

Noble metal catalysts for the upgrading of wood-based pyrolysis oil

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Introduction

The liquid fraction (pyrolysis oil, PO) obtained by the pyrolysis of biomass can be used to produce transportation fuels and chemicals. Wood-based PO is a complex mixture of oxygen-containing compounds. The high concentration of these oxygenates negatively affects the product properties. Upgrading is therefore required to partially or completely remove oxygenates before applications and/or further processing. Hydrodeoxygenation (HDO) is an attractive method for the upgrading of PO. This process is carried out at high H₂ pressures and temperatures, and in the presence of a catalyst. HDO is conventionally performed on sulfided catalysts such as Al₂O₃-supported NiMo and CoMo. Sulfur leaching from the catalysts and the high tendency towards coke formation are the drawbacks of using these conventional catalysts [1]. Reduced ZrO₂-supported mono- and bimetallic Rh, Pt, and Pd (0.5 wt% total metal loading) catalysts have previously [1] been found to be active and selective in the HDO of 2-methoxyphenol (guaiacol, GUA), used as a model component for wood-based PO. It was shown that the HDO of GUA gave lower carbon deposition with the noble metal catalysts than with the sulfided catalyst (CoMo/Al₂O₃). The aim of this work was to study these catalysts in the HDO of wood-based PO.

Materials and Methods

Mono- and bimetallic Rh, Pd and Pt catalysts [1] were tested in a batch reactor at 350 °C and 20 MPa for 4 h. The catalysts were pretreated in-situ before testing. After the experiments, the reactor was cooled down to room temperature and gas and liquid samples were taken. The gas samples were analyzed by gas chromatography (GC). The liquid samples were centrifuged to separate the organic, aqueous, and solid phases. The liquid phases were analyzed by GC and GC-MS, ¹H-NMR, GPC and 2D-GC. The fresh and used catalysts were characterized using chemi- and physisorption, Raman spectroscopy and temperature-programmed oxidation (TPO).

Results and Discussion

The noble metal catalysts were active in the HDO of wood-based PO at 350 °C. The oxygen content of the PO decreased from 51 wt% to values from 7 to 11 wt% (Table 1). Similar concentrations of oxygenates (~ 5 wt%) have been reported with commercial Al₂O₃-supported CoMo and NiMo catalysts in the sulfided form [2]. The O/C molar ratio of the product mixture decreased from 0.6 mol/mol to values close to 0.1 mol/mol. This is in agreement with the decrease in the total concentration of the oxygenated groups detected in the ¹H-NMR measurements. The H/C molar ratio decreased from 1.5 mol/mol to values close to 1 mol/mol with all the catalysts indicating the presence of unsaturated cyclic and aliphatic

compounds. Thus, the degree of hydrogenation was limited at 350 °C, probably because of thermodynamics as calculated for GUA [1].

Table 1. Main properties of PO and upgraded oils.

	PO	ZrO ₂ -supported catalyst					
		Rh	RhPd	RhPt	Pd	PdPt	Pt
Oxygen (mol%, dry)	51.2	7.9	9.3	9.9	9.0	11.3	7.1

Based on the TPO results for the used catalysts, the carbon deposition was from 4 to 8 wt%. The TPO results also demonstrated that temperatures higher than 300 °C are needed to burn the carbon deposited on the catalysts as shown in Figure 1 for the ZrO₂-supported Rh, Pt, Pd, and PdPt catalysts.

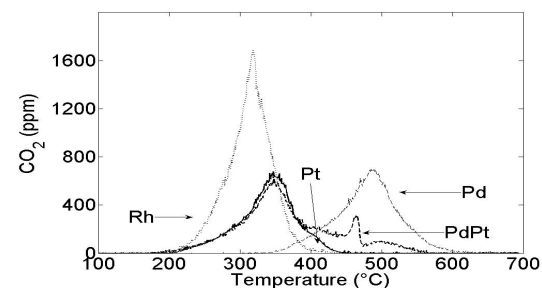


Figure 1. TPO (temperature ramp 5 °C/min) results for the ZrO₂-supported Rh, Pt, Pd and PdPt catalysts after testing in the HDO of PO (350 °C, 20 MPa, 4h).

Raman characterization of the catalysts used in the HDO of PO showed one peak at 1580 cm⁻¹ indicating the presence of graphitic coke and a second peak at 1350 cm⁻¹ attributed to polycrystalline and imperfect graphite and other types of carbon. Graphitic coke is known to block the active sites deactivating the catalyst [3].

Significance

Chemical and physical stability of wood-based PO are expected to improve after the upgrading allowing the oils to be co-fed into existing refinery units. Based on the results presented, noble metal catalysts can be used to replace the conventional sulfided Al₂O₃-supported CoMo and NiMo and thus the contamination of the products with sulfur can be avoided. Also, the carbon deposition is expected to be less with the noble metal than with the sulfided catalysts. The TPO results demonstrated that the coke can be burn at temperatures higher than 300 °C.

References

1. A. Gutierrez, R.K. Kaila, M.L. Honkela, R. Slioor, A.O.I. Krause, *Catal. Today*, (2008), accepted for publication.
2. D.C. Elliott, *Energy Fuels* 21, 1792 (2007).
3. M. Guisnet, P. Magnoux, *Appl. Catal. A*, 212, 83 (2001).