Insitu Regeneration of Metal Catalysts Used for Hydrotreatment of Bio-oil

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Introduction

Several teams around the world are developing technologies capable of producing liquid fuels from lignocellulosic material (woody biomass, grasses, energy crops, etc.). One of the most promising processes is fast pyrolysis of biomass because it can convert a broad variety of feedstocks into liquid fuel products. The bio-oil produced via this process has limited commercial applications because of its poor heating value (~17 MJ/kg), high oxygen content (~45 wt %), high viscosity (>200 cP), and corrosiveness due to acid content (pH ~ 2.5). There is a necessity to upgrade the bio-oil via deoxygenating to fuel that can be used directly in diesel and gasoline engines [1,2]. Active metal catalysts appear to be a promising solution in the deoxygenation of bio-oil, however they get rapidly deactivated. In this paper the performance of Ru/TiO2 combined with Ru/TiO2/ZSM5 is evaluated on fresh and regenerated catalyst over four cycles. The regeneration tests were performed in situ in a two-stage reactor design. The feedstock and product analysis combined with catalyst characterization by different techniques show that the catalyst can be recovered from coke with a solvent rinse and hydrogen treatment.

Materials and Methods

Ru/TiO2 and Ru/TiO2/ZSM5 were prepared using a method developed at Pacific Northwest National Laboratory. Bio-oil feedstock was produced from pine wood sawdust via fast pyrolysis in a pilot scale reactor. Hydrotreating tests were conducted in a 20 ml fixed bed, two-stage hydrotreater with continuous flow. Reactor pressure was approximately 10 MPa, stage I was at 160°C, and stage II at 320°C. The catalysts were regenerated in situ with an organic solvent to remove condensable bio-oil deposited on the catalyst and reactor walls. This was followed by reduction with H2 at moderate temperature. The fresh, spent and regenerated catalysts were characterized by different techniques to determine the root cause of catalyst deactivation and the efficiency of coke removal.

Results and Discussion

The bio-oil hydrotreating tests were conducted in a two-stage reactor design. The first stage consisted of Ru/TiO2 to stabilize bio-oil by hydrogenation at a low reaction temperature and the second stage had the bifunctional catalyst Ru/TiO2/HZSM5 for cleavage of C=O bonds. Figure 1 reports the density of organic phase as a function of time on stream (TOS) for fresh catalyst. The catalysts have good initial performance as indicated by the density of organic phase, oxygen content, total acidity number (TAN) and color. As TOS increased, the density, oxygen content and TAN increased and the color became darker, which reflects progressive deactivation of catalysts. Figure 2 reports the performance of fresh and regenerated catalyst. The regeneration of catalyst was accomplished in two steps: First by rinsing with a polar solvent, such as methanol and acetone, and then followed by reduction with H2. The initial catalyst activity was recovered, but the rate of catalyst deactivation increased from cycle to cycle. The characterization of fresh, spent and regenerated confirms that carbon deposition on the catalyst is not the only cause of catalyst deactivation; we expect that poisoning with heteroatoms is another.

Figure 1. Fuel density, oxygen concentration, and TAN as function of TOS. Fuel produced from bio-oil sawdust pine (Feed: catalytic bio-oil, 12 MPa, Stage I: 150 °C, Stage II 320 °C (<110h) and 340 °C (>110h), LHSV =0.1 dry bio-oil

Figure 2. Density of fuel as function of TOS on fresh (cycle1) and in situ regenerated catalyst cycles (2-4). Regeneration conditions methanol rinse & reduction with H2 at 400 °C. Reaction conditions: 12 MPa, Stage I: 160 °C, Stage II 320 °C, LHSV = 0.2 dry bio-oil

Significance

The catalyst deactivation by carbon deposition can be recovered by solvent wash follow by reduction with hydrogen at temperature between 350°C and 400°C. This process is practical and can be accomplished at commercial scale without damage to the catalyst.


References