

論 文 の 要 旨

題 目 Carbon nanotube as support for the catalyst in supercritical water gasification
(超臨界水ガス化における触媒担体としてのカーボンナノチューブ)

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Biomass gasification is a way of turning things like wood, farm leftovers, or city waste into a gas mix called syngas through a heat-based process. During these processes, the biomass changes from being complex organic stuff to gases that can burn. Syngas, made up of carbon monoxide, hydrogen, and methane, can be used for different things like making electricity, producing heat, and creating biofuels. This provides a sustainable method for getting energy from biomass resources. Using supercritical water gasification (SCWG) is anticipated to be better for breaking down wet biomass compared to other gasification methods. This is because it doesn't need the biomass to be dried beforehand, and the time it takes to complete the process is significantly shorter. SCWG usually needs a catalyst to speed up the reaction. However, this catalyst essentially needs supports to make it work better in terms of activity, stability, selectivity, and cost-effectiveness. This helps advance efficient and sustainable catalytic processes. In the present time, carbon nanotubes (CNT) show promise as a catalyst support due to their tiny structure and large surface area.

Nevertheless, it's essential to investigate the stability of the catalyst support quantitatively. If, for instance, the catalyst support decomposes rapidly during the gasification process, it might not be a suitable support for the catalyst. Thus, evaluating the gasification characteristics of CNT is vital. Subjecting CNT to severe conditions in supercritical water (SCW) is necessary to figure out how fast it decomposes. The goal of this study was to gasify CNT in SCW and quantitatively analyze its reaction characteristics. The CNT was initially prepared by eliminating the surfactant from the original material. This material originally had both surfactants and CNT and was treated with hot compressed water. Thermogravimetric analyzer (TGA) was used to check the CNT purity after removing the surfactants. To observe any changes in the crystalline defects of the CNT prior to and after gasification, Raman spectroscopy has been used. To gasify CNT in SCW, CNT has been placed in the packed bed reactor and subjected to a pressure of 25 MPa and temperatures between 600 °C to 700 °C. As a result, when the temperature increased, the CGE increased, and the reaction rate also increased. It was observed that the CNT reacted at both ends, and the shortening speeds for each temperature were determined. In addition, at the same temperature condition, during the gasification process, the number of CNT ends remained constant, resulting in a steady gasification rate. The CNT's reaction rate was 8.5 times slower than that of activated carbon. Advantageously, due to this sluggish reaction, CNTs can work well as support for catalysts.

Ruthenium (Ru) was an excellent choice as the primary catalyst for CNT support due to its superior dispersion, increased resistance to oxidation and hydrothermal sintering, stability in water, and ability

to reduce coking in conventional gasification. These features positioned Ru as a highly suitable and advantageous catalyst for supporting CNT applications. The study aims to explore Ru/CNT catalyst, which hasn't been investigated in-depth. So, our aim is to create a Ru/CNT catalyst, spherical-like shape, for SCWG and assess its effectiveness in catalyzing reactions. Ru/CNT was created using a wet impregnation method. The catalyst was then characterized using techniques such as TGA, scanning electron microscope (SEM), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). In this study, glucose (5 wt%), a common model compound of biomass, was continuously fed at 2 mL/min and gasified in a packed bed reactor containing the Ru/CNT catalyst at 600 °C and 25 MPa. Ru/CNT exhibited the highest CGE, achieving complete gasification compared to gasification without a catalyst or CNT alone without Ru impregnation. The stability of the Ru/CNT catalyst in supercritical water at 600 °C under 25 MPa pressure was assessed over 6.5 hours at a feedstock flow rate of 2 mL/min, with a consistent zero TOC yield throughout the stability test. Almost complete gasification was attained, and the gas composition remained constant. The slow reaction of the CNTs allowed the Ru nanoparticles to stay in their original positions in the CNT bundles during a long gasification period, which is why consistent complete gasification throughout the test has been observed. This finding supports the idea that CNTs are promising catalyst support for biomass gasification.

When the packed bed reactor was filled with these spherical Ru/CNT catalyst pieces, certain areas of the flow had to navigate through empty spaces without interacting with the catalyst. In these regions, glucose is exposed to gasification through a homogeneous reaction. Conversely, when there was interaction between the catalyst and flow, glucose is exposed to gasification through heterogeneous reactions. Therefore, it's crucial to understand the rates of both these types of reactions. This study aims to clarify the features of both homogeneous and heterogeneous reactions through experiments under various conditions. Glucose (5 and 10) wt% was chosen as the feedstock, and the reaction temperature was set at (500 and 600) °C. The weight hourly space velocity (WHSV) was adjusted (40, 80, or 160) h⁻¹ by maintaining the catalyst loading at 0.15 g and varying the flow rate (2, 4, or 8) mL/min. Overall reaction model, based on changing WHSVs or space time, was developed. The reaction rate constant at 600 °C was 2 times higher than that at 500 °C. Then also a reaction model, where homogeneous and heterogeneous reactions occur simultaneously based on the residence time (not space time), was developed, and the reaction rates were determined. The reaction rate from using CNTs alone without Ru impregnation had little catalytic effect but was negligible compared to that from Ru. It is noteworthy to mention that even at a short residence time in the catalyst bed of 1.8 s, complete gasification was achieved at 600 °C.