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# Elucidation of Hydrogen Mobility in Functional Groups of Coals Using Tritium Tracer Methods

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Hydrogen exchange reactions of coal with tritiated water and gaseous hydrogen were investigated to estimate the mobility of hydrogen in coal using not only a batch type reactor but also a flow type reactor. Specifically, the reactivities of functional groups were traced in these reactions. In the reaction of coal with tritiated water at 100 °C the hydrogen exchange of functional groups such as hydroxyl group in coals could be estimated. In the pressurized system using stainless batch type reactor aromatic hydrogen at ortho- and para-positions of a functional group could also be estimated by the hydrogen exchange reactions of coal and tritiated water at higher temperature. In hydrogen exchange reactions of coals with tritiated gaseous hydrogen using a flow reactor, reaction temperature was controlled exactly. The use of a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst promoted the generation of hydrogen radicals which reacted with coal. This method enables us to estimate the reactivity of a functional group with a hydrogen radical. Further, it was found that the particle size of coal only slightly affected hydrogen exchange ratio of coal in both cases of tritiated gaseous hydrogen and tritiated water.

## 1. Introduction

To obtain useful fuels and chemicals from coal by liquefaction and pyrolysis, it is important to know the coal structure. Especially, the heteroatom functionalities in coal such as hydroxyl group, thiol, and amino group, etc., play a critical role in the processing of coal because they constitute the more polar fraction of the coal and stabilize free radicals.<sup>1,2</sup> Therefore it is important to estimate the amount of the functional group for the development of coal conversion techniques. Generally, the oxygen group is primarily present in the form of the hydroxy group and the ether group and a little in the carbonyl group and carboxylic acid. Fourier transform infrared was available for the measurement of oxygen functional groups.<sup>3,4</sup>

Recently, we have reported that tritium tracer methods were effective to determine the behavior of hydrogen in coal under coal liquefaction conditions.<sup>5-7</sup> In these works, we have performed the reactions of coals with tritiated molecular hydrogen<sup>5-7</sup> where the hydrogen exchange reactions between coal and gas phase and solvent as well as the hydrogen addition were estimated quantitatively. In our course of study, we investigated

the reaction of coal with tritiated water, which can be regarded as a proton donor rather than a hydrogen atom, to estimate the reactivity of hydrogen in coal.<sup>6</sup>

In the present paper, we review our recent studies concerning the hydrogen exchange reaction of various coals with tritiated water and gaseous hydrogen to estimate the amounts of hydrogen in functional groups of coals.<sup>8-11</sup> In the pressurized system with tritiated water using the batch reactor, aromatic hydrogen around the functional groups in coal can be determined. This study is the original contribution for this paper. Further, a pulse flow reactor is developed to control the reaction temperature and to estimate the behavior of hydrogen in functional groups as well as other hydrogen more accurately in the reaction of coals with tritiated gaseous hydrogen in the presence of a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The effect of particle size on the hydrogen exchange reaction of coal with gaseous hydrogen as well as water is also described.

## 2. Experimental Section

**2.1. Materials.** Four kinds of coals of the Argonne Premium Coal Sample Program (<100 mesh), and Wandoan coal (<150 mesh) were used as raw materials. The analytical data of these coals are shown in Table 1. Unless otherwise noted, coal samples were dried under vacuum at 120 °C for 1 h.

**2.2. Reaction of Coal with Tritiated Water.<sup>8,9</sup>** Into a 25 mL glass reactor was added 1.0 g of coal and 1.0 g of tritiated water (initial radioactivity: 1 000 000 dpm). After these

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**Table 1. Ultimate Analysis of Coals Used (% daf)<sup>a</sup>**

coal	C	H	N	S	O	
ND	72.94	4.83	1.15	0.70	20.38	(L)
WA	76.9	6.7	1.1	0.3	15.0	(SB)
IL	77.67	5.00	1.37	2.38	13.58	(HVB)
UF	85.50	4.70	1.55	0.74	7.51	(MVB)
POC	91.05	4.44	1.33	0.50	2.68	(LVB)

<sup>a</sup> Abbreviations: ND: Beulah-Zap, WA: Wandoan, IL: Illinois No. 6, UF: Upper Freeport, POC: Pocahontas No. 3; L: lignite, SB: subbituminous coal, HVB: high-volatile bituminous coal, MVB: medium-volatile bituminous coal, LVB: low-volatile bituminous coal. Except for WA, samples are coals of the Argonne Premium Coal Sample Program.

materials were degassed under vacuum ( $<10^{-4}$  Torr), the reactor was put into an oil bath set to 50 or 100 °C and stirred by a magnetic stirrer for 1 to 24 h. After the reaction, coal and water were separated and coal was dried at 50 or 100 °C under vacuum. The radioactivities of water and coal, which was oxidized to water before measuring radioactivity, were measured with the liquid scintillation counter (Beckman LS6500).

When the reaction was performed at 200, 250, or 300 °C, the reaction of coal with tritiated water was performed in a batch type stainless tube reactor (i.d. 8 mm, length 12 cm). The reactor was put into a furnace heated to the expected temperature. After the reaction, water was removed and the separated coal was dried under vacuum at 120 °C for 1 h. After drying, the coal sample was oxidized to water using the combustion system to measure its radioactivity with a liquid scintillation counter. To determine hydrogen in functional groups, the hydrogen exchange reactions of the tritiated coal and water were performed at 100 °C for 24 h in a glass reactor. After the reaction, suction filtration was performed and tritiated coal was washed with hot water. Further, the separated coal was dried under vacuum at 120 °C for 1 h. After drying, the coal sample was oxidized by a method similar to the above using the combustion system to measure its radioactivity.

The reactions of model compounds with deuterium oxide were performed in a similar way. After the reaction, the deuterated model compounds were isolated by filtration or by distillation. The deuterated position of model compounds was identified by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

**2.3. Reaction of Coal with Tritiated Gaseous Hydrogen.** The detail procedure of the hydrogen exchange reaction between coal and tritiated gaseous hydrogen was described elsewhere.<sup>10,11</sup> About 0.4 g of coal sample and 0.05 g of Pt/ $\text{Al}_2\text{O}_3$  catalyst were put in a flow microreactor and several tritiated gaseous hydrogen pulses were introduced into the reactor until the radioactivity of the recovered pulse approached that of the introduced pulse. The radioactivity of tritiated gaseous hydrogen recovered from the reactor, i.e., unreacted  $^3\text{H}_2$ , was directly monitored with a radioanalyzer in the outlet of the reactor.

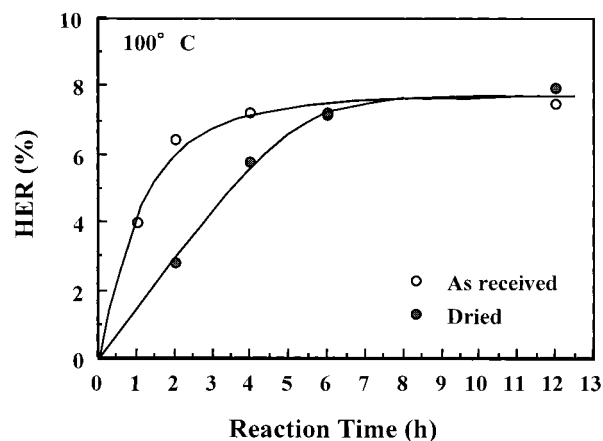
**2.4. Calculation of Hydrogen Exchange Ratio.** The hydrogen exchange ratio (HER) described in this paper means the ratio of the amount of hydrogen exchanged in coal ( $H_{\text{ex}}$ ) to the total amount of hydrogen in an original coal ( $H_{\text{coal}}$ ). The HER between coal and water or gaseous hydrogen was calculated on the basis of eq 1:

$$\text{HER} = H_{\text{ex}}/H_{\text{coal}} \quad (1)$$

$H_{\text{coal}}$  was calculated with the analytical data presented in Table 1. The amount of hydrogen exchanged between water and coal ( $H_{\text{ex}}$ ) was calculated on the basis of eq 2:

$$R_{\text{coal}}/H_{\text{ex}} = R_{\text{water}}/H_{\text{water}}; \quad H_{\text{ex}} = H_{\text{water}} \cdot R_{\text{coal}}/R_{\text{water}} \quad (2)$$

$H_{\text{water}}$  is the amount of hydrogen in water and  $R_{\text{water}}$  is the radioactivity of tritium contained in water. In eq 2, it was

**Figure 1.** Change in the HER of IL coal with reaction time.

assumed that the hydrogen exchange reaction between gaseous hydrogen and coal reached equilibrium. Thus, after the reaction, the ratio of the radioactivity in coal to the amount of the hydrogen exchanged in coal ( $R_{\text{coal}}/H_{\text{ex}}$ ) is equal to the ratio of the radioactivity in water to the amount of hydrogen in water. The similar equation was used for the calculation of HER between gaseous hydrogen and coal.

When as-received coal was used in Figure 1, water contained in the original coal was considered in the calculation of HER.

### 3. Results and Discussion

**3.1. Determination of Functional Groups by Hydrogen Exchange Reaction of Coals with Tritiated Water.**<sup>8</sup> Figure 1 shows the change in HER of Illinois No. 6 coal with reaction time at 100 °C. When coals were dried before the reaction, HER gradually increased with an elapse of time and reached the constant value 7.8% after 6 h. For coal without drying before the reaction, it took 4 h to reach the constant value. This delay may be due to the difference in the rate of diffusion of water into the inside of coal. Even at 50 °C, HER reached 7.8% after 12 h. Therefore, this exchange reaction includes the exchange reaction with hydrogen in functional groups such as the hydroxy group and carboxylic acid. The hydrogen exchange reactions of other coals were performed in the batch reactor at 100 °C. The constant value of HER (HER-OH) for each coal was obtained for more than 6 h of reaction time and was listed in Table 2.

It is well-known that aromatic hydrogen exchanges with deuterium oxide in the presence of acid or base under mild conditions.<sup>12–14</sup> On the other hand, it is also well-known that aromatic hydrogen does not exchange with deuterium oxide or tritiated water under the neutral condition.<sup>6,15</sup> In the present study the hydrogen exchange of coal with tritiated water is related to the exchange with functional groups because the reactions were performed under almost neutral conditions. Further, our results in HER are consistent with the exchange of functional groups determined in the literature. Attar and Hendrickson developed an empirical correlation between the distribution of oxygen functional

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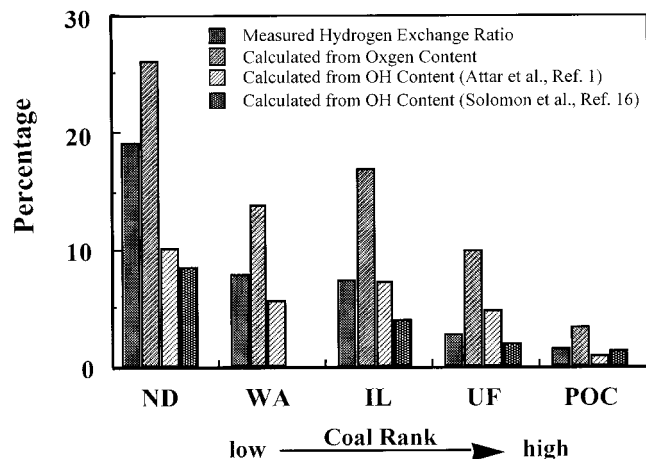
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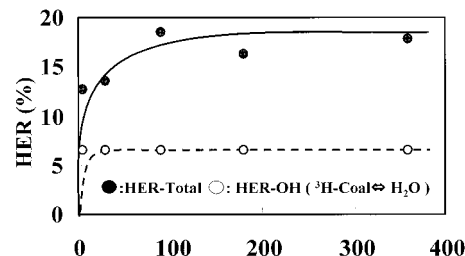
**Table 2. Hydrogen Exchange Ratios of Coals with Tritiated Water in a Batch Reactor**

coal	100 °C	200 °C		250 °C		300 °C		(AR-H/OH mol/mol)
	HER-OH (%)	HER-Total (%)	HER-OH (%)	HER-Total (%)	HER-OH (%)	HER-Total (%)	HER-OH (%)	
ND	19.2	24.2	13.7	36.5	14.1	45.2	8.5	2.7
IL	7.1	10.0	6.1	16.2	6.4	23.4	5.8	2.3
UF	2.8	3.3	1.7	4.6	2.1	5.2	2.4	0.9
POC	1.6	1.6	0.8	2.2	0.9	4.3	0.9	1.7

**Figure 2.** Comparison of hydrogen exchange ratio with content of hydroxy group.

groups and the ultimate analysis of coals.<sup>1</sup> According to this correlation, the contents of the hydroxy group in each coal were estimated. Further, Solomon et al. determined the contents of hydroxy groups in Argonne Premium Coals using FT-IR.<sup>3,16</sup> The maximum content of the hydroxy group can also be calculated from the analytical data listed in Table 1 assuming that all oxygen in coals is present in the form of the hydroxy group. In Figure 2, HERs of coals with tritiated water at 100 °C were compared with the ratios of hydrogen in the hydroxy group to total hydrogen in coal calculated by the several methods mentioned above. Except ND coal, HERs for other coal were very near the values calculated from the literature (Attar et al.<sup>1</sup> or Solomon et al.<sup>16</sup>). ND coal includes a large amount of carboxy group. Therefore HER for this coal, which includes the hydrogen exchange of not only the hydroxy group but also the carboxy group, was larger than the values calculated from the literature.

**3.2. Determination of Aromatic Hydrogen around Functional Groups in Coal.<sup>9</sup>** To determine the amount of aromatic hydrogen around functional groups in coal, reactions of coal with tritiated water were performed in a stainless reactor at elevated temperature. Figure 3 shows the change in hydrogen exchange ratio (HER) of coal with reaction time at 250 °C. Total HER increased with reaction time and reached a constant value at 90 min. At that time, it can be considered that hydrogen exchange reaction has reached the equilibrium state. As shown in this Figure, HER of functional groups (HER-OH) immediately reached the constant value at the beginning of the reaction. The difference between total HER and HER-OH reveals the amount of aromatic hydrogen exchanged. These results show that the

**Figure 3.** Effect of reaction time on hydrogen exchange ratio of IL coal at 250 °C ●: HER-Total, ○: HER-OH ( $^3\text{H-Coal} \rightleftharpoons \text{H}_2\text{O}$ ).

reaction rate is very fast, especially for the functional group, and that the ionic exchange with proton may occur.

All the data are shown in Table 2. For all coals, total HER increased with increasing temperature while HERs of functional group were almost the same with the change in temperature except ND coal. ND coal initially has 19% of exchangeable hydrogen in the functional group, which decreased to about half at 300 °C. This shows that all carboxy groups included in ND coal by about 50% of HER of functional group was decomposed at the higher temperature under high pressure of water. Both total HER and the HER-OH decreased with increasing coal rank. Further the difference between total HER and HER-OH represents the amount of aromatic hydrogen, which also decreased with increasing coal rank. This result suggests that the hydrogen exchange reaction between aromatic hydrogen and tritiated water is closely related to the presence of functional groups on the aromatic ring.

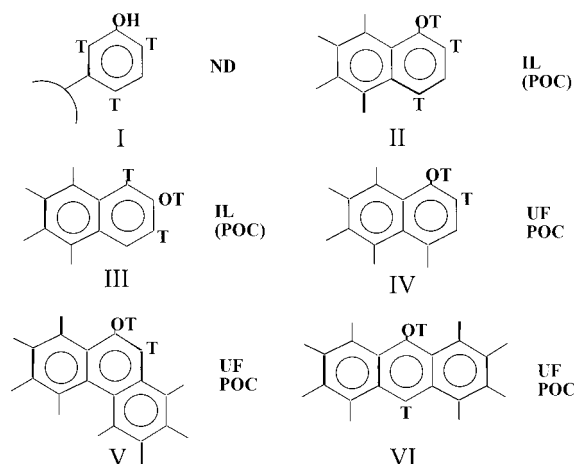
Using total HER at 300 °C ( $\text{HER-Total}_{300^\circ\text{C}}$ ) and HER of functional group at 100 °C ( $\text{HER-OH}_{100^\circ\text{C}}$ ), the ratio of the amount of aromatic hydrogen to the amount of functional group was calculated according to eq 3:

$$\text{AR-H/OH} = \frac{(\text{HER-Total}_{300^\circ\text{C}} - \text{HER-OH}_{100^\circ\text{C}})}{\text{HER-OH}_{100^\circ\text{C}}} \quad (3)$$

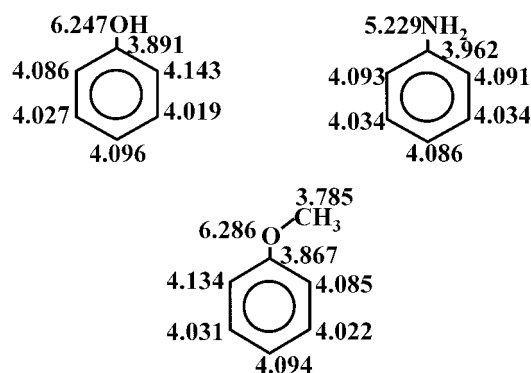
The aromatic hydrogens in a ring with a carboxy group hardly exchange with water which is present later in the reaction of model compound. Therefore in the case of ND coal, half value of HER of functional group was used in the denominator of eq 3. The ratios of the amount of exchangeable aromatic hydrogen to the amount of functional group (phenolic OH group) were 2.7, 2.3, 0.9, and 1.7, for ND, IL, UF, and POC, respectively. The hypothetical exchanged positions in model structures are shown in Scheme 1. For ND coal there may be the structure I with a single ring and one hydroxy group and three exchangeable ortho- and para-hydrogen. In IL coal, there may be a two-ring system where one ring has a hydroxy group, and hydrogen atoms at the ortho- and para-positions are exchangeable



**Scheme 1. Exchanged Positions in Model Structures**



**Scheme 2. Electron Densities in Various Organic Compounds Calculated with WinMOPAC**

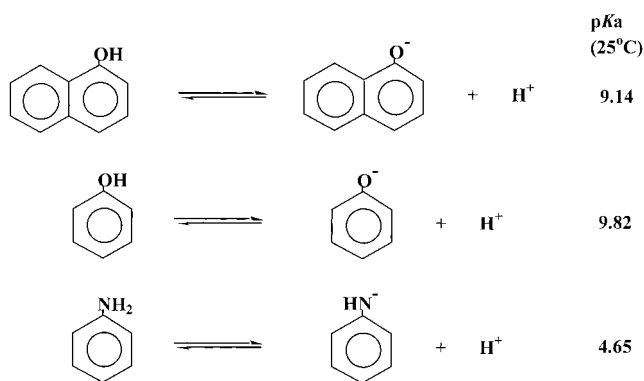


and can be exchanged with tritiated water under high pressure of water at elevated temperature (Structures II and III). The aromatic hydrogen in the other ring without a hydroxy group does not exchange. For higher rank coal such as UF and POC coals, there may be two to three-ring structure (Structures IV, V, and VI). In the structures IV, V, and VI, one hydrogen atom is exchangeable.

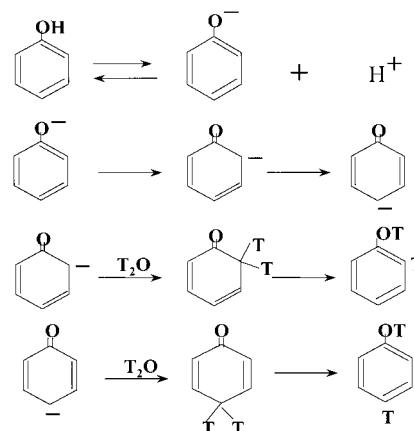
To investigate in detail what kind of hydrogen in coal can be exchanged, the reactions of coal model compound with deuterium oxide were performed. As model compounds, aniline, anisole, benzoic acid, and ethyl benzoate were used. The reaction was performed at 300 °C for 180 min. Deuterium in the compound after the reaction was determined by NMR. Hydrogen at ortho- and para-positions of aniline was exchanged with deuterium oxide and the reaction almost reached the equilibrium state. No aromatic hydrogen exchanged with deuterium oxide in anisole. Although a trace amount of deuterium seemed to be introduced into the ortho-position of benzoic acid, the exact amount could not be traced and only the signal of ortho-carbon in NMR became small slightly.

The electron densities of model compounds were calculated by using the WinMOPAC, a molecular orbital calculation software. The data for phenol, aniline, and anisole are shown in Scheme 2. The electron densities of ortho- and para-positions of phenol and aniline were higher than those of other positions. However, the electron densities of ortho- and para-positions of anisole were also higher than those of other positions and very

**Scheme 3. Dissociation of Naphthol, Phenol, and Aniline**



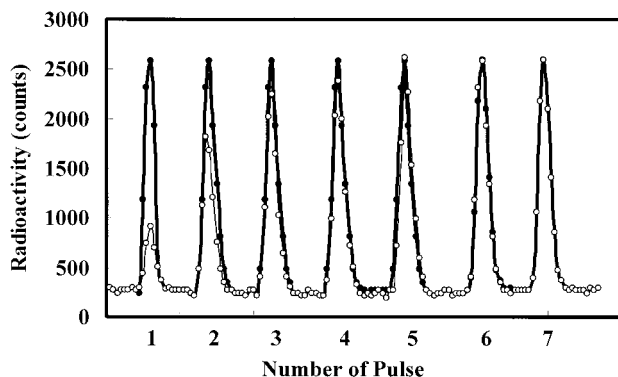
**Scheme 4. Mechanism of Hydrogen Exchange between Phenol and Tritiated Water**



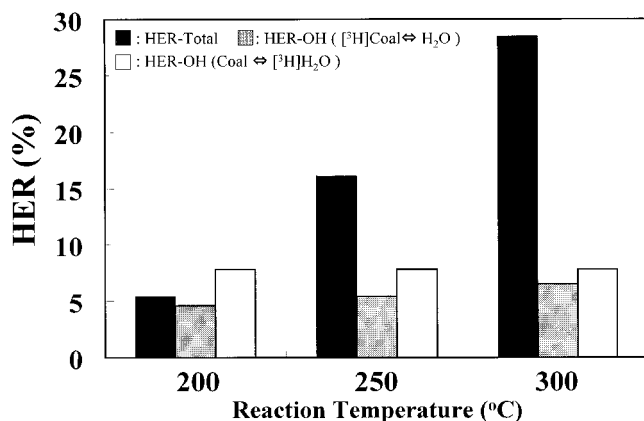
close to the values for phenol and aniline. Therefore, the results obtained in the present study cannot be explained by this electron density of model compounds.

The common feature of phenol and aniline is that they can dissociate to a proton and a counteranion as shown in Scheme 3. The anion structures may be related to the hydrogen exchange with water. As a model compound, phenol is used to explain the exchange mechanisms (Scheme 4). Phenol dissociates to a proton and a phenoxide. This phenoxide anion has these resonance structures. These structures may contribute the hydrogen exchange at ortho- and para-positions. In the reaction of coal with tritiated water, it is expected that the hydrogen exchange of aromatic hydrogen through these routes may occur.

**3.3. Hydrogen Exchange Reaction between Coal and Tritiated Gaseous Hydrogen.**<sup>10</sup> Figure 4 shows the change in radioactivity of tritiated gaseous hydrogen in a recovered pulse with the number of introduced pulse. A pulse of tritiated gaseous hydrogen (9.62 mL) with a constant radioactivity (8792 counts/pulse) was introduced into POC coal with 50 mg of 1%-Pt/Al<sub>2</sub>O<sub>3</sub> at 250 °C every 30 min. After the first pulse was introduced, the radioactivity of the recovered pulse was only 1899 counts. This indicates that some tritium in tritiated gaseous hydrogen was incorporated into coal. Further, the radioactivity in the recovered pulse increased with the number of introduced pulses and approached a constant value (8792 counts) at the fifth pulse. In contrast to this, the amount of recovered gaseous hydrogen, which was monitored by the TCD



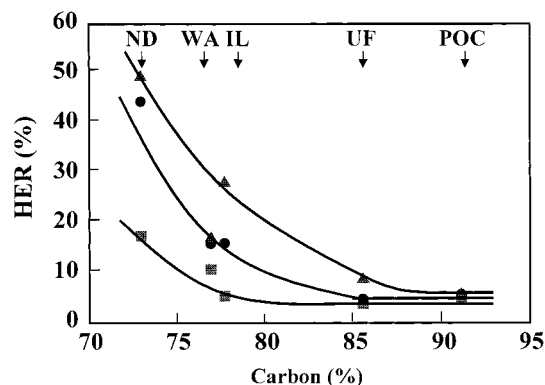
**Figure 4.** Change in radioactivity of tritiated gaseous hydrogen in introduced or recovered pulse: ● Introduced pulse, ○: Recovered pulse.



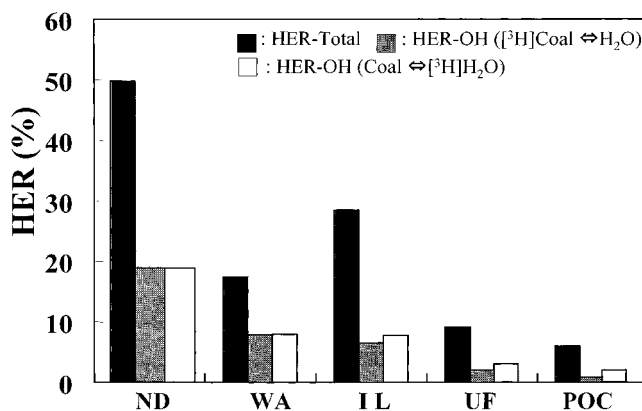
**Figure 5.** Effect of reaction temperature on hydrogen exchange ratio of IL coal: ■ HER-Total, gray box: HER-OH ( $[^3\text{H}]\text{Coal} \rightleftharpoons \text{H}_2\text{O}$ ), □: HER-OH ( $\text{Coal} \rightleftharpoons [^3\text{H}]\text{H}_2\text{O}$ ).

equipped at the outlet of the reactor, approximately remained constant for every introduced pulse. This indicates that the decrease in the radioactivity of the introduced pulse could not be attributed to the adsorption/desorption of gaseous hydrogen in the coal but to the hydrogen exchange between the tritiated gaseous hydrogen and the coal. Meantime, it can be considered that hydrogen exchange between the tritiated gaseous hydrogen and the coal reached equilibrium after introduction of the fifth pulse.

We have already reported that hydrogen in the hydroxy group present in coal exchanges with water at 100 °C. Therefore, to understand the behavior of hydrogen of functional group in coals in hydrogen exchange reactions between coal and gaseous hydrogen, the hydrogen exchange reactions between the tritiated coal, which was obtained in the reaction with tritiated gaseous hydrogen, and water were performed at 100 °C for 24 h in a batch reactor. HER-OH between tritiated IL coal and water is shown with HER-Total between coal and tritiated gaseous hydrogen in Figure 5. HER-Total increased with increasing temperature. However, HER-OH between tritiated coal and water (HER removed with water) only slightly increased with temperature. At 200 °C, HER-Total with tritiated gaseous hydrogen is very similar to HER-OH with water, indicating that most of HER-Total corresponds to the hydrogen exchange of functional group at this temperature. At 300 °C, the HER-OH is very similar to HER-OH<sub>100°C</sub> between coal and tritiated water mentioned



**Figure 6.** Effect of coal rank on hydrogen exchange ratio at several temperatures ■: 200 °C, ●: 250 °C, ▲: 300 °C.



**Figure 7.** Effect of coal rank on hydrogen exchange ratio of coal with tritiated gaseous hydrogen ■: HER-Total, gray box: HER-OH ( $[^3\text{H}]\text{Coal} \rightleftharpoons \text{H}_2\text{O}$ ), □: HER-OH ( $\text{Coal} \rightleftharpoons [^3\text{H}]\text{H}_2\text{O}$ ) 300 °C.

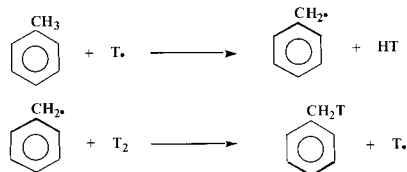
above.<sup>8</sup> These suggest that the hydrogen of functional groups in coal can easily be exchanged with gaseous hydrogen in the presence of the Pt catalyst.

**3.4. Effect of Rank of Coal on HER with Tritiated Gaseous Hydrogen.**<sup>10</sup> Hydrogen exchange reactions in various coals with tritiated gaseous hydrogen were performed in the absence and presence of catalyst at 200 to 300 °C. The results are shown in Figure 6. In the absence of the catalyst, HER is only 1% even in the case of ND coal and the hydrogen exchange reactions hardly occur in the cases of other coals. In contrast, the hydrogen exchange reactions remarkably proceed in the presence of catalyst and HERs are lower for higher coal ranks. HERs of ND, WA, IL, UF, and POC were 45, 16, 16, 5, and 6%, respectively, at 250 °C. As shown in Figure 6, it was observed that HER decreased with increasing coal rank at every temperature.

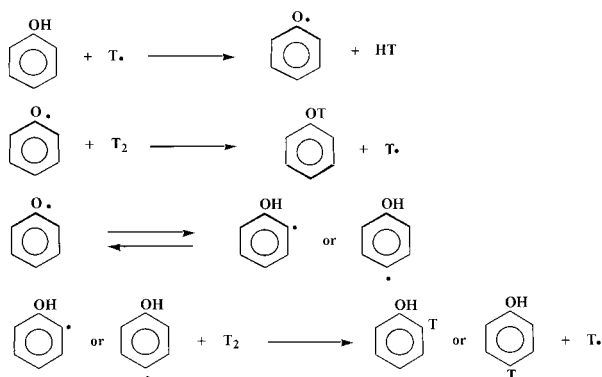
Hydrogen exchange reactions between various tritiated coals and water were also performed in a batch reaction system. In Figure 7 (300 °C), HERs between tritiated coal and water (HER removed with water) were compared with original HERs of tritiated coal and HERs between coals and tritiated water mentioned above.<sup>8</sup> In all cases, HERs between tritiated coal and water are very similar to those between coals and tritiated water. The results show that in all cases the hydrogen of functional group such as hydroxy group in coals is almost exchanged with tritiated gaseous hydrogen at 300 °C. The difference between hydrogen of coal exchanged with gaseous hydrogen and hydrogen of func-

**Scheme 5. Hydrogen Exchange Reaction of Coal with Tritiated Gaseous Hydrogen in the Presence of Catalysts**

a) Hydrogen exchange in an alkyl group when toluene is used as a model compound



b) Hydrogen exchange in a functional group with heteroatom and an aromatic ring with the functional group when phenol is used as a model compound



tional group is larger for lower rank coals. This shows that, besides hydrogen in functional groups, hydrogen of aromatics with functional groups or hydrogen at the alpha position of alkyl groups may be related to this exchange reaction because the low rank coals include a large amount of functional groups and alkyl groups.

Possible mechanisms for hydrogen exchange of coal with tritiated gaseous hydrogen in the presence of catalyst can be considered (Scheme 5). Since hydrogen in low rank coal is more labile in this reaction, hydrogen atoms in alkyl groups, functional groups with a heteroatom, and aromatic rings with those functional groups may be related to the hydrogen exchange. When toluene is used as a model compound, benzyl radical is formed in the reaction with tritium radical (or hydrogen atom). The benzyl radical reacts with tritiated hydrogen to form tritiated toluene. When phenol is used as a model compound, phenoxyl radical is formed in the reaction with tritium radical (or hydrogen atom). The phenoxyl radical reacts with tritiated hydrogen to form tritiated phenol. Phenoxyl radical may be stabilized at equilibrium with hydroxyphenyl radical. The hydroxyphenyl radical reacts with tritiated hydrogen to form the other tritiated phenol which is tritiated at the ortho-para-position.

A similar hydrogen–deuterium exchange reaction using the mixture of a coal and a catalyst packed into a flow reactor has been performed.<sup>17</sup> This method has been used to examine the exchange of gas-phase deuterium with the hydrogen in coal. Several experiments in this work gave evidence that the source of hydrogen

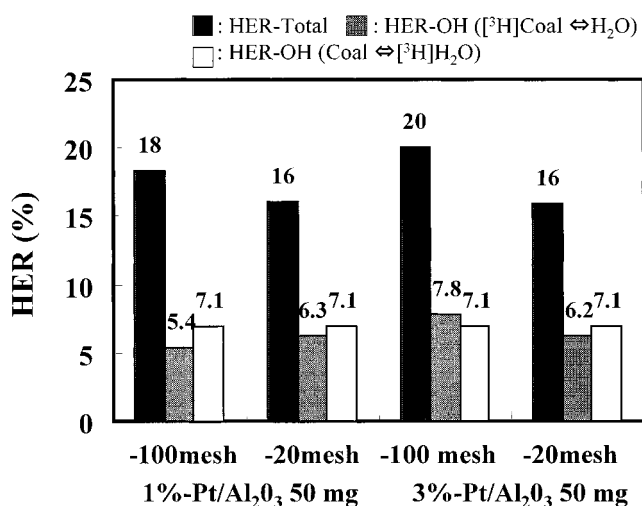
involved in the exchange reaction is hydrogen located on the coal itself and the active catalyst,  $\text{MoS}_2$ , is required for the exchange to proceed at low temperatures. The exchange reaction was observed at 225 °C, similar to the temperature used in our work. The extent of catalyzed hydrogen exchange on coal was reported in another publication.<sup>18</sup> Pd on carbon was used instead of  $\text{MoS}_2$  as the catalyst in these experiments, closer to our system using  $\text{Pt}/\text{Al}_2\text{O}_3$ . Since there was no figures and tables, the experimental detail is not clear. However, only one result concerning the determination of hydrogen exchange between coal and deuterium in the presence of the catalyst was that the exchangeable hydrogen on coal at 140 °C was 3.4 mg-atom/g Illinois No. 6 coal, roughly equivalent to the phenolic OH content of this coal. This value corresponds to 6.8% of HER, our criterion to estimate exchangeable hydrogen in coal and is in good agreement with our result. Further, the same research group reported hydrogen spillover from Pd on carbon to the OH groups of either silica or polyvinylphenol.<sup>19</sup> The structure of solid polyvinylphenol was related to the phenolic groups locked in the solid structure of coal. The amount of hydrogen corresponding to roughly 75% of the phenolic hydrogen on polyvinylphenol took part in the catalyzed hydrogen exchange. The deuterium incorporated could be removed by back exchange with hydrogen, thus confirming transport in to and out of the polymer. This work pointed out the connection between the catalyzed exchange reaction with the large body of work on the topic of hydrogen spillover. In the next section, we present the topic that spillover hydrogen travels over all around surface in coal.

**3.5. Effects of Particle Size on HER with Tritiated Water and Gaseous Hydrogen.**<sup>11</sup> To survey the effect of the diffusion of hydrogen molecules or hydrogen radicals in coal on the hydrogen exchange reactions, the hydrogen exchange reactions of coals having several particle sizes with tritiated gaseous hydrogen were performed. Two IL coal samples with different particle sizes were used: under 100 mesh and under 20 mesh. Figure 8 shows the effect of the particle size of IL coal on the HER in the presence of 1 or 3 wt %  $\text{-Pt}/\text{Al}_2\text{O}_3$  catalyst at 250 °C. As shown in Figure 8, HERs between coal and gaseous hydrogen for under 100 mesh and under 20 mesh samples were about 18% and 16%, respectively, in the presence of 1 wt %  $\text{-Pt}/\text{Al}_2\text{O}_3$  catalyst. When these tritiated coal samples were reacted with water, tritium in functional groups was removed and the HERs corresponding to hydrogen exchanged in functional groups could be estimated to be 5.4% for under 100 mesh and 6.3% under 20 mesh samples, respectively. Further, the amount of functional group can be estimated by the hydrogen exchange reaction of coal and tritiated water at 100 °C and HERs estimated for under 100 mesh and under 20 mesh samples were 7.1% and 7.1%, respectively. Similar results were also obtained in the presence of 3 wt %  $\text{-Pt}/\text{Al}_2\text{O}_3$  catalyst. These results show that in the reaction between coal and tritiated gaseous hydrogen almost all hydrogen in functional groups exchanged with gaseous hydrogen in

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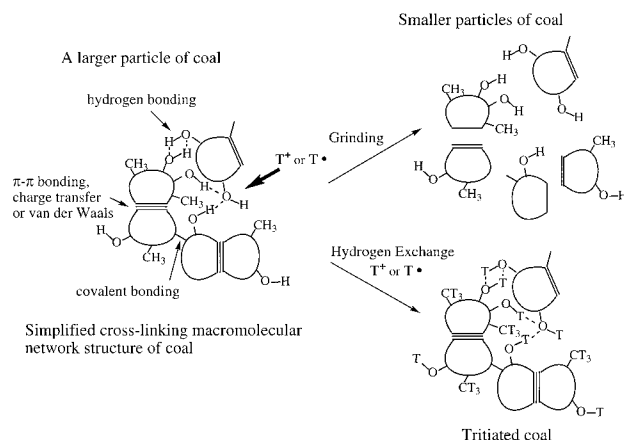
**Figure 8.** Dependence of hydrogen exchange ratio on particle size ■: HER-Total, gray box: HER-OH ( $[^3\text{H}]\text{Coal} \rightleftharpoons \text{H}_2\text{O}$ ), □: HER-OH ( $\text{Coal} \rightleftharpoons [^3\text{H}]\text{H}_2\text{O}$ ).

the presence of the catalyst at 250 °C, and that there were no significant effects of the particle size of coal on the HER between coal and hydrogen or between coal and water. It is suggested that most of hydrogen exchanged with gaseous hydrogen or water, e.g., hydrogen in functional groups and  $\alpha$ -carbon of an aromatic ring, is located on not only the exterior surface but also the interior surface of coal, where hydrogen atom generated in the presence of the catalyst or proton generated from water can easily approach, even in the case of the larger particle size of coal.

Because there was no or very little significant effect of the particle size in the reaction of coal with tritiated gaseous hydrogen and tritiated water, it is suggested that most of exchangeable hydrogens in functional groups and  $\alpha$ -carbon of an aromatic ring are located on not only the exterior surface but also the interior surface of coal or the cross-linking position in the macromolecular network structure of coal,<sup>20,21</sup> where hydrogen atoms generated in the presence of the catalyst or proton generated from water can easily approach, even in the case of the larger particle size of coal. The hypothetical linkage structure of coal is illustrated in Scheme 6. Further it is suggested that there is no pore-like structure where a hydrogen atom or a proton is difficult to approach and that, when broken to smaller size, one coal particle becomes small through coming off from the larger layer structure of aromatics or breaking of cross-linking such as hydrogen bonds in the macromolecular network structure of coal as in Scheme 6.

It has been reported that the diffusion effects of donor solvents on coal conversion is absent.<sup>22</sup> Larsen et al. used 2-*tert*-butyltetralin which is expected to have little effect on the hydrogen-donating ability of the tetralin but is expected to significantly reduce its diffusion into coal. Coal conversions to pyridine extractables and the amount of hydrogen transferred from the donor are essentially the same for both tetralin and 2-*tert*-butylte-

**Scheme 6. Hypothetical Coal Structure. A Larger Particle of Coal, Smaller Particles of Coal, and Tritiated Coal**



tralin, demonstrating that diffusion of the hydrogen donor does not play a significant role in conversion of coal. The results showed the possibility that hydrogen atoms can readily move to the radicals generated in coal. This result supports our results. In our study, it was suggested that most of exchangeable hydrogen in coal at least existed on the coal surface where hydrogen atoms and protons, or hydrogen molecule and water, could be accessible. Since the generation of a large amount of hydrogen (tritium) atoms and the spillover of those hydrogen atoms to the coal surface can occur on the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, those radicals may travel all around the coal structure. In this situation, the hydrogen exchange seems to proceed through direct abstraction of exchangeable hydrogens in functional groups or  $\alpha$ -carbon of aromatic rings by radicals as in Scheme 5a and b.

Buchanan et al. have also demonstrated the ready mobility of hydrogen atoms in anchored systems.<sup>23</sup> In this atom-hopping radical relay mechanism, hydrogen may move from an external donor to a radical site. In our case, however, it seems not to be a major route because the coal surface is not so regulated as their system using surface-immobilized molecules. Further, Malhotra and McMillen reported the implications of the solvent-mediated hydrogenolysis picture for coal liquefaction.<sup>24</sup> They showed that polycyclic aromatic hydrocarbons mediated hydrogen transfer to promote the coal conversion in coal liquefaction. Solvent-mediated hydrogenolyses were also important even under catalytic conditions. Malhotra's solvent-mediated hydrogen transfer does not occur in our case because there is no solvent in the system. However, hydrogen radicals may access exchangeable hydrogens passing over aromatic ring planes or aromatic hydrogens which may play a role like a railway carrying the radicals.

Although the hydrogen-exchange of hydrogen in aromatic rings may occur, it will proceed only to a very small extent. In Buchanan's experiments, the aromatic spacers were inert while spacer molecules containing benzylic C-H bonds were reactive in their radical relay reaction. In our case, HER reached the constant value

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with the addition of 20 mg of the catalyst, and the further addition of the catalyst did not increase the HER. These results suggest that although there is a large amount of aromatic hydrogen in coal, the hydrogen exchange reaction of most of those aromatic hydrogens with hydrogen radicals may be difficult to occur with the observable rate at least in the range 200–300 °C.

#### 4. Conclusions

1. Hydrogen exchange reactions between coal and tritiated water were performed using a batch reactor. The hydrogen exchange ratio of coals with different coal rank at 100 °C was estimated and could be regarded as the hydrogen exchange of functional groups such as hydroxy group in coals.

2. Aromatic hydrogen at ortho- and para-positions of a functional group could be estimated by the hydrogen exchange reactions of coal and tritiated water at higher temperature. The ratios of the amount of exchangeable aromatic hydrogen to the amount of functional group (phenolic OH group) in coal were as follows: ND: 2.7, IL: 2.3, UF: 0.9, POC: 1.7.

3. Hydrogen exchange reactions of coals with tritiated gaseous hydrogen were performed using a flow reactor.

In these reactions, reaction temperature was controlled exactly. The presence of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst remarkably enhanced the generation of hydrogen radical and simultaneously the hydrogen mobility of each coal regardless of coal rank. Further, from the hydrogen exchange reaction of the tritiated coal with water, it was suggested that the hydrogen in functional groups in coal was more easily exchanged with gaseous hydrogen.

4. When the effect of the particle size of coal on the hydrogen exchange reaction was investigated, it was found that the particle size of coal only slightly affected the hydrogen exchange ratio of coal in both cases of tritiated gaseous hydrogen and tritiated water. The results means that proton and hydrogen atom generated in the reactions with water and gaseous hydrogen can reach almost all hydrogen in coal.

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