

Novel class of molybdenum carbide catalysts for bio-oil upgrading

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Introduction

A very important focus of the current research in chemistry and engineering is the development of a clean alternative technology that utilizes a sustainable feedstock and transforms it into fuel. In this respect, the use of biomass as a renewable source of carbon is a promising alternative and the fast pyrolysis is an efficient and inexpensive primary route to produce liquids from lignocellulosic biomass. However the produced liquids are not suitable for direct application in internal combustion engines due to high oxygen (35-40 wt%, dry basis) and water content (15-30 wt%) [1]. The quality of bio-oils can be improved by eliminating oxygenated functionalities, and hydroprocessing is a well-established and widely employed in the current petroleum refineries. The challenge is to be able to utilize the current petroleum refining catalysts under bio-oil conditions. For instance, the active sulfide catalysts (e.g., supported CoMo, NiMo sulfides) [2] utilized in petroleum refinery are not stable under low-sulfur content of the bio-oils. Precious metals such as Ru appear to be more robust and active [3], but cost reduction and improved catalyst selectivity are significant technical challenges. In this work, we investigate molybdenum carbides as catalysts in bio-oil hydroprocessing since it has a noble metal behavior [3] without the scarcity and cost issues related to noble metals. More specifically, we report a novel synthetic method aimed to improve molybdenum carbide stability and performance in the harsh bio-oil reaction conditions. The performance and stability of the carbide catalysts were evaluated and compared to a commercial Ru/C catalyst. The results were promising suggesting that it is possible to design robust and active catalysts for bio-oil hydroprocessing using inexpensive carbides.

Materials and Methods

High-surface area Mo₂C doped with either Ni or Cu were prepared from oxide beads using a classical temperature-programmed method [4]. The novelty derives from the precursor material, sturdy porous oxide beads synthesized using a gelling method [5] in which, first, a catalyst slurry is formed from a suspension of MoO₃ powder in a solution of sodium alginate. Then, the catalyst slurry is dropped in an aqueous solution including nickel chloride, or copper chloride to form a doped oxide bead. The oxide bead is separated from the aqueous solution, rinsed, and dried. After carburization, the doped Mo₂C beads were compared with Mo₂C prepared from Mo oxide powder and commercial Ru/C. Their stability in water (hydrothermal aging) was tested in a batch reactor with distilled water at 250°C for 24-48 h. The catalysts were also characterized using X-ray diffraction, surface area measurements, CO chemisorption, and microscopic imaging to determine morphology and surface composition and structures before and after catalytic performance evaluation. Hydroprocessing was done in a mechanically stirred 300 mL stainless-steel batch reactor. The catalyst was reduced in situ at 250°C in H₂ for 2 h. Hydroprocessing was done with a model bio-oil (5% acetic acid, 5% furfural, 5% guaiacol, water balance) at 250 °C and a total pressure of 1740 psi. After a 4-h

run, the reactor was cooled to room temperature and its solid and liquid contents were collected and separated. Liquid samples were analyzed using a CE and a GC-MS.

Results and Discussion

The kinetics of MoO₃ carburization was affected by the presence and nature of the metal promoter. As expected, shift of the temperature at which O-removal and C-insertion occur affected the final surface area and particle size, although Mo₂C phase was formed in every case. The catalytic behavior (Figure 1) shows that all the samples were equally active for the conversion of furfural. It is noteworthy that catalyst coking was limited (results not shown); ineffective catalysts are known to suffer significant coking due to faster thermal reaction of furfural. Although the carbides were less active for the conversion of acetic acid and guaiacol, they were more selective towards the formation of unsaturated products whereas Ru/C produced fully hydrogenated molecules. Selectivity towards unsaturated products is an advantage in hydroprocessing due to limitations for hydrogen consumption. Additionally, the activity of the promoted Mo₂C beads was generally superior to the traditionally synthesized carbides, indicating the potential of utilizing novel synthetic routes that can yield to highly active molybdenum carbides. In this presentation, we will discuss the influence of hydrothermal environments on carbide structures and implication on performance as well.

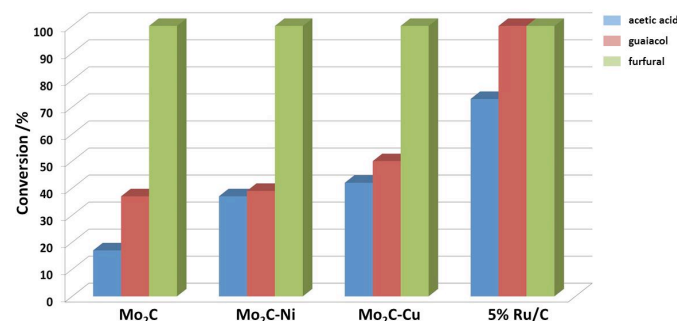


Figure 1. Catalytic activities in the conversion of the model bio-oil (comparison done on a similar number of active sites basis)

Significance

There is a great need of developing novel and robust catalysts for bio-oil upgrading that are effective and inexpensive. Our novel synthetic route yielded doped molybdenum carbides that are active for the model bio-oil hydroprocessing and more robust for the harsh bio-oil environment than traditionally synthesized molybdenum carbides.

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