

Hydrodeoxygenation of guaiacol as model compound for pyrolysis oil on noble metal catalysts

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Abstract: *Pyrolysis oils are an alternative to fossil fuels. The high content of oxygenated compounds makes them thermal and chemically unstable thus, the removal is required. Zirconia-supported mono- and bimetallic Rh and Pt catalysts were tested in hydrodeoxygenation reactions. Tests performed using guaiacol (2-methoxyphenol) as model compound showed that, e.g. the monometallic Rh catalyst was more active than the sulfided CoMo/Al₂O₃ at temperatures lower than 300 °C. The presence of oxygenated compounds indicated that temperatures higher than 300 °C are needed in hydrodeoxygenation. The carbon deposition was lowest on the noble metal catalysts. Noble metal catalysts are a promising alternative to sulfided catalysts.*

Keywords: hydrodeoxygenation, guaiacol, noble metal catalysts.

1. Introduction

Alternative feed stocks for fuels and chemicals are widely investigated due to the imminent depletion of fossil fuels and the increasing concern in environmental protection [1]. The thermal breakdown of the biomass transforms it into liquids (pyrolysis oils) [2]. The energy density of these liquids is higher than biomass, they are CO₂ neutral, and their use does not generate SO_x emissions as the sulfur content of biomass is often negligible [2]. Pyrolysis oils are complex mixtures of chemicals and water [2-4]. The high concentration of oxygenated compounds (close to 40%) makes them thermally and chemically unstable [3,4] and the total or partial elimination of oxygenates is required [3,5,6]. Hydrodeoxygenation (HDO) is an alternative for upgrading of pyrolysis oils [3]. Sulfided CoMo and NiMo catalysts are used in upgrading reactions but they have the disadvantage of sulfur stripping causing the deactivation of the catalyst and the contamination of the products [7]. Furthermore, sulfided catalysts are deactivated due to coke deposition [7]. Therefore, there is a need for more suitable catalysts. Noble metal catalysts are an alternative to sulfided catalysts in upgrading reactions [8]. In this work, guaiacol (GUA) was selected as the model compound for wood-based pyrolysis oils. The performance of ZrO₂-supported noble metal catalysts was compared to that of sulfided CoMo/Al₂O₃.

2. Experimental

Zirconia-supported mono- and bimetallic Rh and Pt catalysts were prepared by dry impregnation. The total metal loading of the catalysts was 0.5 wt-%. The experiments were performed in a 40 ml stainless steel batch reactor heated in a sand bath (100 – 350 °C). The catalysts were pretreated in situ. The drying was performed in air (1 MPa) at 350 °C during 1 h. After this, the noble metal catalysts were reduced in H₂ and the CoMo catalyst was sulfided with 5 vol-% H₂S in H₂. The conditions used for both procedures were 1

MPa, 350 °C, and 1 h. After the pretreatment procedure a solution of 3 wt-% GUA in n-hexadecane was charged to the reactor and the pressure was increased with H₂. Liquid samples were taken after 3 h and they were analyzed with GC and GC-MS. The carbon and sulfur content of the catalysts were measured using a LECO elemental analysis instrument.

3. Results and discussion

At low temperatures, the conversion of GUA was higher with Rh/ZrO₂ than with zirconia-support Pt and RhPt and the sulfided catalyst (Figure 1, A). Complete conversion of GUA was reached after 3 h with Rh/ZrO₂ and CoMo/Al₂O₃ at 8 MPa total pressure and temperatures higher than 200 and 300 °C, respectively, but it was not achieved with Pt/ZrO₂ and with the RhPt/ZrO₂. After 3 h at 300 °C, the main product with the Rh/ZrO₂ was benzene while on the sulfided catalyst a mixture of benzene, phenol, and cyclohexanol was obtained further indicating its lower activity (Figure 1, B). Longer reactions times or temperatures higher than 300 °C could be required with the Pt/ZrO₂ and RhPt/ZrO₂ catalysts to obtain complete conversion of GUA. At low temperatures, the oxygenated reaction intermediates were different with the Rh/ZrO₂ and with the sulfided catalyst suggesting differences in the reaction pathways. Furthermore, the carbon deposition was lowest on the monometallic Rh/ZrO₂ catalyst (0.6 wt-%) and highest (9.7 wt-%) on the CoMo/Al₂O₃.

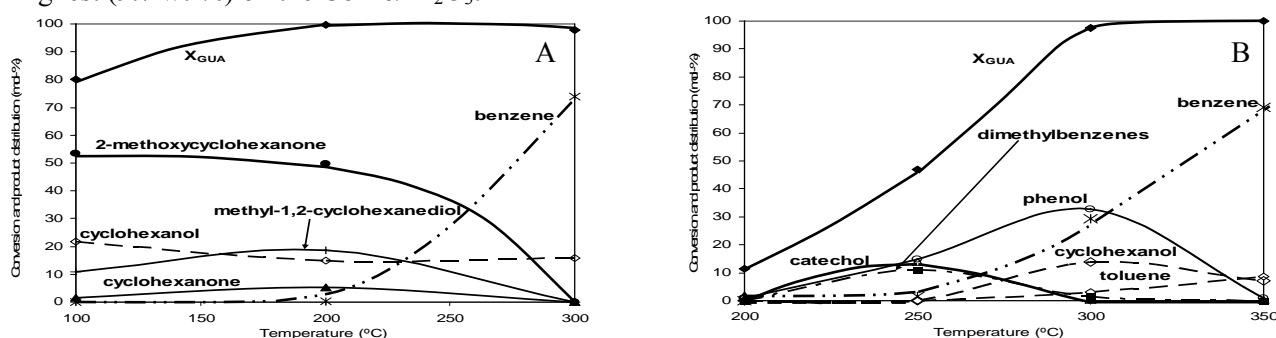


Figure 1. Conversion and product distribution as a function of temperature. A) Rh/ZrO₂ catalysts. B) CoMo/Al₂O₃.

4. Conclusions

Noble metal catalysts have potential in upgrading reactions. However, even though with the most active catalyst (Rh/ZrO₂) high temperatures are needed to achieve the removal of oxygenates. The different intermediates at low temperatures with the noble metal and sulfided catalysts are an indication that HDO proceeds via different intermediates.

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