in the ratio of 1.8/1.0. These constant ratios suggest the assignment of the spectra to two spectroscopic species, as already designated as Components 1 and 2. The second derivative mode analysis indicates that the band for Species 2 consisted of a pair of doublets, i.e. at 19,000 and 19,600 cm^{-1} and at 20,600 and 21,300 cm^{-1} . The wavenumbers given for the individual maxima represent average values from several spectra.

To probe the differences in Co(II) species that give rise to Components 1 and 2, a sample of the 8.2 wt% Co(II) erionite was back-exchanged with Na^+ at ambient temperature. This was carried out by equilibration of 1.0 g of the zeolite with 500 ml of 0.2 M aqueous NaNO_3 solution for 10 hr. After filtering, washing, and drying, it was found that the zeolite contained only 0.14 wt% Co(II). The visible spectrum for this sample after dehydration at 350°C is shown in Figure 4, where the spectrum has been normalized with respect to that of the 8.2 wt% Co(II) sample with which it is compared. It is clear that this spectrum differs

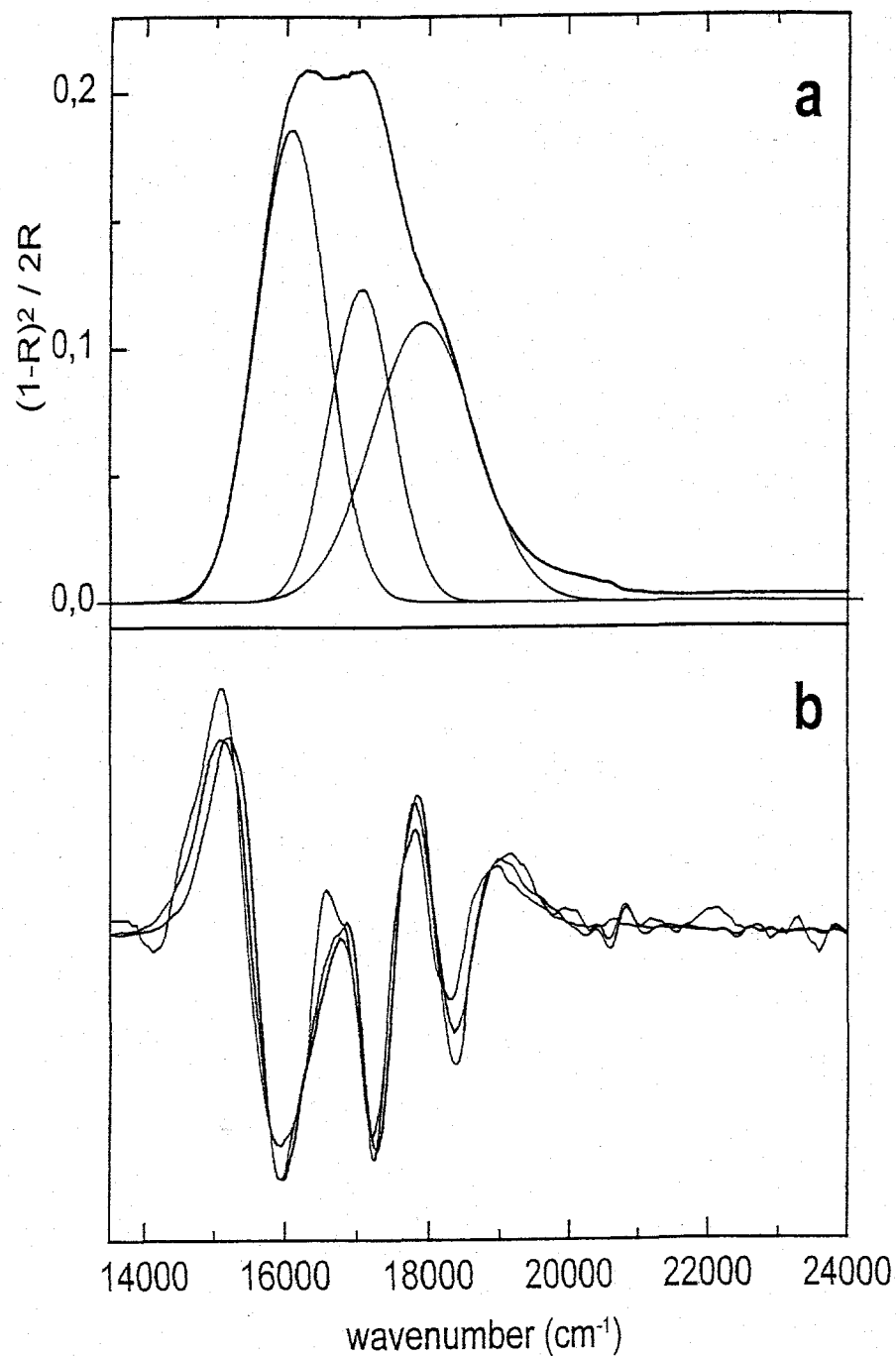


FIGURE 2. (a) The visible spectrum of the 0.15 wt% Co(II) erionite sample dehydrated at 350°C , with deconvolution of the spectrum into Gaussian bands, and (b) the second derivative mode analysis of the visible spectra of Co(II) erionite containing 0.12, 0.15, and 0.30 wt% Co(II).

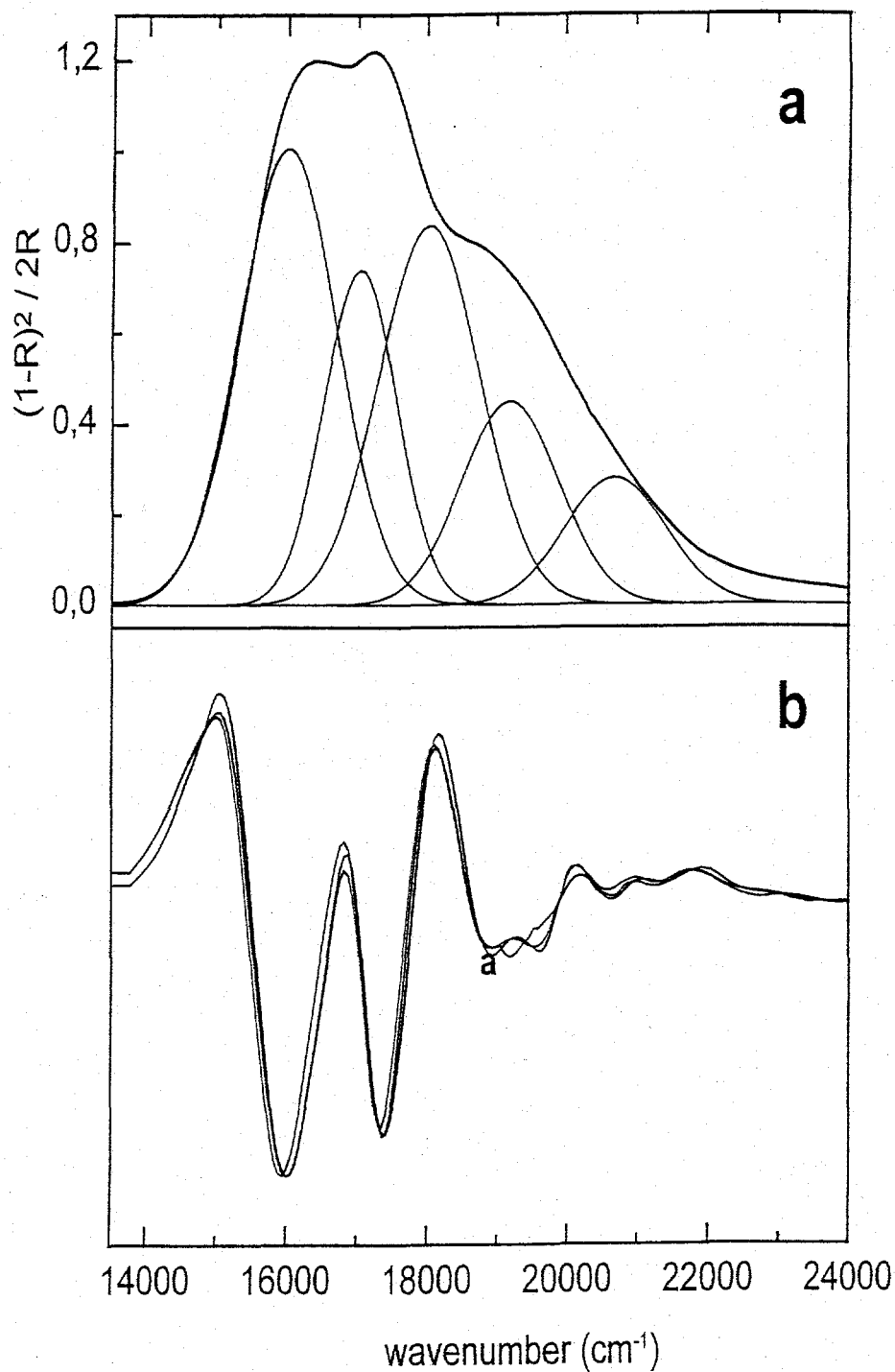


FIGURE 3. (a) The visible spectrum of the 7.9 wt% Co(II) erionite sample dehydrated at 350°C, with deconvolution of the spectrum into Gaussian bands, and (b) the second derivative mode analysis of the visible spectra of Co(II) erionite containing 3.2, 7.9, and 8.2 wt% Co(II).

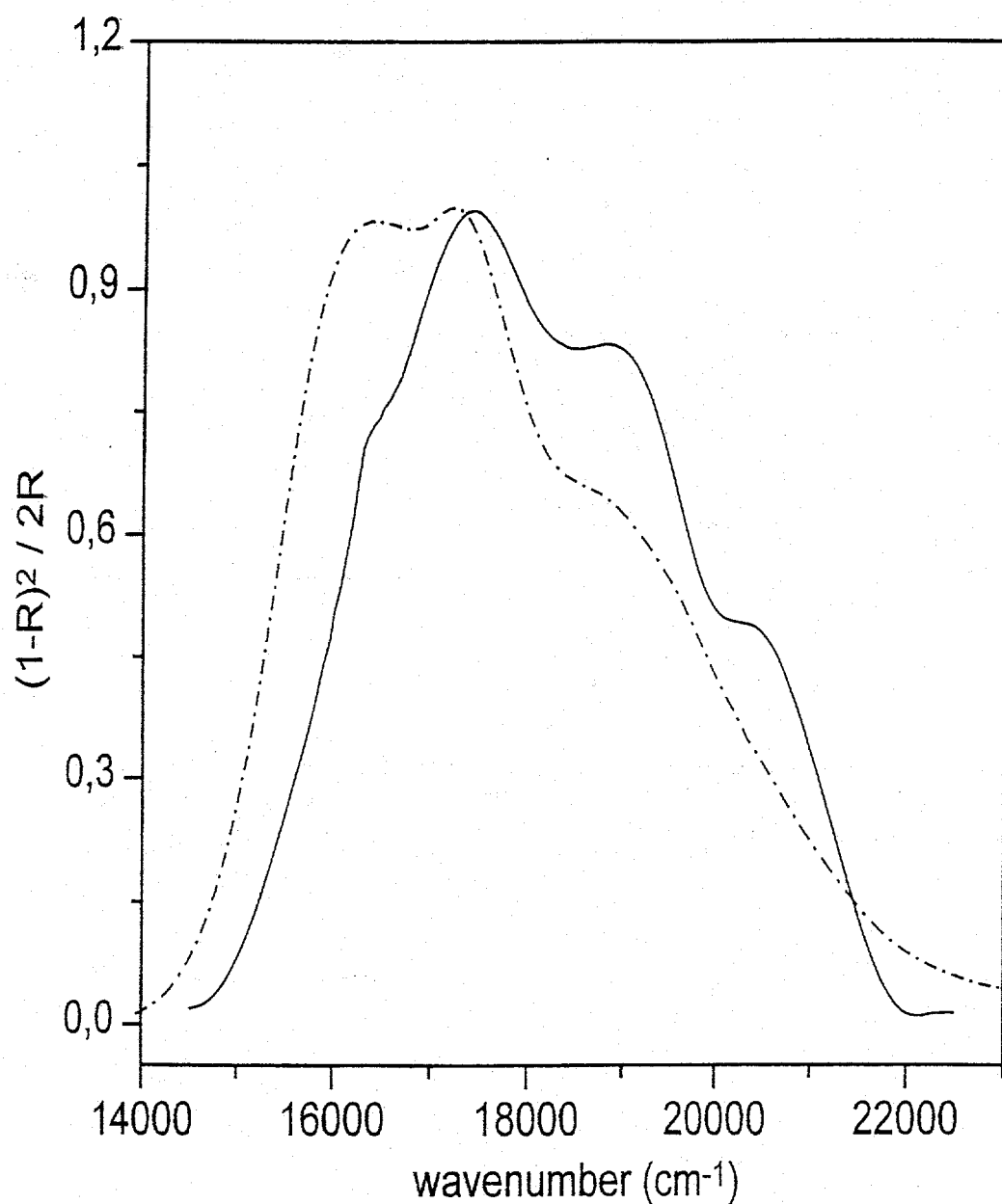


FIGURE 4. The effect of reverse ion exchange of Co(II) by Na⁺ on the normalized visible spectrum of the resultant 0.14 wt% Co(II) erionite sample (—) as compared with the initial 8.2 wt% Co(II) erionite sample (---), both dehydrated at 350°C.

dramatically from that of the forward-exchanged Co(II) erionite containing a similar Co(II) content, as seen by comparing the spectrum in Figure 4 with the spectrum for the 0.15 wt% Co(II) sample shown in Figure 2. In Figure 4, visible bands at 19,250 and 20,600 cm^{-1} dominate the spectrum, and these are attributed to Co(II) Species 2. Thus, Species 2 corresponds to Co(II) cations in sites that are occupied only at high Co(II) concentrations in erionite and from which it is difficult to exchange the Co(II) cations back out of the zeolite.

The optical spectra in the near-infrared (NIR) region were also obtained, in part to monitor bands attributable to molecular water. The NIR DRS of Co(II) in selected Co(II) erionite samples after dehydration at 350°C are shown in Figure 5. The absence of the vibrational combination bands of water at 5,300 cm^{-1} ($\nu + \delta$) and 7,150 cm^{-1} (2ν) [4-6] is evidence that the Co(II) erionite samples are completely dehydrated at 350°C. The NIR bands observed at about 5,800 and 7,600 cm^{-1} in the spectra of samples with low Co(II) concentrations are attributed to electronic transitions of the Species 1 Co(II) ion. The NIR spectra of erionite with higher Co(II) concentrations are dominated by bands at 8,500 and 11,500 cm^{-1} , which correspond to electronic transitions in the Species 2 Co(II) cation.

Diffuse Reflectance Studies of Co(II) Erionite Dehydrated at 525°C

It was previously shown that the spectra of Co(II) ZSM-5 samples were dependent upon the dehydration temperature utilized to remove water from the zeolite [7]. It was found that the spectrum of a Co(II) erionite sample also depended upon the temperature at which dehydration was carried. The UV-Vis-NIR spectrum of 3.2 wt% Co(II) erionite dehydrated at 525°C is compared in Figure 6 with that obtained with a sample dehydrated at 350°C.

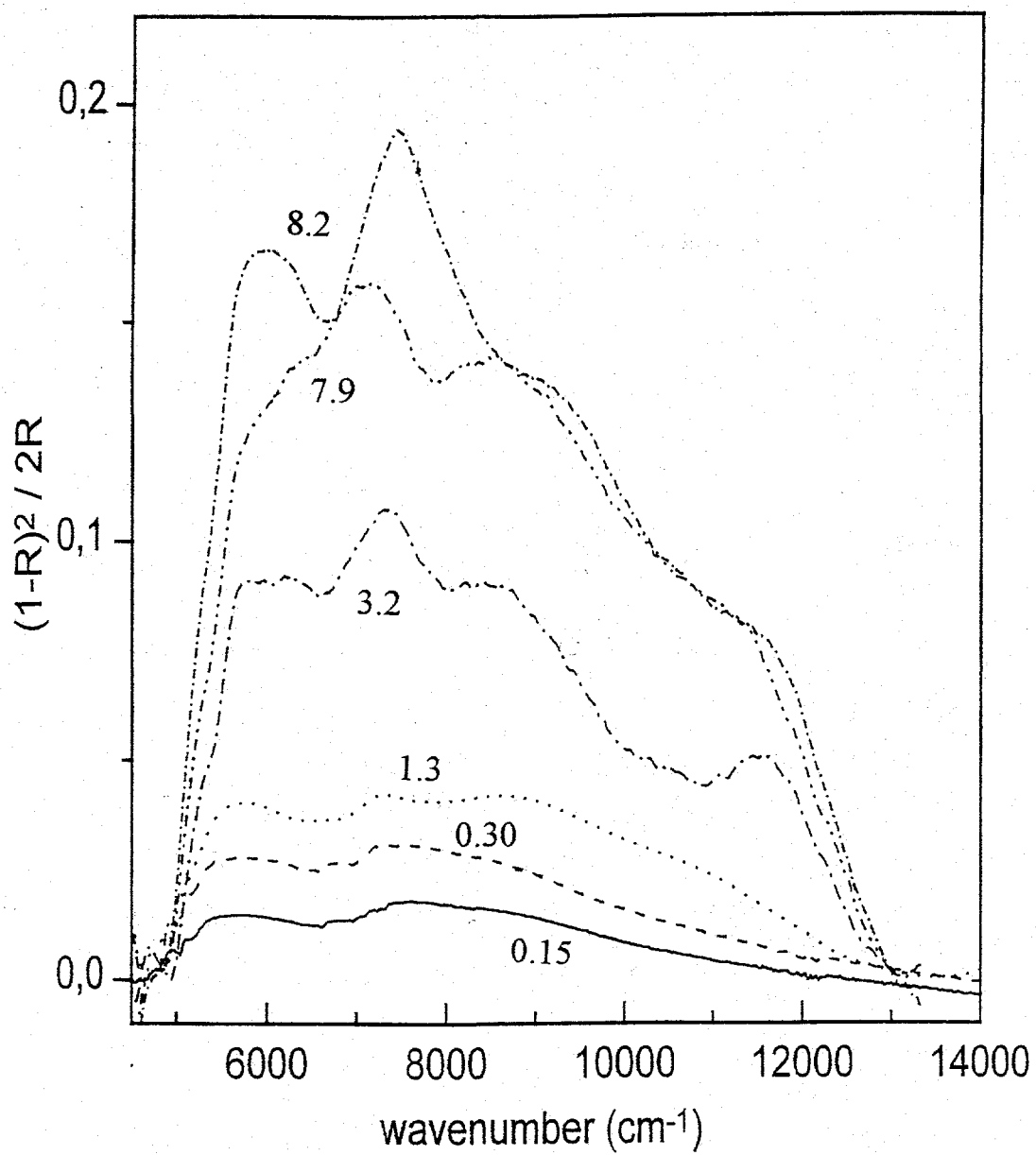


FIGURE 5. The effect of Co(II) concentration on the NIR spectra obtained with Co(II) erionite samples dehydrated at 350°C containing 0.15, 0.30, 1.3, 3.2, 7.9, and 8.2 wt% Co(II).

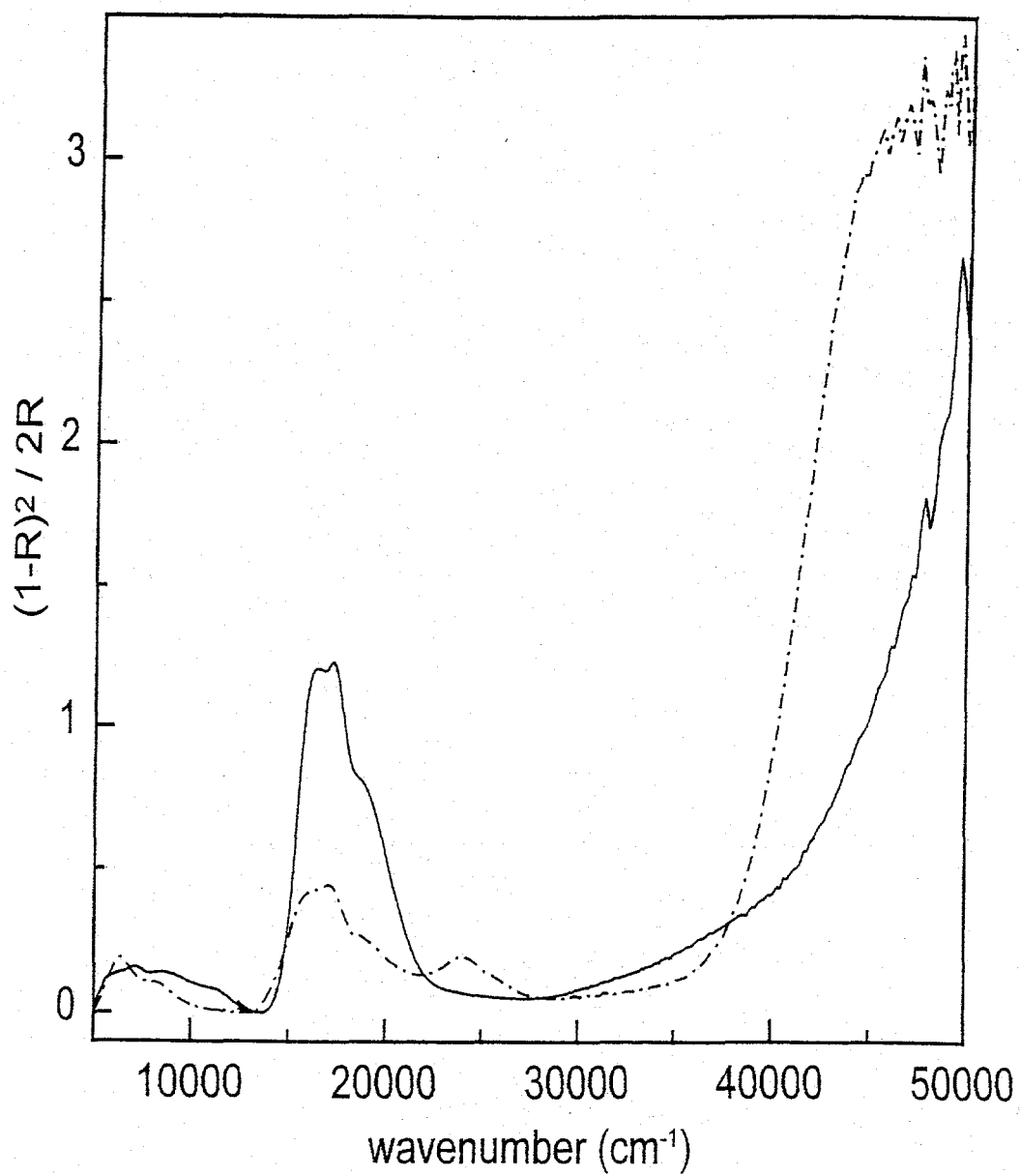


FIGURE 6. The UV-Vis-NIR spectra of 3.2 wt% Co(II) erionite samples dehydrated at 350°C (—) and at 525°C (---).

Further details of the NIR and Vis spectral regions are shown in Figures 7 and 8, respectively, where 0.3, 1.5, 3.2, and 8.2 wt% Co(II) erionite samples were dehydrated at 525°C. It is clear that a new asymmetric band centered at approximately 24,000 cm^{-1} appeared as a result of dehydration at 525°C (compare Figure 8 with Figure 1). It appears that a higher wavenumber shoulder accompanies this band. As can be determined from the spectra in Figure 8, as the Co(II) concentration increased in the erionite, the intensity of the 17,000 cm^{-1} band increased at a faster rate than the 24,000 cm^{-1} band. This indicates that the spectra are composed of at least two components representing different spectroscopic species. In addition to Component 1 (centered at $\approx 17,000 \text{ cm}^{-1}$) and Component 2 (centered at $\approx 19,000 \text{ cm}^{-1}$), a new Component 3 is evident by the presence of the band centered at $\approx 24,000 \text{ cm}^{-1}$.

The NIR spectra of Co(II) erionite samples dehydrated at 350°C and at 525°C can be compared in Figures 5 and 7. Bands at $\approx 8,000 \text{ cm}^{-1}$ and at $\approx 11,500 \text{ cm}^{-1}$ are characteristic of high Co(II) loading levels of erionite, and they are assigned to Component 2. The band at $\approx 6,400 \text{ cm}^{-1}$ (Figure 7) appears to be assignable to Component 3, while the band at $\approx 5,600 \text{ cm}^{-1}$ (Figure 5) appears to correspond to Component 1.

Further studies, including adsorption of CO and ethylene on the ion exchanged Co(II) cations, are being carried out to clarify the assignment of different cation sites in erionite and to determine their accessibilities to reactants.

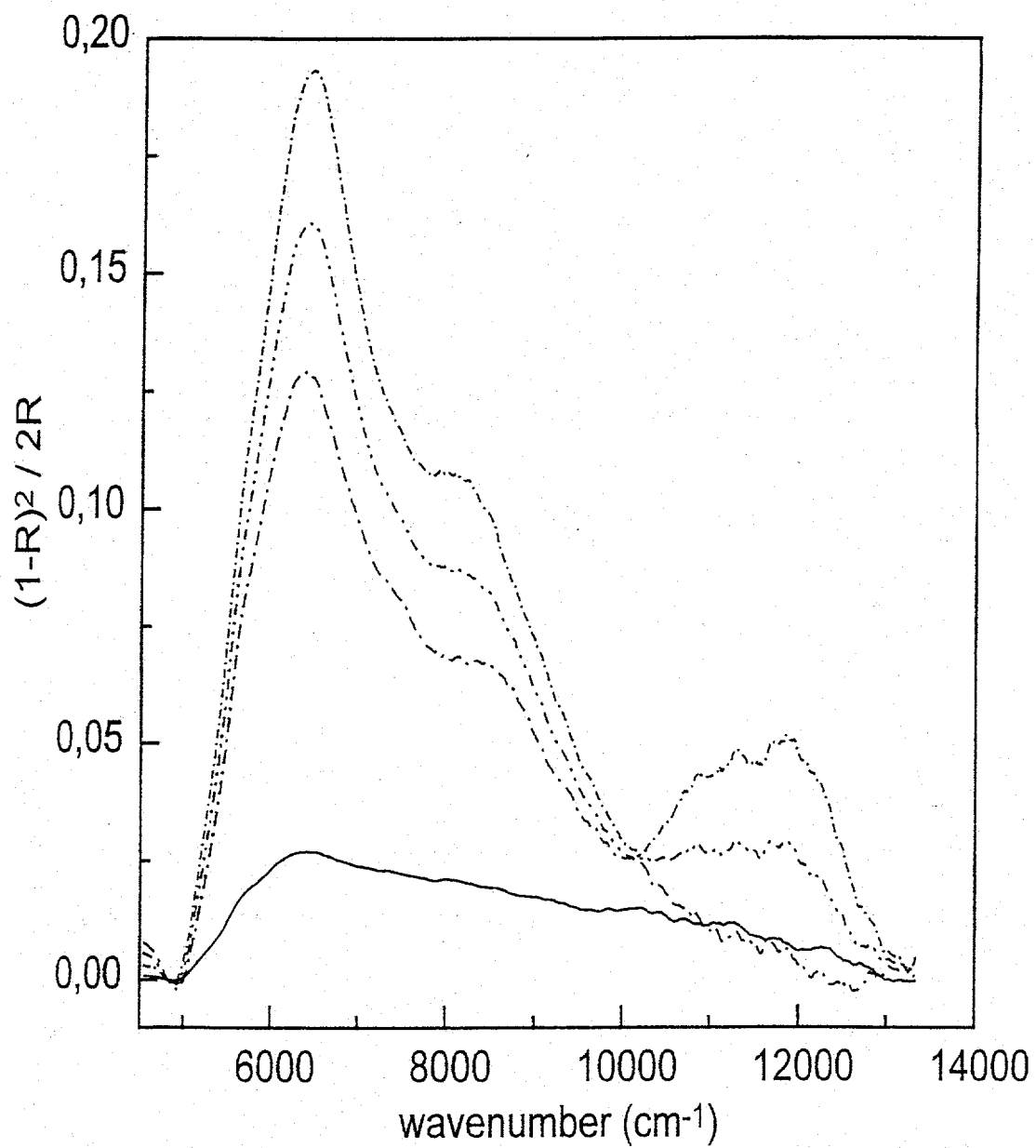


FIGURE 7. The effect of the Co(II) concentration on the NIR spectrum of 0.3, 1.5, 3.2, and 8.2 wt% Co(II) erionite samples dehydrated at 525°C

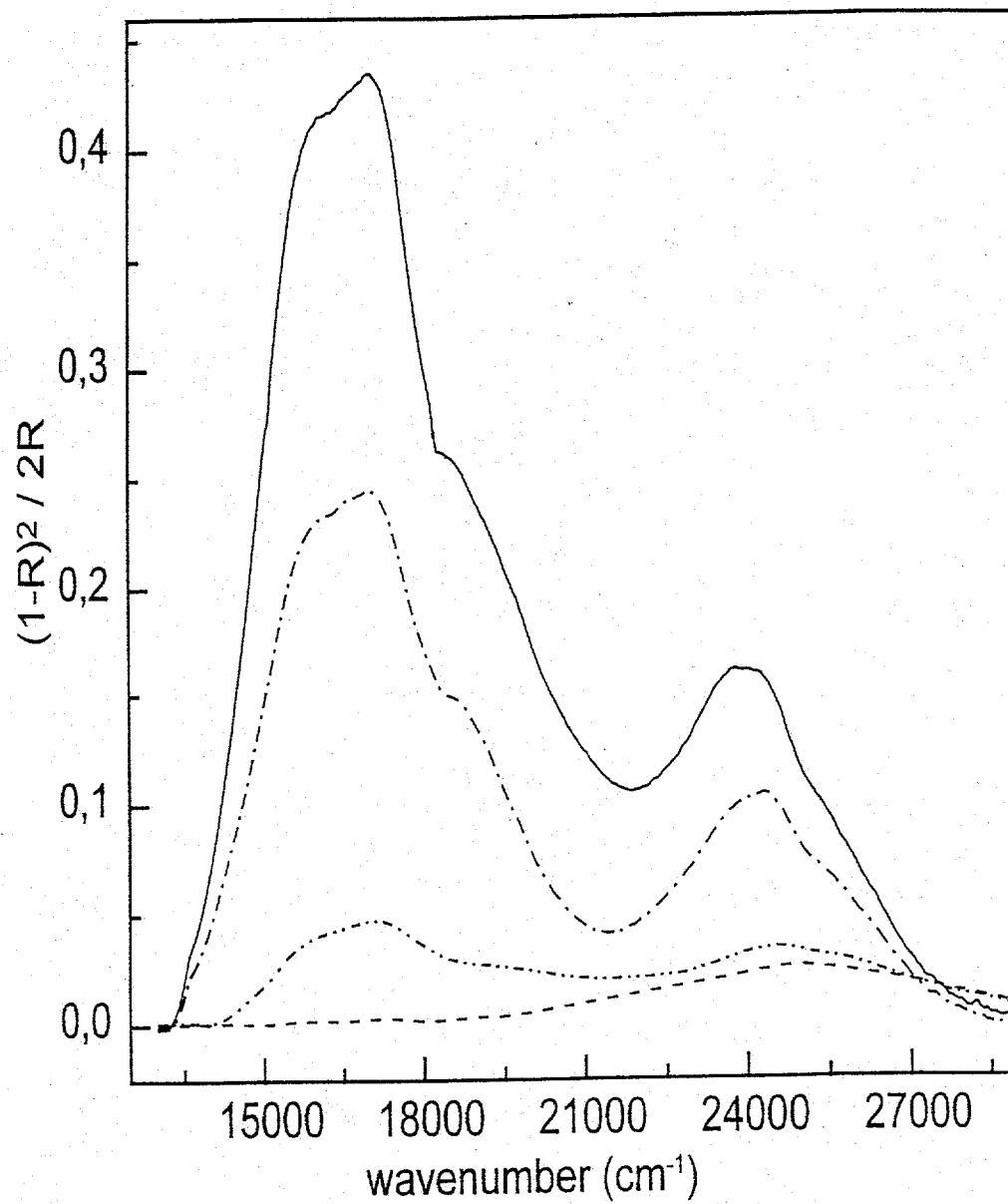


FIGURE 8. The effect of the Co(II) concentration on the Vis spectrum of 0.3, 1.5, 3.2, and 8.2 wt% Co(II) erionite samples dehydrated at 525°C

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