

HYDROGASIFICATION OF BROWN COAL WITH ACTIVE IRON CATALYSTS FROM FERRIC CHLORIDE

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INTRODUCTION

It would be necessary nowadays that coal is converted into the environmentally acceptable fuels. Gasification of coal with hydrogen is an important process for producing clean SNG. Since the reaction rate is very slow, high temperature and high pressure are required in the absence of catalyst [1], and thus an active and inexpensive catalyst should be developed. Iron is one of the most promising catalysts for the hydrogasification of coal. We have been trying to utilize acid wastes from metal pickling and titanium oxide production plants as Fe catalyst sources, because the wastes are cheap and abundant. When Fe chlorides or sulfates of the major components are added onto coal by the conventional impregnation method, they are inactive for the gasification in H_2 at low temperatures [2], and Cl- or S-containing gases evolved during gasification may result in serious problems such as corrosion. However, we have recently found that Cl-free Fe catalysts finely-dispersed on low-rank coals can be successfully prepared from an aqueous solution of $FeCl_3$ using several additives, and exhibit high activities for the low temperature gasification with steam [3,4].

In the present work, these Fe catalysts are applied to the gasification of brown coal in atmospheric H_2 at low temperatures below 1200 K. The relationship between the catalytic activity and the preparation method and the catalytic state is examined.

EXPERIMENTAL

Coal and Catalyst. Australian Loy Yang brown coal with a particle size of 0.15 - 0.25 mm was employed in this study. The proximate analysis was ash, 0.5; volatile matter, 52.4; fixed carbon, 47.1 wt% (dry), and the ultimate analysis was C, 66.7; H, 4.6; N, 0.5; S, 0.3; O, 27.9 wt% (daf).

Three kinds of Fe catalysts were precipitated onto brown coal from an aqueous solution of $FeCl_3$ with different additives, that is, urea $((NH_2)_2CO)$, $Ca(OH)_2$, and NH_3/NH_4Cl buffer solution. These catalysts are abbreviated as Fe(U), Fe(C), and Fe(A), respectively. In the preparation of Fe(U), urea was added to the mixture of coal and $FeCl_3$ solution so that fine particles of $FeOOH$ could be precipitated onto coal [5], and the resulting mixture was stirred at 370 K. For Fe(C) and Fe(A) $Ca(OH)_2$ powder and NH_3/NH_4Cl solution were added instead of urea, respectively, and the aqueous mixture was stirred at room temperature. After each precipitation, the solution was filtered off, and the Fe-bearing coal was washed with deionized water repeatedly to remove the Cl^- or Ca^{+2} ions. The preparation methods have been described in detail elsewhere [3,4].

Hydrogasification. Gasification runs were isothermally conducted in a thermobalance under atmospheric H_2 at 873-1173 K. Since all the samples were quickly heated up to a predetermined temperature, the coal devolatilization first took place, and after the completion within a few minutes char gasification started. The activity of Fe catalyst in the latter stage will be discussed throughout the paper. The reactivity of char after devolatilization is expressed by using both char conversion on a dry ash free and catalyst free basis and the specific rate of char, that is, the gasification rate per unit

weight of remaining char.

X-ray diffraction. X-ray diffraction (XRD) measurements of Fe-bearing coals and chars were made with Mn-filtered Fe-K α radiation to clarify the chemical form and dispersion state of Fe catalyst. The average crystallite size of Fe species was determined by the Debye-Schörrer method.

RESULTS AND DISCUSSION

Catalyst Components. The actual Fe loading of each sample was 3.4, 4.7, and 4.6 wt% for Fe(U), Fe(C), and Fe(A), respectively. The chlorine content determined by a standard Eschka method was nearly equal to that in the original coal (0.08 wt%) in every catalyst, indicating the complete removal of Cl ions from FeCl₃ with water washing. A small amount of Ca²⁺ (0.5 wt%) from Ca(OH)₂ was retained with Fe(C).

Catalytic Activity for Hydrogasification. Table 1 shows char conversion after 30 min in the hydrogasification at 873 K. The enhancement of the gasification rate by Fe catalyst was observed only in the early period of reaction, though not so high, and all the catalysts seemed to lose the activity in the latter stage. Char conversion showed that the order of the catalytic effectiveness was Fe(A) < Fe(C) < Fe(U).

Figure 1 illustrates the change in char conversion with reaction time at 1073 K. Every catalyst promoted the gasification, and the effectiveness was strongly dependent on the preparation method. The order of the activity was Fe(A) < Fe(U) < Fe(C), which is the same order as observed in the steam gasification [4]. With the most active Fe(C) char was completely gasified within about 100 min. The conversion at 120 min with Fe(U) and Fe(A) increased from 18 % without iron to 52% and 37%, respectively. Figure 2 shows the specific gasification rate as a function of char conversion at 1073 K. The rates for Fe(A) and the original coal were low and almost constant. The initial rates for Fe(U) and Fe(C) were almost the same, and they were about 20 times that without iron. The specific rate for Fe(U) decreased steeply with increasing conversion. On the contrary, the rate for Fe(C) increased gradually as the gasification proceeded. This rate increase was also observed at 1173 K. The change in specific rate with conversion may be determined by the balance between catalyst agglomeration and enrichment due to the consumption of char. When the catalyst enrichment is predominant as in the K-catalyzed gasification [6], the specific rate would increase with increasing conversion. The rate increase observed in the latter part of gasification with Fe(C) may be this case.

Thus, it is found that these precipitated Fe catalysts, especially Fe(C), exhibit high activities for the gasification of brown coal in atmospheric H₂ even at a temperature as low as 1073 K.

Catalyst State. Since no XRD lines of Fe species were detectable for each catalyst, the chemical form of Fe catalyst on coal could not be identified. However, other analytical techniques such as elemental analysis, ESCA, and FT-IR suggested that the catalyst exists as finely dispersed FeOOH [3,4].

The catalyst state immediately after devolatilization in H₂ at 873 K is summarized in Table 1. Major XRD species were α -Fe irrespective of the catalyst type. Small peaks due to cementite (Fe₃C) were also observed for Fe(C). The degree of catalyst dispersion evaluated from the average crystallite size of α -Fe increased in the order of Fe(A) < Fe(C) < Fe(U). This order corresponded to that of the gasification activity, which suggests that the dispersion may be a key factor determining the catalytic effectiveness in this temperature region.

Figure 3 shows the XRD patterns for Fe-bearing chars devolatilized at 1073 K. When the devolatilization temperature was raised from 873 K to 1073 K, the main species for Fe(C) changed from α -Fe to Fe₃C and strong XRD lines of unidentified iron carbides

appeared with small signals of α -Fe for Fe(U), whereas the major species for Fe(A), α -Fe, remained unchanged, though weak peaks of unidentified carbides were observed. As is seen in Figure 1, Fe(C) was the most active catalyst at 1073 K, and it achieved the complete gasification of char. Although Fe₃C is not always the actual active species because of the bulk chemical form identified by XRD, these observations suggest that the formation of iron carbide, perhaps Fe₃C, may be essential for such the high activity in the temperature region of around 1100 K. In other words, the hydrogasification may proceed through the carbon dissolution mechanism [7,8]. On the other hand, the hydrogen spill-over mechanism [1,9] might be predominant in the Fe-catalyzed hydrogasification in the temperature region of around 850 K.

CONCLUSIONS

Hydrogasification of brown coal with Cl-free Fe catalysts precipitated from FeCl₃ solution using different additives is carried out at ambient pressure. The activity depends strongly on the preparation method and the gasification temperature. The use of urea as an additive seems to give the most effective catalyst at 873 K. The iron prepared with Ca(OH)₂ shows the largest rate enhancement at 1073 K, and realizes complete gasification within a short time. The formation of Fe₃C may be related to the catalytic activity in this case.

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Table 1 Activity and state of Fe catalysts at 873 K.

Sample	Additive	Conv. ^{a)} (wt%)	Chem. form ^{b)}	Size ^{b),c)} (nm)
Fe(U)	(NH ₂) ₂ CO	20	α-Fe	10
Fe(C)	Ca(OH) ₂	13	α-Fe, (Fe ₃ C)	28
Fe(A)	NH ₃ /NH ₄ Cl	8	α-Fe	45
Original	—	5	—	—

a) Char conversion after 30 min.

b) Immediately after devolatilization in H₂.

c) Average crystallite size of α-Fe.

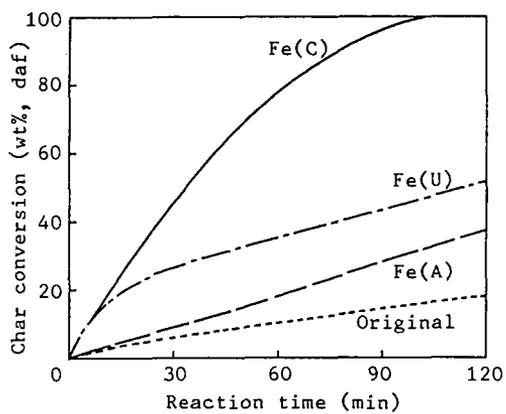


Figure 1 Hydrogasification of Loy Yang coal with iron catalysts at 1073 K.

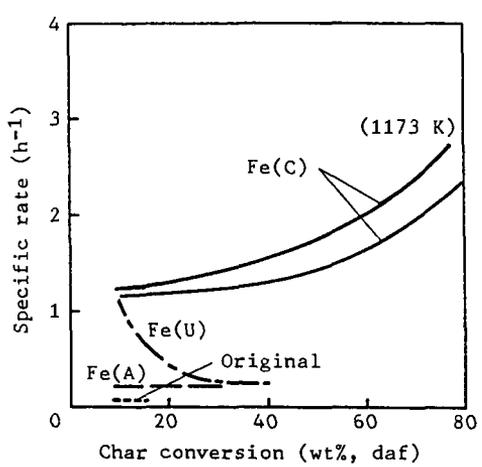


Figure 2 Profiles of specific gasification rates at 1073 K.

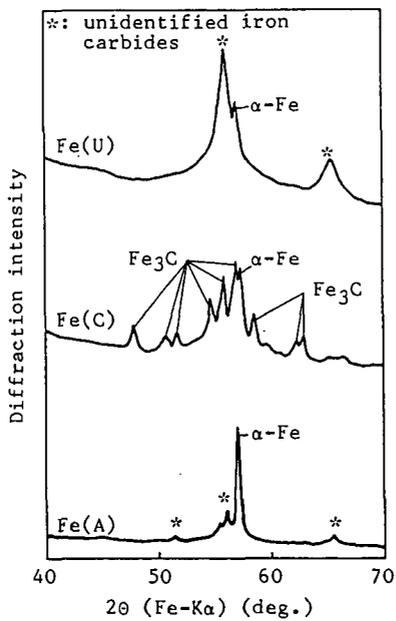


Figure 3 XRD patterns of iron catalysts on the chars devolatilized at 1073 K.