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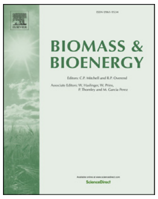

Research paper

Durability studies of limonite ore for catalytic decomposition of phenol as a model biomass tar in a fluidized bed

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A B S T R A C T

The development of highly active, durable, tar decomposition catalysts is desirable for practical application of biomass gasification at low temperature. In this study, limonite ore calcinated at 900 °C was used as bed material in a fluidized bed for catalytic decomposition of phenol (biomass tar model) at 650 °C. The limonite showed catalytic activity for the decomposition of phenol to produce combustible gases (H_2 and CO). A long-term durability test of phenol decomposition with O_2 regeneration treatment was conducted for 25 h using the limonite catalyst. The O_2 treatment repeatedly removed the deposited carbon, allowing H_2 and CO to be generated constantly for 25 h. Steam reforming of phenol using the limonite catalyst was also conducted with various steam/carbon ratios ($S/C = 0$, 0.4, and 0.8), of which $S/C = 0.4$ was the best for suppressing carbon deposition and producing higher volumes of H_2 and CO gases. Continuous steam reforming for 24 h could be achieved using a limonite catalyst with $S/C = 0.4$, while maintaining the production of H_2 and CO gases, even though carbon deposition occurred steadily. These results indicated that limonite ore is a promising bed material for use in internally circulating fluidized-bed systems for long-term catalytic decomposition of biomass tar.

1. Introduction

Biomass has attracted much attention as an energy resource because it is a carbon-neutral resource that is readily available worldwide. Thermochemical conversion of biomass by gasification is an effective way to produce combustible gases (H_2, CO, CH_4, and other hydrocarbons) that can be used for the production of electricity via fuel cells, internal combustion gas engines, and turbines, or for the synthesis of liquid fuel by the Fisher-Tropsch reaction. This process is generally conducted at high temperatures (>1000 °C); however, low-temperature gasification is desired to increase the cold gas efficiency of the gasifier. The problem with low-temperature gasification is the formation of tarry compounds (tar), composed of a complex mixture of aromatic hydrocarbons, because the condensation of tar causes plugging of lines and filters, leading to major operation problems in the gasification process.

To overcome these problems regarding low-temperature gasification, metal catalysts, which possess catalytic activity for the decomposition of tar and increase the gas yield, have been widely used. Generally, transition metals, such as Ni, Fe, and Co loaded onto metal oxides show high catalytic activity for the decomposition of tar [1]. From a point of a practical view, catalysts should be satisfactory with regard to both activity and cost. Our group has developed highly active and inexpensive catalysts, such as Ni-loaded chicken droppings [2], Ni-loaded brown coal char [3,4], and limonite ore [5], for decomposition of tars derived from biomass and coal.

Limonite ore is a low-grade, inexpensive iron ore that includes iron species having catalytic activity for tar decomposition [6]. Li et al. [5] reported that an Indonesian natural limonite ore showed catalytic activity for coal tar decomposition to produce light fuel gas. Moreover, Zhao et al. [7] studied the catalytic reformation of biomass volatiles derived from corncob pyrolysis using an Indonesian limonite and found that the reforming activity of the limonite at 650 °C was comparable to a commercial Ni/Al_2O_3. One of the critical problems using catalysts for tar decomposition is the formation of deposit carbon on the active metal, which leads to the deactivation of the catalyst.

We also developed an internally circulating fluidized-bed gasifier for biomass gasification [8,9]. This system consists of two chambers (gasification and combustion chambers) and a bed

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material that circulates between the two chambers. This process can utilize the heat from the combustion of biomass char for the gasification of biomass as follows. In the former chamber, the biomass is gasified to produce combustible gases and biomass char. The char formed is moved to the combustion chamber by a circulating bed material and burned with air to generate heat in the combustion chamber. The generated heat and the hot bed material are then supplied to the gasification chamber for application as a thermal source for gasification. During this process, if we used the catalyst for tar decomposition with the bed material, the carbon deposited on the catalyst during the gasification could be burned away, and the heat generated from this process could be used as the thermal source for biomass gasification. Therefore, the durability of the catalyst for O_2 regeneration in the fluidized bed is important for the success of this process.

In this study, we evaluated the durability of the catalyst for long-term decomposition of biomass tar with O_2 regeneration treatment and introduction of steam. The catalytic decomposition was conducted at a low temperature (650 °C) in a fluidized bed including a calcinated limonite ore. As a model tar, we used phenol, one of the main components of the tar in woody biomass [10]. The effects of the O_2 regeneration treatment for the catalyst and introduction of steam during the tar decomposition on durability were evaluated in terms of gas production, tar formation, and carbon deposition.

2. Materials and methods

2.1. Materials

Limonite is a natural iron-containing ore; the limonite used in these experiments was produced in Indonesia. The elemental composition of the limonite ore analyzed using X-ray fluorescence spectroscopy (XRF, EDX-700; Shimadzu Corp., Japan) is shown in Table 1. The limonite ore was calcinated by the following procedure before being used as a catalyst. First, the limonite powder was kneaded with distilled water to form balls 2–3 cm diameter. The obtained balls were calcinated at 900 °C for 30 min in a muffle furnace. The calcinated limonite balls were allowed to cool down to room temperature and then pulverized and sieved into fractions 0.25–0.50 mm diameter.

Sand (JFE MINERAL Co. Ltd.) was used as an inert bed material. The average particle size of the sand was 0.225 mm. Phenol (Wako Pure Chemical Industries Ltd.) was used as a model compound of biomass tar.

2.2. Tar decomposition in a fluidized bed reactor

The tar decomposition test was performed using phenol as model tar in a fluidized bed reactor, as shown in Fig. 1. The bed material was a mixture of limonite ore and sand (volume ratio, 1:1), or only sand. Phenol was fed into the reactor by bubbling N_2. After passing through the fluidized bed, the gas was collected in an aluminum gas bag located after tar traps. The detailed procedure was as follows.

The bed material was set on a mesh filter located in the middle of a quartz tube (internal diameter: 4.0 cm). The static bed height was 3.0 cm. After purging air using N_2, the bed material was heated to 650 °C in a N_2 stream and kept at this temperature. Phenol heated at 70 °C by an oil bath was fed into the reactor at a rate of 0.4 mmol min^{-1} by bubbling 1.5 l min^{-1} N_2 gas to start the phenol decomposition. The feeding rate of phenol was controlled by maintaining phenol at a constant temperature (70 °C) based on the Antoine equation. The bed material was bubbled using N_2 gas for which the superficial velocity was approximately three times higher than the minimum fluidization velocity. During phenol decomposition, the gas passed through five tar traps containing distilled water (two traps were at room temperature, and the other traps were at 0 °C using an ice bath) and was collected for 9 min every 30 or 60 min in a gas bag. After reaching the desired reaction time, the gas was switched to N_2 gas from phenol/N_2 gas to stop the reaction, and the reactor was cooled down to room temperature. The gas collected during the phenol decomposition was analyzed by gas chromatography-thermal conductivity detector (GC-TCD, GC-2014; Shimadzu Corp.) and GC-flame ionization detector (GC-FID, GC-2014; Shimadzu Corp.) with a methane converter to detect H_2, CO, CO_2, CH_4, and hydrocarbons. The total amount of gas during the phenol decomposition was calculated by integrating the gas production rate. The carbon content of water-soluble tar was measured using a total organic carbon analyzer (TOC-V; Shimadzu Corp.). The deposited carbon on the bed material was combusted at 650 °C for 40 min in an O_2 stream to form CO and CO_2. The gas collected during the combustion was analyzed using GC-FID to calculate the carbon content of the deposited carbon. The combustion procedure was repeated until carbon oxide gases were not detected by the GC-FID. The carbon balance was calculated based on the ratio of carbon content of phenol to that of the gas (C_{gas}), the deposit ($C_{deposit}$), and the tar (C_{tar}).

Table 1
Elemental composition of limonite ore analyzed by XRF.

Elemental composition (wt%)									
Fe	Si	Al	Ni	Co	Cr	Ca	Mg	Na	S
41.4	1.7	6.1	1.7	0.1	1.5	<0.01	0.3	<0.01	0.1

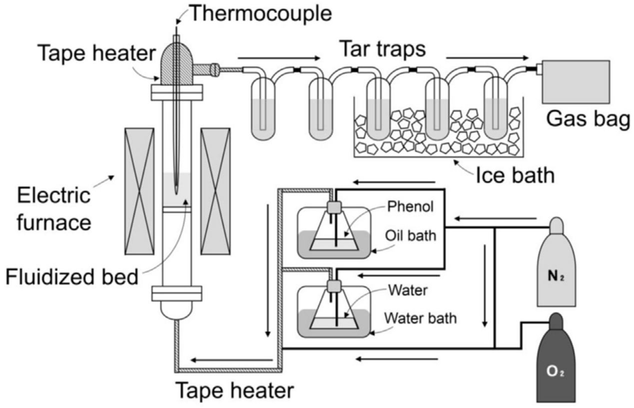

Fig. 1. Schematic of the fluidized-bed reaction system.

Steam reforming of phenol was also performed using the same procedure, but in the presence of steam introduced by bubbling of water with the N_2 gas (Fig. 1). The steam/carbon molar ratio (S/C) was set to 0.4 or 0.8, and the feeding rate of steam was controlled by maintaining water at constant temperatures based on the Antoine equation.

2.3. O_2 regeneration treatment of the catalysts

The catalyst bed was regenerated every 5 h by O_2 treatment after the phenol decomposition without steam (S/C = 0) to remove the carbon deposited on the catalyst. The cycle of the decomposition and regeneration was repeated five times (the total time of phenol decomposition was 25 h). After every decomposition test, the catalyst bed was regenerated by combustion at 650 °C for 40 min in an O_2 stream. After treatment, the catalyst bed was