Studies on Chemical Structural Change of Pyrolyzing Coal and Real-time Analysis of Volatiles

張，露

(様式3)

氏　　名　：　張　露

論　文　名　：　Studies on Chemical Structural Change of Pyrolyzing Coal and Real-time Analysis of Volatiles

（熱分解における石炭の化学構造変化ならびに揮発成分のリアルタイム分析に関する研究）

区　　分　：　甲

論文内容の要旨

Pyrolysis is a most generally used technology for down-stream processing and clean utilizations of coal. Pyrolysis of coal produces three main products, i.e., light gases, tar, and char. Deep insight into the reaction processes during the coal pyrolysis is critical to develop this technology. Real-time analysis is a most effective approach to explore the mechanisms of the pyrolysis accurately, however, has not been sufficiently developed. In addition, the study on the detailed processes of coke formation during the coal pyrolysis is an attractive subject to coke industry, and also an important topic to the community of the low rank coal utilization. In this thesis, the author applies a series of off-line characterizations to coal-to-coke, in order to explore the chemical structural change of coal during the pyrolysis, and carries out the real-time quantitative analysis to volatiles from the pyrolysis.

Chapter 1 reviews existing technologies for the coal pyrolysis, real-time analysis, and also so for proposed models of chemical structure of coal and its pyrolysis mechanism.

In order to study the chemical structural change of coal during the pyrolysis, in Chapter 2, the samples of caking coal (CC), non-caking coal (NCC) and their cokes which were gotten from pyrolyzing coal at the temperature range from 400 to 900°C were evaluated by solid state ^{13}C-NMR, FT-IR, XPS and Raman, respectively. Sizes of aromatic clusters with pyrolyzing coal were estimated via ^{13}C-NMR. It was found that CC has less substituents, but higher aromaticity and condensation degree than those of NCC. During the pyrolysis, NCC would be deprived more substituents and then produced more gases than CC to evolve an aromatic structure similar to CC. Eventually, it was impossible to distinguish the coking products of NCC and CC in terms of both aromaticity and condensation degree. Other three characterizations indicated that, compared with CC, NCC contained more O-containing functional groups, in particular hydroxyl and ester groups, which were related to the cross-linking reactions during the pyrolysis. It was also found that those reactions related to O-containing groups mainly occur before 500°C.

In Chapter 3, to investigate the strict relationship between the substituents or functional groups attached to the coal macromolecules and the generation of the volatile products, e.g., CH_4, H_2O, CO, CO_2, etc., during the coal pyrolysis, quadrupole mass spectrometry, gas chromatography, and ^{13}C nuclear magnetic resonance were applied to real-time monitoring the formations of volatile products, off-line quantitative determination of the total products from the pyrolysis of

NCC, and the changes of diverse substituents in the NCC along with coke formation, respectively. These measurements were also performed for the pyrolysis of CC to contrast NCC. Qualitative formation rates as a function of temperature of gas products were achieved, and then were deconvoluted and assigned to several peaks based on the possible reactions occurred during the pyrolysis. These data revealed that, during the pyrolysis, the functional groups related to the formation of CO, i.e., ether, carbonyl, and anhydride, can directly generate CO via bond breaking, or take a detour of the formation of other intermediates via condensation and recombination firstly. Moreover, the formations of CO_2 and CH_4 were related to the direct removal of -COO- and -CH_3, respectively.

In order to real-time analyze the formation of tar during the coal pyrolysis, Chapter 4 describes a prototype device for Li^+ ion-attachment mass spectrometry (IAMS) was developed for real-time quantitative monitoring of the vapor produced from thermochemical conversion of coal. Simulated tar vapor containing a suite of aromatics and the real vapor produced from the pyrolysis of coal were monitored by IAMS with a Li^+ source. It was confirmed that both the simulated and real vapors are ionized without undergoing fragmentation and the sensitivities of these detected aromatic molecules are similar to one another. In addition, when the feeding rate of the coal sample was changed from 0.5 to 1.0 g/min, the peak intensities increased nearly twice as much. These results showed the possibility of applying IAMS to the quantitatively monitoring of coal-derived volatiles.

The general conclusions of this thesis are proposed in Chapter 5. First, during the pyrolysis, NCC was removed more substituents and then produced more gases than CC to evolve a coke structure. The degree of crystallinity of NCC was much lower than that of CC, as well as their derivative cokes. Second, during the coal pyrolysis, the CO formation can be mainly attributed to the cleavage of ether group, the removal of anhydrides, oxygen free radicals reaction, and cleavage of carbonyl groups. The removals of carboxyl, ester, and anhydride groups were the main reasons for the CO_2 formation. The quantity of aromatic oxygen during the pyrolysis would temporarily increase due to some secondary reactions, as well as the quantity of aliphatic oxygen. Third, the advantages (no occurrence of fragmentary ions) of Li^+–IAMS enabled real-time qualitative analysis of the simulated tar vapor. Li^+–IAMS performed well to the quantitative analysis of the simulated tar vapor because of its equivalent sensitivities of the aromatics with Li^+ affinities above 1 eV. Moreover, the results of real vapor from the coal pyrolysis monitored by Li^+–IAMS coincided very well with those of the simulated tar vapor.