Original Paper

Dispersion State of Catalytic Metal Supported on Bio-Char Elucidated Using Energy Dispersive X-ray Spectroscopy: Effects of Catalyst Type and Heating Process

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Bio-chars loaded directly with catalytic metals such as K and Fe were gasified with CO₂ at atmospheric pressure after being heated to 1023-1323 K under an Ar flow. The gasification rate constant (K_p) of K-loaded bio-char was extremely higher than that of Fe-loaded bio-char. The structure such as surface and cross section of these bio-chars after (1) metal ions were supported on bio-char by the impregnation method (*i.e.* before heating) and (2) heating under an Ar flow (*i.e.* just before gasification) were observed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Before heating, the K atoms were uniformly distributed with no crystal formation. Even after heating under an Ar flow, the distribution of K atoms on the surface and inside of bio-chars remained uniform, suggesting the efficient formation of active sites for CO₂ gasification, although the K content on the surface decreased because of releasing. In contrast, even before heating, the Fe atoms were nonuniformly supported as α -FeOOH and α -Fe₂O₃ particles on the surface. After heating under an Ar flow, the Fe content on the surface decreased because Fe oxide particles moved into mesopore, suggesting the decrease in the number of active sites and the restriction of the accessibility of CO₂ to active sites because of the existence of large Fe oxide particles in mesopores.

バイオマスを熱分解して得られたバイオチャーにガス化触媒金属 (K および Fe) を直接担持し、熱天秤を用いて 1023-1323 K の範囲で CO₂ ガス化反応特性を調べた。その結果、K 担持バイオチャーにおいて、高いガス化速度定数が得られた。その原因を調べるため、(1) 水分を蒸発させ、金属イオンを担持した直後、(2) アルゴン気流中でガス化温度まで昇温させた直後 (ガス化直前)、の 2 種類のバイオチャーについて、表面および断面の触媒金属の存在状態を SEM-EDS を用いて観察した。金属イオンを担持した直後は、K 原子はバイオチャー表面および内部に均一に担持されていた。また、ガス化温度まで昇温した場合、K 原子の一部は放出したものの、ほぼ均一に担持されたままであった。一方、Fe イオンを担持した直後は、 α -FeOOH および α -Fe₂O₃ 粒子が主にバイオチャー表面上に担持されていた。アルゴン気流中でガス化温度まで昇温した後は、バイオチャー表面の Fe 原子の濃度が減少した。Fe 酸化物の沸点を考慮すると、ガス化温度への昇温により、Fe 酸化物の形態を持つ粒子が、粒子内部に移動したことが観察された。従って、K 原子を担持した場合、昇温しても均一に分散した状態が保たれ、多くの活性点が存在する。一方、Fe 原子を担持した場合は、粒子を形成しやすいため、活性点が少なくなる傾向である。また、昇温によりその粒子がバイオチャー内部に移動し、CO₂ が細孔内へ拡散しにくくなる。金属担持バイオチャーに及ぼすこのような昇温の影響により、K 担持バイオチャーのガス化反応特性が高いと考えられた。

Key Words

Potassium, Iron, Bio-char, Cross section, CO₂, Gasification

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1. Introduction

Gasification technologies are receiving attention since they allow the effective use of biomass resources. Gasification at low temperatures is essential for constructing exergy-recuperative biomass gasification systems^{1) 2)}. However, simultaneous “rapid gasification” and “low-temperature operation” would be difficult because of the contradictory nature of the two processes.

The gasifiers employed in most gasification processes have pyrolysis, combustion, and reduction zones^{3) ~ 5)}. Biochars produced from biomass feedstock in the pyrolysis zone are gasified with CO₂ and steam in the reduction zone. Since endothermic reactions have to proceed in both zones, the heat produced in the combustion zone (approximately 1273-1473 K) is employed.

In the kinetic studies on biomass pyrolysis^{6) ~ 9)}, the pyrolysis rate of biomass was much higher than the reduction rate of bio-char. Therefore, the gasification of bio-char in the reduction zone is often the rate-determining step in biomass gasification^{10) 11)}.

The utilization of catalysts in the gasification process is one of the most promising measures to realize rapid gasification rates at low temperatures. Alkali and alkaline earth metallic species (AAEMs) have led to increases in the gasification rates of bio-char^{12) ~ 15)}. In these cases, the inherent metal species played a catalytic role. However, by-products such as tarry compounds and sulfur compounds would have negative influences on the following steps such as gas cleaning and liquid fuel synthesis. In contrast, authors have reported that CO₂ gasification of K- and Fe-loaded bio-chars was promoted by supporting such metals on bio-chars directly¹⁶⁾. The gasification of metal-loaded bio-chars has the advantages of fewer negative effects to the following steps. The metal catalyst can be collected after cleaning the product gas and then recycled for further use. However, how the direct addition of metal catalysts to bio-chars promotes gasification has not been fully discussed because it was not clear how the supported metal behaved until heating to gasification temperature.

In the present study, the surfaces and cross sections of metal-loaded bio-chars were observed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). On the basis of the findings, the

relationship between the structure of bio-chars and the CO₂ gasification rate was discussed to suggest a structure of metal-loaded bio-chars, especially dispersion state of catalytic metal supported on bio-char, that is effective for gasification at low temperatures.

2. Experimental

2.1 Preparation of metal-loaded bio-chars

Douglas fir (1-4 mm) was used as a biomass sample. **Table 1** shows the results of analysis of the feedstock. The procedure for the preparation of K- and Fe-loaded bio-chars was reported previously in detail¹⁶⁾. The biomass samples with/without demineralization were heated under an Ar flow to obtain the bio-chars. As metal catalyst precursors, potassium acetate and iron(II) acetate were employed, respectively. Bio-chars were immersed in aqueous solutions and then dried overnight at 378 K to obtain the K- and Fe-loaded bio-chars before heating. The metal content on a total weight basis was regarded as the total metal content and was calculated as follows:

$$\begin{aligned} \text{Total metal content [wt\%]} \\ &= \text{Weight of supported metal [g]} \\ &\quad / (\text{Weight of bio-char [g]} \\ &\quad + \text{Weight of supported metal [g]}) \times 100 \end{aligned} \quad (1)$$

The total K contents were 0, 2.1, 6.0, 10, and 20 wt% (denoted as K0, K2.1, K6.0, K10, and K20, respectively) and the total Fe contents were 0, 2.2, 4.6, 10, and 23 wt% (denoted as Fe0, Fe2.2, Fe4.6, Fe10, and Fe23, respectively).

2.2 CO₂ gasification of catalytic metal-loaded bio-char

In the gasification experiments, CO₂ was selected as a gasifying agent because it is easy to handle (i.e., single phase) and can induce the CO₂ gasification of bio-char ($\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$), which is the endothermic reaction in the reduction zone and has to proceed at lower temperatures to allow the design of an effective process for liquid fuel synthesis from biomass^{18) 19)}.

The bio-char samples were gasified using a thermobalance (TGD-9600, ULVAC), shown in **Fig. 1**. **Table 2** shows the gasification conditions. The bio-chars were sifted to obtain samples with nearly identical diameters (1.5-2.0 mm) and lengths (2.0-3.0 mm). Approximately 6.0 mg of char samples was used for each run. In order to

Table 1 Ultimate and proximate analysis of feedstock

Ultimate analysis (daf wt%)					Proximate analysis (wt%)			HHV ²	
C	H	N	S	O ¹	Moisture	Volatile matter	Fixed carbon	Ash	(MJ/kg)
49.16	5.53	0.04	0.00	45.27	7.9	72.0	19.9	0.2	16.4

¹ By difference

² Higher heating value, calculated using Dulong's formula¹⁷⁾

Fig. 1 Experimental apparatus

Table 2 Gasification conditions

Gasifying agent	Flow rate mL/min	Temperature K	Pressure MPa
CO ₂	400	1023, 1073, 1173, 1273, 1323	0.1

obtain accurate gasification rates, the char particles were distributed independent of one another (hereinafter referred to as “the single char particle distribution”). The bio-char samples were heated under an Ar flow at a heating rate of 10 K/s until the gas temperature became constant, and then the atmospheric gas was changed from Ar to CO₂. The gasification experiments were carried out more than three times independently under isothermal conditions.

The kinetics of char gasification have been estimated using several models such as the volume reaction model (VRM), non-reactive core model (NRC), shrinking core model (SCM), and random pore model (RPM). Seo *et al.*²⁰⁾ and Sadhwani *et al.*²¹⁾ have reported that in the CO₂ gasification of metal-loaded chars, the RPM was the best at predicting experimental data. Therefore, in the present study, the RPM, expressed as Eq. (2), was applied to the weight-loss curve of K- and Fe-loaded bio-chars:

$$\frac{dX}{dt} = K_p (1 - X) \sqrt{1 - \psi \ln(1 - X)} \quad (2)$$

where X , K_p , and ψ are the bio-char conversion on a dry-ash-free basis, the gasification rate constant, and a parameter related to the pore structure of the bio-char sample ($X = 0$), respectively. Solving Eq. (2) analytically, we obtain

$$X = 1 - \exp \left\{ -K_p t \left(1 + \frac{\psi K_p t}{4} \right) \right\} \quad (3)$$

By transforming Eq. (3) and taking logarithms on both sides, it can be rewritten as Eq. (4):

$$\frac{-\ln(1 - X)}{t} = K_p + \frac{\psi K_p^2}{4} t \quad (4)$$

K_p and ψ can be derived by determining the intercept and gradient of the straight line of $-\ln(1 - X)/t$ versus t given by Eq. (4).

2.3 Preparation of metal-loaded bio-chars just before gasification

The gasification of K- and Fe-loaded bio-chars was carried out with CO₂ after heating to a specific temperature under an Ar flow. Supported catalytic metals may be released during the heating of metal-loaded bio-chars under an Ar flow. Therefore, metal-loaded bio-chars were heated to 1173 and 1273 K under an Ar flow at a heating rate of 10 K/s and kept for 5 s, and then were immediately cooled to room temperature to obtain bio-char samples just before gasification.

2.4 SEM and EDS observation

The state of the catalytic metal supported on bio-char was analyzed using SEM and EDS. Analyses were performed using a JSM-7100F (JEOL Ltd.). In the present study, both the surfaces and cross sections of bio-chars were observed. Fig. 2 shows the method for the preparation of bio-char samples for cross section observation. Bio-chars were sandwiched between carbon double-sided tape (P/N: 781173159), and the tape was cut at an appropriate location with a cutter to enable observation of the cross section of the samples. After confirming that the cross section was that of the char particle using SEM, EDS analysis was performed. The same EDS parameters, including the accelerating voltage, emission current, and preset number

Fig. 2 Preparation of SEM samples for cross section observation

Table 3 EDS analysis conditions

Accelerating voltage	Emission current	Preset number of scans	Number of pixels
kV	μA	-	-
15	42.4	10	512×364

of scans, were used for all samples (Table 3). The preset number of scans represents the number of scans while the material's surface is irradiated with an electron beam and the generated characteristic X-ray is measured. The number of pixels indicates the image resolution of an element. The JSM-7100F database contained standard data that corresponded to 100% concentration for each pure element. Therefore, the absolute concentrations of K and Fe atoms in the EDS images were calculated using the standard data.

The cut-off and grinding of fine particle samples immersed in resin and wax is the typical SEM preparation method. In some cases, rigid samples were cut with a diamond cutter^{22) 23)}. In the present study, a new preparation method was employed. Since bio-char samples in the present study had identical diameters of 1.5-2.0 mm and lengths of 2.0-3.0 mm, which were cut appropriately, a clear cross-section was obtained.

3. Results

3.1 Effect of total metal content on gasification rate constant

Fig. 3 shows the effects of total metal contents of K- and Fe-loaded bio-chars on K_p in the CO_2 gasification. For both cases, the K_p values increased as the metal contents increased up to 10 wt%, and were almost constant at greater than 10 wt%. The K_p values of K10 at 1073 and 1173 K were 133 and 300 times those of K0, respectively (Fig. 3(a)). The K_p values of Fe10 were between 3.3 and 6 times those of Fe0 at all temperatures (Fig. 3(b)).

Comparison of the K_p values at the same temperatures showed that the addition of K to bio-char led to a drastic increase in the K_p values even when the metal

content was almost the same. At 1173 K, the K_p value of K10 (5.4 min^{-1}) was approximately 90 times that of Fe10 (0.06 min^{-1}). The K_p value of K10 at 1023 K (0.09 min^{-1}) was higher than that of Fe10 at 1173 K. Taking the gasification temperature into account, the addition of K with a total content of 10 wt% was effective for promoting the CO_2 gasification at low temperatures.

3.2 SEM and EDS observation of metal-loaded bio-chars

In the present study, both the surfaces and cross sections of bio-chars were observed. The values of the surface atomic concentration were measured using the EDS function of the electron microscope. The atomic concentration was regarded as the metal content on the surface or in the cross section, and was calculated as an average value from several EDS images. This result will be discussed later.

3.2.1 K-loaded bio-char before heating

Fig. 4 shows the results of the observation of the cross section of K2.1. The EDS images, (b), (c), (d), (e), and (f), represent element maps of C, O, Na, K, and Fe, respectively. These figures show the concentration distribution of each element. The concentration is indicated by the color bars shown in the lower-left corner of each EDS image. Namely, the concentration of each element decreases in the order red > yellow > green > black. A higher number of colors indicate a greater difference between concentrations of supported atoms. In the cross section of K2.1, the concentration of C was the highest, followed by O and K. Na and Fe atoms were originally included in the woody biomass, while a large portion of K atoms was added to bio-

Fig. 3 Effect of total metal content on rate constant of CO_2 gasification of K-loaded bio-chars (a) and Fe-loaded bio-chars (b)

Fig. 4 SEM and EDS results of cross section of K2.1: (a) SEM image of cross section and element maps of (b) C, (c) O, (d) Na, (e) K, and (f) Fe

chars through impregnation. Fig. 4(e) indicates a uniform distribution of K even in the cross section.

Fig. 5 shows SEM and EDS images of the surfaces and cross sections of K2.1, K10, and K20. Here, the EDS images ((b), (d), (f), (h), and (j)) represent element maps of K. For both the surface ((b) and (f)) and the cross section ((d), (h), and (j)), the concentration of K increased with increasing the total K content. The EDS images of the surfaces of K2.1 and K10 ((b) and (f)) indicated that the K atoms supported

in K10 were locally condensed while those in K2.1 were uniformly distributed. The increase in the total K content caused the K atoms to be condensed. The EDS images of the cross sections of K2.1 and K10 ((d) and (h)) indicated that the K atoms were uniformly distributed even in the cross section while they were locally condensed for K20 ((j)).

The BET surface area, average pore diameter, and mesopore area of these K-loaded bio-chars were in the 0.6-1.4 m²/g, 13.3-32.5 nm, and 0.7-1.4 m²/g ranges, respectively ¹⁶.

Fig. 5 SEM and EDS images (surface and cross section) of K-loaded bio-chars: (a) SEM image of K2.1 surface, (b) element map of K (K2.1 surface), (c) SEM image of K2.1 cross section, (d) element map of K (K2.1 cross section), (e) SEM image of K10 surface, (f) element map of K (K10 surface), (g) SEM image of K10 cross section, (h) element map of K (K10 cross section), (i) SEM image of K20 cross section, and (j) element map of K (K20 cross section)

The BET surface areas were almost the same as the mesopore areas, indicating that mesopores were dominant in the char samples. The X-ray diffraction (XRD) patterns of these K-loaded bio-chars indicated that no crystal structure of K had formed¹⁶⁾. These results indicated that the bio-chars had large enough pore diameters to support the K atoms, and the supported K atoms were distributed inside the bio-chars as the total K content increased up to 10 wt%. At 20 wt%, the difference in the concentration of K became

large without crystal formation, even inside the bio-chars.

3.2.2 Fe-loaded bio-chars before heating

Fig. 6 shows the results of the observation of the surface of Fe2.2. The EDS images, (b), (c), (d), (e), and (f), represent element maps of C, O, Na, K, and Fe, respectively. The concentration of C was the highest, followed by O and Fe. The tendency was the same as those of other Fe-loaded bio-chars.

Fig. 7 shows SEM and EDS images of the surfaces

Fig. 6 SEM and EDS results for Fe2.2 surface: (a) SEM image of cross section and element maps of (b) C, (c) O, (d) Na, (e) K, and (f) Fe

Fig. 7 SEM and EDS images (surface and cross section) of Fe-loaded bio-chars: (a) SEM image of Fe2.2 surface, (b) element map of Fe (Fe2.2 surface), (c) SEM image of Fe2.2 cross section, (d) element map of Fe (Fe2.2 cross section), (e) SEM image of Fe10 surface, (f) element map of Fe (Fe10 surface), (g) SEM image of Fe10 cross section, (h) element map of Fe (Fe10 cross section), (i) SEM image of Fe23 surface, (j) element map of Fe (Fe23 surface), (k) SEM image of Fe23 cross section, and (l) element map of Fe (Fe23 cross section)

and cross sections of Fe2.2, Fe10, and Fe23. Here, the EDS images ((b), (d), (f), (h), (j), and (l)) represent element maps of Fe. Fig. 7(b), 7(f), and 7(j) indicate that the concentration of Fe on the surface increased monotonously as the total Fe content increased. In contrast, Fig. 7(d), 7(h), and 7(l) indicate that inside the bio-chars, the Fe atoms were hardly detected at 2.2 and 10 wt%. The Fe content in the cross section estimated using EDS images was only 5%, although the total Fe content was 23 wt% (Fig. 7(l)). These results indicated that a large portion of Fe atoms was supported on the surface of the bio-chars.

In the XRD patterns of the Fe-loaded bio-chars, clear peaks attributed to α -FeOOH and α -Fe₂O₃ were observed, and the crystal diameters determined using the Scherrer equation increased from 11.7 to 14.8 nm and from 17.9 to 24.6 nm, respectively, as total Fe content increased¹⁶. The BET surface area, average pore diameter, and mesopore area were in ranges of 0.7-5.5 m²/g, 13.5-27.0 nm, and 0.9-5.0 m²/g, respectively, and the pore diameters of Fe4.6, Fe10, and Fe23 were smaller than the diameter of α -Fe₂O₃¹⁶. These results supported the findings that the Fe atoms were nonuniformly supported as α -FeOOH and α -Fe₂O₃ particles on the surface from EDS observation shown in Fig. 7.

3.2.3 K-loaded bio-char after heating

Alkali compounds in biomass feedstock were released during heating under inert gas flow^{24) ~ 26)}. In the present study, the gasification of K- and Fe-loaded bio-chars was carried out with CO₂ after heating to a specific temperature under an Ar flow. Supported catalytic metals may be released during the heating of metal-loaded bio-chars under an Ar flow. Therefore, metal-loaded bio-chars were heated to 1173 and 1273 K under an Ar flow, and then were immediately cooled to room temperature to obtain bio-char samples just before gasification.

Fig. 8 shows SEM and EDS images of the cross sections of K-loaded bio-chars after heating under an Ar flow. The K atoms remained inside the bio-chars even after heating. Comparison of Fig. 5(h) and Fig. 8(f) showed that the concentration of K in the cross section decreased upon heating to 1173 K. These EDS images reflect the local situation; however, it is suggested that the K atoms supported inside the bio-char moved and were released without crystal formation upon heating.

3.2.4 Fe-loaded bio-char after heating

Fig. 9 shows SEM and EDS images of the surfaces and cross sections of Fe-loaded bio-chars after heating to 1173 K under an Ar flow. Like with Fe-loaded bio-char before heating, the concentration of Fe on the surface increased with increasing total Fe content; that inside the

bio-char ((d), (h), and (l)) was hardly detected. Comparison of element maps of Fe before and after heating (Fig. 7(f) and Fig. 9(j)) showed that the concentration of Fe on the surface decreased because of heating. Here, comparison of Fig. 7(b) and Fig. 9(b) suggested that the supported Fe atoms present in low amounts (Fe2.2) were hardly affected by heating.

Figs. 10 and 11 show SEM and EDS images including both surface and cross section before and after heating with respect to Fe10 and Fe23, respectively. For both Fe-loaded bio-chars before heating, the Fe and O atoms condensed on the surface while those atoms hardly existed in the cross section (Fig. 10(c), 10(d), 11(c), and 11(d)). In contrast, the C atoms were observed in the cross section while they hardly existed on the surface (Figs. 10(b) and 11(b)). After heating, the thickness of Fe atoms observed on the surface increased (Figs. 10(h) and 11(h)), suggesting that the heating process led to the penetration of Fe atoms inside bio-chars. For both Fe-loaded bio-chars, the O contents in the cross section (Figs 10(g) and 11(g)) were apparently lower than Fe contents on the same section (Figs. 10(h) and 11(h)).

3.2.5 Effect of heating on metal content on the surface

Fig. 12 shows the K and Fe contents on the char surface before and after heating under an Ar flow. The horizontal axis represents the total metal content. The

Fig. 8 SEM and EDS images of cross section of K-loaded bio-chars after heating to 1173 K: (a) SEM image of K2.1, (b) element map of K (K2.1), (c) SEM image of K6.0, (d) element map of K (K6.0), (e) SEM image of K10, and (f) element map of K (K10)

Fig. 9 SEM and EDS images (surface and cross section) of Fe-loaded bio-chars after heating to 1173 K: (a) SEM image of Fe2.2 surface, (b) element map of Fe (Fe2.2 surface), (c) SEM image of Fe2.2 cross section, (d) element map of Fe (Fe2.2 cross section), (e) SEM image of Fe4.6 surface, (f) element map of Fe (Fe4.6 surface), (g) SEM image of Fe4.6 cross section, (h) element map of Fe (Fe4.6 cross section), (i) SEM image of Fe10 surface, (j) element map of Fe (Fe10 surface), (k) SEM image of Fe10 cross section, and (l) element map of Fe (Fe10 cross section)

vertical axis indicates the atomic content on the surface of bio-chars measured using the EDS function of the electron microscope. The content was calculated as an average value from several EDS images. In both figures, straight lines with slopes of 1 are also shown. If the metal catalysts were uniformly supported on bio-chars and not released during heating, the metal contents on the char surface measured by EDS should be plotted along the straight line.

Comparison of Figs. 12(a) and 12(b) indicates the Fe content on the surface before heating was much higher than the K content before heating. This result indicates that a large portion of supported Fe atoms was distributed on the surface of bio-char while the K atoms were supported on and inside the bio-char at 2.1 and 6.0 wt%. This fact supported the results of SEM and EDS observation in Figs. 5, 7, 10, and 11. Interestingly, the K content on the surface of K20 was lower than the total K content (Fig. 12(a)), suggesting that the K atoms were likely condensed without crystal formation inside the bio-char.

When the temperature was increased to 1273 K, in most cases, the metal content on the surface decreased. These results were supported by the fact that for Fe10 and Fe23, the heating process led to the penetration of Fe atoms inside the bio-chars (Figs 10 and 11). On the contrary, the Fe content on the surface of Fe2.2 increased slightly with

increasing temperature (Fig. 12(b)).

Taking into account that the melting points are higher than 1643 K²⁷⁾, no release of Fe oxide would take place because the gasification temperature was much lower than the melting point. Leijenhorst *et al.* reported that the Fe atoms in the biomass feedstock remained largely on the solid char in pyrolysis²⁸⁾. The increase in temperature to 1173-1273 K would lead to the phase transition of α -FeOOH and α -Fe₂O₃ to Fe oxide compounds such as FeO because the O contents were lower than the Fe contents (Figs. 10(g) and 11(g)). The increase in the temperature also would lead to the aggregation of Fe oxide particles. The average pore diameter of Fe2.2 before heating was 27.0 nm, which was larger than the diameters of α -FeOOH (11.7 nm) and α -Fe₂O₃ (17.9 nm)¹⁶⁾, therefore, small particles might migrate from the inside to the surface, and then aggregate during heating. In contrast, it would be more difficult for the Fe oxide particles to move because the sizes of Fe oxide particles for Fe4.6, Fe10, and Fe23 were comparable to the average pore diameter¹⁶⁾.

4. Discussion

Fig. 13 shows a schematic of the structure change as K and Fe atoms were supported on bio-chars. Here, mesopores were dominant in the char samples. In order

Fig. 10 SEM and EDS images of Fe-loaded bio-chars before and after heating to 1273 K: (a) SEM image of Fe10 surface and cross section before heating, (b) element map of C (Fe 10 surface and cross section before heating), (c) element map of O (Fe 10 surface and cross section before heating), (d) element map of Fe (Fe10 surface and cross section before heating), (e) SEM image of Fe10 surface and cross section after heating, (f) element map of C (Fe10 surface and cross section after heating), (g) element map of O (Fe10 surface and cross section after heating), (d) element map of Fe (Fe10 surface and cross section after heating)

to emphasize sizes of the K atoms and Fe oxide particles compared with the mesopore diameter (mentioned later), Fig. 13 does not depict SEM/EDS images.

Bio-chars were immersed in aqueous solutions of potassium acetate and iron(II) acetate and then dried. For K-loaded bio-chars, the K ions moved into the mesopores and were distributed not only on the surface, but also the inside of the bio-char (Fig. 13(a)). The K content on the surface decreased by 21-59% as the temperature increased to 1273 K (Fig. 12(a)). The boiling point of metallic K is 1047 K²⁹⁾. In a study on pyrolysis of biomass, the release of K from bio-char was observed³⁰⁾. In the present study, a portion of supported K atoms would be released from the surface and the inside of the bio-char (Fig. 13(a)), followed by the decrease in the K content on the surface. Then, the

residual K atoms would be bound to carbon atoms to form active sites (K-C) for CO₂ gasification.

For Fe-loaded bio-chars (Fig. 13(b)), Fe²⁺ is easily oxidized to Fe³⁺ at room temperature. In the aqueous solution, Fe³⁺ was converted to α -FeOOH and α -Fe₂O₃ via ferrihydrite above 373 K³¹⁾. In the present study, during drying, large α -Fe₂O₃ particles formed on the surface. In drying step, the aqueous solution in which Fe ions was dissolved was heated. The crystallization of Fe oxide would be faster than the evaporation of water, followed by prompt formation of large particles. Therefore, the large α -FeOOH and α -Fe₂O₃ particles remained on the surface because their sizes were comparable to the average pore diameter.

It is possible that a portion of Fe oxide particles of Fe₂O₃ move from the inside to the surface with an increase

Fig. 11 SEM and EDS images of Fe-loaded bio-chars before and after heating to 1173 K: (a) SEM image of Fe23 surface and cross section before heating, (b) element map of C (Fe23 surface and cross section before heating), (c) element map of O (Fe23 surface and cross section before heating), (d) element map of Fe (Fe23 surface and cross section before heating), (e) SEM image of Fe23 surface and cross section after heating, (f) element map of C (Fe23 surface and cross section after heating), (g) element map of O (Fe23 surface and cross section after heating), (d) element map of Fe (Fe23 surface and cross section after heating)

Fig. 12 Metal content on the char surface of K-loaded bio-char (a) and Fe-loaded bio-char (b) before and after heating

Fig. 13 Schematic of structure changes of metal-loaded bio-chars: (a) K-loaded bio-char and (b) Fe-loaded bio-char

in the temperature. In contrast, the Fe content on the surface of Fe4.6, Fe10, and Fe23 decreased by 28-58% as the temperature increased to 1273 K (Fig. 12(b)). The Fe atoms were observed inside the bio-char more deeply than the O atoms while both atoms existed on the surface before heating. This result suggests that the reduced Fe oxide such as FeO formed and the size decreased, and then moved into the mesopores because of reduction atmosphere during heating under Ar flow (Fig. 13(b)).

Huang et al. has reported the effect of catalyst type such as K, Na, Ca, Mg, and Fe on CO₂ gasification of metal-loaded bio-char³²⁾. Taking into account that the reactivity decreased in the order of K > Na > Ca > Fe > Mg, the trend was the same as that in the present study (K > Fe). The intrinsic catalytic performance for the K atoms would have higher compared to that for Fe.

The following mechanism of CO₂ gasification using K as a catalyst has been proposed^{33) 34)}:

KC_(site) and K(s) represent an active site combining K with C and mobile K atoms, respectively. CO₂ is adsorbed on the active site leading to the formation of KC-O and release of CO. Subsequently, KC-O forms K(s) and releases CO, and K(s) comes into contact with carbon atoms to form KC_(site).

In order to increase the CO production rate, an increase in the number of KC_(site) and easy accessibility of CO₂ to the site are required. For the K-loaded bio-char

employed in the present study, the K atoms were distributed on the surface and inside of the bio-char. K-loaded bio-chars had large pore diameters compared to the volume of CO₂ molecules.

The K_p values of K10 were almost identical to those of K20 (Fig. 3(a)). The average pore diameter of K20 was 32.5 nm¹⁶⁾, which was larger than the volume of CO₂ molecules. Therefore, the result is attributed to the lack of increase in KC_(site) even when the total K content is increased from 10 and 20 wt%. This assumption is also supported by an increase in the concentration of K as determined through EDS observation (Fig. 5(h), 5(j), and Fig. 12(a)).

For Fe-loaded bio-chars, the active site (Fe-C) should form for effective CO₂ gasification. However, the number of Fe-C sites would be much lower than that of KC_(site) because the Fe atoms were supported as Fe oxide particles. Moreover, it is likely that the Fe oxide particles aggregate due to an increase in the temperature. The size of the Fe oxide particles just before gasification is the important issue. Therefore, in the near future, we will measure the size of the Fe oxide particles by XRD.

In the present study, the direct addition of K to bio-char was effective for promoting CO₂ gasification. Not only the intrinsic high performance for the K atoms, but also the number of active sites just before gasification was focused on because of high dispersibility even after heating. Therefore, in order to enhance the reactivity of K-loaded bio-char, utilization of bio-char with a larger pore diameter and surface area and distribution of K atoms without

condensation are required. Hanaoka *et al.* reported that biochars with large surface areas were produced under a $N_2/CO_2/O_2$ flow, and the char yield was almost the same as that without CO_2/O_2 ¹⁸⁾. If the K atoms are impregnated using methanol instead of water as a solvent, they can move deeper into the mesopores and would be distributed uniformly because the surface tension is lower than that of the aqueous solution.

5. Conclusions

The K_p value of K10 was approximately 90 times that of Fe10. The K_p value of K10 at 1023 K was higher than that of Fe10 at 1173 K. The gasification rate constant at a low temperature such as 1023 K was drastically enhanced by the addition of an appropriate amount of K to bio-char. With regard to metal-loaded bio-chars, the structure changes were observed using SEM and EDS. The obtained results can be summarized as follows:

- (1) For K-loaded bio-char, the K_p values increased as the total K content increased to 10 wt% and remained constant at greater than 10 wt%. Before heating, the K atoms were distributed without crystal formation even inside the bio-char as the total K content increased to 10 wt%. When the content was 20 wt%, the K atoms were locally condensed on the surface and inside of the bio-char. After heating under an Ar flow, the distribution of K atoms uniformly remained as the total K content increased to 10 wt%, although the K content on the surface decreased by 21-59% because a portion of K atoms was released.
- (2) For Fe-loaded bio-char, the K_p values increased slightly with increasing total Fe content. However, the K_p values were considerably lower than those of K-loaded bio-chars. Even before heating, the Fe atoms were nonuniformly supported as α -FeOOH and α -Fe₂O₃ particles on the surface, and the Fe contents on the surface became much higher than those on a total weight basis because the particle sizes were comparable to the average pore diameter. After heating under an Ar flow, the Fe content on the surface decreased by 28-58%. Taking the melting points of Fe oxide compounds into account, it was suggested that the Fe oxide particles would move into the mesopores without being released and the existence of large Fe oxide particles restricted the accessibility of CO₂ to active sites.
- (3) The direct addition of an appropriate amount of K to bio-char and the distribution of K atoms on the surface and inside of the bio-char were effective for promoting CO₂ gasification at low temperatures.

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