Effect of Sulfur on Gasification of Lignin over Supported Metal Catalysts in Supercritical Water

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Introduction

Lignin gasification in supercritical water could be a potential technology that can operate at low temperatures because of the high solubility and hydrolysis rates of biomass in supercritical water. This would also lead to minimization of the mass-transfer limitations of the reactant and rinsing effect of supercritical water for washing out coke precursors from the active catalyst sites. We have reported that supported ruthenium catalysts are effective for lignin gasification [1]. It has been reported that as much as 0.5 wt% sulfur can be present in waste biomass [2]. In this paper we report the effect of sulfur on the lignin gasification over supported ruthenium catalysts in supercritical water.

Methods

Catalytic gasification was conducted in a stainless steel 316 bomb reactor. A weighted amount of catalyst, sulfur, and water were loaded into the reactor [3]. The reactor was submerged into a preheated sand bath. Gaseous products were collected by a syringe through sampling loops attached to gas chromatograph for analysis by TCD. The other products from the reactor were recovered with pure water and separated as water-soluble and water-insoluble fractions, which were analyzed by GC-FID [4].

Results and Discussion

The product yield verses time profile for lignin gasification with and without sulfur is shown in Figure 1. The molar ratio of sulfur to surface ruthenium was 0.4. The gas yield reached 100% in about 120 min in the absence of sulfur, while it reached 90% in 360 min even with the concentration of sulfur at 0.4, indicating that almost complete gasification occurred, but at a slow rate. Both in the presence and absence of sulfur, the products were gas and THF-soluble, and the yields of water soluble and THF-insoluble products were below 0.1 C%.

Figure 2 shows the effect of water density on lignin gasification in the presence and absence of sulfur. Total gas yield increased with water density both in the presence and absence of sulfur. However, the gas yield in the presence of sulfur was lower than that in the absence of sulfur, indicating the sulfur poisoning of the ruthenium active sites. The formation of THF-insoluble products was observed below 0.33 g cm³ of water density both in the presence and absence of sulfur. We have reported that the increase in the gas yield with the increase in water density for lignin gasification in the absence of sulfur was the results of the following: the increase of water density enhanced the hydrolysis of lignin to produce low

molecular-weight fragments, which were decomposed over ruthenium surface [1]. The same reasons hold true even in the presence of sulfur.



Figure 1. Product yield vs. reaction time for lignin gasification over Ru/C at 673 K with a water density of 0.5g cm⁻³, 0.1 g of Ru/C, and 0.1 g of lignin, without (a) or with (b) elemental sulfur.



Figure 2. Product yield vs. water density for lignin gasification over Ru/C at 673 K, 180 min of reaction time, 0.15 g of Ru/C, and 0.1 g of lignin.

Significance

Sulfur atoms present in waste biomass poisoned the ruthenium catalysts in supercritical water gasification. The gas yield increased with an increase in water density.

References

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