Effect of demineralization on hydrogen transfer of coal with tritiated gaseous hydrogen

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Received 26 April 2003; received in revised form 28 August 2003; accepted 20 October 2003

Abstract

Roles of mineral matters and oxygen functional groups of coal on hydrogen transfer reaction with gaseous hydrogen were investigated by using a tritium tracer technique in a fixed-bed reactor system. Mineral matters in coal were removed by HCl or HCl/HF treatments. Alkali metals and a part of pyrite were removed by HCl treatment. SiO2 and Al2O3 were removed only by HCl/HF treatment. A large part of pyrite was removed by HCl/HF treatment but about 20% of them still remained even after the treatment. It was observed that the efficiency of hydrogen transfer of coal decreased to some extent when cations and mineral matters were removed by HCl treatment. Further decrease in hydrogen transfer was observed after HCl/HF treatment. These results suggested that iron species from pyrite may catalyze the hydrogen transfer reaction with H2 gas. Mineral matters assist the H-transfer to the carbon network of coal but does not promote hydrogen transfer to hydroxy groups.

Keywords: Demineralization; Hydrogen transfer; Coal; Tritiated gaseous hydrogen; Acid treatment

1. Introduction

The transfer of hydrogen atoms from H-sources (H-donor solvent or gaseous H2) to coal would be one of the important processes for efficient conversion of coal molecules into liquids and soluble products; the conversion of coal into liquids or gases necessarily involves breaking of chemical bonds [1,2]. Some research groups have also suggested that, in addition to the function of the H-sources as radical scavenger, hydrogen transfer
from H-sources, especially from the solvent, also engenders bond scission \[3–9\]. Their studies on reaction mechanisms of the hydrogen transfer during liquefaction reactions have offered a useful knowledge for the development of efficient coal liquefaction process.

The type of hydrogen affects the coal liquefaction performance in the absence of a catalyst under mild conditions (at \(< 400 \, ^\circ\text{C}\)). There is the substantial difference in bond strength between H—H bond of hydrogen molecule and C—H bond of solvent; H—H bond strength is 104 kcal/mol, while the benzylic C—H bond strength in tetralin is about 82 kcal/mol \[10–12\]. The 22 kcal/mol difference in bond dissociation energy between these H-sources would result in the much favored abstraction of H\(_1\) from tetralin than from hydrogen molecule. However, our previous work in the liquefaction of Datong coal in the presence of tetralin and tritium-labeled gas has shown greater hydrogen transfer to the coal from the gas than from tetralin at 300–350 \(\, ^\circ\text{C}\) \[13\]. Furthermore, the liquefaction of Illinois No. 6 coal under mild condition at 350 \(\, ^\circ\text{C}\), as reported by Korda et al. \[12\] also demonstrated that the presence of H\(_2\) enhanced conversion to pyridine-extractable products and decreased the amount of hydrogen transfer from tetralin. A possible candidate to enhance the transfer of hydrogen atom from hydrogen molecule is mineral matter present in coal. Coal mineral matter generally enhances the liquefaction of coal. Some studies have focused on the addition and role of pyrite in the conversion of coal to liquid products \[14–16\]. Pyrite has shown to enhance the coal conversion and to increase selectivity to lighter products. Iron compounds, such as Fe\(_2\)O\(_3\) and sulfided Fe\(_2\)O\(_3\), were also reported to act as catalysts in coal liquefaction \[17,18\].

Catalysis of exchangeable cations in liquefaction of low-rank coals is reported by Joseph and Forrai \[19\]. They have shown that Fe-cation substantially catalyzes the reaction, while exchangeable alkali and alkaline earth metal cations such as Na\(^+\), K\(^+\), and Ca\(^{2+}\) are detrimental to liquefaction \[19\]. On the other hand, the study reported by Korda et al. \[12\] has shown that in comparison of liquefaction behavior of untreated Wyodak coal with successive HCl/HF-treated one, mineral matter originally present in coal promotes H\(_2\) dissociation.

The objective of the present study is to seek that the hydrogen transfer from H\(_2\) gas to coal is enhanced not only by coal mineral matter, as suggested by Korda et al. \[12\] but also by intrinsic structure of coal molecules because the presence of oxygen functionalities often affected the hydrogen transfer of coal in the presence and absence of catalyst \[20–23\]. The reaction of coal with H\(_2\) was conducted in a fixed-bed reaction system under mild conditions of 300–400 \(\, ^\circ\text{C}\), a gas pressure of 5 MPa and a reactant gas flow rate of 50 ml/min, in the absence of catalyst. In our laboratory, radioisotope tracer techniques, using tritium and \(^{14}\)C tracers, have been developed extensively to monitor the mechanism of hydrogen transfer reaction in coal liquefaction and to provide quantitative information on the mobility of hydrogen in coal \[13,20–27\]. In the present study, we applied the tritium tracer technique to provide further perspective on the nature of the interactions between coal molecules and H\(_2\). This work was done primarily to study the effect of coal mineral matter on hydrogen transfer. Metal cations of each coal were eliminated partly by an HCl treatment, and ash components were removed completely by successive HCl/HF treatment. Furthermore, to study the influence of functional groups on the hydrogen transfer, coals with different ranks, from lignite to low volatile bituminous coal, were selected.
2. Experimental

2.1. Materials

Four coal samples (lignite Beulah Zap coal (ND), high volatile bituminous Illinois No. 6 coal (IL), medium volatile Upper Freeport coal (UF), and low volatile bituminous Pocahontas No. 3 coal (POC)) were obtained from the Argonne Premium Coal Sample Bank. The elemental analysis and mineral matter content of the coals are given in Table 1. All coal samples were dried at 105 °C for 4 h under 10^-1 Torr before use. Tritiated H2 gas (tritium-labeled H2 gas) was obtained by electrolysis of tritiated water using HG-225 Hydrogen Generator. The tritiated water was purchased from Japan Isotope Association (185 MBq/ml) and was diluted with water to 6 × 10^7 dpm/ml. Tritiated H2 gas obtained was further pressurized with H2 gas before use.

2.2. Preparation of demineralized coal

Mineral matter in the coal samples was removed by conventional methods using HCl and successive HCl/HF treatments [12]. In the HCl treatment, the coal sample was mixed with 6 N HCl (20 ml/g coal) and stirred for 1 h at 60 °C under nitrogen atmosphere. Then it was filtered, washed with distilled water until the filtrate became neutral, and dried at 105 °C for 4 h. The successive HCl/HF treatment was carried out by adding 40 wt.% HF solution (20 ml/g coal) to the HCl-washed coal. This mixture was also stirred for 1 h at 60 °C under nitrogen atmosphere, and then filtered, washed, and dried based on the procedure above. Untreated, HCl-demineralized and HCl/HF-demineralized coal samples were analyzed by XRF, where each sample was fused using a hydraulic press to form a disk prior to analysis. Each sample was also oxidized slowly at temperature up to 950 °C with an automatic combustion system (Aloka ADS-113R) to measure the total ash content.

2.3. Reaction procedure

The reaction of each coal sample with tritiated H2 gas was carried out in a fixed-bed reactor (volume of 15 ml). The reactor system is presented schematically in Fig. 1. One gram of the coal sample was charged into the reactor, and then the gas was passed

Table 1

<table>
<thead>
<tr>
<th>Coal</th>
<th>Ultimate analysis (% daf)</th>
<th>Mineral and ash contents (% dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>ND</td>
<td>72.9</td>
<td>4.8</td>
</tr>
<tr>
<td>IL</td>
<td>77.7</td>
<td>5.0</td>
</tr>
<tr>
<td>UF</td>
<td>85.5</td>
<td>4.7</td>
</tr>
<tr>
<td>POC</td>
<td>91.1</td>
<td>4.4</td>
</tr>
</tbody>
</table>

through the reactor at a constant flow rate of 50 ml/min and pressure of 5.0 MPa in all reactions. Radioactivity of the gas introduced was also approximately constant at about 1500 counts/min and the change in radioactivity of the recovered gas from the reactor was monitored continuously by a radioanalyzer (Aloka RLC-701). The reactor was heated up to a temperature between 250 and 400 °C and was kept for 1 h at a certain reaction temperature. Change in ratio of radioactivity of the recovered gas to the feed gas for the reaction with the bituminous IL coal at various temperatures is presented in Fig. 2. The profile of the radioactivity includes heat-up zone to reaction temperature. In fact, for all the reactions the radioactivity of the gas phase went back to the initial value within 1 h, thus it should be considered that the system reached an equilibrium within 1 h. The tar produced was completely trapped by an ice-cooled trap. Total yield of volatile matters was determined by weighing the reactor before and after the reaction. The recovered solid residue and tar were combusted by the automatic sample combustion system. The tritiated water produced in the combustion was dissolved into a monophase scintillator reagent; its radioactivity was measured by a liquid scintillation counter (LSC, Beckman LS 6500). The radioactivity measured is correlated to the amount of tritium incorporated into the product. The error of analysis was usually within 1%. Furthermore, reproducibility of the data was determined by repeating the same experiments at a specified set of reaction conditions. Generally, the data were reproducible within 2–3% for the radioactivity and with the variations of 1–2% for the total yields of volatile matters and tar.

2.4. Calculation of the amount of tritium transferred

The amount of tritium transferred from the gas to coal was calculated with an assumption that hydrogen transfer reaction between coal and tritiated H₂ gas reached
equilibrium. Thus, after the reaction, the ratio of the radioactivity in the reacted coal to the amount of tritiated H$_2$ gas transferred ($R_{\text{coal}}/H_{\text{tr}}$) is equal to the ratio of the radioactivity in the gas to the amount of hydrogen in the gas ($R_{\text{gas}}/H_{\text{gas}}$).

$$R_{\text{coal}}/H_{\text{tr}} = R_{\text{gas}}/H_{\text{gas}} \quad \text{or} \quad H_{\text{tr}} = H_{\text{gas}} R_{\text{coal}}/R_{\text{gas}}$$

$R_{\text{coal}}$: the radioactivity in the reacted coal; $H_{\text{tr}}$: the amount of tritiated H$_2$ gas transferred; $R_{\text{gas}}$: the radioactivity in the gas; $H_{\text{gas}}$: the amount of hydrogen in the gas.

The total amount of transferred hydrogen is based on the weight of dry ash-free (daf) coal.

2.5. Determination of hydrogen in functional groups and tritium incorporated into these groups after the reaction with tritiated H$_2$ gas

The total amount of hydrogen in the functional groups of the raw and acid-treated coal samples was determined by exchanging hydrogens in the functional groups such as phenolic and carboxylic groups with tritium-labeled water at 100 °C for 24 h. This procedure has been verified by the previous studies in the exchange reaction of coal-like model compounds with D$_2$O or T$_2$O, in which the exchange reaction at 100 °C occurs selectively with hydrogen in the hydroxy groups, [21,27] while hydrogen in an aromatic ring substituted by functional groups become exchangeable at higher temperature of 300 °C [28,29]. The reaction was performed in a glass reactor immersed into an oil bath with stirring, and then followed by filtration and vacuum drying of the tritiated sample. The concentration of tritium in the coal was measured by similar procedure described
above. On the other hand, the amount of tritium incorporated into the functional groups of coal after the reaction with tritiated $\text{H}_2$ gas was determined by exchanging the tritiated coal with excess amount of water under the same condition above. A decrease in the radioactivity of the tritiated coal after the exchange with water would correspond to the amount of tritium incorporated into hydroxy groups, and the remaining tritium concentration would be equal to the amount of tritium incorporated into the carbon network.

3. Results and discussion

3.1. Demineralization of coal

The total ash content and metal concentration of ND, IL and UF coals before and after acid treatments are summarized in Tables 2, Tables 3, Tables 4, respectively. Raw lignite ND coal contains relatively large amounts of alkali and alkaline earth metals, especially calcium. The literature [30] shows that these metals in low rank coals are associated mostly as cations in carboxylic acid salts, and these inorganics are reduced in higher rank coals. This trend is also shown in these tables. On the other hand, inorganic components of higher rank IL and UF coals consist mainly of discrete mineral matters associated with Si and Al. Furthermore, these coals involve a significant amount of pyrite, as shown in Table 1.

Aqueous HCl treatment was done to remove the exchangeable alkali and alkaline earth cations. Table 2, Table 3 and Table 4 show that these cations in ND and IL coals are almost removed by the treatment. The Fe-component was also decreased drastically, depending on the coal rank. Since the degree of removal of Fe-component was higher in lower rank coals, the Fe removed by the HCl treatment may be associated to its form as exchangeable cation. On the other hand, other remaining elements such as Si, Al, Ti are assumed to be mainly associated with the minerals such as alumina, silica, titania, etc.,

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>Removed by HCl</th>
<th>Removed by HC/HF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration</td>
<td>% Removed</td>
</tr>
<tr>
<td>Ca 18,350</td>
<td>1870</td>
<td>89.8</td>
</tr>
<tr>
<td>Mg 4780</td>
<td>0</td>
<td>100.0</td>
</tr>
<tr>
<td>Na 6420</td>
<td>470</td>
<td>92.7</td>
</tr>
<tr>
<td>K 660</td>
<td>0</td>
<td>98.5</td>
</tr>
<tr>
<td>Si 11,340</td>
<td>10,300</td>
<td>8.9</td>
</tr>
<tr>
<td>Al 8540</td>
<td>6590</td>
<td>22.8</td>
</tr>
<tr>
<td>Ti 620</td>
<td>450</td>
<td>27.4</td>
</tr>
<tr>
<td>Fe 9825</td>
<td>3880</td>
<td>60.5</td>
</tr>
<tr>
<td>Total ash 92,000</td>
<td>35,000</td>
<td>62.0</td>
</tr>
</tbody>
</table>

* Metal and total ash concentrations are expressed as $\mu$g/g dry coal.
and they are almost completely removed from the coals by the successive HCl/HF treatment.

3.2. Content of hydroxy group in raw and demineralized coals

Our previous study has indicated that hydrogen atoms in functional groups such as phenolic and carboxy groups are readily exchanged with tritiated H₂ gas in the presence of a catalyst, even at 200 °C [20–23]. Therefore, in the present work, it is necessary to know the change in the amount of hydrogen atom in these groups after treating with acids. The total amount of hydrogen in the functional groups was determined by hydrogen exchange between coal and tritiated water at 100 °C. It is noteworthy to note that, in our previous study of exchange reaction of coal or coal model compounds with tritiated water and model compound with D₂O, relatively acidic hydrogen such as the hydrogen in phenolic groups was exchangeable at lower temperatures (up to 100 °C), while hydrogen in an aromatic ring substituted by functional groups became exchangeable at a higher temperature of 300 °C [21,29]. This is also in good agreement with the result reported by Werstiuk and Ju [28].

The data for the amount of hydrogen in the hydroxy group of untreated and acid-treated coals obtained by exchange reaction and by FTIR analysis in literature [31] are presented in Fig. 3. The results show that demineralization does not affect the amounts of functional groups. These data suggested that little exchangeable alkali and alkaline earth cations might be present in the functional groups. These cations may be present as isolated salts. Values obtained by the tritium tracer method were higher than those by FTIR analysis in low rank coals, indicating that the former includes carboxy groups as well as hydroxy groups.

Fig. 3. Content of hydrogen in functional groups for untreated and acid-treated coals. T-exchange: React. Temp. 100 °C; H₀ff by FTIR analysis [31].
3.3. Effect of demineralization on the efficiency of hydrogen transfer reaction

To investigate the possibility that mineral matter catalytically affects the hydrogen transfer from H$_2$ gas to the coal organics, we compared the efficiency of hydrogen transfer reaction between untreated and acid-treated coals in the reaction with a tritiated H$_2$ gas without catalyst at 300–400 °C for 1 h. The amount of hydrogen transferred to coal ($H_{tr}$) was determined by measuring the tritium concentration in the recovered products of tar and char.

Fig. 4 presents a change in the amount of hydrogen transfer from the gas phase to lignite ND coal as a function of reaction temperature for the untreated and acid-treated coals. In the reaction with the untreated coal, a perceptible level of hydrogen transfer to the coal ($H_{tr}$ = about 0.6 wt.%) was observed even at temperature as low as 300 °C, and then the $H_{tr}$ increased significantly to reach a level of $\approx 3.6$ wt.% at 400 °C. Partial demineralization with an HCl solution (denoted as HCl Dem.) decreased the hydrogen transfer reaction from the tritiated H$_2$ gas to coal, in which the reduction degree depended upon the reaction temperature. The $H_{tr}$ of the HCl-treated coal was lowered by about 50% at 300 and 350 °C, but by a lesser degree of 26% at 400 °C, relative to the $H_{tr}$ obtained with the untreated coal. Further removal of mineral matters by HCl/HF treatment (denoted as HCl/HF Dem.) did not result in a further decrease of $H_{tr}$ (at a perceptible level) at all the reaction temperatures. For example, with HCl/HF treatment the $H_{tr}$ was lowered by about 36% of that of the untreated coal or by 12% of that of the HCl-treated coal.

The results in Fig. 4 show that the presence of some mineral matters in lignite ND coal catalytically enhances the hydrogen transfer reaction with H$_2$ gas. In this case, the mineral matters removed by HCl treatment seem to be more active catalyst than the remained mineral matters.

![Graph showing change in amount of H-transfer for untreated and acid-treated lignite ND Beulah-Zap coals with temperature.](image-url)
mineral matters. Table 2 and the literature [30] show that lignite ND coal contains a significant amount of the exchangeable cations such as Fe, Ca, and Mg, and these mineral matters can be completely removed from the coal by washing with an HCl solution. Joseph and Forai [19] have investigated the influence of these cations on liquefaction of low rank coals, and they revealed that iron deposited on a lignite by ion exchange with FeCl₂ was active liquefaction catalyst which enhanced the conversion and product quality, while exchangeable alkali and alkaline earth metal cations, such as Na⁺, K⁺ and Ca²⁺, were detrimental to liquefaction. Furthermore, the enhancement of both the liquefaction yield and quality of products did not depend on whether the iron has been introduced into the coal from an iron(II) or iron(III) salt [32]. Therefore, the observed decrease in the Htr by the HCl treatment may be due to the removal of Fe cations from the coal. On the other hand, pyrite is well known as an active catalyst in the coal liquefaction, but its removal from the coal reduces the efficiency of hydrogen transfer from H₂ gas.

Fig. 5 shows the change in the amount of hydrogen transfer for the untreated, HCl-treated, and HCl/HF-treated IL coals with reaction temperature. Table 1 shows that IL coal has relatively high mineral and pyrite contents. However, the activity of the coal to react with H₂ gas was not as high as that of ND coal. The Htr value of IL coal increased from 0.4 to 2.2 wt.% daf as the temperature went up from 300 to 400 °C, in which these values were by about 60% lower than the Htr obtained for ND coal. These results suggest that, in addition to the effect of mineral matter, the coal structure also affects the efficiency of the hydrogen transfer reaction. Furthermore, the HCl treatment lowered the Htr of the coal by ≈ 30–40% relative to the Htr of the untreated coal at any temperatures from 300 to 400 °C. As shown in Table 3, the treatment reduced the iron concentration of IL coal by ≈ 35%, which may be as Fe-cations, and hence the decrease in Htr may be expected as a result of their removal. In contrast with the results of lignite ND coal, further treatment of

![Graph showing the change in amount of H-transfer for untreated and acid-treated Illinois No. 6 coals with temperature.]

Fig. 5. Change in amount of H-transfer for untreated and acid-treated Illinois No. 6 coals with temperature.
the HCl-treated IL coal with an HF solution resulted in a significant decrease in the activity of the coal to react with H₂, where the \( H_{tr} \) was lowered to the levels of \( \approx 45-60\% \) of the \( H_{tr} \) of the untreated coal at 300–400 °C. The decrease would be due to the removal of pyrite from the coal because the further decrease in a large amount of Fe content was detected with HCl/HF treatment.

The hydrogen transfer efficiency of higher rank UF coal is presented in Fig. 6. The efficiency of hydrogen transfer reaction for UF coal was significantly small compared to two lower rank coals above. For example, the \( H_{tr} \) level was not more than 35\% of the \( H_{tr} \) obtained for untreated ND coal. The HCl treatment also decreased the activity of the hydrogen transfer reaction, but the decrease was not as extensive as the other two coals. A significant decrease in the \( H_{tr} \) was observed when the coal was treated by the HCl/HF

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>Removed by HCl</th>
<th>Removed by HC/HF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration</td>
<td>% Removed</td>
</tr>
<tr>
<td>Ca 14,230</td>
<td>1040</td>
<td>92.7</td>
</tr>
<tr>
<td>Mg 1210</td>
<td>0</td>
<td>100.0</td>
</tr>
<tr>
<td>Na 1470</td>
<td>0</td>
<td>100.0</td>
</tr>
<tr>
<td>K 2680</td>
<td>2490</td>
<td>6.9</td>
</tr>
<tr>
<td>Si 36,870</td>
<td>36,320</td>
<td>1.5</td>
</tr>
<tr>
<td>Al 19,280</td>
<td>18,700</td>
<td>3.0</td>
</tr>
<tr>
<td>Ti 1230</td>
<td>1230</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe 26,730</td>
<td>17,270</td>
<td>35.4</td>
</tr>
<tr>
<td>Total ash 158,000</td>
<td>121,000</td>
<td>23.4</td>
</tr>
</tbody>
</table>

\( ^a \) Metal and total ash concentrations are expressed as \( \mu g/g \) dry coal.
The above situation was in agreement with the data in Table 4, where Fe component in UF coal is mainly as pyrite which is not effectively removed by the HCl treatment.  

### 3.4. Effect of coal structure on the efficiency of hydrogen transfer reaction

Since HCl/HF demineralization removed over 96% of mineral matters, those remained after the demineralization would have a negligible effect on the catalytic enhancement of the reaction with H₂ gas, and therefore observed level of $H_t$ for the HCl/HF treated coal would be directly related to the reaction efficiency between the coal organics and the gas. Korda et al. [12] compared the liquefaction behaviors between untreated and HCl/HF-treated Wyodak sub-bituminous coals at 350 °C, and concluded that the hydrogen transfer

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**Table 4**

| XRF analysis of mineral matter in MV bituminous UF coal before and after acid treatments$^a$ |
|---------------------------------|-----------------|-----------------|-----------------|
| Initial concentration | Removed by HCl | Removed by HCl/HF |
|---------------------|-----------------|-----------------|-----------------|
| Ca                  | 7120            | 690             | 50              |
| Mg                  | 1520            | 0               | 0               |
| Na                  | 550             | 0               | 0               |
| K                   | 2890            | 2680            | 7.3             |
| Si                  | 31,280          | 31,030          | 0.8             |
| Al                  | 22,970          | 22,500          | 2.1             |
| Ti                  | 770             | 770             | 0.0             |
| Fe                  | 17,850          | 15,100          | 15.4            |
| Total ash           | 13,200          | 113,000         | 14.4            |

$^a$ Metal and total ash concentrations are expressed as µg/g dry coal.

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**Fig. 7.** Effect of oxygen content of various coals on amount of H-transfer at different reaction temperature.
was catalyzed only by mineral matters in the coal. However, present results obtained by use of the tritium tracer technique have showed direct thermal reaction between the coal organics and H₂ gas which caused the incorporation of tritium into the HCl/HF-treated coal. Furthermore, as the amounts of H₅ obtained for the HCl/HF-treated coals are plotted against the oxygen content, Fig. 7 shows that the H₅ increased linearly with increase in the oxygen content of coal at 350 °C, and increased remarkably over 13.5 wt.% of oxygen content at 400 °C. This strongly suggests that oxygen functional groups also play an important role for enhancing the hydrogen transfer reaction with H₂ gas.

Stein revealed that phenoxy radical was much more reactive in H abstraction reaction than benzylic radical, even though ArO—H and ArC—H bonds have similar strength [1]. Indeed, studies on pyrolysis of model compound such as benzyl phenyl ether, as reported by Stock [2] showed that more phenol was formed than toluene; this indicates that phenoxy radical is a stronger abstractor than benzylic radical. The previous studies show

![Graph A. H-transfer to oxygen functional groups](image)

![Graph B. H-transfer to carbon network](image)

Fig. 8. Amount of hydrogen transferred to oxygen and carbon network for untreated and acid-treated ND Beulah-Zap coals.
that the exchange reaction between hydroxy groups in coal and tritiated H₂ gas in the
presence of a catalyst has already taken place, even at temperature as low as 200 °C [20,22].
These results lead to the conclusion that acidic groups such as phenolic groups may be
crucial in the transfer reaction with H₂ gas.

To get the information on the relative reactivity between oxygen-containing functional
groups and carbon network in the coal structure, we examined the amount of tritium
incorporated into acidic groups of coal samples after the reaction with tritiated H₂ gas.
Here, the amount of tritium incorporated to hydroxy groups was determined by exchang-
ing tritium in the functional groups with water at 100 °C [20–23]. Consequently, tritium
remained in coal after the exchange reaction was assigned to the tritium incorporated into
the carbon network of coal. The data for ND and IL coals are shown in Figs. 8 and 9,
respectively. In general, the data for the two coals show that tritium can be incorporated
into the hydroxy groups, even at temperature as low as 300 °C, and even with reducing the
mineral matter concentration by HCl and HCl/HF treatments. Furthermore, the amount of

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**Fig. 9.** Amount of hydrogen transferred to oxygen and carbon network for untreated and acid-treated Illinois No. 6 coals.
to the functional groups is hardly changed with the mineral matter concentration of coal at each reaction condition. In contrast, the hydrogen transfer to the carbon network is evidently affected by the mineral matter content in both cases, where the \( H_{tr} \) decreases continuously with the reduction in the concentration of mineral matter. The independence of the tritium incorporation to the hydroxy groups on the concentration of mineral matter may suggest that the hydroxyl radical formed during the reaction is capable of abstracting hydrogen from the gas phase, as shown by the following sequence:

\[
\begin{align*}
\text{Coal} - \text{Coal} &\rightleftharpoons \text{Coal}^\cdot + \text{Coal}^\cdot \\
\text{ArO} - \text{H} + \text{Coal}^\cdot &\rightleftharpoons \text{ArO}^\cdot + \text{H} - \text{Coal} \\
\text{ArO}^\cdot + \text{T}_2 &\rightleftharpoons \text{ArO} - \text{T} + \text{T}^\cdot
\end{align*}
\]

In this sequence, the formation of hydroxyl radicals should be initiated by coal radicals (Eq. (2)). The coal molecules have thermally labile linkages and thermally sensitive oxygen functional groups which generate coal radicals (denoted as Coal\(^\cdot\)) as shown in Eq. (1). On the other hand, a certain extent of the hydrogen transfer to the carbon network of coal may occur as a result of mineral matter catalysis.

4. Conclusions

The hydrogen transfer behaviors of untreated and acid-treated coals in the reaction with tritiated H\(_2\) gas were investigated. The results were as follows:

1. Pyrite present in coal catalytically enhances the hydrogen transfer from the gas.
3. Hydrogen transfer to hydroxy groups is independent of the mineral matter catalysis.
4. Hydroxy groups also play an important role in the transfer reaction from H\(_2\) gas to coal.

Acknowledgements

This study was supported by the Research for the Future Project of the Japan Society for the Promotion of Science (the 148 Committee on Coal Utilization Technology) under Contract JSPS-RFTF96R14801.

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