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In situ Diffuse Reflection FT-IR Spectroscopic Study of Lignite Gasification

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Among various spectroscopic techniques, infrared spectroscopy has been utilized as the most important tool in the characterization of coal because most of its organic and mineral components absorb in the infrared region.¹ However, infrared spectra of coals has been traditionally obtained by the transmission method after dispersing the sample in an infrared transparent medium (usually KBr) and then pressing into a glassy pellet.² Owing to its inherent disadvantage requiring mechanical mixing with other matrix, the infrared spectroscopic method has thus been regarded inappropriate for *in situ* studies. This changed with the pioneering work of Fuller and Griffiths,³ who successfully developed diffuse reflectance technique for infrared spectroscopy and demonstrated its usefulness in coal characterization studies. In this NOTE, we wish to report the usefulness of diffuse reflectance infrared Fourier transform (DRIFT) technique for *in*

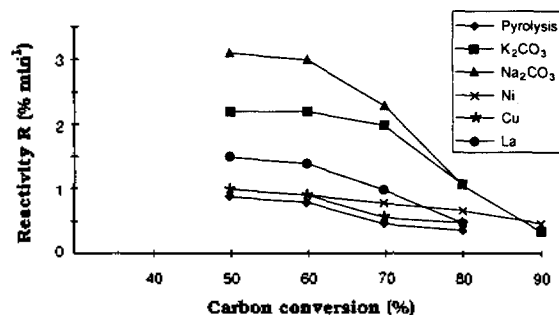


Figure 1. Reactivity vs. weight loss in steam gasification of lignite at 1073 K. See text. When preparing the Ni, Cu, and La incorporated samples, nitrate salts were used due to their solubilities in water.

situ studies of coal by interfacing the DRIFT optics with a reaction chamber. In this regard, the gasification of lignite has been investigated by recording the infrared spectra at various temperature.

Diffuse reflectance infrared spectra were measured with a vacuum-purged Bruker model IFS 113v 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 4π solid angles was fitted to the sampling compartment of the FT-IR spectrometer. A reaction chamber made of stainless steel (Harrick Model HVC-DR2) was located inside the reflection attachment. The position of sampling cup was adjusted to match with the focal point of incident radiation. CaF₂ crystals were used as the infrared transparent windows. The temperature of sampling cup was regulated by a home-made temperature controller, and the chamber was flushed continuously with a wet nitrogen (*ca.* 100 ml/min) prepared by bubbling through a water trap.

Impregnation method has been used to incorporate the metallic species to lignite sample. After drying at 373 K overnight, its infrared spectra were measured at a nominal resolution of 4 cm⁻¹ by co-adding 128 scans. The temperature of sampling cup was raised at a rate of 3°C/min and kept for 4 min at each specified temperature to take the spectra. 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 at room temperature. The spectrum was then converted to the Kubelka-Munk (K-M) function.⁴ The triangular squared function was used in the apodization of measured interferograms. The proximate and ultimate analyses of the lignite sample have been reported previously.⁵

Prior to taking the *in situ* infrared spectra, the relative catalytic effectiveness of several metals in the steam gasification has been tested in a separate reactor. In this experiment, the weight % of metal was kept constant at below 10%. It was found that at below 773 K the weight loss of lignite occurred mainly by pyrolysis rather than by catalytic gasification. At higher temperatures above 873 K, the latter reaction seemed, however, to be more favorably to occur. Letting the amount of lignite, remaining after reaction at a higher temperature, be *W* based on the dry-ash-free state, the relative catalytic effect may then be comparatively stu-

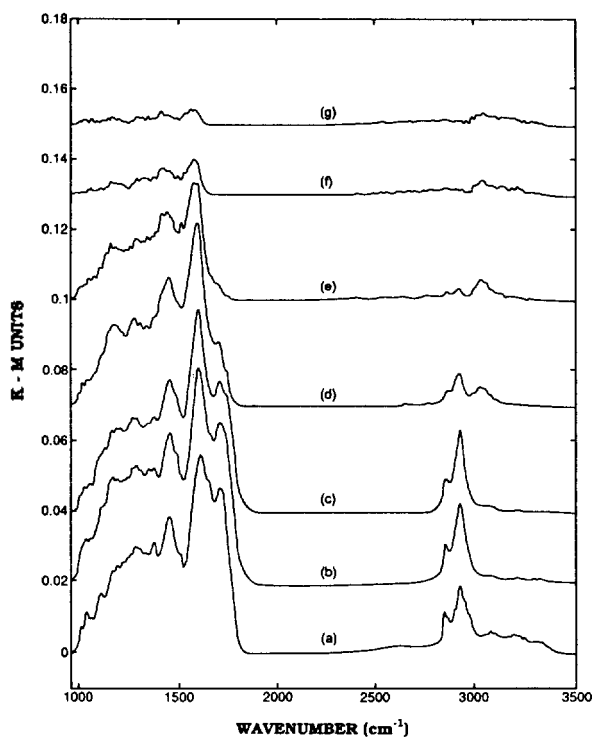


Figure 2. Diffuse reflectance infrared spectra of lignite during pyrolysis under dry nitrogen atmosphere. Spectra were obtained at (a) 298, (b) 473, (c) 573, (d) 673, (e) 773, (f) 873, and (g) 923 K.

died by examining the reactivity R defined as the time derivative of W , i.e., $R=(1/W)(dW/dt)$, in terms of the weight loss. A typical Reactivity-to-Weight Loss behavior at 1073 K is shown in Figure 1. It can be seen that the reactivity decreases as the weight loss increases. This can be understood by invoking that the sample surface should be covered with ash as the gasification reaction proceeds. The catalytic effectiveness is observed in the order of $\text{Na} > \text{K} \gg \text{La} > \text{Ni} > \text{Cu}$. The catalytic effect of sodium is noteworthy while that of copper is minimal.

The catalytic mechanism of transition metals has been a matter of dispute. Lopez-Peinado *et al.*⁶ reported that nickel was catalytically active when presenting as a metallic state, but inactive in an oxidized state. We have observed previously⁷ that nickel nitrate dispersed in amorphous carbon was decomposed to nickel oxide and then reduced to nickel metal at far below 773 K. Considering that char with a high carbon content will be formed when gasification occurs at above 973 K and that carbon is a very strong reducing agent, the possibility of presence of nickel in an oxidized state should be very scarce. In fact, the residue obtained after gasification of lignite at 1073 K was found not to contain nickel oxide species from the x-ray diffraction. This implies that the catalytic activity of nickel is much lower than that of alkali metals.

Although the pyrolysis reaction is more favorable to occur at below 773 K, the catalytic effect of metals would be reflected in the infrared spectra. Namely, the catalytic activity at high temperature (above 973 K) may have some relevance with the variation of infrared peak intensities of organic functional groups at a relatively low temperature (below 773 K). Figure 2 shows the *in situ* DRIFT spectra of pure lignite

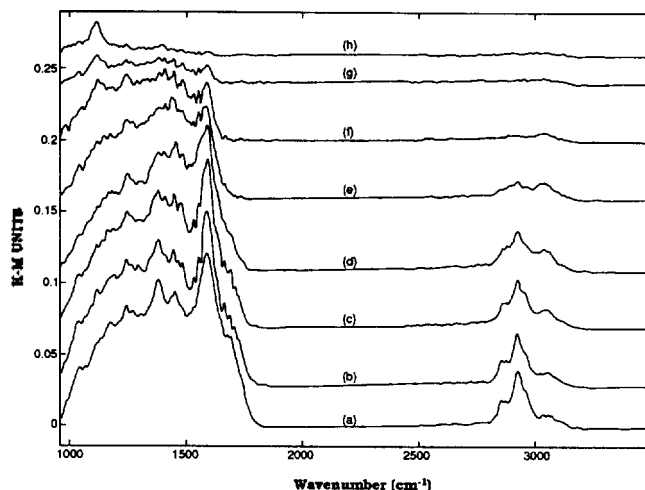
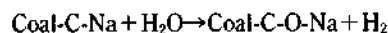


Figure 3. Diffuse reflectance infrared spectra of sodium carbonate incorporated lignite during steam-gasification. Spectra were obtained at (a) 473, (b) 523, (c) 573, (d) 623, (e) 673, (f) 723, (g) 773, and (h) 823 K.

obtained during pyrolysis under dry nitrogen medium. Figure 3 shows the same kinds of spectra obtained during steam gasification of sodium incorporated lignite. It can be seen from Figure 2 that the aromatic C-H stretching band at 3050 cm^{-1} grows at 673 K by pyrolysis and becomes more dominant at 773 K than the aliphatic C-H stretching bands in the 2800-2950 cm^{-1} region. The carbonyl stretching bands at near 1700 cm^{-1} become weakened at 673 K. In contrast, it is seen from Figure 3 that the increase of aromaticity factor occurs evidently even at 473 K when sodium is incorporated in the lignite. Decarboxylation appears also to occur at 473 K. While the lignite-to-char conversion occurs at *ca.* 923 K during pyrolysis, the corresponding temperature is observed to be lowered by as large as 150 K when sodium is incorporated. However, when catalytically inactive metals like copper were incorporated into lignite, the DRIFT spectra were hardly different from those in Figure 2. The present observation indicates that the catalytic effect of metals at high temperature is in fact reflected in the DRIFT spectra at low temperature.

Yuh and Wolf⁸ have reported transmission infrared spectra of thin wafers of KBr mixed with carbon and coal char samples after impregnation with potassium salts, devolatilization, and partial gasification at 1023 K. All catalytically activated salts like KOH, K_2CO_3 , and KNO_3 were informed to show two characteristic bands at 1400 and 1650 cm^{-1} while no such bands appeared in the case of catalytically inactive KCl. By noticing that the bands can be correlated with those of KHCO_3 , C-O-K and C-O-H bonds were argued to participate in the gasification as common active intermediates. Similarly, the same authors⁹ reported that when catalytically active sodium salts such as Na_2CO_3 , NaOH, and NaNO_3 were incorporated into coal chars, devolatilized and partially gasified samples at 1023 K showed absorption bands at 1675, 1450, and 880 cm^{-1} . By assigning the 1450 and 880 cm^{-1} bands to carbonate and the 1675 cm^{-1} band to carbonyl group, the following reactions were suggested to occur:



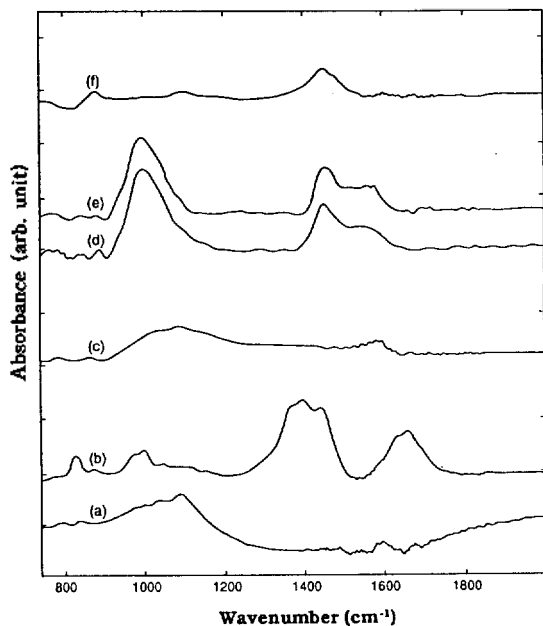
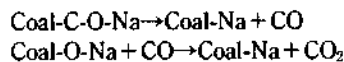


Figure 4. Transmission infrared spectra of chars of lignite after dispersing in KBr matrices. The spectra were obtained for (a) char itself, (b) K_2CO_3 incorporated char, (c) K_2CO_3 incorporated char after steam gasification for 10 min at 1023 K, (d) Na_2CO_3 incorporated char, and Na_2CO_3 incorporated char after steam gasification for 10 (e) and 30 (f) min at 1023 K.



Namely, the 1675 cm^{-1} band was argued due to the complex resulting from the combination of coal-Na and/or coal-O-Na with CO_2 .

In order to test whether the characteristic peaks reported by Yuh and Wolf⁹ are in fact related with the gasification of coal chars, we have attempted to obtain similar infrared spectra. Coal chars were prepared by treating the lignite sample under dry nitrogen at 1173 K, and then either K_2CO_3 or Na_2CO_3 was added to them by impregnation method. Figure 4(a) shows the transmission infrared spectrum of char dispersed on KBr matrix. The peak at near 1100 cm^{-1} is due to ash component. Figure 4(b) shows the infrared spectrum of char recorded after impregnating with K_2CO_3 . As reported by Yuh and Wolf, the absorption peaks appeared distinctly at near 1400 and 1650 cm^{-1} . However, when the sample was steam-gasified for 10 min at 1023 K, such peaks became completely absent as can be seen from Figure 4(c). In a separate weight-loss experiment, it was found that gasification reaction was continuously occurring even after 10 min. The present observation may indicate that the 1400 and 1650 cm^{-1} peaks are not due to characteristics of catalytically active surface complex. A somewhat different observation was made, however, for the Na_2CO_3 incorporated sample. Figure

4(d) corresponds to the transmission infrared spectrum of char obtained after impregnating with sodium salt. As reported by Yuh and Wolf, bands are observed at 880 and 1450 cm^{-1} . However, the 1675 cm^{-1} band is barely seen. Instead, previously unnoticed bands appeared distinctly at 1000 and 1550 cm^{-1} . As can be seen from Figure 4(e), the spectral pattern was hardly affected by steam-gasification for 10 min at 1023 K. This is in contrast with what observed for the K_2CO_3 incorporated char. Even after 30 min gasification, the 880 and 1450 cm^{-1} bands are still kept distinctly. Hence, at least for the sodium incorporated chars, the 880 and 1450 cm^{-1} bands seem to have relevance with the high catalytic activity of sodium metal in the coal gasification. Although the present observation appears to be consistent with the idea of a salt-surface complex introduced by Mims and Pabst,¹⁰ the identity of those peaks is, however, a matter of conjecture at this moment.

In summary, we have investigated the steam gasification of lignite *in situ* at below 923 K by the diffuse reflectance infrared spectroscopy along with a weight-loss measurement at above 973 K. Although a detailed spectral analysis could not be performed due to the overlapping of bands, at least the qualitative information seemed to be possibly to obtain from the *in situ* spectra. The catalytic activity at higher temperatures appeared to be reflected in the DRIFT spectra at relatively lower temperatures. The most significant contribution of this work would be to demonstrate that the temperature and atmospheric effects on the physicochemical properties of powdered materials can be readily investigated by interfacing the infrared reflectance optics with a controlled environment reaction chamber.

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