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단 신

석탄 확산-반사 적외선 스펙트럼의 C-H 신축띠 분석

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Analysis of C-H Stretching Bands in Diffuse Reflectance Infrared Spectra of Coals

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The need for efficient utilization of fossil fuel reserves has made stringent demands on chemists to better elucidate and understand the chemical and physical structure of coals. In this respect, infrared spectroscopy has been used as the most important tool because most organic and mineral components in coal absorb in the infrared region[1]. Since absorption bands in the infrared spectra of coals are, however, rather broad and featureless[2,3] ,the spectra often have to be mathematically manipulated to obtain useful structural information.

A spectrum is completely described when the number of constituent bands and their shapes, positions, widths, and amplitudes are specified. Although curve-fitting can be used to determine those parameters, its success depends on the quality of the information used in the calculation. Curve fitting should be attempted only if the number of bands is known, and the accuracy of the calculation relies on the correctness of the models for the band shapes[4,5].

We are currently investigating the metal-catalyzed coal gasification reactions by in-situ diffuse reflectance FT-IR spectroscopy. In conjunction with the above implications, we present in this note the details on the vibrational structures of coals in the C-H stretching region.

Spectra were measured with a vacuum-purged Bruker Model 113 V FT-IR spectrometer. The source was a water-cooled Globar and a liquid nitrogen cooled mercury-cadmium telluride detector was used. The diffuse reflection attachment (Harrick Model DRA-2CO) designed to use the 6 : 1, 90° off-axis ellipsoidal mirrors subtending 20% of the 4 π solid angles was fitted to the sampline compartment of the FT-IR spectrometer. The sampling cup made of stainless steel was 3.2 mm deep with 9.5 mm diameter. The spectra were measured at a nominal resolution of 4 cm^{-1} by co-adding 4096 scans for the signal to noise ratio (SNR) to be better than 300 : 1. Diffuse reflectance spectra at infinite depth were calculated by taking ratio of the single-beam spectrum of the sample to that of the KBr reference placed in the same cup. The spectrum was then converted to the Kubelka-Munk (K-M) function[6]. The coal samples were lignite and high volatile bituminous originating from Indonesia and China, respectively, both of which are currently being used in the domestic industry plants. Their proximate and ultimate analyses are given in Table 1. The mineral contents of high temperature (1023 K) ashes analyzed by X-ray fluorescence method are also included in *Table* 1. Initially, the samples having particle sizes less than 78 μm (325) mesh) were dried in an oven at 380 K overnight and

Table 1. Proximate, ultimate, and ash analyses of coal samples (wt%)

	Lignite	Bituminous
Proximate Analysis[a]		
Moisture (ad)	4.56	8.14
Ash (ad)	4.81	7.13
Volatile Matter (daf)	45.9	37.8
Elemental Analysis[b]		
Carbon (dmmf)	69.1	76.1
Hydrogen (dmmf)	5.17	5.02
Oxygen (dmmf)	23.9	16.7
Nitrogen (dmmf)	1.13	0.86
Sulfur (dmmf)	0.66	1.26
Ash Analysis[c]		
SiO_2	47.51	55.28
Al_2O_3	32.59	19.15
Fe_2O_3	6.73	14.99
TiO_2	3.74	0.96
MnO	0.11	0.39
CaO	2.88	4.17
MgO	1.29	2.34
K_2O	1.18	1.32
Na_2O	0.24	0.36
P_2O_5	3.94	0.18

[a]ad: as analyzed (air dry) basis, daf: dry, ash free basis, [b]dmmf: dry, mineral free basis, [c]high temperature (1023 K) ashes.

then loosely packed in the sampling cup to record the diffuse reflectance spectra. The rectilinear baseline correction has been made to adjust the spectra between 3100 and 2700 cm^{-1}.

To determine the peak positions, one can use various techniques such as second derivative[5] and Fourier self-deconvolution (FSD)[7]. The former technique has disadvantage that the converted spectra are difficult to interpret, because of the presence of secondary negative-going lobes. On the other hand, recent work has shown that the widths of absorption bands can be reduced through the use of a technique called Fourier self-deconvolution (FSD)[8], permitting effective resolution enhancement. It is known[9,10] that the form of the band shape is not crucial for determining band positions by FSD. Hence, the peak positions were determined in this work by FSD and their appropriateness was confirmed by comparing with the corresponding values obtained from the second derivative spectrum. The initial estimates for the bandwidths were determined also from the second derivative spectra. The curve-fitting calculation to obtain the refined bandwidths and amplitudes was performed by minimizing the squared difference between the measured and fitted spectra. We employed the linear constrained optimization algorithm (Nelder-Mead downhill simplex fitting algorithm[11]) to minimize the difference. Gaussian, Lorentzian, and Voigt functions were used as possible models for the band shape. The suitability of the assumed band shape was verified by deconvoluting the fitted spectrum with the same parameters as for the measured spectrum. When the two deconvoluted spectra were compared favorably, the assumed band shape could by regarded as a reasonable representation of the true one.

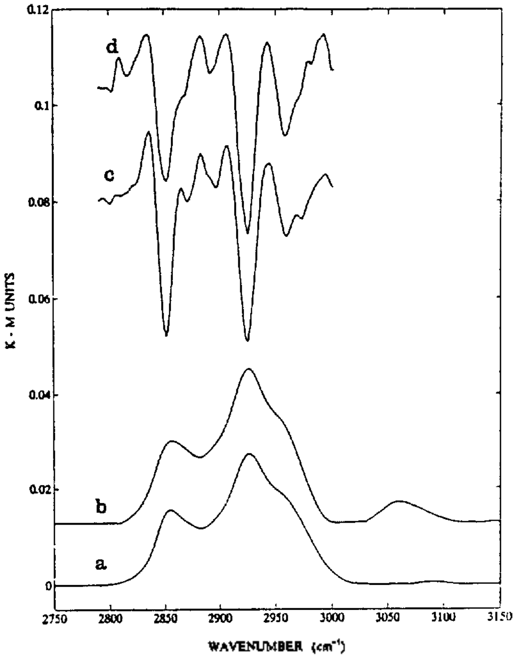

Fig. 1. Diffuse reflectance infrared spectra of lignite (a) and bituminous (b) coals in the C-H stretching region. (c) and (d) represent second derivative spectra of (a) and (b), respectively.

Fig. 1a and 1b show the infrared spectra of lignite and bituminous coals in the C-H stretching region. Two distinct bands are observed at 2853 and 2920 cm^{-1}, which can be assigned[12], respectively, to the symmetric and asymmetric C-H stretching vibrations of CH_2 group. Appearacne of very weak peak at near 3055 cm^{-1} indicates that aromatic rings the highly substituted and/or highly crosslinked. Its intensity is nonetheless stronger in *Fig.* 1b than in *Fig.* 1a. This can be attributed to the fact that aromaticity increases with rank[12]; high volatile bituminous coal is ranked higher than lignite. In order to resolve the broad spectral feature in *Fig.* 1a and 1b into component bands, second derivative spectra are obtained. The resulting spectra are shown in *Fig.* 1c and 1d. From the figure, we can identify the presence of several peaks, for instance, at 2853, 2872, 2893, 2920 and 2953 cm^{-1}. By using the FSD method, identical peak positions have been determined. This can be evidenced from *Fig.* 2 which shows a series of increasingly self deconvoluted spectra with a 15 cm^{-1} wide Lorentzian line and a triangular squared[7] apodization. Since the SNR was very large, the second derivative and FSD methods should provide the peak positions rather consistently with each other as actually observed. The 2953 and 2872 cm^{-1} peaks can be assigned[12], respectively, to the asymmetric and symmetric C-H stretching vibrations of CH_3 group. The relatively weak band at 2893 cm^{-1} can be attributed to lone CH group[3]. The band may also have a contribution from the overtone and combination bands of lower frequency bending modes, probably intensity enhanced by Fermi resonance interactions. Another very weak shoulder peak at near 2975 cm^{-1} (see *Fig.* 1c and 1d) appears to be assignable to methyl groups in a different environment[8].

The peak positions determined as above were used in the curve-fitting calculations. Bacause the correct band shape was unknown, the observed spectrum was fitted with Lorentzian, Gaussian, and Voigt (1 : 1 Gauss-Lorentz sum) functions, ob-

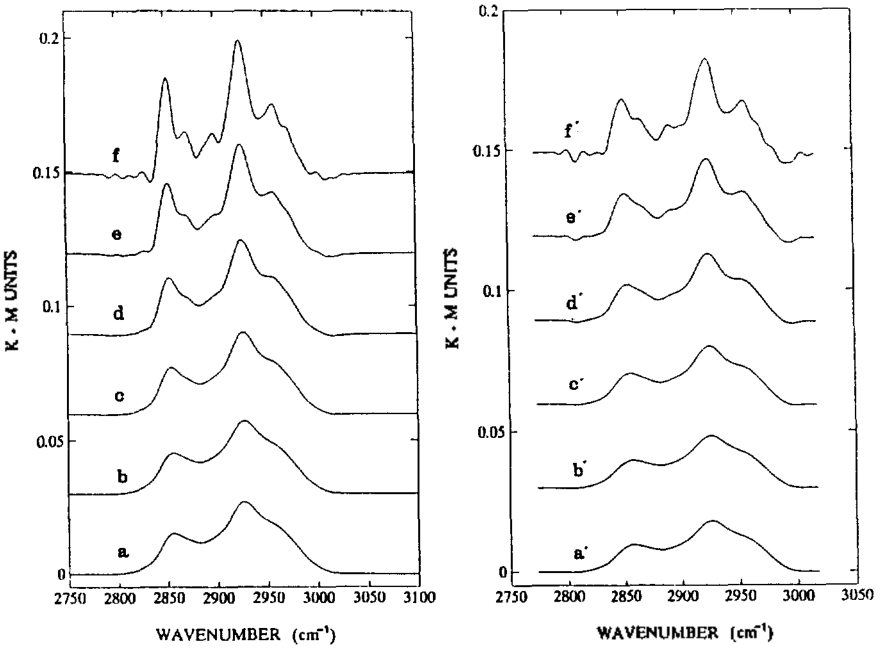

Fig. 2. Fourier self deconvolution of the C-H stretching region with Lorentzian line and triangular squared (D_a^2) apodization. Experimental spectra of lignite (a) and bituminous (a') coals with 4 cm^{-1} resolution. (b)~(f) and (b')~(f') are calculated by multiplying the Fourier transform (FT) of (a) and (a'), respectively, by $D_a^2(x)\exp(\gamma x)$ and computing the reverse FT. Values of γ (cm^{-1}): (b) and (b') 3; (c) and (c') 6; (d) and (d') 9; (e) and (e') 12; (f) and (f') 15.

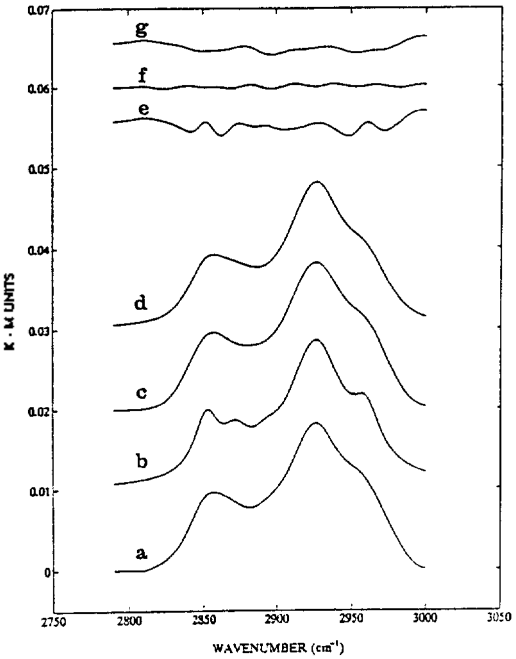

Fig. 3. Diffuse reflectance spectra of bituminous (a) in the C-H stretching region, and its curve-fitted spectra with Lorentzian (b), Gaussian (c), and Voigt (d) functions. (e), (f), and (g) are difference between measured and curve-fitted spectra: (e)=(b)−(a); (f)=(c)−(a); (g)=(d)−(a).

taining the results for bituminous labeled as curves b, c, and d in *Fig.* 3. The difference between the curve-fitted and measured (*Fig.* 3a) spectra are drawn in *Fig.* 3e, 3f, and 3g. It is seen that Gaussian function would be the most probable band shape. Since deconvolution is known extremely sensitive to the details of the components bands even when they overlap severely[10], the suitability of Gaussian band shape has been verified, as mentioned earlier, by deconvoluting the fitted spectrum with the same parameters as for the meassured spectrum. *Fig.* 4 shows a series of deconvoluted spectra obtained with a bandwidth of 7 cm^{-1}. It can be seen that a Gaussian band shape yields in fact the best agreement of the deconvoluted fitted-spectrum with the deconvoluted measured-spectrum. Although the results on the lignite coal are not graphically presented, same observation has been made. From the curve-fitted spectra with

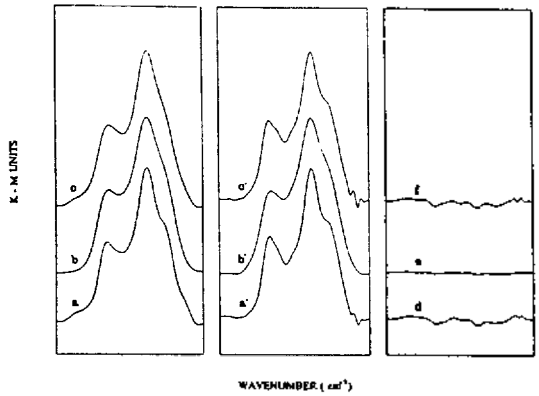

Fig. 4. Deconvolution of bituminous spectra using a 7 cm^{-1} bandwidth. Curve-fitted spectra with Lorentzian (L), Gaussian (G), and Voigt (V) functions (see *Fig.* 3) are deconvoluted, respectively, with L (a), G (b), and V (c) functions. (a'), (b'), and (c') are deconvolution of experimental spectrum with L, G, and V functions, respectively. (d), (e), and (f) are difference between (a-a'), (b-b'), and (c-c')

Gaussian functions, the relative intensities of component bands in lignite are then estimated to be 9 : 14 : 22 : 23 : 31 for the bands centered at 2853, 2872, 2893, 2920, and 2953 cm^{-1}, respectively. The corresponding relative intensities in bituminous coal are 10 : 12 : 20 : 37 : 21. The intensities of CH_3 group vibrational bands are in a relative sense more intense in lignite than in bituminous coal. This is consistent with the general view that the methyl group is more abundant in a low ranked coal[8]. these relative peak intensities will certainly change by catalyzed cal reactions. Such changes will depend on the kinds of catalysts. One could correlate the changes with the specific catalyst activity, and this will provide a useful basis for one to design a more effective catalyst. That is, present mathematical manipulation concepts can be directly applied to the coal-gasification, and can be a starting point for the production of modified catalysts with higher activity and selectivity.

In summary, we have combined curve-fitting with a deconvolution technique to examine the C-H stretching region of the infrared spectra of two different coal samples. The diffuse reflectance spectra of lignite and bituminous coals have been concluded to be made of Gaussian bands. The present work is believed to provide the basis for an extensive infrared study of the chemical changes in coals brought about by in-situ reactions under different conditions. Changes in concentrations of specific functional groups could be more confidently monitored as function of catalysts by fitting spectra with the proper band shape. Such information should be useful in designing a more effective multi-functional catalyst.

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