12. Tritium Tracer法を用いた石炭の水素移行挙動の解析：脱灰処理の影響
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Elucidation of Hydrogen Transfer Behavior of Coal Using a Tritium Tracer Method:
Effect of Demineralization
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Synopsis
The roles of mineral matter and intrinsic parameters of each coal in term of hydrogen transfer reaction with H₂ have been investigated using a tritium tracer technique. Variations of the mineral matter content were achieved by removing gradually the mineral matter with HCl and HCl-HF treatments.

Introduction
Hydrogen transfer reactions that occur during coal liquefactions are essential for the conversion of intractable coal molecules into liquids and soluble products. In fact, the hydrogen transfer pathways have received special attention by many researchers because practical considerations virtually require that the hydrogen content of the coal be increased. Therefore, control of the hydrogen transfer processes is central to achievement of control of product distributions and the economic of coal liquefaction.

There is little doubt that H₂ affects the coal liquefaction processes, especially under mild conditions (at <400 °C), because of substantial different in bond strength between it and C-H in solvent; H-H bond strength is 104 kcal/mol, while the benzylic C-H bond strength in tetralin is about 82 kcal/mol. In fact, in the liquefaction of Datong coal, we have shown greater hydrogen transfer to the coal from H₂ than from tetralin at 300 – 350 °C, and comparable transfer at 400 °C.¹ However, this behavior is not universal; for example, Wandoan coal behaves differently.² These results are fascinating and important to be elucidated because it should give enlightenment in effective utilization of H₂. Larsen et al. have addressed us to the nonradical hydrogen transfer pathway that is catalyzed by mineral matter exist in coal for the utilization of H₂.³

In the present study, we have further sought the roles of mineral matter and intrinsic parameters of each coal in term of hydrogen transfer reaction with H₂ using a tritium tracer technique.

Experimental Section
Materials. Coal samples (lignite Beulah Zap (ND), hvb Illinois No. 6 coal (IL), mvb Upper Freeport (UF), and lvb Pocahontas No. 3 (POC) coals) were obtained from the Argonne Premium Coal Sample Bank. Demineralized coal samples were prepared by standard methods of HCl and successive HCl-HF treatments. Tritiated molecular hydrogen was obtained by electrolysis of tritiated water (6 x 10⁶ dpm/mL), using HG-225 Hydrogen Generator and pressurized with hydrogen gas before use.

Reaction procedure. The reactions were carried out in a fixed bed reactor (reactor volume of 15 mL). The reaction conditions were as follows: coal sample, 1.0 g; at 300-400 °C; under the gas pressure of 5.0 MPa, at flow of 50 mL/min; reaction time, 1h. The concentration of tritium in the reacted coal was measured by oxidizing it into water followed by measuring the radioactivity of the water with a liquid scintillation counter (LSC, Beckman LS 6500). The radioactivity measured is correlated to the amount of tritium transferred to coal. The amount of hydrogen in hydroxy groups of raw and the treated coals was determined by means of hydrogen exchange reaction with tritiated water at 100 °C for 24 h.³ The composition of mineral matter in the coal samples was analyzed by an XRF.

Results and Discussion
The present work is focused to elucidate the roles of mineral matter in term of hydrogen transfer reaction with gas phase H₂. The content of mineral matter was varied by which the mineral matter was removed gradually from the coal samples by HCl and successive HCl/HF treatments. XRF analyses of the samples before and after the treatments showed that HCl treatment removed almost all alkali and...
alkaline earth metals, and HCl-HF treatment removed almost completely all the mineral matter.

In a study of hydrogen transfer, it is necessary to determine the change in the amount of acidic hydrogen in hydroxyl of phenolic and carboxyl groups of coal before and after the acid treatments, since they are very reactive in the hydrogen exchange reaction with tritium in the presence of a catalyst.3 The data are shown in Figure 1. The HCl-treatment is intended to remove cations associated carboxylic groups; consequently, the treatment should result in increase of the amount of the acidic hydrogen. However, we observed that the amount of this hydrogen in the HCl and HCl/HF treated coals hardly increased, in fact, its amount decreased slightly in the HCl/HF-treated coals, as compared to that of the untreated coals. A reasonable explanation for this evidence is that some discrete mineral matter that lost during the acid treatments, such as alumina and silica, may originally carry hydroxyl.

Figure 2 shows the level of hydrogen transfer (Htr) of untreated- and the treated-ND coals as a function of temperature. The HCl-treatment has decreased the ability of organics in this coal to H-transfer reaction with the gas-phase at all temperature. A more decrease in their ability was observed in the HCl-HF treated coal. This result, therefore, gives the indication that both cations and discrete mineral matter affect catalytically the transfer of hydrogen from the gas phase to the organics in coal. There are evidences that Fe cation (as Fe2+ or Fe3+) catalytically enhances the transformation of coal into liquid products under coal liquefaction conditions.5 Furthermore, pyrite associated with discrete mineral matter should also be expected to show some catalytic activity in the hydrogen transfer reaction because it has shown moderate activity in previous liquefaction processes.

As shown in Figure 2, a significant level of hydrogen transfer to the organics of lignite ND coal was still observed even though the mineral matter had been completely removed from this coal, indicating that some structural elements in coal may also play a role in the hydrogen transfer reaction with H2. Furthermore, as the Htr of coal is plotted against the oxygen content of coal (Figure 3), it shows that the Htr increases with increasing the oxygen content for all cases of raw and the treated coals. This gives the indication that oxygen functional groups which may be hydroxy groups have also a role for enhancing the reaction.

Conclusion

The results have given the indications as follows: (1) both cations and discrete mineral matter present in coal catalytically enhanced the transfer of hydrogen from the gas, and (2) oxygen functional groups have also a role for the utilization of H2.

References