

GASIFICATION OF ACTIVE CARBON WITH ALUMINA-SUPPORTED POTASSIUM CARBONATE CATALYST

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INTRODUCTION

It was shown in our previous work that carbonaceous residues from petroleum were gasified with extremely high efficiency in the fluidized bed of alumina-supported alkali catalysts.¹ In the present work, we applied the same fluidized bed system to the gasification of solid carbon. Many works have been reported on the catalytic activity of alkali for the gasification of solid carbon such as coal, char and graphite.²⁻⁸ Recent studies have showed that alkali-catalyzed gasification of graphite and char proceeds via oxygen transfer mechanism where the redox of alkali salt is essential.^{3,9-11}

In the gasification of petroleum residues, the intermediate was carbon deposited on the catalyst. In the case of solid carbon, however, catalytically active species must travel from catalyst to the surface of solid carbon, and may hopefully return to catalyst after gasification. It is the purpose of the present work to investigate how effectively the alumina-supported potassium carbonate catalyst functions in the gasification of solid carbon.

EXPERIMENTAL

Apparatus and Procedure

Steam gasification of active carbon was carried out in a fluidized-bed and a fixed-bed reactor at 850°C and atmospheric pressure. The fluidized-bed reactor was made of a 40mm diameter and 400mm height stainless steel tube. Steam was supplied in a rate of 4.5 moles/hr at the bottom part of the reactor. Details of the reactor were described in the previous paper.¹ Fixed-bed gasification was studied using five different packing modes of catalyst and carbon, as shown in Fig. 1. Type A and B beds consisted of carbon-catalyst-carbon and catalyst-carbon layers with thin separating layers of alumina, respectively. In Type C bed, a mixture of K_2CO_3 and a small amount of carbon was packed in the upper layer with the major part of carbon in the lower. Type D and E beds contained a carbon-catalyst mixture and carbon impregnated by K_2CO_3 , respectively. Each packed-bed contained 4.48×10^{-3} moles K_2CO_3 . The feed rate of steam or CO_2 was 0.33 moles/hr.

To investigate the behavior of K_2CO_3 supported on alumina, thermogravimetric analyses were performed by use of Shimadzu thermal analyser DT-30. Measurements were carried out under atmospheric pressure. The sample was heated at a rate of 10°C/min in a stream of H_2 , CO or He.

Materials

An active carbon was used in the present work as a feedstock. It was prepared from coconut shell and was supplied by Tsurumi Coal CO. Ltd. The ultimate analysis showed 95% C, 1.7% O, 0.3% H, 0.1% N, 0.1% S and 2.8% ash. An alumina-supported K_2CO_3 catalyst containing 1.28×10^{-3} moles K_2CO_3 /g-catalyst, was used in this work. The catalyst was prepared as follows: alumina was impregnated by a solution of K_2CO_3 , and dried at 100°C. Alumina was obtained by calcining γ -alumina at 1200°C for 2 hr. The catalyst was dried at 350°C for 2 hr followed by screening and a

portion of the particles in the range of 32-65 mesh were used in the catalytic studies.

RESULTS AND DISCUSSION

Fluidized Bed Gasification

The catalytic activity of K_2CO_3 supported on alumina was compared with that of K_2CO_3 supported on carbon itself. As given in Fig. 2, the variation of gasification rate with reaction time for both cases overlapped in the whole range of carbon conversion. When carbon was completely gasified, another dose of carbon was charged to the residual fluidized bed. In both cases, the carbon was gasified in the same rate with the first run, and it was reproduced on repeated several doses of additional carbon charge. These results seem to show that catalytically active species rapidly transfer from catalyst to the surface of carbon and return to alumina surface after gasification. As the reaction temperature ($850^\circ C$) was far below the melting point of K_2CO_3 ($891^\circ C$), decomposition or reduction of K_2CO_3 should be involved in the transfer of the active species. The gasification rate was found to be a function of the amount of carbon in the fluidized bed, being independent of the catalyst amount in the range tested (bulk $K/C \geq 0.015$). Thus, the amount of active species required is not very large.

Thermogravimetric (TG) Study

Reactions of K_2CO_3 on alumina in a stream of reducing or inert gas were investigated, the results being shown in Fig. 3. In flowing He or CO, K_2CO_3 decomposed above $650^\circ C$ to CO_2 and K_2O which was retained by alumina. In a stream of H_2 , the weight reduction exceeded that of decarboxylation, showing a further reduction of K_2O to K. Carbon physically mixed with the catalyst was also found to reduce K_2CO_3 to potassium metal in flowing He.

Packed-bed Gasification

TG experiments showed that K_2CO_3 in the catalyst was reduced by flowing H_2 but not by CO. To examine the effect of catalyst reduction on gasification, C- H_2O and C- CO_2 reactions were performed using packed-beds of Type A and Type B. The results are shown in Fig. 4. For C- H_2O reaction, the carbon/catalyst/carbon triple-layer bed (Type A) was gasified with a greater rate than the catalyst/carbon double-layer bed (Type B). The rate of C- CO_2 reaction was not influenced by the mode of bed-packing. It is thus deduced that non-catalytic C- H_2O reaction in the upper layer of Type A bed to yield H_2 is effective to form K in the middle layer and to make the gasification in the lower layer catalytic.

Further evidence for the transport of K vapor was obtained by the run using a Type C packed-bed where K_2CO_3 was mixed with a small amount of carbon in the upper layer. The solid contact reduction of K_2CO_3 by carbon was very rapid and K was mounted on carbon in the lower layer in a stream of nitrogen. As shown in Fig. 5, transferred K gave a rate of gasification greater than non-catalytic one. As gasification proceeded and K/C ratio increased to some extent, the rate of gasification decreased with decreasing amount of carbon. When the catalyst instead of K_2CO_3 was packed with carbon in the upper layer, no appreciable enhancement of gasification rate was observed probably due to the adhesion of K on alumina which did not enable the distant transport of K in gas phase.

Figure 6 shows the rate of gasification in a uniform mixture of carbon and catalyst, compared with that of carbon impregnated by K_2CO_3 . With increasing amount of carbon in the bed and decreasing K/C ratio, the rate of gasification increased and saturated at a bulk K/C ratio around 0.03-0.05. Reduction of K_2CO_3

and transfer of K would create active centers on carbon surface. The rate of gasification should be proportional to the number of active centers. At K/C ratios above saturation, the number of active centers seemed to be determined by the amount of carbon, and the gasification rates in both cases coincided. At K/C ratios below saturation, however, K_2CO_3 on alumina seems to create larger numbers of active centers than K_2CO_3 on carbon.

Overall Kinetics

Recent studies of Mims et al.^{5,6} have indicated that the rate of K_2CO_3 -catalyzed gasification of amorphous carbon is proportional to the $(H_2O)/(H_2)$ ratio, in agreement with their gasification mechanism. The results obtained in the present work were also found to obey the following rate expression meaning product inhibition:

$$\text{rate} = k \cdot C_x \cdot (H_2O/H_2) \quad 1)$$

where C_x meant the number of active centers. Figures 7 and 8 show $\text{rate} \cdot (H_2/H_2O)$ vs the amount of total carbon (C_t) for packed-bed and fluidized-bed experiments, respectively. Here, (H_2/H_2O) was obtained by averaging ratios at reactor-inlet and outlet. Assuming that $C_t = C_x$ in the region of large K/C ratio, the rate coefficients for packed-bed and fluidized-bed gasification were determined to be 0.54 and 0.48 (hr^{-1}), respectively. Roughly coincident rate coefficients seem to mean a common gasification mechanism operating in the packed-bed and fluidized-bed gasification.

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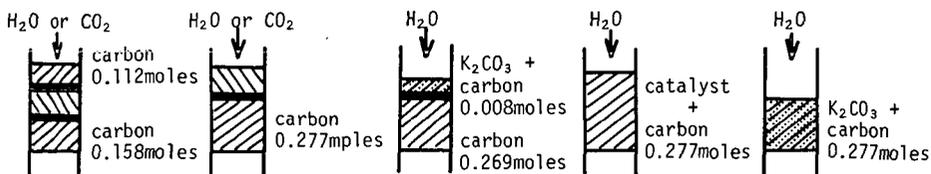


Figure 1. Packed bed reactors of different types A-E. The amount of catalyst in packed beds A, B and D were 3.5g which contained 4.48×10^{-3} moles K_2CO_3 . The same amount of K_2CO_3 were packed in beds C and E. ■, Al_2O_3 isolater; ▨, carbon; ▩, catalyst; ▤, K_2CO_3 .

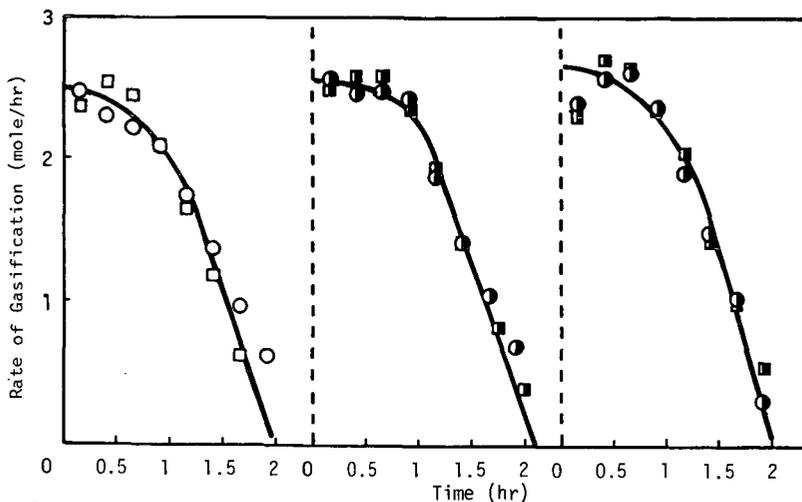


Figure 2. Rate of fluidized-bed gasification in Runs; A (○) with K_2CO_3 (0.123 moles) on alumina (83g) + carbon (3.96 moles) followed by Run B (●) with freshly charged carbon (3.96 moles) after a complete consumption of carbon in the preceding run; and C (□) with K_2CO_3 on carbon (3.96 moles) + alumina (83g) followed by D (■) as Run B after Run A.

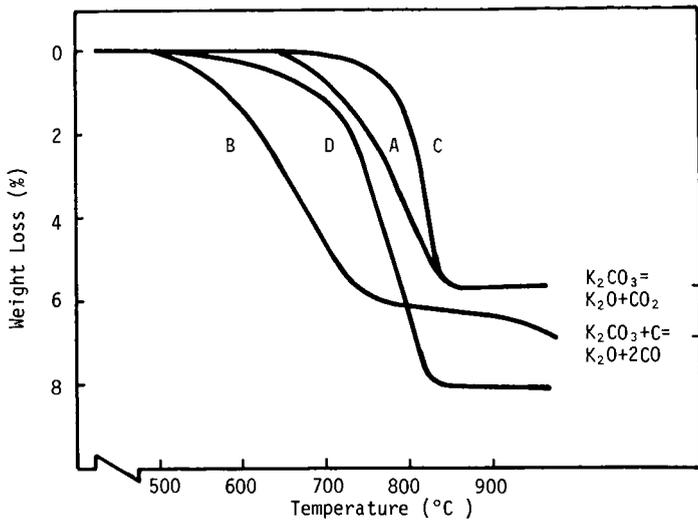


Figure 3. Thermogravimetric analyses on decomposition and reduction of K_2CO_3 supported on alumina: A, in He; B, in H_2 ; C, in CO; D, mixed with active carbon ($K/C=0.17$) in He.

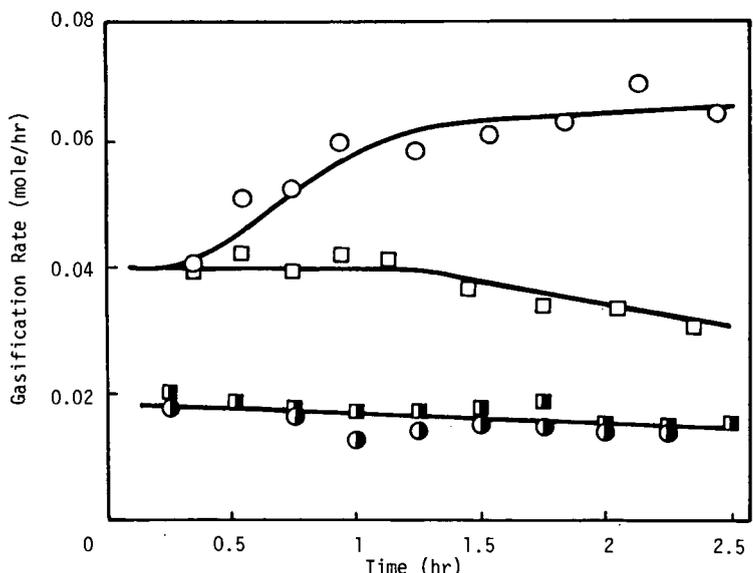


Figure 4. Variation in rates of $C-H_2O$ and $C-CO_2$ reactions in packed-beds Type A (catalyst-carbon-catalyst) and Type B (catalyst-carbon) with reaction time: ○ and ●, $C-H_2O$ and $C-CO_2$ reactions in Type A, respectively; □ and ■, those in Type B. Initial amounts of carbon and catalyst were 0.277 moles and 3.5g, respectively.

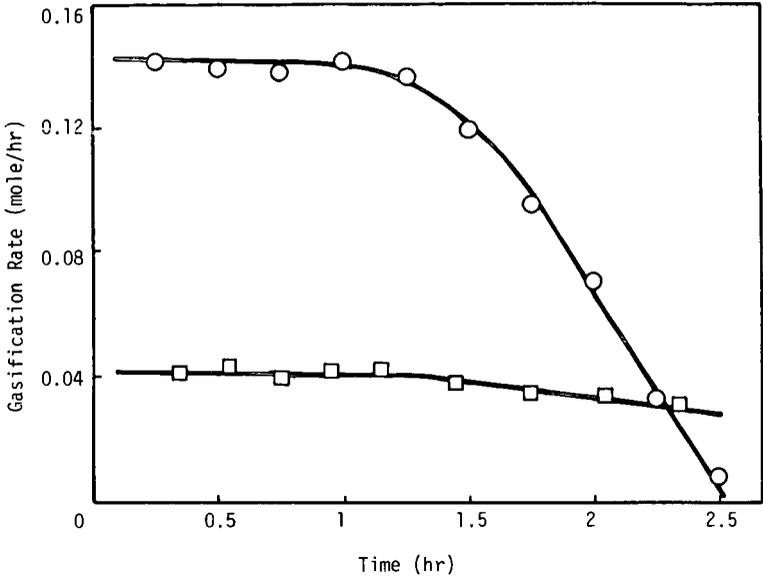


Figure 5. Enhancement of gasification rate in packed-bed Type C (○) where K_2CO_3 was reduced by a small amount of carbon in the upper layer, in comparison with Type B (□).

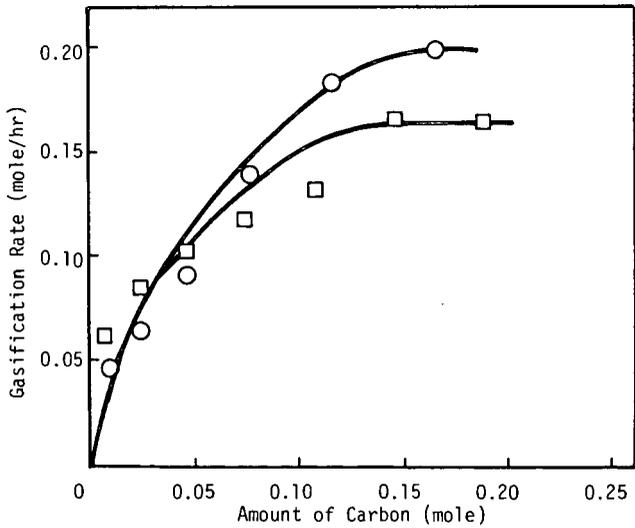


Figure 6. Rates of packed-bed gasification of carbon mixed with catalyst (Type D, ○) and K_2CO_3 (Type E, □) as a function of the amount of carbon in the beds.

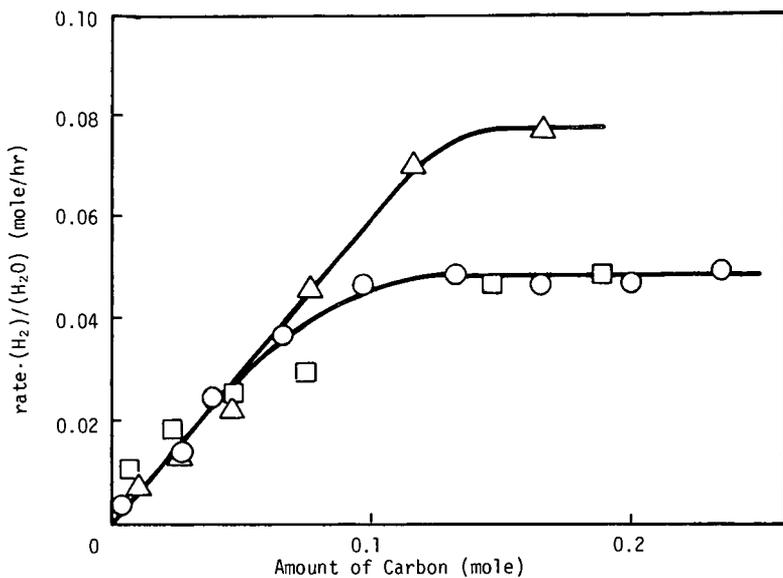


Figure 7. Plots between $\text{rate} \cdot (\text{H}_2)/(\text{H}_2\text{O})$ and C_t for data from packed-bed experiments: \circ , Type C; \triangle , Type D; \square , Type E.

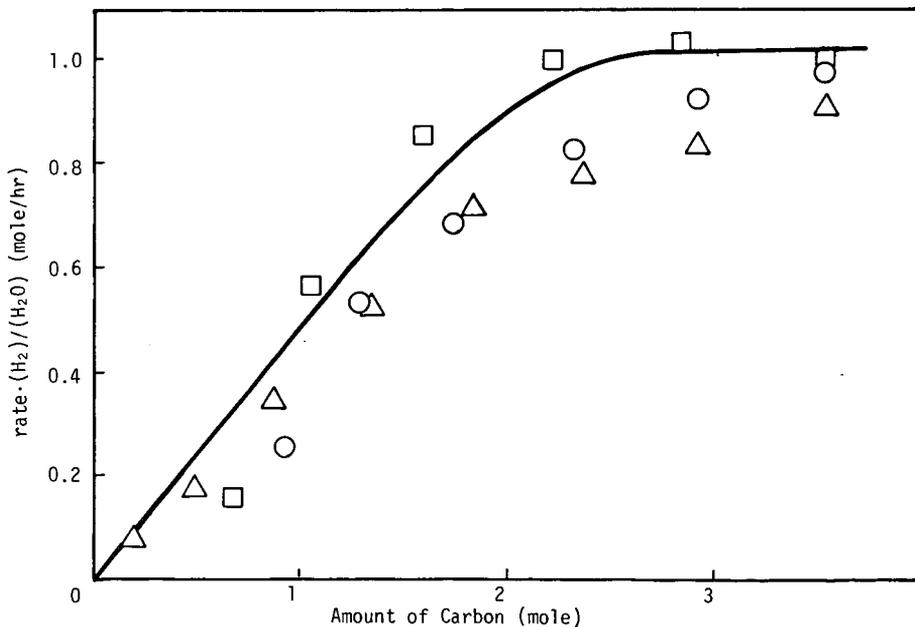


Figure 8. Plots between $\text{rate} \cdot (\text{H}_2)/(\text{H}_2\text{O})$ and C_t for data on fluidized-bed gasification: catalyst weight \circ , 150g; \triangle , 100g; \square , 25g.