

CATALYTIC STEAM GASIFICATION OF COAL BY PHYSICAL MIXING OF K-EXCHANGED BROWN COAL

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The application of KCl to the catalytic gasification of higher-rank coal char was investigated. K-exchanged brown coal was prepared from KCl using an ion-exchange method. The K-loaded coal was physically mixed with a higher-rank coal. The mixture was gasified in steam with a thermobalance.

The effects of the mixing pattern and the caking property of higher-rank coal on the catalytic effectiveness of K-exchanged coal were examined. The catalytic effectiveness of physical mixing of K-loaded brown coal was compared with that of physical mixing of Ni-loaded brown coal.

Rate enhancement by physical mixing of K-exchanged Yallourn coal was almost independent of both the caking property of higher-rank coal and the chemical state of potassium catalyst before mixing. Direct contact between K-exchanged coal and higher-rank coal was required for this catalytic coal gasification system. EPMA analysis showed that potassium catalyst easily transferred from Yallourn coal to higher-rank coal char surface, whereas no transfer of Ni catalyst was observed. Potassium was a highly suitable catalyst for catalytic gasification by the physical mixing method.

Introduction

The use of catalyst in coal gasification can decrease the gasification temperature. Since a reduction in gasification temperature would result in several advantages, a number of studies have been carried out on the catalysis of coal gasification. Alkali-metal compounds and nickel show high catalytic activities in the gasification of coal. In steam gasification, nickel catalyst is the most active catalyst for several low-rank coals, and the catalyst efficacy of potassium carbonate is extremely high for almost all coals¹²⁾. In the Exxon catalytic coal gasification process, potassium carbonate is used as a catalyst. It is well known that potassium catalyst reacts readily with alumino-silicate compounds which are present in most coals as minerals^{2,4,7)}. Therefore, recovery of the potassium catalyst by leaching of ash is incomplete. From the practical point of view, it is desirable to develop cheap catalysts.

Alkali metal chlorides are attractive as raw materials of gasification catalysts, because they are quite cheap. However, their catalytic activities are generally quite low compared with those of corresponding carbonates because of the strong affinity between alkali metal ion and chloride ion⁶⁾. It has been reported that active, chlorine-free catalysts can be prepared from NaCl and

KCl solutions by using the ion-exchange technique^{13,14,16)}. This method has been found to be effective for activating ferric chloride¹⁾. The ion-exchange technique, however, is restricted to low-rank coals, since the amount of surface functional groups which act as cation-exchange sites is insufficient to enhance the gasification rate of coal in higher-rank coals.

Very recently, we have developed a method utilizing KCl as the raw material for the catalytic gasification of higher-rank coals¹⁷⁾. K-exchanged brown coal prepared from KCl solution using the ion-exchange technique was physically mixed with a higher-rank coal, and the mixture was gasified. The potassium catalyst incorporated into low-rank coal enhanced the reactivity of not only low-rank coal char but also higher-rank coal char.

In this study, the effects of the mixing pattern and the caking property of higher-rank coal on catalytic effectiveness are investigated to clarify the mechanism of rate enhancement by the physical mixing method. The catalytic effectiveness by physical mixing of K-loaded brown coal is compared with that by the physical mixing of Ni-loaded brown coal.

1. Experimental

1.1 Coal

Yallourn coal, an Australian brown coal, was used to load catalyst components using the ion-exchange

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method. It was received in the form of briquettes. Liddell coal and Taiheiyo coal were used as higher-rank coals. The analyses are shown in Table 1. Coal size was 100–200 mesh, except for the experiment of SEM observation described later.

1.2 Method of catalyst addition

The method of catalyst addition essentially consists of a cation-exchange step and a water-washing step. Thus, 20 g of low-rank coal was soaked in 300 ml of 2 N-KCl aqueous solution and the pH of the solution was adjusted by adding an adequate amount of 4 N-NH₃ solution. The cation exchange was carried out by stirring the mixture of coal and alkaline aqueous solution of KCl at room temperature until no further change in pH was observed. The final pH was 10.8. The coal was separated from the solution by filtration, washed twice with deionized water and dried at 380 K. The amount of potassium metal incorporated into the coal was determined by back-exchange with a dilute HCl solution followed by flame spectrochemical analysis. The details of the ion-exchange procedure have been described elsewhere^{13,14,16}.

Ni-loaded Yallourn coal was prepared by impregnation from an aqueous solution of hexammine nickel(II) carbonate.

The K and Ni loadings were 9.4 and 10 wt%, respectively.

1.3 Gasification procedure

The gasification reaction was conducted in a thermobalance. A schematic diagram of the experimental apparatus is shown in Fig. 1. The main components of the apparatus were a thermobalance (Shinku-riko, TGD-7000RH), steam generator and gas feeding system. After evacuation and substitution with nitrogen gas, the temperature was raised to 423 K, where steam was introduced. Then the sample was raised to gasification temperature at a heating rate of around 500 K/min. The partial pressure of steam was 0.03 MPa. K-exchanged low rank coal and the higher-rank coal (total weight of about 20 mg) were physically mixed (1/1 on the basis of fixed-carbon weight) in a quartz cell. The reaction consisted of a devolatilization stage and a subsequent char gasification stage. The reactivity of char in the latter stage will be discussed in this paper.

1.4 SEM observation and EPMA analysis

Catalyst on the surface of higher-rank coal char was observed with a scanning electron microscope (JEOL JSM-820) and examined with an electron-probe microanalyzer (JEOL JXA-8600). In this experiment, Liddell coal of 9–16 mesh and metal-loaded Yallourn coal of 32–60 mesh were used. A particle of Liddell coal was placed in a quartz cell in contact with a particle of metal-loaded Yallourn coal. The sample was partially gasified and the residual

Table 1. Analyses of coals

Coal	Carbon content (wt%, daf)	Proximate analysis (wt%)				C.S.N.
		Mois.	V.M.	Ash	F.C.	
Yallourn	65.4	14.3	45.7	1.4	38.6	0
Taiheiyo	77.0	5.8	46.5	10.8	36.9	0
Liddell	83.5	3.6	33.5	7.2	55.7	3.5

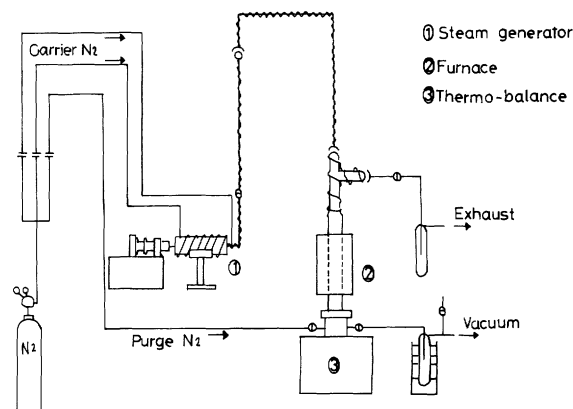


Fig. 1. Schematic diagram of experimental apparatus

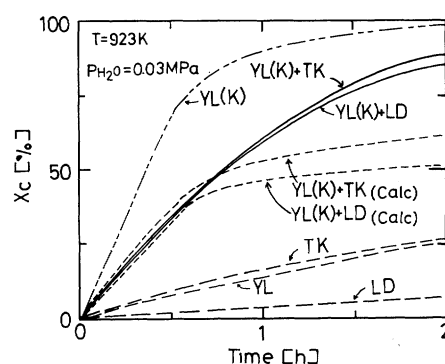


Fig. 2. Fixed-carbon conversion of sample during stream gasification

Liddell char surface was examined.

2. Results and Discussion

2.1 Coal type

Steam gasification was carried out in a thermobalance at 923 K. The reactivities of raw coals (Yallourn (YL), Liddell (LD) and Taiheiyo (TK)), K-exchanged Yallourn coal (YL(K)) and mixtures (YL(K)+LD, YL(K)+TK) are shown in Fig. 2. The mixing ratio of K-exchanged Yallourn coal/higher-rank coal is 1/1 on the basis of fixed-carbon weight. The reaction rate of YL(K) is much higher than that of Yallourn raw coal. This means that an active potassium catalyst was prepared from KCl solution by using the ion-exchange technique, as already reported^{14,16}. Such a potassium catalyst exhibits a high activity comparable to that of the corresponding

carbonate catalyst, which is known as the most effective catalyst in steam gasification¹⁶⁾.

The fixed-carbon conversion of the mixture YL(K)+LD smoothly increases with increase in reaction time and reaches about 90% within 120 min. The calculated fixed-carbon conversion (YL(K)+LD(calc.)) is also shown in Fig. 2. The calculated value was based on the assumption that the K-exchanged Yallourn coal char and Liddell coal char were independently gasified. The conversion obtained in this experiment is much higher than the calculated value. The potassium catalyst incorporated into low-rank coal enhances the reactivity not only of low-rank coal char but also of higher-rank coal char. In the case of YL(K)+LD the sample was lumped in the quartz cell during the gasification because of the caking property of Liddell coal. Thus, the rate enhancement of Liddell coal char may be explained as follows. Liddell coal adhered to K-exchanged Yallourn coal at the gasification stage; thus the potassium acts as a catalyst for the gasification of Liddell coal char. Then the gasification of the mixture was carried out by using a non-caking coal, Taiheiyo coal. The result is also shown in Fig. 2. The catalytic effect of the K-exchanged Yallourn coal on the gasification rate of Taiheiyo coal char was clearly recognized in a manner similar to that for Liddell coal. It is concluded that rate enhancement by physical mixing of K-exchanged Yallourn coal is independent of the caking property of higher-rank coal.

2.2 Mixing pattern

The potassium catalyst incorporated into Yallourn coal by the ion-exchange technique is mainly bonded to carboxyl groups as COO-K. It is transformed to potassium carbonate¹⁶⁾ or combined to char surface as surface complexes, C-O-K and C-K^{3,9)}, during devolatilization. The potassium catalyst at the gasification stage is quite uniformly dispersed on a char surface¹²⁾. After gasification, the potassium catalyst remains as potassium carbonate in the ash.

To clarify the mechanism of rate enhancement by co-processing, several kinds of mixing patterns were examined.

At first, to clarify which state of potassium catalyst is effective for the gasification of higher-rank coal, char (YL(K)_{char}) or ash (YL(K)_{ash}) obtained from the K-exchanged Yallourn coal was mixed with Taiheiyo coal or char (TK_{char}). The char was prepared with the thermobalance in N₂ atmosphere at 923 K. The mixing ratio of K to fixed carbon in Taiheiyo coal was 0.052 wt/wt. The results for the gasification of the mixture are shown in Fig. 3. The rate per initial char weight ($-1/W_0 \cdot dW/dt$) was used as a means of expressing the rate profiles shown in Fig. 3. There is a slight difference in the gasification rate among the mixtures examined, but the difference is not so

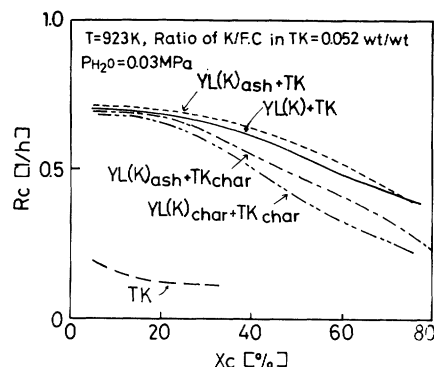


Fig. 3. Rate profiles of several kinds of mixture in steam gasification

important. The catalytic effectiveness of potassium is markedly observed for all the mixing systems. The reaction rate of Taiheiyo coal char was enhanced by mixing of not only the K-exchanged Yallourn char but also the ash prepared from K-exchanged coal. It has been reported that the physical mixing of ash obtained from bituminous coal did not result in a large catalytic effect on the gasification of bituminous coal¹⁸⁾. In the case of K-exchanged Yallourn coal, the ash contains about 90% potassium carbonate by weight. The effectiveness of the mixing of ash obtained from K-exchanged coal is due to the high content of potassium carbonate. It is concluded that the effect of the physical mixing of potassium catalyst on the gasification rate of higher-rank coal is almost independent of the chemical state of the potassium catalyst before mixing.

Samples were gasified without mixing in order to examine the effect on catalytic effectiveness of the contact pattern between K-exchanged Yallourn coal and higher-rank coal. K-exchanged Yallourn coal particles were placed on a layer of Taiheiyo coal particles in the quartz cell (YL(K)/TK) and the sample was gasified without mixing. The reverse case, Taiheiyo coal particles on the K-loaded coal (TK/YL(K)), was also examined. The mixing ratio of K to fixed-carbon in Taiheiyo coal was 0.052 wt/wt. The gasification profiles for samples without mixing are compared with that for the sample with mixing in Fig. 4. In the case of sample without mixing, the rate falls steeply at a conversion of about 40%, which approximately corresponds to the amount of Yallourn char. After that, the rate for the sample was essentially similar to that for Taiheiyo raw coal. This result means that the potassium catalyst incorporated into Yallourn coal enhances only the reactivity of that coal and hardly affects the gasification rate of Taiheiyo coal. It was found that direct contact between K-exchanged coal and higher-rank coal is indispensable for this catalytic coal gasification system.

Some researchers have pointed out that part of the

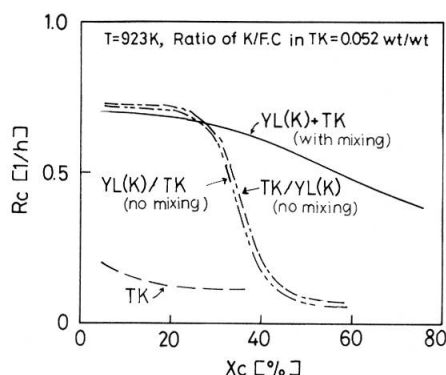


Fig. 4. Rate profiles for steam gasification of YL(K)+TK

K catalyst is lost to the gas phase through vaporization^{8,10,11}. Morita¹⁰ reported that K catalyst was transferred to other carbon particles via gas phase and enhanced the gasification rate of the carbon. In that study, direct contact between catalyst particle and carbon particle was not required for the transfer of K catalyst. In our study, the contact between K-exchanged coal and higher-rank coal was essential for the transfer of K catalyst. This discrepancy may be due to the difference in gasification temperature. In this study, the sample was gasified at 923 K. Morita¹⁰ carried out the gasification of active carbon at 1123 K. McKee *et al.*⁸ carried out the TG-DTA measurement of a graphite- Na_2CO_3 mixture and reported that a rapid loss in weight was observed above 1173 K, accompanied by the evolution of copious amounts of sodium vapor. On the other hand, there was essentially no catalyst loss during the steam gasification of alkali metal-loaded Yallourn coal at 923 K¹⁶. It seems that K catalyst loaded on carbon particle can be transferred to other carbon particles via gas phase at higher gasification temperatures and via contact point between K-loaded carbon particle and other carbon particle at lower gasification temperatures.

A fluidized-bed reactor is one of the most promising reactor, for coal gasification. In a fluidized-bed reactor, char particles are fluidized by fluidizing gas. In this catalytic coal gasification system, K-exchanged coal and higher-rank coal can be mixed by fluidizing gas in the fluidized bed. From the practical point of view, it is necessary to examine the catalytic effect of co-processing in a fluidized-bed reactor.

2.3 Comparison with Ni catalyst

A mixture of Ni-loaded Yallourn coal and Liddell coal (YL(Ni)+LD) was reacted for comparison with the case of K-exchanged coal. The mixing ratio of Ni to fixed carbon in Liddell coal was 0.056 wt/wt. The results are shown in Fig. 5. As already reported^{12,15,19,20}, Ni-loaded Yallourn coal (YL(Ni)) showed a peculiar rate profile. The fixed carbon was gasified in two stages and the rate for the first stage

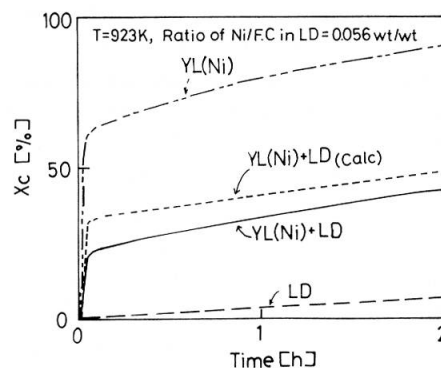


Fig. 5. Fixed-carbon conversion of YL(Ni)+LD during steam gasification

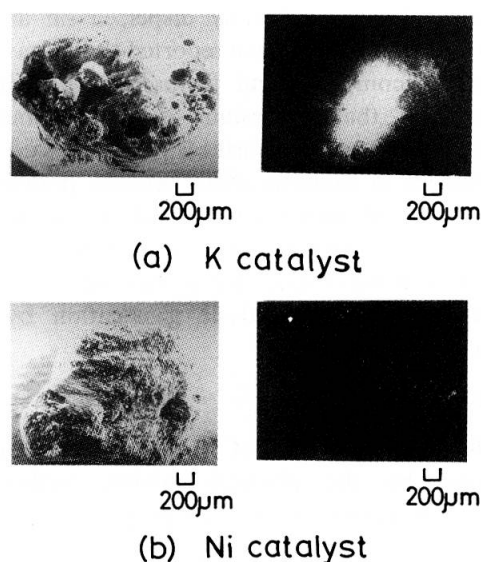


Fig. 6. SEM photograph and X-ray analysis of catalyst on Liddell char surface

was extremely high. About 60 wt% of char was gasified within a few minutes. The rapid gasification is due to a good dispersion of Ni on the Yallourn char surface^{5,12}. The conversion of the mixture was slightly lower than that calculated on the assumption that the Ni-loaded Yallourn char and Liddell char were independently gasified. In short, little rate enhancement by physical mixing of Ni-loaded Yallourn coal was found.

2.4 SEM observation and EPMA analysis

To clarify the difference in catalytic effectiveness between nickel and potassium, a SEM observation and an EPMA analysis were conducted. A particle of Liddell coal (9–16 mesh) was placed in a quartz cell in contact with a particle of K-loaded Yallourn coal or Ni-loaded Yallourn coal (32–60 mesh). The sample was partially gasified in steam until the fixed-carbon conversion of metal-loaded Yallourn coal reached about 60 wt% and the residual Liddell char surface was examined. The SEM images and the X-ray analyses of potassium and nickel for the Liddell char surface are shown in Fig. 6. Potassium catalyst was

obviously recognized in the neighborhood of the contact point on the Liddell char surface. The surface area covered with potassium catalyst is larger than the contact area between the Liddell char and K-exchanged Yallourn char. It is concluded that potassium catalyst is easily transferred from Yallourn coal char to Liddell coal char and spread out over Liddell char surface in the gasification stage. On the other hand, nickel catalyst was scarcely found on Liddell char surface where contacted with Ni-loaded Yallourn coal. This means that nickel catalyst in Yallourn coal hardly transferred to Liddell char. It is generally accepted that nickel catalyst is gradually agglomerated during gasification⁵⁾, whereas potassium catalyst is uniformly dispersed on a char surface¹²⁾. Mims *et al.*⁹⁾ have reported that potassium carbonate decomposes and forms a surface intermediate, and that potassium is thus atomically dispersed on the carbon surface. It can be said that the difference in catalytic effect between potassium-loaded coal and nickel-loaded coal is due to the difference in behavior of the catalyst during gasification. It was found that potassium is a highly suitable catalyst for catalytic gasification by the physical mixing method.

Conclusion

1. Rate enhancement of K-exchanged Yallourn coal by the physical mixing method is independent of the caking property of higher-rank coal.
2. The effect of physical mixing of potassium catalyst on the gasification rate of higher-rank coal is almost independent of the chemical state of the potassium catalyst before mixing.
3. Direct contact between K-exchanged coal and higher-rank coal is essential for this catalytic coal gasification system.
4. Potassium is a highly suitable catalyst for catalytic gasification by the physical mixing method.

Nomenclature

P_{H_2O}	= partial pressure of steam	[MPa]
R_c	= gasification rate	[1/h]
t	= reaction time	[h]
T	= gasification temperature	[K]
W_0	= initial char weight	[g]
W	= char weight	[g]
X_c	= fixed-carbon conversion	[—]

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