Catalytic Hydrodeoxygenation of 4-Methyl-1,2-Benzenediol over Supported Metal Catalysts

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Introduction
The next-generation biofuels will be derived from non-edible sources, possibly via conversion to bio-oils using pyrolysis reactors. As produced, these bio-oils are thermally unstable and they need to be upgraded in order to reduce their oxygen content and be stabilized. Conventional hydrotreating catalysts, sulphided Co-Mo and Ni-Mo supported on alumina, have been commonly investigated for hydrodeoxygenation (HDO) of biomass-derived liquids [1]. Different metal catalysts including nickel and noble metals have also been studied in HDO of model compounds typical of bio-oils [2-3]. For low-sulphur biomass-derived liquids, these metal catalysts can be attractive because the presulphiding step is eliminated and that no minimum S level is required in the feed in order to maintain catalyst activity.

Model compounds found in bio-oils such as phenol, 4-methylphenol, 4-methoxyphenol, methoxybenzene (anisole) and 2-methoxyphenol (guaiacol) have been used to investigate the hydrodeoxygenation reactions and identify promising catalysts [1, 2-4]. However, the HDO of 4-methyl-1,2-benzenediol was not systematically studied although it has been identified as one of the most abundant compounds in bio-oils [5]. The effects of catalyst composition, reaction temperature, H₂ pressure, reaction time and initial hydrogen to oxygen molar feed ratio were examined in terms of conversion and product yields.

Materials and Methods
The catalytic hydrodeoxygenation of 4-methyl-1,2-benzenediol [CH₃C₆H₄(OH)₂] was investigated in a 300-mL semi-batch autoclave using a variety of supported platinum, nickel and nickel-molybdenum catalysts. The Pt and Ni catalysts were prepared by incipient wetness impregnation of a commercial γ-Al₂O₃ support (crushed to 60-100 mesh size). Their performance for hydrodeoxygenation was evaluated using a blend of 10 wt% CH₃C₆H₄(OH)₂ in hexadecane (reaction medium/diluent). A commercial Ni-Mo/γ-Al₂O₃ catalyst (60-100 mesh size) was also tested. We characterized the liquid products by GC-MS and GC-FID to determine the alkylenynes (C₁-C₅ aromatics), the cyclopentane ring C₅ aromatics, the light oxygenates and the compounds heavier than trimethylphenols.

Results and Discussion
Sulphided Ni-Mo/γ-Al₂O₃ and 2.44%Pt/γ-Al₂O₃ catalysts showed excellent HDO activity at 380°C, 1600 psig and 4 h in terms of low yields of undesired products (light oxygenates and heavy compounds) and high yields of desired products (aromatic and cyclopentane ring hydrocarbons). In general, Pt catalysts (2.44 and 1.06 wt% Pt) generated more than 61 g hydrocarbons/100 g CH₃C₆H₄(OH)₂. The simplified HDO reaction pathway of 4-methylbenzenediol with sulphided Ni-Mo/γ-Al₂O₃.

Figure 1. HDO reaction pathway of 4-methylbenzenediol with sulphided Ni-Mo/γ-Al₂O₃.

Significance
This work contributes to identify promising HDO catalysts for the upgrading of biomass-derived feedstocks to hydrocarbon biofuels as well as desired operating conditions.

References