Guaiacol transformation over unsupported molybdenum-based nitride catalysts

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ABSTRACT

Unsupported Mo_2N catalysts were prepared by thermal decomposition of ammonium heptamolybdate to form MoO_3 followed by nitridation in either flowing ammonia or a N_2/H_2 mixture. The nitridation was achieved at two different space velocities for each reaction mixture. This resulted in Mo_2N catalysts with different surface areas as well as different phases present as were determined by X-ray diffraction (XRD). The activity and selectivity of the catalysts were evaluated for hydrodeoxygenation (HDO) of guaiacol in a batch autoclave at $300\,°C$ and 5 MPa hydrogen pressure. The catalyst prepared with flowing ammonia and a space velocity of $29\,h^{-1}$ displayed the highest activity (guaiacol conversion) and highest phenol/catechol ratio within the products indicative of HDO activity. This highest activity was attributed to the catalyst containing only γ-Mo_2N phase (as measured by XRD) and having the highest N/Mo atomic ratio. An initial attempt to promote this catalyst with Co, similar to that done for hydrodesulfurization and hydrodenitrogenation catalysts was unsuccessful in forming a single phase cobalt molybdenum nitride, however did show modest improvements in the production of deoxygenated compounds, and suggests further studies into this material for HDO catalysis.

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1. Introduction

Legislations stipulating increases in the production of fuels, chemicals and energy from renewable resources such as biomass have been passed by the United States and the European Union, owing to issues related to increases in total energy consumption, depletion of fossil fuels, and environmental concerns [1–3]. For that reason, processes for the transformation of biomass into fuels and value-added chemicals are being extensively investigated by researchers worldwide. Catalytic hydrodeoxygenation (HDO) is an important reaction, which partially or completely removes oxygenates from biomass-derived oil, or pyrolysis oil, in order to improve its fungibility as a fuel. For this reason, several HDO studies of model oxygenates observed in pyrolysis oils have been conducted to gain valuable insights into reaction mechanisms of different functional groups present in bio-oil, as well as the development of improved catalysts and processes.

Most HDO studies have been conducted over classical sulfided catalysts originally developed for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions in petroleum refining processes. Despite the high activity of these catalysts for HDO of model compounds such as guaiacol, they require the addition of sulfur to the feed to prolong the catalyst lifetime, which leads to contamination of products. Another principal disadvantage of sulfided catalysts is the high level of hydrogen consumption due to the consecutive transformation of guaiacol to catechol and to phenol. These limitations have led to the study of new active phases, which will eliminate the necessity to add a sulfur source to the feed, potentially consume less hydrogen, and lower the formation of coke by permitting the rapid conversion of guaiacol into phenol. Transition metal nitrides [4] and phosphides [5] have been identified as phases that show promising activities for HDO of guaiacol.

Bulk transition metal nitrides prepared from the temperature-programmed reaction of a metal oxide precursor and NH_3 [6] or N_2/H_2 mixtures [7] have compared favorably to traditional catalysts for HDS and HDN reactions [8–10]. However, only very few studies have been reported demonstrating the performance of bulk metal nitrides for HDO catalysis [11,12]. In those previous