Journal of Industrial and Engineering Chemistry 20 (2014) 194–201

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Low-temperature catalytic conversion of lignite: 2. Recovery and reuse of potassium carbonate supported on perovskite oxide in steam gasification

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ARTICLE INFO

Article history:
Received 19 March 2013
Accepted 5 April 2013
Available online 17 April 2013

Keywords:
Catalytic steam coal gasification
K_2CO_3
Catalyst recovery
Perovskite

ABSTRACT

Catalytic recovery after repeated uses of unsupported K_2CO_3 or K_2CO_3 supported on 3 kinds of perovskites ($LaMn_{0.8}Cu_{0.2}O_3$, $LaMn_{0.8}Cu_{0.2}O_3/\gamma$-alumina, and $La_{0.9}K_{0.1}MnO_3$) was investigated during steam gasification of an Indonesian lignite (Adaro) at 700 °C. Perovskite supports effectively retained K_2CO_3 and maintained higher catalytic activity than K_2CO_3 alone. The supported catalysts were recovered from the ash after gasification based on their size and ferromagnetism. Quartz and alumina accumulation on the catalyst poisoned the ash due to reactivity with potassium. Catalytic activity as high as 90% carbon conversion was maintained up to seven cycles, and separation from the ash after gasification regenerated the activity.

1. Introduction

Coal gasification is an effective use of coal for power generation and syngas production [1–12]. Hydrogen, the main product of coal gasification, is an attractive fuel with no greenhouse gas emissions [13]. Steam gasification of coal through the reduction of H_2O is an attractive method for increasing H_2 yield. However, it is a slow, highly endothermic reaction that requires high temperatures above 1000 °C under pressure [14]. At temperatures below 800 °C, the commercially established rate requires a catalyst to enhance steam gasification.

Recently, lots of catalysts have been reported to the steam gasification area [15–22]. Besides iron and nickel, alkali salts and alkaline earth salts are the most frequently used catalysts in steam gasification of coals; the catalytic activity of sodium, potassium, and calcium salts has been investigated extensively. Even catalysts of so-called "high activity," such as potassium carbonate or potassium hydroxide, are required at 10 wt.% or more relative to the amount of coal to achieve effective catalysis, leading to considerable process costs. Therefore, in the Exxon catalytic coal gasification process [23], for example, a separate recovery procedure that makes use of multi-stage aqueous leaching of gasification residues has been considered. However, simple water leaching results in partial recovery because of the formation of water-insoluble potassium compounds; thus, the solution of recovered catalyst must be highly concentrated before reuse. These limitations could be overcome using a completely new approach to catalyst recovery on particular supports during coal gasification in a fluidized-bed reactor. In a previous study [24,25], we reported that K_2CO_3 supported on perovskite oxides showed high catalytic ability than each of perovskite and K_2CO_3 in combustion, and maintained K_2CO_3 on the support after reaction.

In the present study, we investigated catalyst recovery from ash after steam gasification of coal using size separation and the magnetic properties of the supports. $LaMn_{0.8}Cu_{0.2}O_3$ (LMC82), $LaMn_{0.8}Cu_{0.2}O_3/\gamma$-alumina (LMC82/A), and $La_{0.9}K_{0.1}MnO_3$ (LKM91) supports were investigated. For LMC82 and LMC82/A, size separation was used for recovery, while magnetic separation from ash was used for LKM91. Catalysts carrying 10 wt.% K_2CO_3 impregnated on the supports (K10@support) were investigated during steam gasification of an Indonesian lignite, Adaro coal. Catalysts were separated from ash after each cycle during several cycles of coal gasification. Recovered catalysts were reused and

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http://dx.doi.org/10.1016/j.jiec.2013.04.007

Table 1
Properties of Adaro coal.

Sample	Proximate analysis (wt.%)			Elemental analysis (wt.%, dry and ash free base)					Calorific value (as received) (cal/g)
	VM	Water	Ash	C	H	N	S	O_{diff}	
Adaro coal (prepared)	43.3	3.7	4.4	70.9	5.1	1.0	0.1	22.9	6010

analyzed by inductively coupled plasma mass spectrometry (ICP-MS) to quantify the residual potassium and by X-ray diffraction (XRD) and scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS) to confirm catalytic poisoning of the ash.

2. Experimental

2.1. Materials

Adaro coal, an Indonesian lignite, was investigated in this study. Raw coal was ground to a size of 45–125 μm and dried at 80 °C for 24 h in an oven. Table 1 shows the selected properties of the prepared 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 the sol–gel method [26,27]. A flow chart of catalyst preparation is shown in Fig. 1, and the elemental analyses (La, Mn, Cu, and Al in top layer of 5 μm) were carried out by X-ray fluorescence (XRF, EDX-800) using Na–Sc Ti–U radiation, as shown Table 2. Quantitative amounts of lanthanum nitrate, manganese nitrate, and copper nitrate were mixed and stirred for 8 h in citric acid aqueous solvent. 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 added during this step at a LMC82/γ-alumina ratio of 0.2/0.8). The gel was kept at 110 °C overnight, and the resultant mass was ground and calcined at 750 °C for 5 h. K_2CO_3 (10 wt.%) was impregnated onto the supports by immersing the supports in K_2CO_3–ethanol/H_2O. The solvent was removed at 110 °C under vacuum according to the wet impregnation method [24]. The catalysts were double-sieved to select a size range from 125 to 250 μm after calcination and K_2CO_3 impregnation (the amount of K_2CO_3 powder was estimated because sieving K_2CO_3 from the deliquescent was limited).

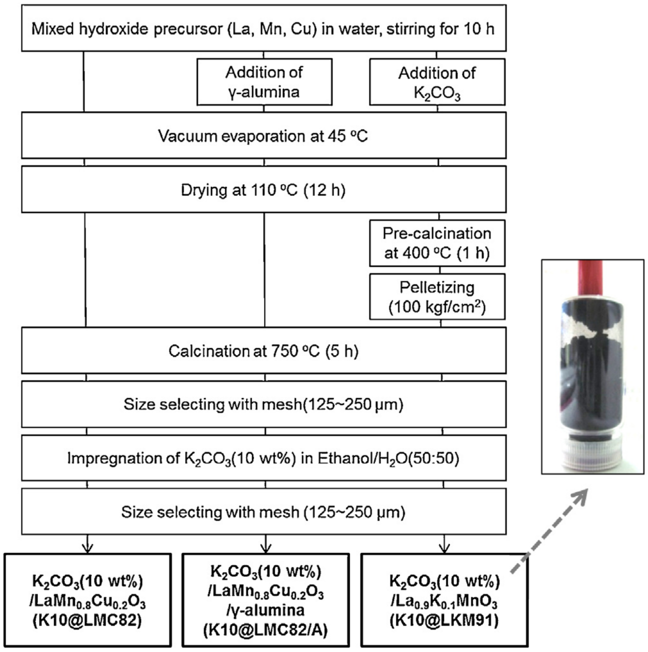

Fig. 1. Preparation of the catalysts (the right picture shows the ferromagnetism of LKM91).

Table 2
Elemental analyses and surface areas of catalysts.

Catalyst	Specific area (m^2/g)	Components (%)				
		La	Mn	Cu	Al	K
$LaMn_{0.8}Cu_{0.2}O_3$ (LMC82)	9.5	64.762	24.128	11.110	–	–
$LaMn_{0.8}Cu_{0.2}O_3$/ γ-alumina (LMC82/A)	107.3	16.642	8.855	3.101	71.403	–
$La_{0.9}K_{0.1}MnO_3$ (LKM91)	12.9	59.152	43.309	–	–	2.461

Table 3 summarizes the particle size ranges, densities, and surface areas of the coal and catalysts used in the experiments, together with the minimum fluidization velocity (U_{mf}) calculated according to a previous study [28]. This formula predicted the U_{mf} of the particles in our reactor with sufficient accuracy.

2.2. Apparatus

A circular stainless steel reactor (15.7 mm ID, 0.3 m high) was used for the catalytic steam gasification of Adaro coal (Fig. 2). The fluidization gas distributor consisted of 10 pieces of nickel mesh with holes 50 μm in diameter piled at the bottom of the reactor. The same pile was also used as the upper-side separator of the fluidized bed. The fluidization column (0.1 m high) and the preheating section (0.1 m high) were heated by a 2.4 kW cylindrical electric furnace. The temperature of the bed, measured by a K-type thermocouple placed 30 mm above the distributor, was kept constant by a proportional–integral–derivative (PID) controller. Temperature variation in the fluidization column was maintained within ±1 °C of the set temperature.

The syngas product, including steam, was sent to a micro-gas chromatograph (GC) through a series of three condensers, which collected heavier tar at 25 °C in the first condenser, steam and light tar at −10 °C in the second condenser (the first two condensers were filled with tetrahydrofuran, THF), and lighter tar through a quartz filter at 25 °C in the third condenser. The transfer lines between the steam generator and the reactor, as well as between the reactor and the first condenser of the tar collector, were heated to 200 °C to prevent the condensation of tarry products in the lines.

Table 3
Particle size ranges, densities, and surface areas of coal and catalysts.

Material	Size range	Density (kg/m^3)	S_{BET} (m^2/g)	U_{mf} (m/s)	U/U_{mf}
Adaro coal	45 μm < d < 125 μm	1390	6.6	0.0034	12.7
K_2CO_3	125 μm < d < 250 μm	2290	2.6	0.0056	7.7
K10@LMC82		6090	7.3	0.0150	2.9
K10@LMC82/A		3910	89.9	0.0095	4.5
K10@LKM91		5860	9.9	0.0143	3.0