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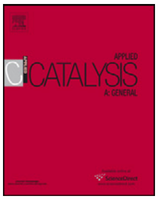

Comparison of alumina- and SBA-15-supported molybdenum nitride catalysts for hydrodeoxygenation of guaiacol

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ABSTRACT

The hydrodeoxygenation of guaiacol (2-methoxyphenol) has been studied in a batch reactor over alumina- and SBA-15 silica-supported molybdenum nitride catalysts at 300 °C and 5 MPa of hydrogen pressure. The catalysts were prepared by nitriding supported Mo oxide precursors with ammonia gas or nitrogen–hydrogen mixtures via temperature-programmed reaction. The alumina-supported catalysts had a higher activity relative to the SBA-15 silica-supported catalysts which was essentially due to catechol production, an effect of the alumina support. The SBA-15 silica-supported catalysts transformed guaiacol directly to phenol by demethoxylation without noticeable catechol production. On both supports, nitridation by ammonolysis increased the activity by a factor of ∼1.1 relative to nitridation by nitrogen–hydrogen. On SBA-15, ammonolysis preferentially produced the γ-Mo_2N phase while the N_2/H_2 mixture produced the β-$Mo_2N_{0.78}$ phase. The incorporation of Co led to a marginal improvement in exposed Mo species but generally had a diminishing effect on HDO activity. The lack of catechol production using the SBA-15 silica support is important in minimizing coking reactions and also opens up possibilities for utilizing silica supports with highly controlled pore sizes to possibly influence product distribution in HDO of more diverse feed streams derived from biomass conversion processes.

1. Introduction

The removal of oxygen from biomass-derived oils through catalytic hydrodeoxygenation (HDO) is receiving considerable attention because of its potential as feedstock for the production of fuels and value-added chemicals. Most of the initial studies on HDO reactions have been conducted over metal sulfides supported on alumina [1,2]. However, recently there have been significant efforts on the development of catalysts, based on new or modified supports and new active phases, with minimal hydrogen consumption and high selectivity toward direct oxygen removal [1]. Guaiacol (2-methoxyphenol) has commonly been used as a model compound for the HDO studies because it is known to exist significantly in bio-oils, because of its propensity for coke formation, and also because of its intransigence to deoxygenation [2]. Several of the studies have reported that the HDO activity and selective transformation of guaiacol to phenol is distinctively influenced by the nature of the support [3,4]. Catalysts supported on alumina (Al_2O_3) displayed higher activity compared with alternative supports such as silica and carbon owing to higher dispersion of the active phase [3]. However, alumina-supported catalysts suffer from coke formation which limits the lifetime of the catalyst [3]. The benefits of using silica and carbon supports lie in the minimal coke formation and greater selectivity toward phenol production over catechol [3].

Interests in exploring non-sulfided catalysts for HDO have increased due to issues related to contamination of the feed by the sulfiding agent [5,6]. Novel active phases such as metal nitrides have been shown to be an effective catalyst for HDS [7] and HDN [8] reactions. However, only a limited number of studies have reported their performance for HDO reactions. Recently, Monnier et al. [9] reported activity on γ-Al_2O_3-supported Mo, W, and V nitride catalysts for HDO of oleic acid and canola oil. In a recent study, we demonstrated high activity and rapid demethoxylation of guaiacol

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