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Tar Reforming of Lignite at Low Temperatures Using Supported Potassium Carbonate

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Alumina-supported K_2CO_3 - $LaMn_{0.8}Cu_{0.2}O_3$ was investigated for use in the catalytic conversion of tar, produced from lignite, into syngas under inert and steam-reforming conditions. A double-bubble fluidized bed reactor system, equipped with a micro gas chromatograph to analyze permanent gases and a collecting system to analyze condensable species, was developed to screen the catalytic conversion of tar components at 700°C. Samples of Adaro coal were characterized based on elemental, proximate, and thermal analyses. The redox properties of catalysts, estimated by hydrogen temperature programmed reduction analyses, were correlated with their catalytic performance in tar conversion. The synthesized catalyst effectively converted tars into hydrogen-rich syngas and also improved tar reforming by inhibiting coke deposition.

1. Introduction

At low temperatures, the steam coal gasification process produces hydrogen by reducing H_2O . However, the low reactivity of coal leads to very slow conversion rates and tar emission. In addition, at temperatures lower than its dew point, tar formation severely limits the stability of the system by blocking up and/or fouling system components such as fuel lines, filters, engines, and turbines. Therefore, the removal or conversion of tar compounds is required to transform coal (or other biomass) into a suitable fuel for internal combustion engines, fuel cells, or feed stock for chemical synthesis.

Due to the advantages inherent to converting tar into useful gases and adjusting the composition of the product gases, both mechanical and thermal cracking methods have been proposed¹⁾. Mechanical methods do not allow energy recovery from tars, while thermal cracking requires temperatures higher than 1100°C to convert the tars into lighter gases. Catalytic decomposition has been proposed to overcome these drawbacks. In addition, the use of a catalyst can yield hydrogen-rich product gas compositions, which promotes reforming reactions.

Various catalysts, such as nickel-based catalysts, dolomites, olivine, and zeolites, have been investigated for use in catalytic tar decomposition. However, these catalyst systems have mostly been employed in secondary reactors, where volatile tars generated from the thermal decomposition of coal or biomass²⁻⁵⁾ and from coke oven gas (COG)⁶⁻⁹⁾ in the primary gasifier are broken down into product gases on the catalyst surface in the presence of gasifying agents such as steam, oxygen, or air. Dolomites and nickel-based catalysts are the most conventional catalysts for tar decomposition in secondary reactors at 700–900°C. Nevertheless, dolomites suffer from low mechanical strength and poor activity in the modification of gaseous hydrocarbons. Ni-based catalysts have

tar-conversion efficiencies higher than 99 % and very effective reforming capabilities for light hydrocarbons in gaseous products. However, the lifetime of Ni-based catalysts is limited due to the deposition of large amounts of carbon on the catalyst surface¹⁰⁾.

In the present study, catalysts consisting of an alumina - supported K_2CO_3 , perovskite oxide - supported K_2CO_3 were prepared, and their ability to catalyze the conversion of tar which could be produced through the pyrolysis of Adaro coal under steam-reforming conditions was investigated. A double-bubble fluidized bed reactor system equipped with a micro gas chromatograph to analyze synthesized gases and a tar collecting system to analyze condensable species, was designed and self-manufactured to study the catalytic conversion of tar components at 700°C. To confirm the catalytic tar conversion into syngas without the formation of deposited coke on the catalyst surface is another objective of this study.

2. Experimental

2.1 Materials

Indonesian lignite, also known as Adaro coal, was ground into 45–125 μm particles and dried at 80°C for 24 h in an oven. Table 1 shows selected properties of the prepared Adaro coal.

Table 1 Properties of Adaro coal.

Coal	Proximate analysis (wt.%)				Elemental analysis (wt.%, dry & ash free base)				
	VM	Water	Fixed carbon	Ash	C	H	N	S	O _{diff}
Adaro Coal	43.3	3.7	48.6	4.4	70.9	5.1	1.0	0.1	22.9

Perovskite-type oxides, $\text{LaMn}_{1-x}\text{Cu}_x\text{O}_3$ (LMC82, $x = 0.2$), and $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ (LKM91, $x = 0.1$) were prepared according to a sol-gel method^{11,12}. Quantitative amounts of lanthanum nitrate, manganese nitrate, and copper nitrate were stirred for 8 h in a solution of citric acid and water. The water was evaporated from the mixed solution by a rotary evaporator at 45°C until a viscous gel was obtained. For LMC82/ γ -alumina, γ -alumina was mixed in at this step. The ratio of LMC82/ γ -alumina was 20/80 wt.%. The gel was kept at 110°C overnight and the resultant mass was ground and then calcined at 750°C for 5 h. All of the prepared supports impregnated with a 10 wt.% K_2CO_3 by immersion in a mixture of K_2CO_3 and ethanol/ H_2O . The solvent was removed under vacuum at 110°C in accordance with a previously published method of wet impregnation¹³. The catalysts were double-sieved to select an appropriate size range after calcination and K_2CO_3 impregnation. Table 2 reports the particle size ranges and the surface area of the coal samples and catalysts.

Table 2 Particle size ranges, densities, and surface area.

Material	Size range	S_{BET} (m^2/g)
Adaro coal alone	$45\mu\text{m} < d < 125\mu\text{m}$	6.6
γ -alumina (A)	$12\mu\text{m} < d < 250\mu\text{m}$	149.9
10 wt.% $\text{K}_2\text{CO}_3/\gamma$ -alumina (K10@A)		115.5
LMC82 (L)		9.8
10 wt.% $\text{K}_2\text{CO}_3/\text{LMC82}$ (K10@L)		7.3
10 wt.% $\text{K}_2\text{CO}_3/\text{LMC82}/\gamma$ -alumina (K10@L-A)		89.9

The specific surface areas of prepared catalysts were calculated using the BET method applied to N_2 adsorption isotherms at 77 K. Redox activities were measured by TPR. Briefly, a sample (~50 mg) was heated at a constant rate (5 K/min) in a U-shaped quartz reactor from room temperature to 1000°C in a flowing hydrogen/helium mixture (50 mL/min, 5 % H_2 in He). Hydrogen consumption was monitored using a quadruple mass detector.

2.2 Apparatus

A circular stainless steel steam bubbling fluidized bed reactor (15.7 mm ID and 0.3 m high) was used for the catalytic steam gasification of Adaro coal, as shown in Figure 1. The fluidization gas distributor and separate fluidized bed were 1 mm thick and composed of 10 stacked pieces of nickel mesh with holes 50 μm in diameter. The fluidization columns (50 mm) and preheating section (0.1 m) were heated by a cylindrical 2.4 kW electric furnace. The temperature of the bed, measured by a K-type thermocouple placed 30 mm above the distributor, was kept constant by a PID controller. Temperature variation in the two continuous fluidization columns was always within $\pm 1^\circ\text{C}$ of the set point.

The syngas-containing steam flowed to a three-stage condenser. Heavier tars were collected at 25°C by the

first condenser, and steam and light tar were collected at -10°C by the second condenser. The first and second condensers were filled with THF (tetrahydrofuran), respectively. Lighter tars were collected through a quartz filter at 25°C by the final condenser. The lines running between the steam generator and the reactor, and those between the reactor and the first condenser of the tar collector, were heated to 200°C to prevent tar products from condensing.

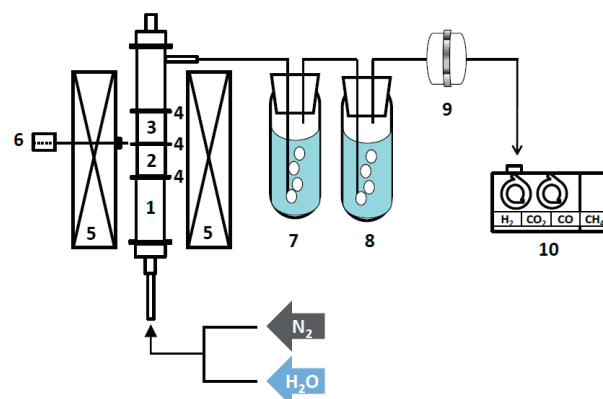


Fig. 1 Experimental apparatus. (1) Gas preheating section, (2) fluidization column 1 for coal, (3) fluidization column 2 for catalyst, (4) gas distributor and separator, (5) electric furnace, (6) thermocouple, (7) condenser 1, (8) condenser 2, (9) quartz microfiber filter, (10) gas analyzer.

2.3 Procedures

To investigate tar reforming ability, Adaro coal (1 g) was introduced into the bottom (first) reactor. Catalyst (1 g) was introduced into the upper (second) reactor separated by nickel mesh, as illustrated in Figure 1. The temperature of the reactor was raised at $200^\circ\text{C min}^{-1}$ in N_2 (400 $\text{mL}\cdot\text{min}^{-1}$ flow rate, $U = 0.035\text{ m}\cdot\text{s}^{-1}$) or $\text{N}_2/\text{H}_2\text{O}$ vapor flows (320/80 $\text{mL}\cdot\text{min}^{-1}$) and kept at 700°C for 30 min. The resulting syngas (H_2 , CO , CO_2 , and CH_4) was sent to the micro GC through the three condensers. The collected tars were dissolved in THF. Then the steam and THF were evaporated at 105°C for 24 h in an oven, and the collected tars were weighed. At the end of each experiment, the amount of coke formed on the catalysts was quantified by thermogravimetric analysis.

3. Results and discussion

3.1 Catalyst characterization

In Table 2, LMC82 exhibited a very low BET surface area of 9.8 m^2/g . The surface areas of the supports, LMC82, and γ -alumina decreased following K_2CO_3 impregnation and LMC82 coating.

The redox properties of the catalysts were evaluated by TPR, as shown in Figure 2. The redox properties of each catalyst were correlated with catalyst performance. LMC82 yielded two main reduction peaks at 250°C and 700°C. The peaks shifted to slightly higher temperatures following K_2CO_3 impregnation. Although γ -alumina had

a larger surface area than LMC82, almost no reduction activity was observed. The reduction of γ -alumina increased slightly after K_2CO_3 impregnation and LMC82 coating. K10@L-A exhibited broad reduction peaks below 700°C.

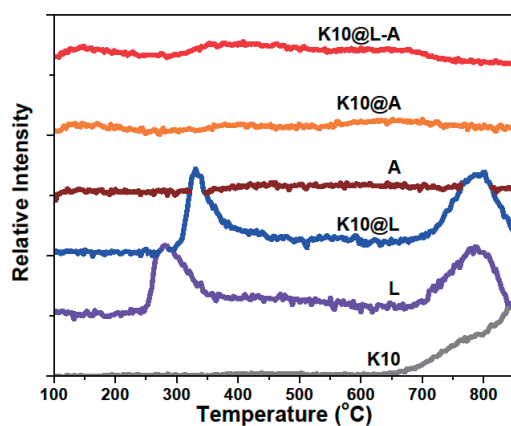


Fig. 2 TPR analyses of catalysts.

3.2 Volatile products and tar formation at low temperatures

Before the catalytic reforming tests, blank pyrolysis experiments with Adaro coal were performed under inert and steam reforming conditions. The release of volatiles under inert conditions was mostly complete in 30 min, as shown in Figure 3. Under steam reforming conditions, slow char gasification progressed with a regular slope following volatile release.

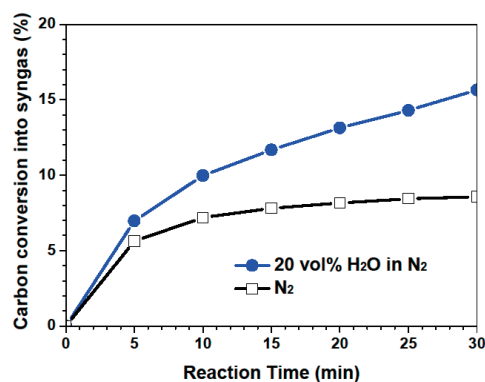


Fig. 3 Comparison of carbon conversion for Adaro coal under pyrolytic and steam reforming conditions at 700°C.

Tar formations were observed in inert and steam atmospheres at 700°C. Table 3 shows the amounts of tar compounds collected by the three-stage condenser. Without any catalyst, tar compounds represented 10.9 % of the total carbon in the coal sample under inert gas flow, and about 10.1 % in the presence of 20 vol.% steam.

The inevitable carbon loss (shown in Table 3) is generally conjectured to come from the coke formation on the reactor wall and light aromatics, which are undetectable in our system. However, at the present state, the exact reason is hard to be clear. More precious GC-MS analysis of the aromatics should be established to close to the complete carbon balance in future work.

Table 3 Tar collected from Adaro coal without catalysts.

Contents	Amount (g for 1 g coal, at 700 °C)	
	Pyrolysis	20 vol.% steam in N ₂
Condensed tar	0.0772 (10.9 %)	0.0718 (10.1 %)
Char	(67.8 %)	(66.2 %)
Syngas	(8.5 %)	(15.6 %)
Carbon loss	(12.8 %)	(8.1 %)

(): Carbon percent for whole carbon

3.3 Catalytic tar reforming and coke formation on catalysts

The use of γ -alumina under pyrolytic conditions resulted in the removal of large amounts of tar, as shown in Table 4. However, about 20 % of the available carbon was deposited as coke on γ -alumina, as shown in Table 5.

Table 4 Tar collected after reforming in the presence of catalysts.

Catalyst	Condensed tar amount (g for 1 g coal)	
	Pyrolysis	Steam reforming
A	0.0246 (3.47 %)	0.0302 (4.26 %)
K10@A	0.0231 (3.26)	0.0218 (3.08)
L	0.0442 (6.24)	0.0403 (5.69)
K10@L	0.0274 (3.87)	0.0246 (3.47)
K10@L-A	0.0203 (2.87)	0.0167 (2.36)

Table 5 Coke formation on the catalyst surface.

Catalyst	Coke formation (g on 1 g catalyst)	
	Pyrolysis	Steam reforming
A	0.141 (19.90 %)	0.124 (17.50 %)
K10@A	0.105 (14.82)	0.072 (10.16)
L	0.047 (6.63)	0.005 (0.71)
K10@L	0.010 (1.41)	< 0.001
K10@L-A	0.023 (3.25)	< 0.001

This means that while tar compounds were captured by the high surface area of γ -alumina, tar reforming was not remarkable. The reactivity of γ -alumina was improved by K_2CO_3 impregnation, but large amounts of coke, constituting 10.16 % of the available carbon, still remained on the K10@A catalyst surface under steam reforming conditions. LMC82 exhibited lower tar removal but also lower coke formation than γ -alumina. This shows that the lower surface area of LMC82 did not

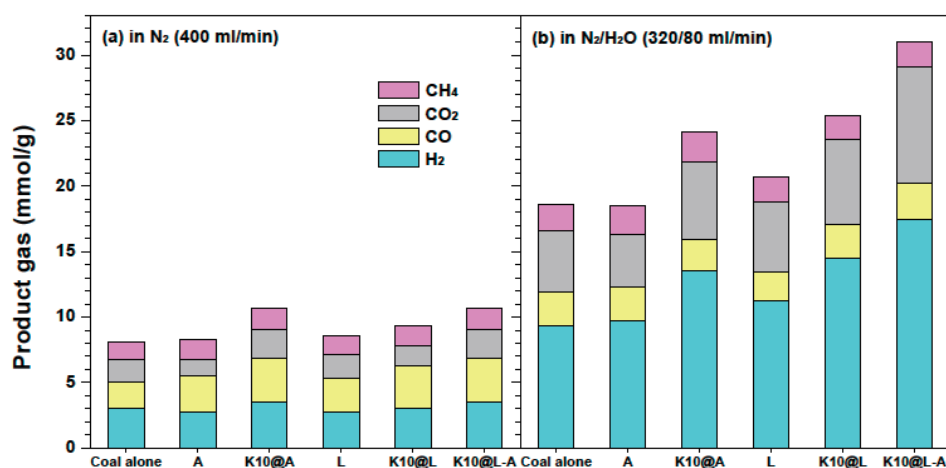


Fig. 4 Composition of syngas produced under (a) pyrolytic and (b) steam reforming conditions.

effectively adsorb tar even though the surface reactivity was higher than that of γ -alumina. K_2CO_3 impregnation of LMC82 improved its surface reactivity by effectively inhibiting coke formation on the catalyst surface. However, the potential for tar removal was limited by its relatively low surface area. K_2CO_3 impregnation resulted in a further decrease in surface area. Catalysts consisting of γ -alumina (high surface area) hybridized with K_2CO_3 -LMC82 (high surface reactivity) showed the highest degree of tar reforming and relatively low amounts of deposited coke on the catalyst surface. Under steam reforming conditions, this hybrid catalyst showed remarkably high performance with regard to both tar reforming and the inhibition of coke (below 0.1 % of the available carbon) formation.

3.4 Changes in syngas composition by tar reforming

Figure 4 shows the results of a syngas analysis after tar reforming tests in inert and steam reforming conditions. γ -alumina barely affected syngas production under any conditions. The addition of K_2CO_3 increased the hydrogen production of γ -alumina. This enhancement was the result of coke reforming on the catalyst surface because the composition of condensed tars in the presence of γ -alumina with or without K_2CO_3 impregnation varied only slightly (Table 5). Although LMC82 had relatively little impact on syngas composition under inert conditions, similar to that of γ -alumina, hydrogen-rich syngas was obtained under steam reforming conditions. The use of K10@LMC82 resulted in higher hydrogen production than K10@A. K10@L-A was the highest-performing catalyst with regard to hydrogen-rich syngas production with minimal tar and coke formation under steam reforming conditions.

4. Conclusions

Tar reforming can be achieved in two steps: adsorption of tar compounds onto the catalyst surface after the release of volatile materials, followed by catalytic reforming of these tar compounds into syngas. In this

way, adsorbed tar compounds can be converted into hydrogen-rich syngas. The remaining compounds form coke on the surface of the catalyst. In the present study, a catalyst composed of γ -alumina (high surface area) hybridized with K_2CO_3 -LMC82 (high surface reactivity) showed the highest degree of tar reforming with minimal coke formation. Consequently, catalysts for effective tar reforming should be of high surface area and high surface reactivity. The feasibility of various catalysts requires further study for use with brown coal and biomass tar reforming with NO_x and SO_x emissions.

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