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Hydrodeoxygenation of pyrolysis oils derived from kraft lignin using Ru-based catalysts in a continuous flow reactor

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Highlights

- Bimetallic RuRe/C catalysts are highly active and stable for the HDO of real lignin oils.
- Medium temperature and low WHSV exhibit the highest deoxygenated hydrocarbon yield.
- The formation of soft coke was the main cause of catalyst deactivation.

1. Introduction

The hydrodeoxygenation (HDO) of pyrolysis oils derived from lignin is considered to be the most effective method for improving the quality of oil by selectively removing oxygen functionalities [1]. Although the effectiveness of noble metal-based catalysts such as Ru/C and RuRe/C for the HDO of lignin model compounds (e.g., phenol, guaiacol) are demonstrated, HDO studies with real pyrolysis oil are relatively unexplored [2-3]. Due to its complex composition and mineral impurities such as sulfur, the activity and stability of the catalysts for the HDO of pyrolysis oil would be significantly different from those for the model compounds. In this work, the HDO of pyrolysis-oils derived from kraft lignin using ruthenium-based catalysts (i.e., bimetallic RuRe/C) was studied in a continuous flow trickle bed reactor system. The effects of reaction temperature and space velocity were investigated, and a detailed analysis of the reaction products were performed to understand the fundamental reaction chemistry. The spent RuRe/C catalysts were also characterized by using X-ray photoelectron spectroscopy, high-resolution TEM, chemisorption, and ICP analyses to elucidate the main cause of catalyst deactivation.

2. Methods

Pyrolysis oil was obtained from fast pyrolysis of kraft lignin at 500 °C in a bench-scale fixed bed reactor. Bimetallic RuRe catalysts with 4 wt% Ru and 3.64 wt% Re content were prepared by successive impregnation of dried Ru/C with an aqueous solution of NH_4ReO_4. This metal loading was corresponded to an atomic Ru : Re ratio of 1 : 0.5, which was found to be the optimal composition of the RuRe catalyst in our previous study [2]. The HDO of lignin pyrolysis oil was performed in a fixed bed reactor, and the size of the reactor tube was 18 mm ID and 14 cm in length. The powder catalyst was supported by a double metal filter (0.5 ㎛ pore size) installed at the bottom of the reactor. For a typical run, a reactor was loaded with a RuRe/C catalyst of 4−8 g and treated with hydrogen at 350 °C for 2 h. The reactor were then cooled down to the desired reaction temperatures. The system was then slowly pressurized to 100 bar and the pyrolysis-oil/tetrahydrofuran mixture (50:50 vol%) was fed to the reactor with H_2. A typical reaction lasted for 6−8 h.

3. Results and discussion

The yield of liquid product and the degree of deoxygenation of pyrolysis-oil were strongly dependent on the reaction temperature and weight hourly space velocity (WHSV). At 300 °C, the liquid yield was very low, and the majority of carbon was deposited on the surface of the catalyst, indicating that strong adsorption of phenolics on active sites makes catalyst deactivation more severe at lower reaction temperature. In contrast, at 350 °C or above, the liquid products were biphasic mixtures composed of an organic phase and aqueous phase, and the organic phase primarily consisted of cyclic alkanes (naphthenes) ranging from C6 to C20 as evidenced by GCxGC-MS and 2D-HSQC NMR analyses of the organic phase. Although higher temperature (i.e, 400 °C) leaded to an enhanced deoxygenation of pyrolysis-oils (i.e., lower O/C ratio), the organic phase yield decreased due to the cracking of oils to light gases (C2-C6). Low WHSV (<0.2 h^{-1}) was also crucial to achieve a high degree of deoxygenation of pyrolysis-oil and prolong the catalyst lifetime. Catalyst deactivation and reactor plugging by tar formation were observed at high WHSV (~ 1.0 h^{-1}) even after ~ 6 TOF. The characterization of spent RuRe/C catalysts with ICP and HR-TEM revealed the existence of sulfur species on the catalyst surface due to the high sulfur impurities in the lignin oil, which can result in the catalyst deactivation. However, XPS analysis indicated that there were no RuS_x and ReS_x phases in the catalysts. These results suggests that sulfur species are adsorbed mainly on the carbon support and are not the cause of deactivation. Meanwhile, TGA analysis indicated the presence of high amount of soft coke on the spent catalyst. However, this coke was readily removable by washing with acetone, suggesting that the majority of the coke formed can be strongly adsorbed phenolic reactants, occupying the surface sites.

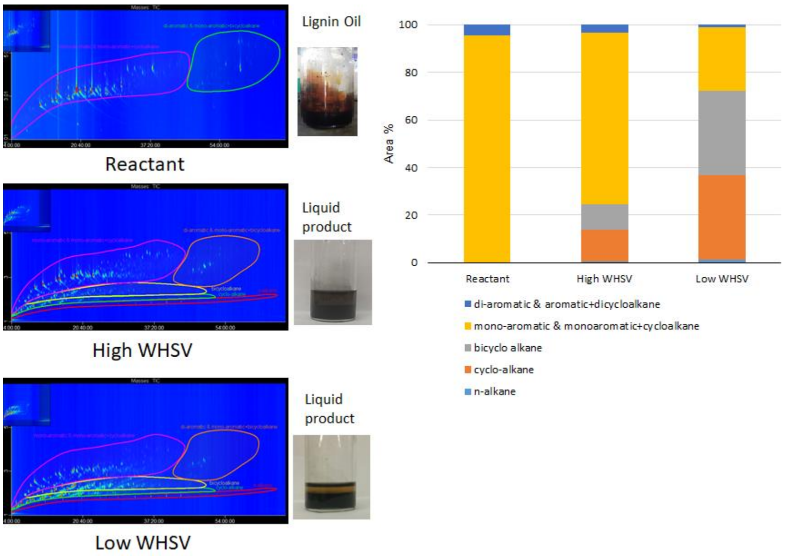

Figure 1. GCxGC-MS analysis of liquid products obtained from HDO of lignin oils at different WHSV.

4. Conclusions

In conclusion, we studied the hydrodeoxygenation (HDO) of lignin pyrolysis oil into liquid hydrocarbon fuels using RuRe/C catalysts in a continuous flow reactor. The HDO activity and stability of RuRe/C catalysts were largely dependent on the reaction temperature and weight hourly space velocity (WHSV). Medium temperature (350 °C) and low WHSV (0.2 h^{-1}) exhibited the higher yield of deoxygenated hydrocarbons and the longer catalyst lifetime (> 10 TOS). The formation of soft coke was the main cause of catalyst deactivation rather than sulfur poisoning.

References

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Keywords
Hydrodeoxygenation, Lignin, Pyrolysis, Noble metals