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Short communication

Low-temperature catalytic conversion of lignite: 3. Tar reforming using the supported potassium carbonate

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ABSTRACT

Alumina-supported K_2CO_3–$LaMn_{0.8}Cu_{0.2}O_3$ was investigated for 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 and a collecting system to analyze permanent gases and condensable species, was developed to screen the catalytic conversion of tar components below 700 °C. 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 [1–12]. 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 proposed [13]. 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 [14–22]. However, these systems have mostly been employed in secondary reactors, where volatile tars generated from the thermal decomposition of coal or biomass [23–26] and from coke oven gas (COG) [27–30] 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 surface [31].

In the present study, a catalyst consisting of an alumina-supported K_2CO_3, perovskite-type oxide was prepared, and its ability to catalyze the conversion of tar produced from the pyrolysis of Adaro coal under steam-reforming conditions was investigated [32]. 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,

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Table 1
Properties of Adaro coal.

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

was developed to study the catalytic conversion of tar components at 700 °C. The catalyst converted tar into syngas without the formation of deposited coke on the catalyst surface.

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.

Perovskite-type oxides, $LaMn_{1-x}Cu_xO_3$ (LMC82, $x = 0.2$), and $La_{1-x}K_xMnO_3$ (LKM91, $x = 0.1$) were prepared according to a sol–gel method [33,34]. 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 point. 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. Alumina supports were 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 impregnation [35]. 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.

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 Fig. 2. 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 ±1 °C of the set point.

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

Material	Size range	S_{BET} (m^2/g)
Adaro coal alone	45 μm< d <125 μm	6.6
γ-alumina (A)	125 μm< d <250 μm	149.9
10 wt% K_2CO_3/γ-alumina (K10@A)		115.5
LMC82 (L)		9.8
10 wt% K_2CO_3/LMC82 (K10@L)		7.3
10 wt% K_2CO_3/LMC82/γ-alumina (K10@L-A)		89.9

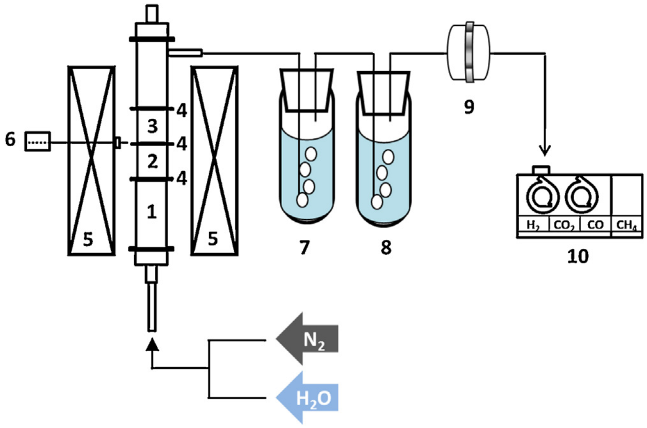

Fig. 1. Experimental apparatus. (1) Gas preheating section, (2) fluidization column 1 for coal, (3) fluidization column 2 for catalyst, (4) gas distributor and separator, (5) electric furnace, (6) thermocouple, (7) condenser 1, (8) condenser 2, (9) quartz microfiber filter, (10) gas analyzer.

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.

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 Fig. 1. The temperature of the reactor was raised at 200 °C min^{-1} in N2 (400 mL min^{-1} flow rate, $U = 0.035$ m s^{-1}) or N_2/H_2O vapor flows (320/80 mL 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

Table 2 summarizes the surface areas of the prepared catalysts. 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 Fig. 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 are than LMC82, almost no reduction