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Estimation of Hydrogen Mobility in Coal Using a Tritium Tracer Method. Hydrogen Exchange Reaction of Coal with Tritiated Water

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The reaction of coal with tritiated water was investigated under the coal liquefaction conditions to estimate the mobility of hydrogen in coals. In the reaction of Wandoan coal with tritiated water, the hydrogen exchange ratio of coal increased with a rise in temperature and was 30% at 300 °C and 36% at 400 °C, respectively. The results suggested that the hydrogens attached to aromatic carbons in coal was able to exchange with water even at 300 °C.

The research of the reactivity of hydrogen in coal is one of the most interesting and important problems in coal science, especially, the hydrotreating techniques such as coal liquefaction. A number of attempts have been made to estimate the reactivity of hydrogen in coal under coal liquefaction conditions by using deuterium tracer, NMR and MS methods.[1-6] Because of the poor solubility of a part of coal products and the difficulty of quantification of the deuterium tracer, however, there were few examples which enable the quantitative analysis of the hydrogen mobility in coal.

We have already reported that tritium and carbon-14 tracer techniques were effective to trace the hydrogen quantitatively in the coal liquefaction.[7-10] In our course of studies, we investigated the reaction of coal with tritiated water to estimate the reactivity of hydrogen in coal. In the present paper, we now report the hydrogen exchange reaction of hydrogen attached to aromatics in coal with tritiated water under coal liquefaction conditions. The reaction of coal with molecular hydrogen in the absence of solvent was also investigated and was compared with that of water.

The sample of Wandoan coal (C, 76.9; H, 6.7; N, 1.1; S, 0.3; O, 15.0 wt%, daf; ash, 7.7 wt%, dry basis) was ground to <200 mesh particles and dried for 3 h in 10 Torr at 100 °C. Into a 500 ml autoclave equipped with

a glass liner were added 30 g of coal and 15 g of tritiated water (initial radioactivity: 10 000 000 dpm). The autoclave was heated at a heating rate of 10 °C/min, and maintained at the chosen reaction temperature (100-400 °) for 0-6 h. After the reaction, the reaction mixture was separated into gas, tritiated water and coal. The gas was analyzed by GC and oxidized into water to measure the radioactivity. After a distillation, the tritiated water was measured for the radioactivity. The coal was dried under vacuum (3 mmHg) at 120 °C for 1 h and oxidized into water to measure the radioactivity. When tritiated molecular hydrogen was used instead of tritiated water, an initial pressure was 60 kg/cm^2 (initial total radioactivity, 1000000 dpm). The reactions of model compounds (1-naphthol and phenol) with water or molecular hydrogen were performed in the similar way.

The hydrogen exchange ratio (HER) was calculated on the basis of Eq. 1. The amount of hydrogen exchanged between water and coal ($H_{ex(W\leftrightarrow C)}$) was calculated on the basis of Eq. 2, in which the extent of hydrogen exchange between water and coal was regarded as the equilibrium (vide infra).

$$HER = H_{ex(W\leftrightarrow C)} / H_{coal} \quad (1)$$

$$H_{ex(W\leftrightarrow C)} = \frac{H_{water} \times R_{coal}}{R_{water}} \quad (2)$$

HER: Hydrogen exchange ratio; $H_{ex(W\leftrightarrow C)}$: The amount of hydrogen exchanged between water and coal (g); H_{coal}: The amount of hydrogen in coal (Wandoan, 1.86g); H_{water}: The amount of hydrogen in water (1.67g); R_{coal}: Radioactivity in coal after the reaction; R_{water}: Radioactivity in water after the reaction.

In the reaction of coal with tritiated water, tritium transferred from water to coal and the hydrogen exchange reaction between coal and water proceeded in the range of 100-400 °C. Fig. 1 shows the change in the hydrogen exchange ratio of Wandoan coal with reaction temperature. The hydrogen exchange ratio of Wandoan coal was 6% at 100 °C and increased with an increase in temperature to reach 30% at 300 °C and 36% at 400 °C, respectively. Since hydrogens of hydroxyl groups in phenolics and carboxylic acids are easy to exchange with hydrogen in water, the hydrogen exchange reaction at 100 °C is related to such functional group. It has been reported that bituminous coals or high-rank coal, which have a chemical composition of C: 75-85 wt% and H: 5.0-6.4 wt%, contain 3-12 atom% of phenolic (OH) hydrogen and hydrogen in carboxylic acid (COOH) for

total hydrogen.[11-13] In the present results, however, the hydrogen exchange ratio over 300 °C can not be explained by the hydrogen exchange of functional groups in coal. These results suggest that hydrogens attached to carbons in coal are able to exchange with water. As shown in Fig. 2, the hydrogen exchange ratios of Wandoan coal at 200 °C and 300 °C slightly increased over 2 h. However, they were kept almost constant after 2 h. This also suggests that the exchange reaction of coal with water approached the pseudo-equilibrium at each temperature and that it would proceed through the ionic exchange reaction.

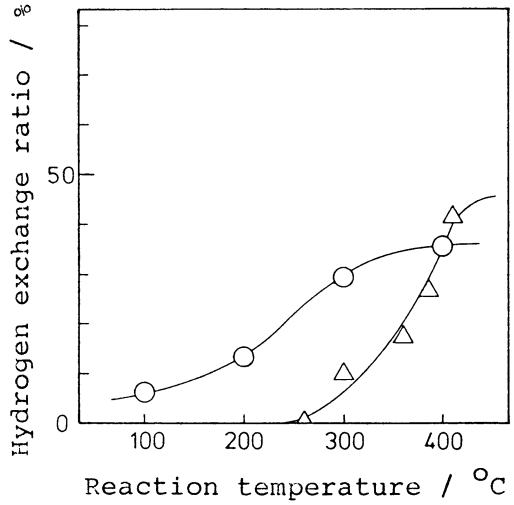


Fig. 1. Change in the hydrogen exchange ratio with reaction temperature.
○: Wandoan coal with water,
△: Wandoan coal with molecular hydrogen, Reaction time, 2 h.

For better understanding of the reaction of coal with water, the reaction of 1-naphthol, one of the model compounds of coal having functional groups, with tritiated water was performed. At 300 °C, 38% of hydrogen in 1-naphthol was able to exchange with water. On the other hand, in the reaction of tetralin which does not have any functional groups, the hydrogen exchange ratio was less than 1% even at 400 °C. These results also shows that hydrogens attached to aromatics having hydroxyl groups are exchangeable even at 300 °C. Therefore, it can be suggested that in the reaction of coal with water, hydrogens attached to aromatics having hydroxyl groups are possible to exchange with water in the following way:

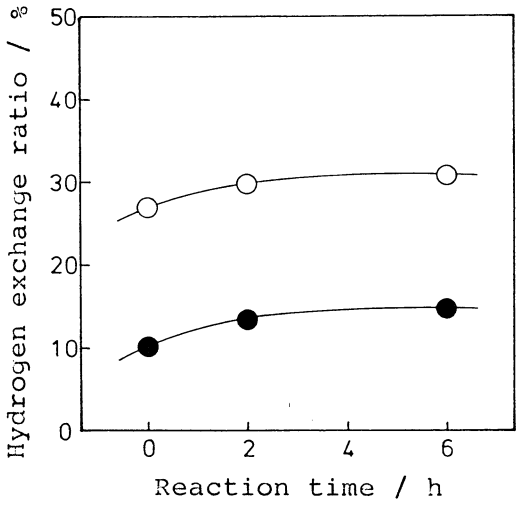
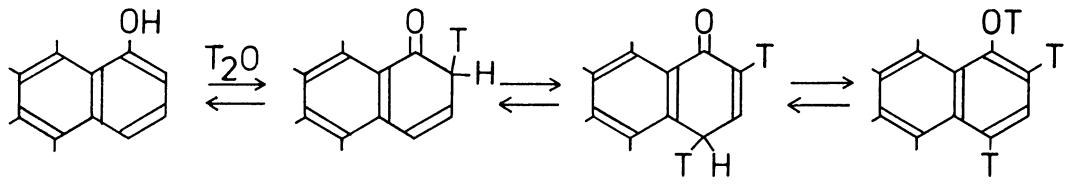


Fig. 2. Effect of reaction time on the hydrogen exchange ratio between Wandoan coal and water.
●: 200 °C; ○: 300 °C.



The reaction of Wandoan coal with molecular hydrogen was compared with the case of water. As shown in Fig. 1, the hydrogen exchange ratio was 10% at 300 °C and increased remarkably with increasing temperature to reach 42% at 410 °C. These results are completely different from that of water and can be explained by the radical mechanism as we have already reported similar results in coal liquefaction systems.[10] The hydrogen exchange of coal with molecular hydrogen at 300 °C is related to hydrogens of the functional group in coal. We have reported the similar results in the reaction of coal with molecular hydrogen in which the solvent, tetralin, was added.[10b] Further, in the reaction of phenol with molecular hydrogen, 50% of hydrogen of the hydroxyl group in phenol was exchangeable at 340 °C.[10b] This also explains the small hydrogen exchange ratio of coal with molecular hydrogen at 300 °C. At 400 °C, many hydrogens attached to carbon will be able to exchange through radicals generated in coal. On the contrary, in the reaction of coal with water, hydrogens attached to carbons was exchangeable even at 300 °C by the ionic mechanism.

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