

Mossbauer Study on Local Structural Change of Iron Species during Stream-Gasification of Iron-loaded Brown Coal

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Many studies have reported on the iron-catalyzed gasification of carbon and coal with steam and CO₂. Since most of the previous studies were made using XRD method with a large amount of iron, the observation of the chemical forms of the highly dispersed iron has not been carried out at all. In the present study, the effects of catalyst loading and char conversion on the change of iron species during the steam gasification are determined by using Mössbauer and EXAFS spectroscopy^{1,2}. The chemical form of highly dispersed iron species which may be responsible for high catalytic activity is clarified.

Loy Yang brown coal from Victoria, Australia, was used in this study. Several coal samples with different catalyst loadings, 0.5, 2 and 10 wt% as metal, were prepared by impregnation with Fe(NO₃)₃. The reactivities for the steam gasification were measured by using a thermobalance at 650°C under H₂O (66 kPa)/N₂ mixture (48 ml(STP) min⁻¹). Mössbauer spectra were measured by a constant acceleration type spectrometer using a 512-multi channel spectrum analyzer in Cyclotron and Radioisotope Center (CYRIC) of Tohoku University. ⁵⁷Co in a rhodium matrix (20 mCi) was used as γ -ray source. X-ray absorption spectra (EXAFS and XANES) of Fe K-edge were obtained at BL-7C facility of the Photon Factory in the National Laboratory for High-Energy Physics (KEK-PF).

The activities for steam-gasification are shown in Figure 1 as a function of char conversion. The catalytic activity of iron in the 0.5 wt% sample is much higher than those of the 2 and 10 wt% samples especially in the region of low char conversion. The activity decreased with char conversion in all the cases.

The chemical forms of iron compounds were identified by XRD method. No iron compounds were detected with the 0.5 wt% samples, and the peaks due to Fe₃O₄ were observed with others.

Figure 2 illustrates Mössbauer spectra of the 0.5 wt% sample which showed only a doublet (D). This doublet was observed for all the samples shown in Figure 2 with different degrees of intensity. The spectra of the 2 and 10 wt% samples (Fig. 2b-e) showed not only this doublet but also two magnetic sextets assigned to crystalline Fe₃O₄. The estimated

concentrations of D species and Fe₃O₄ are summarized in Figure 3. The D species was predominant when the loading was low and the char conversion was small. The content of Fe₃O₄ component became larger with increasing iron loading and char conversion.

Figure 4 shows the Fourier transforms (FTs) of the k^3 -weighted EXAFS spectra. A peak at 1.5-1.6 Å and peak at 2.7 Å can be assigned to the Fe-O and Fe-Fe distances in oxidized species, respectively. Fe₃O₄ has twin peaks at around 2.7 Å, while α-FeOOH has a single peak in this region. The 0.5 wt% sample heated under N₂ (Fig. 4c) exhibits an intense Fe-O peak and a very small Fe-Fe peak, indicating that iron species are highly dispersed. 0.5 wt% sample after gasification (Fig. 4d) exhibits two intense peaks due to Fe-O and Fe-Fe, suggesting the formation of oxide particle. The Fe-Fe peak is a singlet and has a very similar feature of that of Fe-Fe peak of α-FeOOH. The 2 and 10 wt% samples also exhibit two intense peaks due to Fe-O and Fe-Fe. The shoulder of Fe-Fe peak becomes more intense with the longer reaction time and with the higher loading samples.

By combining all data, the variation of chemical form of the iron catalyst can be summarized in Figure 5. Iron species dispersed atomically in the Fe(NO₃)₃-impregnated coal. During the steam gasification, this atomically dispersed iron species transformed to either highly dispersed ultrafine FeOOH or crystalline Fe₃O₄. The concentration of each species depended not only on iron loading but also on char conversion. The ultrafine FeOOH was predominant with low loading samples and at low char conversions. This species seems to be responsible for the catalytic activity. In the highly loaded sample, the concentration of Fe₃O₄ crystallite was high even at a low char conversion, and the transformation of FeOOH to Fe₃O₄ with conversion occurred more easily.

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References

- 1) Yamashita H. et al., *Energy Fuels*; **3** (1989) 686.
- 2) Yamashita H. et al., *Energy Fuels*; **5** (1991) 52.

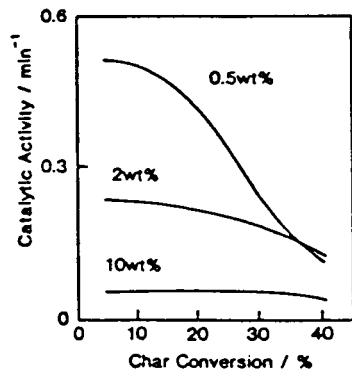


Fig. 1. Specific catalytic activity vs char conversion.

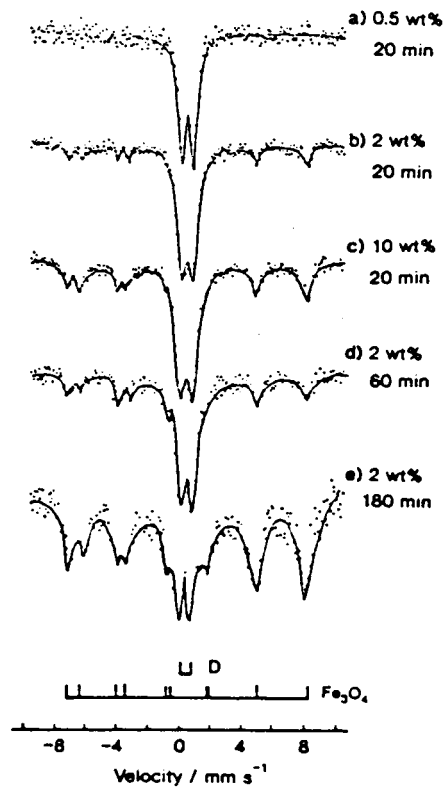


Fig. 2. Mössbauer spectra of iron-loaded samples after steam gasification at 650°C.

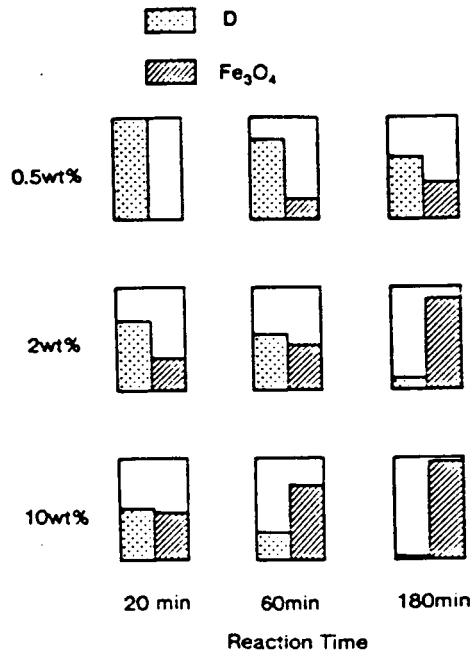


Fig. 3. Relative amount of iron species determined by Mössbauer spectra. D represents iron species that give a doublet in Mössbauer spectra.

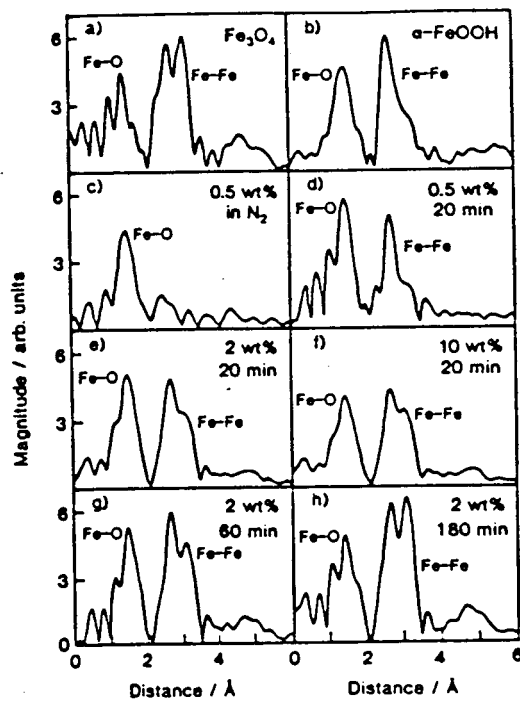


Fig. 4. FTs of EXAFS. Reference iron compounds; (a) Fe_3O_4 and (b) $\alpha\text{-FeOOH}$. Iron-loaded samples: (c) 0.5 wt% sample heat-treated in N_2 at 650°C, and (d-h) samples with different loading after steam gasification at 650°C for different periods.

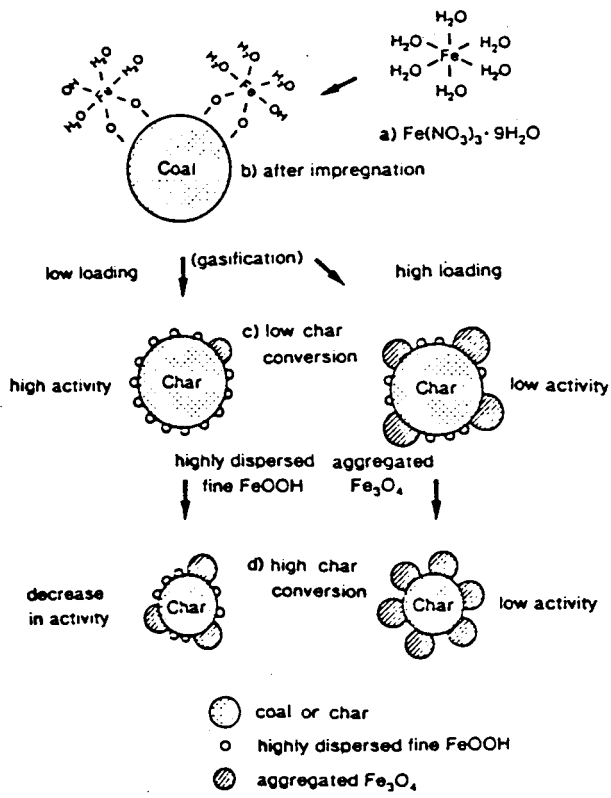


Fig. 5 Change of chemical form of iron species during gasification.