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Quantitative Interpretation of Infrared Diffuse Reflectance Spectra over Whole Concentration Range

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The infrared diffuse reflectance spectra of $CaCO_3$ dispersed in KBr and Si were measured over a wide concentration range. The relation between relative reflectance and concentration varies with dispersing medium. The relation follows the Kubelka-Munk (K-M) equation only in the low concentration region. The deviation in the high concentration region from the K-M equation changes with wavelength and dispersing medium. The results over the whole concentration range can be interpreted by means of a modified K-M equation in which the difference in the scattering coefficients between the sample and the dispersing medium is taken into account. The tendency of scattering coefficients of $CaCO_3$, KBr, and Si calculated by the modified Kubelka-Munk equation agrees with that of refractive indexes.

The diffuse reflectance spectroscopy is widely used in the ultraviolet and visible regions.[1] The infrared diffuse reflectance spectroscopy would also be useful, several equipments having been succesfully developed.[2,3] We have constructed an emissionless infrared diffuse reflectance spectrometer (EDR) for *in situ* determination of reacting species on catalyst surface at elevated temperature.[4] Several theories have been proposed for the quantitative interpretation of the diffuse reflectance spectra.[5,6] The Kubelka-Munk equation is most widely used for analysis, but it should be regarded as a limiting law which holds only in a low concentration range.[6] A convenient equation is desirable for quantitative analysis over a wide concentration range.

We would like to show that the infrared diffuse reflectance spectra over the whole concentration range can be interpreted by means of a modified K-M equation, and that the factor determinig the intensity of absorption band is not only the absorption coefficient but also the scattering coefficient of the sample in the high concentration region.

Experimental

Fine powder of commercial calcium carbonate was used without further purification. Potassium bromide crystals for spectroscopy (Japan Spectroscopic Co.) and silicone wafers (99.9999%, Shin-Etsu Chem. Co. Ltd.) were ground to fine powder and used as dispersing media. Mixtures of the sample and a dispersing medium with predescribed ratios were packed in a sample holder, and the spectra were measured with an emissionless infrared diffuse reflectance spectrometer (Japan Spectroscopic Co., EDR-31) at an ambient temperature and at 200 °C. The details of the spectrometer were reported.[4]

Results

Figure 1 shows typical diffuse reflectance spectra of mixture of $CaCO_3$ and KBr. The absorption bands at 873 and 711 cm^{-1} can be ascribed to characteristic vibrations of carbonate ion, and the band at 2520 cm^{-1} to a combination band.[7] Even when the concentration of $CaCO_3$ was as low as 0.19%, the absorption bands were conspicuous. The band intensities increase with increase in concentration, but the relation between band intensity and concentration differs with wavelength. The band intensity of 100% $CaCO_3$ at 2520 cm^{-1} was much greater than that of 10% $CaCO_3$; the difference in band intensity at 873 cm^{-1} was not so great. On the other hand, the difference in band intensity between 0.19% and 1% $CaCO_3$ samples was greater at 873 cm^{-1} than that at 2520 cm^{-1}. The relation between band intensity

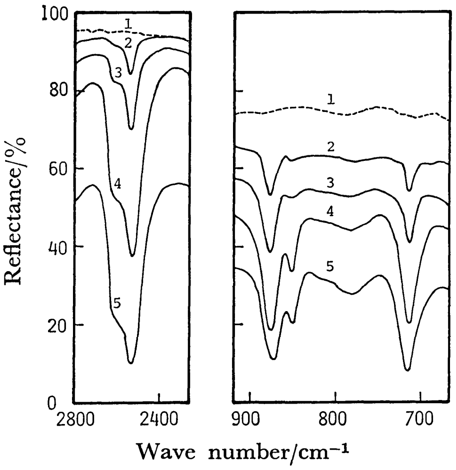

Fig. 1. IR diffuse reflectance spectra of $CaCO_3$ dispersed in KBr. Wt fraction of $CaCO_3$: (1) 0%, (2) 0.19%, (3) 1.0%, (4) 10%, and (5) 100%.

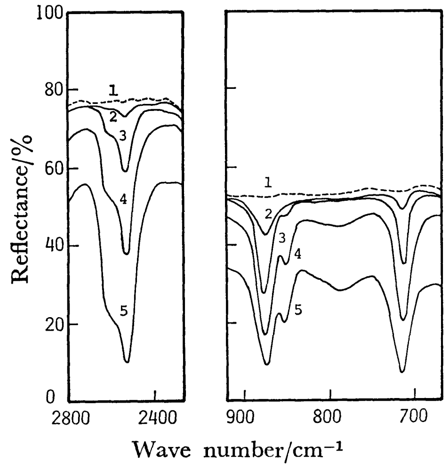

Fig. 2. IR diffuse reflectance spectra of $CaCO_3$ dispersed in Si. Wt fraction of $CaCO_3$: (1) 0%, (2) 1.0%, (3) 10%, (4) 40%, and (5) 100%.

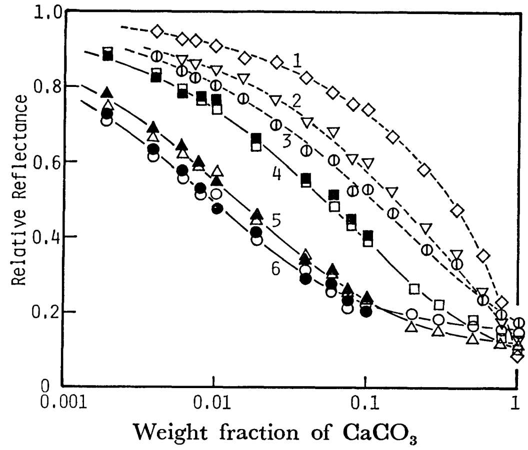

Fig. 3. Variation of relative reflectance with wt fraction of CaCO$_3$. Wavenumber and dispersing medium: (1) 2520 cm^{-1} in Si, (2) 711 cm^{-1} in Si, (3) 873 cm^{-1} in Si, (4) 2520 cm^{-1} in KBr, (5) 711 cm^{-1} in KBr, and (6) 873 cm^{-1} in KBr. Solid marks, at 200 °C; and empty marks, at ambient temp.

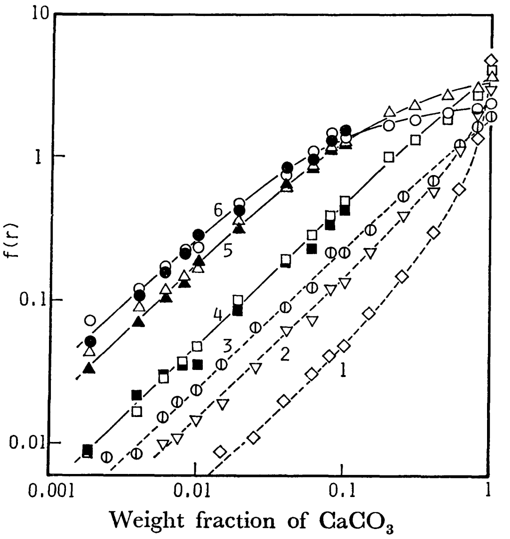

Fig. 4. Variation of K-M function with wt fraction of CaCO$_3$. For the symbols, see the legend of Fig. 3.

and concentration changes with dispersing medium. When Si was used as a dispersing medium, the band intensity changes a great deal with concentration in the high concentration region, as shown in Fig. 2. The difference in band intensity between 10% and 100% samples was much greater than that shown in Fig. 1. The band intensity does not change much with concentration in the low concentration region. The absorption bands of the 0.15% sample at 2520 and 711 cm^{-1} could not be observed.

The variation of band intensity with dispersing medium is shown in Fig. 3, in which the relative reflectance, defined as the ratio of reflectance at peak minimun to the reflectance of pure dispersing medium, is plotted against the weight fraction of CaCO$_3$ in a mixture of CaCO$_3$ and the dispersion medium. With increase in concentration the relative reflectance decreases remarkably in the low concentration region, when KBr is used as the disperison medium. In the case of Si, the relative reflectance decreases remarkably in a high concentration region. In both cases, the relative reflectance at 2520 cm^{-1} decreases in a higher concentration region as compared with that at 873 and 711 cm^{-1} (the results at ambient temperature ○, at 200 °C ●). Agreement between results indicates that the quantitative relation in the emissionless diffuse reflectance spectrometer does not change with temperature.

In the K-M theory, the reflectance is related to the absorption constant K and the scattering constant S of the mixture of the sample and dispersion medium:

$$f(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}, \tag{1}$$

where f(R) is the Kubelka-Munk function and R the absolute reflectance. In practice, the relative reflectance r defined as above is used in place of R. The following assumptions are usually made. The absorption constant K is equal to the product of the absorption coefficient ε_s and the concentration X of the sample, and the scattering constant S is equal to the scattering coefficient of the scattering medium σ_m. Thus, we have

$$f(r) = \frac{(1-r)^2}{2r} = \frac{\varepsilon_s X}{\sigma_m}. \tag{2}$$

Figure 4 shows the relation between the logarithm of the K-M function and the logarithm of the sample concentration. In all cases, the plots give straight lines with the slope of unity only in the low concentration region. This is in line with the fact that the K-M equation is regarded as a limiting law which holds only in the low concentration region. The plots deviate from the straight lines in the high concentration region depending on the wavelength and dispersion medium.

Hecht[6] found that the reflectance in the ultraviolet and visible regions sometimes follows the Rozenberg equation, though a constant in the equation is too large to be physically interpreted. The results in the present study do not follow the Rozenberg equation, according to which the second derivarive of the reflectance with respect to the concentration should be positive. In the infrared diffuse reflectance spectra of NaCO$_3$, NaNO$_3$, and Na$_2$SO$_4$ dispersed in KI, Ishii *et al.*[2] found a linear relationship between the reflective absorbance and logarithm of the concentration in the low concentration region. The intensities of absorption bands at 711 and 873 cm^{-1} of CaCO$_3$ in KBr appeared to obey their relation in the low concentration region, but not the intensities of the other bands.

Discussion

In the K-M theory it is assumed that the absorption constants of a mixture of the sample and the dispersion medium is proportional to the concentration of the sample and the scattering constant is independent of concentration. However, both constants would depend on the concentrations of both sample

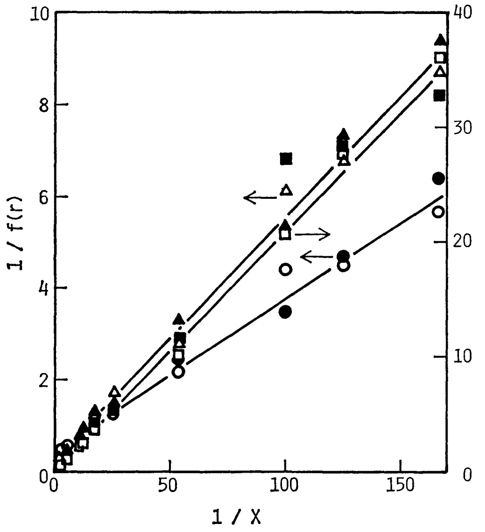

Fig. 5. Reciprocal plot of K-M function *vs.* wt fraction of $CaCO_3$ dispersed in KBr. (○,●) 873 cm^{-1}, (□,■) 2520 cm^{-1}, and (△,▲) 711 cm^{-1}.
Solid marks, at 200 °C; and empty marks, at ambient temp.

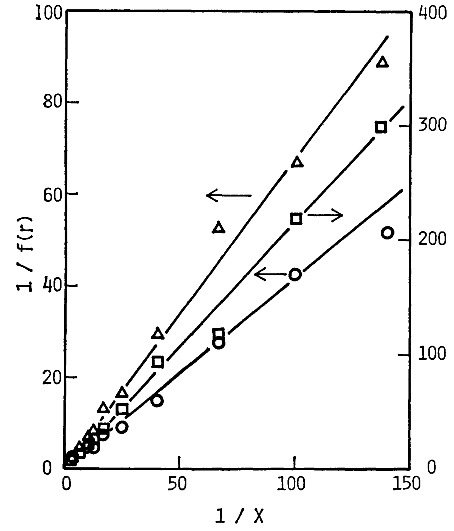

Fig. 6. Reciprocal plot of K-M function *vs.* wt fraction of $CaCO_3$ dispersed in Si. For the symbols, see the legend of Fig. 5.

and diepersion medium.[6,8] Thus, the K-M equation should be written as

$$f(r)=\frac{(1-r)^2}{2r}=\frac{\varepsilon_s X+\varepsilon_m(1-X)}{\sigma_s X+\sigma_m(1-X)}, \tag{3}$$

where σ_s and σ_m are the scattering coefficients and ε_s and ε_m the absorption coefficients of the sample and the dispersion medium, respectively. The absorption coefficient of the dispersion medium can be neglected, when the dispersion medium has no characteristic absorption. Thus we have

$$f(r)=\frac{(1-r)^2}{2r}=\frac{\gamma X}{1+(\delta-1)X}, \tag{4}$$

where δ is the ratio of the scattering coefficient of the sample to that of the dispersing medium, σ_s/σ_m, and γ is the ratio of the absorption coefficient of the sample to the scattering coefficient of the dispersion medium, ε_s/σ_m. Equation 4 indicates that the plot of the inverse K-M function against the inverse concentration would give a straight line.

$$\frac{1}{f(r)}=\frac{\delta-1}{\gamma}+\frac{1}{\gamma X} \tag{5}$$

TABLE 1. RATIO BETWEEN ABSORPTION AND SCATTERING COEFFICIENTS

Band position	711 cm^{-1}	873 cm^{-1}	2520 cm^{-1}
$\gamma(CaCO_3\text{-}KBr)$[a]	9.5	15.0	2.40
$\delta(CaCO_3\text{-}KBr)$[b]	6.0	13.5	1.30
$\gamma(CaCO_3\text{-}Si)$	0.73	1.20	0.23
$\delta(CaCO_3\text{-}Si)$	0.52	1.30	0.10
σ_{KBr}/σ_{Si}[c]	0.087	0.096	0.077
σ_{KBr}/σ_{Si}[d]	0.076	0.080	0.096

a) $\varepsilon_{CaCO_3}/\sigma_{KBr}$. b) $\sigma_{CaCO_3}/\sigma_{KBr}$. c) $\gamma(CaCO_3\text{-}Si)/\gamma(CaCO_3\text{-}KBr)$. d) $\delta(CaCO_3\text{-}Si)/\delta(CaCO_3\text{-}KBr)$.

Figures 5 and 6 show the relations between the inverse K-M function and the inverse weight fraction. We see that the plots give straight lines. Although the intercepts are not obvious, they can not be neglected; the scattering constant of the mixture changes with the concentration of sample.

The constants in Eq. 5 were calculated from the slopes and the intercepts (Figs. 5 and 6), and are given in Table 1. The curves (Fig. 4) calculated by substituting the constants into Eq. 4 agree with the experimental results over the whole concentration range. In the ratios of the scattering constant of KBr to that of Si (Table 1), two groups were calculated from the ratio of γ in the $CaCO_3$–Si mixture to that in the $CaCO_3$–KBr mixture and from the corresponding ratio of δ at each wavelength. The ratios thus obtained agree with each other, *i.e.*, $\sigma_{KBr}/\sigma_{Si}=0.086\pm0.010$. The scattering coefficient varies with the refractive index, shape, size and the packing of the particles.[2,5] The refractive index of KBr is *ca.* 1.52 in the present wavelength region, and that of Si, *ca.* 3.42. The fact that the refractive index of KBr is smaller than that of Si is in line with the result that the scattering coefficient of KBr is smaller than that of Si. The effect of the shape and the size of particles also would be significant. The reflected light from the powder layer consists of the specularly reflected light at the surface of the powder layer as well as the diffusely reflected light.[9] The refractive index might have a predominant effect on the specular reflection and the shape and the size of powder on the diffuse reflection. The ratio of scattering coefficient of KBr to that of Si is fairly constant, but the ratio of the scattering coefficient of $CaCO_3$ to that of the dispersing medium varies with the wave length. This is in line with the fact that the refractive index of the substance which absorbs the light changes with wavelength in a complicated manner near the absorption band.[1]

In the K-M equation, the K-M function is proportional to the sample concentration (Eq. 2). Thus the Kubelka-Munk spectrum, or the plot of the K-M function against wavenumber, would be the same as absorbance spectrum in transmission spectroscopy. Actually, however, discrepancy has been observed both in the ultra-violet and visible regions[6] and the infrared region.[3] Equation 4 indicates that the intensity of the absorption band in the diffuse reflectance spectrum also depends on the scattering coefficient of the sample, especially when the sample concentration is high. Since the scattering coefficient of the substance which absorbs the light appears to vary with the wavelength near the absorption band, the Kubelka-Munk spectrum is not always the same as the absorbance spectrum.

The modified K-M equation would also be useful in the ultraviolet and visible regions. The deviation of the K-M function from linearity appears to be greater in the ultraviolet and visible regions than in the infrared region. The variation of the scattering coefficient with the substance might be large in the ultraviolet and visible regions.

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