

Kideco 석탄의 스팀 가스화 반응에서 K_2CO_3 촉매의 비활성화 거동

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Deactivation Behavior of K_2CO_3 Catalyst in the Steam Gasification of Kideco Coal

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Abstract >> The present work investigates the effect of K_2CO_3 catalyst on steam gasification of Kideco coal and the deactivation of the catalyst due to thermal exposure and interaction with coal ash. The gasification reactivity at 700°C is highly enhanced by K_2CO_3 , which is not deactivated by the heat treatment at $T \leq 800^\circ\text{C}$. TGA and XRD results prove minor decomposition of K_2CO_3 after the calcination at 800°C. K_2CO_3 is, however, evaporated at the higher temperature. Assuming the conversion of K_2CO_3 into K_2O by the decomposition and into $K_2O \cdot 2.5SiO_2$ and $KAlO_2$ by the interaction with coal ash, the reactivity of the gasification is evaluated in the presence of K_2O , $K_2O \cdot 2.5SiO_2$ and $KAlO_2$. Among them, K_2O is the most active, but much lower in the activity than K_2CO_3 . XRD results show that K_2CO_3 could react readily with the ash above 700°C.

Key words : Steam gasification(스팀가스화), Catalyst(촉매), Coal(석탄), Deactivation(비활성화), Potassium(칼륨)

1. INTRODUCTION

Coal is one of the most important energy sources, currently accounting for ~70% of proven fossil fuel resources and also ~25% of worldwide energy consumption¹⁻³. In the medium to long-term aspect, coal is expected to remain a main energy source for

the traditional industries such as electricity generation, iron smelting, and cement manufacturing, thanks to its widespread abundance and economic benefit.

Gasification of coal has gained popularity, as it is more energy-efficient and can reduce the GHGs emission⁴⁻⁷. Many of the commercial gasification processes are being operated at $T > 1200^\circ\text{C}$ in order to boost gasification rate⁸⁻¹⁰. This severity requires exothermic combustion of coal and therefore lowers the overall efficiency. The conversion kinetics at the lower

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temperature ($T < 900^{\circ}\text{C}$) can be improved by introduction of catalytically active potassium¹¹⁻¹³. Potassium catalyst is fed to the reactor, typically in the form of potassium carbonate (K₂CO₃)¹⁴. However, the repeated use of K₂CO₃ seems to be difficult, mainly due to deactivation of the catalyst by both thermal degradation and irreversible interaction with the mineral matters in coal¹⁵⁻¹⁷. In the process of the catalytic coal gasification, K₂CO₃ can be decomposed into K₂O. Moreover, K₂CO₃ can react with coal ash that is composed of mostly Al₂O₃ and SiO₂, forming minerals such as K₂O·xSiO₂, KAlO₂, Sanidine (K₂O·Al₂O₃·6SiO₂), Osumilite (K₂O·4.4MgO·4.6Al₂O₃·20.4SiO₂), and etc. The catalytic behavior of these potassium compounds is not well known.

In this work, the catalytic activity of K₂CO₃ calcined at 800°C, compared to that of fresh K₂CO₃, is evaluated and discussed based on the results from TGA, SEM, and XRD. In addition, the activity of various deactivated forms of K₂CO₃ (K₂O, K₂O·2.5SiO₂, and KAlO₂) is tested at 700°C, feeding steam, and compared with non-catalytic case. After 5 hr steam gasification of Kideco raw coal in a fluidized bed (FB) reactor, the used K₂CO₃ catalyst, and the unreacted coals residing in the reactor and the back filter were collected¹⁸. The chemical composition of the used K₂CO₃ as well as the reactivity of the unreacted coals were then evaluated.

2. EXPERIMENTAL

2.1 Materials

Kideco coal was used as a gasification sample. It is low rank coal, and its proximate/ ultimate analysis and calorific value are tabulated in Table 1. K₂CO₃ (Showa Chemical Inc.), K₂O (96.5% purity, Alfa Aesar),

Table 1 Proximate/ultimate analysis and calorific value of Kideco raw coal

sample	Proximate analysis (wt.%)				Ultimate analysis (wt.%) daf					CV (kcal/kg)
	M	VM*	Ash*	FC*	C	H	N	O	S	
Kideco	27.2	45.9	6.3	47.7	70.3	5.1	1.2	23.2	0.2	4,410
Posco	1.3	21.3	9.8	68.9	86.2	4.1	1.5	1.1	7.1	8,596

(M: moisture, VM: volatile matter, FC: fixed carbon, *: dry basis, daf: dry & ash-free, CV: calorific value)

K₂O·2.5SiO₂ (Alfa Aesar) and KAlO₂ (high purity, Kojundo Chemical Laboratory Co.) were chosen as potassium source for the catalytic reaction. Thermally stressed K₂CO₃ was prepared by heat treatment for 3 hr at four different temperatures (600, 700, 800, and 900°C) with 0.36 mL/hr steam flow in 100 cc/min N₂.

Coal ash was obtained from combustion of Posco coal and its composition is given in Table 1 (proximate/ultimate analysis and calorific value) and Table 2 (chemical composition of Posco coal ash). Two different locations in a SEM image in Fig. 1 were chosen for the composition analysis using EDS. The main components are SiO₂ and Al₂O₃. A small quantity of other metals, such as K, Fe, Na, Ti, and Mg is also included.

2.2 Steam Gasification of Coals

Steam gasification of Kideco coal was performed

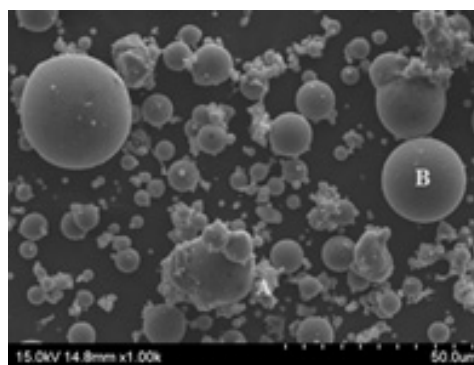


Fig. 1 SEM image of ash from Posco coal

Table 2 Chemical composition of ash from Posco coal

wt.%	SiO ₂	Al ₂ O ₃	K ₂ O	Fe ₂ O ₂	Na ₂ O	TiO ₂	MgO
A-site	83.3	10.6	2.5	1.9	1.6	-	-
B-site	63.5	27.0	3.7	3.4	0.5	0.6	1.4

in a fixed bed reactor⁷⁾. A coal was pulverized solely or together with a catalyst and meshed to < 75 μm. The sample (0.1 g) was introduced into a quartz reactor. The gasification was carried out at 700°C with 30 vol.% steam in 100 cc/min N₂. Temperature was increased to the target at a ramp rate of 30°C/min. Produced gases (H₂, CH₄, CO, and CO₂) were quantified every 12 min using a gas chromatography (GC, Agilent 6890). GC used for this experiment has two separation columns: a front column was porapak N to quantify H₂ and CH₄ using N₂ reference gas, and a back column was porapak Q in series with molsieve to quantify CO and CO₂ using helium reference, where thermal conductivity detectors (TCD) were adapted for both columns. The oven temperature was set to 35°C and the sampling interval of 12 min was used. Water was supplied to the reactor by a syringe pump, which was vaporized in heated stainless steel tubing (150°C) and delivered to the reactor by 100 cc/min N₂. Side products, such as water and tar, were removed by 2-step cold traps (2°C) and an oil filter. Only gaseous products were transferred to the GC. GC was calibrated with standard gas 0.1% and 3.0% containing H₂, CH₄, CO and CO₂ with N₂ carrier. The conversion percentage was calculated as the accumulated amount of the product gases divided by the total amount of the gases produced.

2.3 Characterization

Proximate analysis was done by TGA-701 Thermogravimeter (LECO Co., USA) base on ASTM D3172,

while ultimate analysis was done by using CHN-2000 Elemental Analyzer (LECO Co., USA). Calorific value was determined using Parr 1261 Calorimeter (PARR Co., USA). Thermogravimetric analysis (TGA) of K₂CO₃ was performed under air, N₂, and CO₂ atmosphere using SDT 2960 simultaneous DTA-TGA (TA instruments). About 10 mg sample was loaded and temperature was increased to 900°C at 10°C/min ramp rate. SEM image of fresh and 800°C calcined K₂CO₃ was taken using Hitachi S-4800 machine. XRD pattern was obtained using Rigaku Dmax-2500 for K₂CO₃ calcined at 600, 700, and 800°C, and a mixture of K₂CO₃ and coal ash calcined at 700, 800, and 900°C.

3. RESULTS AND DISCUSSION

3.1 Thermally Treated K₂CO₃ Catalyst

The conversion profile of steam gasification at 700°C is provided for Kideco raw coal without, and with fresh and 800°C-calcined K₂CO₃ catalyst (5.7 wt.%, metal basis) (Fig. 2).

Potassium carbonate was chosen as a catalyst, since

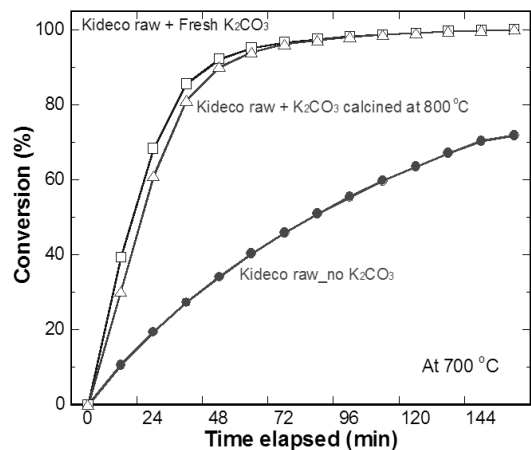


Fig. 2 Steam gasification of Kideco coal at 700°C without, and with fresh and 800°C-calcined K₂CO₃ catalyst

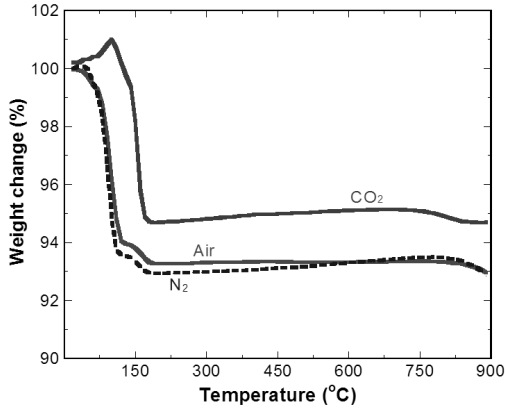


Fig. 3 TGA profile of K_2CO_3 under air, N_2 , CO_2 atmosphere

it is one of the most pronounced catalysts for coal gasification and is free from the mass transport limitation¹³⁾. The calcination temperature ($800^\circ C$) was set to be higher than the reaction temperature ($700^\circ C$) in order to see the sole effect of thermal stress on the catalytic activity of K_2CO_3 . The reaction catalyzed by fresh K_2CO_3 shows much faster kinetics than the non-catalytic one. This happens via the catalytic dissociation of the oxygen-containing molecules, which provides a lower energy pathway and thereby increases the oxygen concentration on the carbon surface through an oxidized catalyst-carbon intermediate¹⁹⁾. The deactivation is not found by calcination of K_2CO_3 at $800^\circ C$. The conversion reaches $> 90\%$ after 60 min similarly for both fresh and the thermally stressed K_2CO_3 . On the other hand, without the catalyst, $\sim 40\%$ of Kideco coal is gasified after 60 min and $\sim 72\%$ after 156 min. Further analysis on the thermal behavior of K_2CO_3 was done using TGA, SEM and XRD.

TGA analysis was done to determine the behavior of K_2CO_3 at the elevated temperature under air, N_2 and CO_2 atmosphere. Fig. 3 shows thermal variation of weight of K_2CO_3 .

In general, similar TGA profiles are shown between

the different atmospheres; a steep drop at $T < 200^\circ C$ followed by a flat region at $T = 200 \sim 800^\circ C$ and a mild fall at $T > 800^\circ C$. A rapid loss at $T < 150^\circ C$ for air and N_2 is most likely due to evaporation of adsorbed water, and which does not appear after $200^\circ C$. A peculiar increase of the weight is shown up to $100^\circ C$ under CO_2 , seemingly indicating the carbonate formation or physisorption of CO_2 ²⁰⁾. It loses weight from 100 to $160^\circ C$ like under air and N_2 . An absolute quantity of the loss under CO_2 is $\sim 2\%$ less than under air and N_2 . In the temperature range of $200 \sim 800^\circ C$, no significant change is found for all the cases. Further weight loss happens above $800^\circ C$ possibly because of the decomposition of K_2CO_3 by reaction (1) and the evaporation near a melting point ($891^\circ C$)²¹⁾.



Based on the TGA results, K_2CO_3 is stable against thermal treatment at $800^\circ C$, in terms of the chemical composition. Therefore, catalytic gasification using K_2CO_3 can be performed below $800^\circ C$ without worrying about the degradation due to the chemical decomposition.

The effect of thermal treatment on microstructure of K_2CO_3 was studied by looking at SEM images of fresh and $800^\circ C$ -calcined K_2CO_3 (Fig. 4).

Compared to amorphous and continuous surface of fresh K_2CO_3 , the heat-treated one contains well-defined grains ($< 1 \mu m$) with pores that might work as a pathway of gaseous participants. Cracks are found at the surface of fresh K_2CO_3 . The microstructural effect on the reactivity seems to be minor in this system, since the solid-solid contact of Kideco coal and K_2CO_3 happens with larger size of the particles ($10 \sim 75 \mu m$) rather than microstructural grains. Moreover, consid-

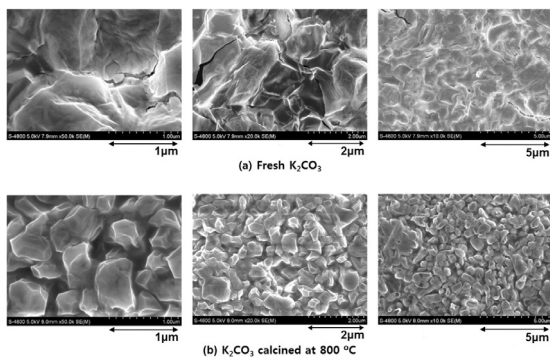


Fig. 4 SEM images of (a) Fresh K_2CO_3 and (b) 800°C-calcined K_2CO_3

eration of the microstructure becomes insignificant in case of the gasification in a fluidized bed reactor. Because a bead-type catalyst sized > 1 mm would contact with coal reactants.

XRD patterns of heat-treated pure K_2CO_3 were obtained (Fig. 5). It was calcined at 600, 700, and 800°C. After calcination at $T = 600$ and 700°C, the peaks corresponding to K_2CO_3 and $K_2CO_3 \cdot 1.5H_2O$ appear and the two temperatures exhibit about the same profile. K_2CO_3 calcined at 800°C shows the peaks mainly due to $K_2CO_3 \cdot 1.5H_2O$ with much weaker K_2CO_3 and there is no peaks indicative of the decomposition (reaction (1)).

When heat-treated at 900°C under steam/ N_2 atmos-

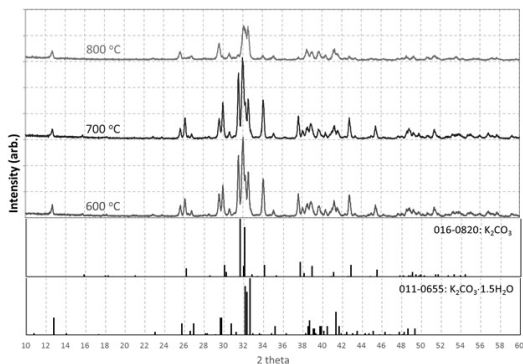


Fig. 5 XRD patterns of thermally treated K_2CO_3 at 600, 700 and 800°C

phere, solid K_2CO_3 was completely evaporated and all gone²². Considering the melting point of K_2CO_3 (891°C), it seems to be safe that the catalytic gasification using K_2CO_3 is performed below 850°C, since the volatility of K_2CO_3 varies depending on the atmospheric condition²¹. This result points out that a weight loss shown in TGA profile at $T > 800^\circ C$ (Fig. 3) might be partly due to the evaporation along with the decomposition (reaction (1)).

3.2 Deactivation of K_2CO_3 by Irreversible Interaction with Coal Ash

K_2CO_3 has been known to catalyze the coal gasification via its redox cycle, being reduced by carbon and oxidized by steam²³. However, it would be easily deactivated^{15,24}. Either the decomposition or mineralization happens, forming new potassium compounds probably containing Si and Al, since the major components in coal ash are silica and alumina. The minerals produced are typically complicated, sometimes combined with other metallic species; for example, Osumilite ($K_2O \cdot 4.4MgO \cdot 4.6Al_2O_3 \cdot 20.4SiO_2$), Sanidine ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$), and Nepheiline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$)¹⁵. In this work, simplified products of the deactivation of K_2CO_3 , such as K_2O , $K_2O \cdot 2.5SiO_2$ and $KAlO_2$, are evaluated as a source of potassium at 700°C (Fig. 6).

Potassium content (metal basis) is 4.6~7.1 wt.%; 5.7 wt.% for K_2CO_3 and K_2O , 4.6 wt.% for $K_2O \cdot 2.5SiO_2$, and 7.1 wt.% for $KAlO_2$. As expected, K_2CO_3 shows the best performance with $> 90\%$ conversion within 60 min. Both K_2O and $K_2O \cdot 2.5SiO_2$ give $\sim 45\%$ conversion after 60 min. Since then, K_2O exhibits higher conversion ($> 90\%$ at 132 min) than $K_2O \cdot 2.5SiO_2$, ($\sim 76\%$ at 132 min). On the other hand, $KAlO_2$ is almost non-catalytic, showing a conversion profile similar to Kideco coal

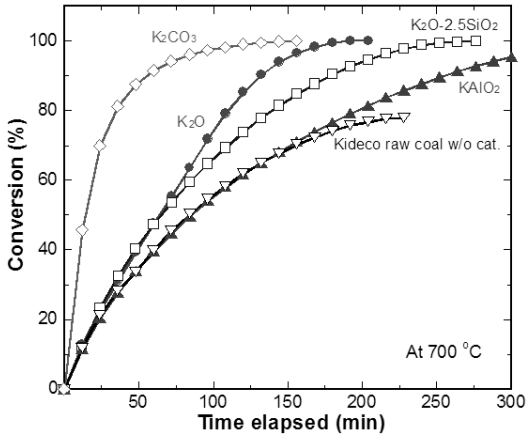


Fig. 6 Comparison of K_2CO_3 , K_2O , $K_2O \cdot 2.5SiO_2$, $KAlO_2$ as a catalyst for gasification of Kideco coal at 700°C

without a catalyst. The deactivation of K_2CO_3 via the decomposition to K_2O and the K_2CO_3 -ash reactions observed in the work agrees with the previous works^{15,25}. In reality, even more severe and broader deactivation due to the reactions with various ash components are expected, limiting repeated use of K_2CO_3 . It seems to be very difficult to overcome the deactivation if ash-containing coals are gasified. Use of ash-free coal substrates could be a solution for the issue⁷.

Ash from Posco coal was mixed with K_2CO_3 and the mixture (1:1 weight ratio) was calcined at 600, 700, 800, and 900°C for 3 hr under 30 vol.% steam in N_2 . In order to investigate the K_2CO_3 -ash reactions, XRD of the samples was taken, as shown in Fig. 7. No significant reactions are observed from the mixture at 600°C, such that the peaks arise from hydrous K_2CO_3 and silica. XRD profile at $T \geq 700^\circ C$ is different from at 600°C. The peaks show the new phases, especially at $2\theta = 29.5^\circ$ and 34.2° and reduced intensity of K_2CO_3 and silica is also shown. The general profile at $T = 700 \sim 900^\circ C$ is about the same with each other, showing that the K_2CO_3 -ash reactions start from 700°C.

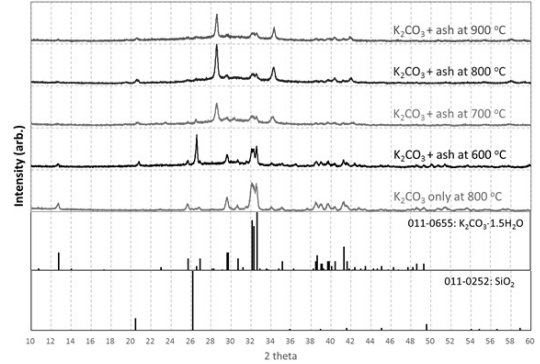


Fig. 7 XRD pattern of a mixture of K_2CO_3 and ash heat-treated at 600, 700, 800 and 900°C

3.3 Used K_2CO_3 Catalyst at 5 hr Gasification in a Fluidized-bed Reactor

Steam gasification of Kideco coal catalyzed by K_2CO_3 was done for 5 hr in a fluidized bed (FB) reactor under the following condition; 800°C, 4 atm, coal feed rate = 1 kg/hr, oxygen to carbon ratio (O_2/C) = 43%, and steam to carbon ratio (H_2O/C) = 108.7%¹⁸. At the completion of the reaction, used K_2CO_3 catalyst was collected from the FB reactor and its chemical composition was analyzed using XRD (Fig. 8). It shows similar profile with K_2CO_3 calcined at 800°C and most of

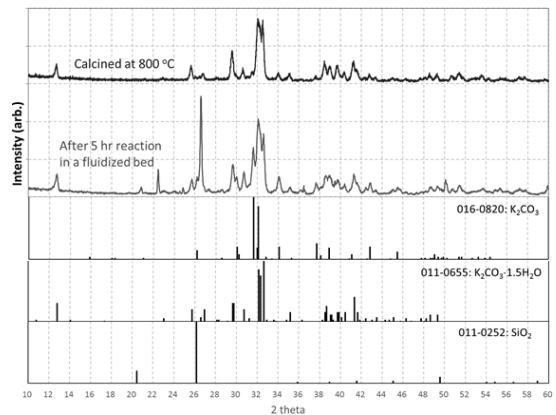


Fig. 8 XRD pattern of used K_2CO_3 after 5 hr reaction in a fluidized bed at 800°C

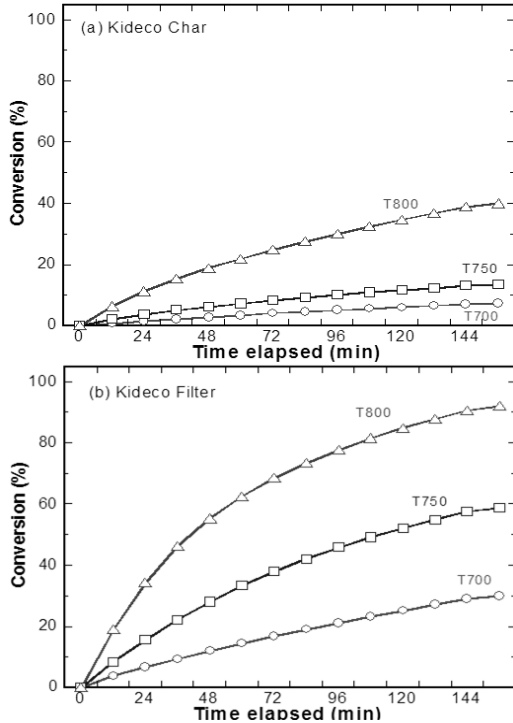


Fig. 9 Steam gasification of unreacted Kideco coal (after 5 hr gasification at 800 °C in a FB reactor) using a fixed bed reactor. (a) Recovered in a FB reactor (Char) and (b) Recovered in a metal filter (Filter)

the peaks correspond to K_2CO_3 and silica. The new phases as a result of K_2CO_3 -ash reactions, such as the peaks at $2\theta = 29.5^\circ$ and 34.2° in Fig. 7, are not detected even after the 5 hr reaction. Insufficient contact between the catalytic bead and the coal seems to minimize the irreversible reaction and thus the deactivation.

Unreacted Kideco coal both in a FB reactor (namely Char) and a metal filter (namely Filter) were also recovered. When the samples are gasified in a fixed bed reactor, much reduced reactivity, compared to the raw coal, appears for both of the coals (Char and Filter), as shown in Fig. 9. “Char” is gasified so slowly that the conversion is only ~8% at 700°C, ~13% at 750°C, and ~40% at 800°C after 156 min. “Filter” is a little faster than “Char”: ~30% at 700°C, ~59% at 750°C,

and ~92% at 800°C. Both of them are much slower than Kideco raw coal that shows > 70% conversion at 700°C after 156 min (Fig. 2). Obviously, a reactive portion of the coal is gasified earlier in the FB process and the remaining “Char” and “Filter” become less reactive.

4. CONCLUSION

Commercial catalytic gasification of coal has not been maximally achieved because of thermal and chemical deactivation of the catalyst. In the work, stability of K_2CO_3 , one of the most popular catalysts, is evaluated. The enhanced kinetics is observed for fresh K_2CO_3 , which maintains the activity even after the calcination at 800°C. TGA and XRD results confirm that no decomposition of K_2CO_3 happens below 800°C. However, K_2CO_3 should be used probably below 850°C, due to the loss of the catalyst by evaporation at the higher temperature. The reactivity is not decreased by the grain growth of K_2CO_3 . XRD results identify the reaction of K_2CO_3 with coal ash above 700°C, deactivating the catalyst. The activity of potassium varies according to its chemical forms and it decreases in the order; $K_2CO_3 > K_2O > K_2O \cdot 2.5SiO_2 > KAlO_2$ where $KAlO_2$ is almost non-catalytic. Repeated use of K_2CO_3 catalytic bead might be possible when gasified at < 800°C in a fluidized bed.

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