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Thermo-catalytic decomposition of propane over carbon black in a fluidized bed for hydrogen production

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ABSTRACT

Thermo-catalytic decomposition of propane to solid carbon and hydrogen was examined for hydrogen production without CO_2 emission. The reaction was carried out over a carbon black catalyst in a bench-scale fluidized bed reactor. Effects of reaction temperature on the propane conversion and product distribution were examined. Catalytic activity of the carbon black was maintained stable for longer than 8 h in spite of carbon deposition. From 600 to 650 °C, the propane conversion increased sharply with propylene produced in a considerably larger amount than methane. As the reaction temperature further increased up to 800 °C, the major hydrocarbon product was methane; the production of propylene decreased rapidly and ethylene was the next most abundant product. The surface area of the carbon black was decreased as the reaction proceeded due to carbon deposition. Surface morphology of the used carbon black was observed by TEM and the change of the aggregates size was measured.

Introduction

Hydrogen is widely regarded as the energy carrier of the future because it is the most acceptable one for the environment. However, conventional processes of hydrogen production, such as the steam reforming and partial oxidation of natural gas and other fossil fuels, accompany simultaneous production of CO_2, which is to be reduced due to the greenhouse effect. Clean processes for hydrogen production, water electrolysis using renewable energy as a typical example, are not competitive with current energy costs. To produce hydrogen without any associated CO_2 emission, thermo-catalytic decomposition of methane with carbon catalysts has been studied by many investigators in recent years [1–12], and the catalytic characteristics such as the reaction kinetics and mechanisms have been studied intensively by the research groups of Muradov [2,6], Yoon [3–5,7–9], Moliner [10] and Serrano [11,12]. Besides pure methane, pure ethane, mixtures of methane and ethane, and mixtures of methane and propane have also been investigated for the thermo-catalytic decomposition over carbon black catalysts [13–15], and the reaction mechanism of ethane decomposition in the presence of carbon black was proposed [13].

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In addition to natural gas whose predominant component is methane, LPG (liquefied petroleum gas) composed of propane and butane is also another important hydrocarbon feedstock which can be thermo-catalytically decomposed for hydrogen production without CO_2 emission [16–18]. Therefore, based on the results of methane and ethane decomposition, a further study for the decomposition of higher hydrocarbons into hydrogen and carbon without CO_2 emission was required, and propane was employed in this study as another feedstock to test the thermo-catalytic decomposition over a carbon black catalyst. Similarly to methane decomposition, propane decomposition to hydrogen and carbon is an endothermic reaction, and the energy requirement per mole of hydrogen produced (26.0 kJ/mol H_2) is considerably lower than that for methane decomposition (37.8 kJ/mol H_2) [5,16–18].

Previous studies on decomposition of ethane, propane and butane over carbon black catalysts were performed in a fixed bed reactor system [13–18]. In this study, the characteristics of thermo-catalytic decomposition of propane were investigated by using a bench-scale fluidized bed reactor (FBR), and the results obtained were compared with those obtained by using a fixed bed reactor [16–18]. In order to compare the reaction characteristics of propane decomposition with those of methane decomposition, the same carbon catalyst and FBR for methane decomposition performed in our laboratory were employed [19,20]. The FBR was selected because it is the most promising reactor for large-scale, continuous powder-handling operations [17]: that is, carbon particles can be continuously added to and withdrawn from the reactor. In an FBR, the bed of carbon catalysts behaves like a well-mixed body of liquid, giving rise to high heat and mass transfer rates from particles to gas. The bed can also buffer any instability that arises during continuous operation. Particularly, the FBR was proposed in order to overcome the reactor plugging problem due to carbon deposition. During fluidization, the gas is allowed to reside a certain time in the reaction zone, and the residence time can easily be controlled by adjusting the ratio of the gas feed rate to the solid weight, which was one of the main variables in this study.

Experimental

Propane (99.999%, Hanmi Gas Ltd.) was used as the reactant. A domestic rubber-grade carbon black (N330 from OCI) was comprised with a particle size of 26–30 nm and a surface area of 77 m^2/g, and used as the catalyst because it showed very stable catalytic activity compared with activated carbons investigated in the previous studies on methane decomposition [4,7,19]. The carbon black was dried at 200 °C for 24 h in an oven before the propane decomposition test and for the characterization.

As shown in Fig. 1, the catalytic decomposition of propane was carried out in an FBR which consisted of a quartz-tube reactor heated with an electric furnace; the reactor

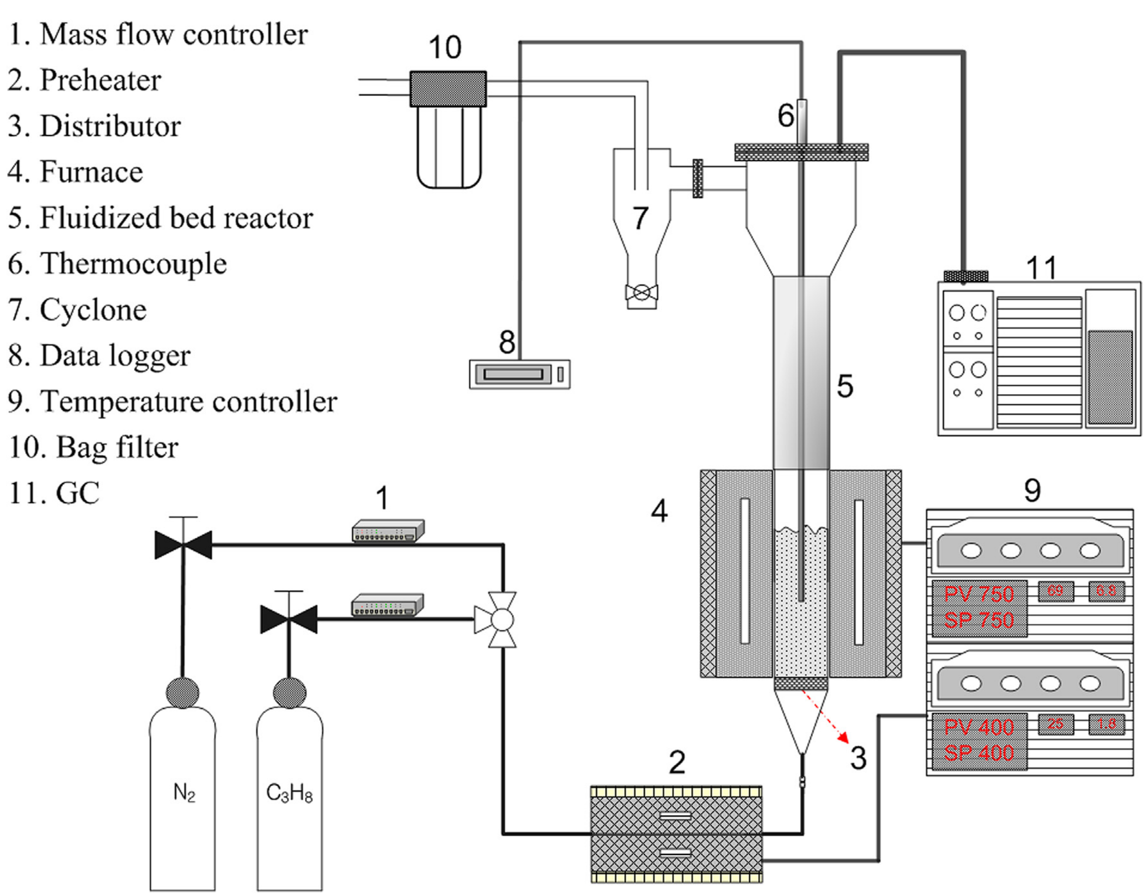

Fig. 1 – Schematic diagram of the experimental test facility.