

ENHANCED REACTION STABILITY OF METAL-MODIFIED ZSM-5 FOR UPGRADING OF BIOMASS PYROLYSIS VAPORS

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Abstract

A ZSM-5 zeolite was impregnated with metals (Ni, Pt, Cu, Co, and Ga) selected for their ability to assist in hydrogen transfer reactions. The catalysts were tested for biomass pyrolysis vapor upgrading at 500°C in H₂ and inert to determine how the production of hydrocarbons and destruction of oxygenates was affected. The most promising of the metal-impregnated materials was found to be Ni/ZSM-5, due to its high yield of aromatics, high deoxygenation activity (>10% reduction in oxygenates), low coke formation (50% reduction in coke), and stability relative to ZSM-5. Characterization of fresh and spent catalysts, and studies on reaction/pretreatment procedures indicate that the presence of metallic Ni increases the methane production rate through hydrogenation of surface alkyl groups, which decreases the rate of ZSM-5 deactivation by coking and maintains pore and acid site accessibility. Additionally, if nickel was initially present as NiO, the pyrolysis vapors led to an *in situ* reduction to form Ni. Promising catalysts (Ni/ZSM-5, Ga/ZSM-5, and ZSM-5) were also evaluated at on three reaction systems spanning a 100,000x scale (10 mg, 500 mg, and 1 kg) and the correlations across the three scales are discussed.

Keywords

Biomass, Pyrolysis, Vapor phase upgrading, ZSM-5, Catalytic deoxygenation, Multi-scale reactions

Introduction

One of the essential requirements in developing a low-cost thermochemical process for converting raw biomass into usable hydrocarbon-based chemicals and fuels is an efficient and stable catalyst technology. This requirement arises due to the poor quality of pyrolysis bio-oil, which predominantly consists of oxygenated organic compounds (Talmadge et. al., 2014).

To this end, various types of microporous zeolites (ZSM-5, beta, mordenite, Y) and mesoporous materials (MCM-41, SBA-15) have been investigated for upgrading biomass vapors and oils (Stöcker, 2008). Acid zeolites, and ZSM-5 in particular, have received much attention for biomass pyrolysis VPU due to their ability to simultaneously reduce the amounts of oxygenated species

and produce organic, aromatic compounds that could be used for transportation fuels (Mukarakate et. al., 2014). Because of the rapid deactivation of ZSM-5, studies looking at the incorporation of metals for their added hydrogen transfer reactions and oxygen rejection have shown that Cu, Ga, and Ni promoted ZSM-5 could lead to reduced coking and improved hydrocarbon yields as compared to ZSM-5 (French and Czernik, 2010). In this study, we have prepared ZSM-5 impregnated with Ni, Pt, Cu, Co and Ga in order to evaluate their reactivity towards hydrocarbon production, oxygen rejection, and stability during the catalytic upgrading of biomass pyrolysis vapors.

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Experimental

Catalyst Synthesis

The base catalyst used in this study was a ZSM-5 zeolite with a SiO₂-to-Al₂O₃ ratio of 30. The metal-promoted catalysts were prepared by incipient wetness impregnation of an aqueous solution containing the metal precursor (Ni, Pt, Cu, Co, or Ga). An equal molar quantity of metal was added to each catalyst, corresponding to (1 mol metal)/(2 mol aluminum). Following impregnation, the catalysts were calcined at 550°C for 3 hours in air.

Pine Pyrolysis Vapor Upgrading Reactions

The metal catalysts were evaluated for biomass pyrolysis vapor phase upgrading at 500°C in 33% H₂ and inert environments by pyrolyzing 14 consecutive 35 mg pine boats over 500 mg of catalyst. The vapors were analyzed with a molecular beam mass spectrometer.

Results and Discussion

Figure 1 compares the aromatic hydrocarbon production and oxygenate breakthrough of ZSM-5 with Ni/ZSM-5 and NiO/ZSM-5. The presence of both Ni and NiO led to enhanced stability (corresponding to enhanced aromatic production and decreased oxygenate formation). These findings were also consistent with characterization results that showed a decrease in coke formation, higher maintained surface area (especially microporosity), and higher maintained acidity when Ni was present on the ZSM-5. The catalyst improvements were most pronounced for the Ni-modified zeolite, but similar findings were observed for those modified with Pt, Co, Cu, and Ga. The enhanced stability is attributed to hydrogen activation, which leads to the hydrogenation of surface alkyl groups, thereby reducing coke deposits. Characterization by XRD indicates that an *in situ* reduction of NiO to Ni results in the same active phase at the end of the reaction, thereby eliminating the necessity of a pre-reduction of the Ni catalyst.

Conclusions

Metal-modified ZSM-5 catalysts were evaluated for pine pyrolysis vapor phase upgrading. In general, the presence of the metals aided in H transfer reactions, which resulted in decreased coking, decreased oxygenate breakthrough, and enhanced stability/lifetime (relative to ZSM-5). These findings were attributed to increased ability to hydrogenate surface alkyl groups, thereby reducing the deposition of carbon which leads to coke and catalyst deactivation. The catalysts were scaled-up and evaluated at larger (1 kg) scales and the results were consistent with the bench-scale studies.

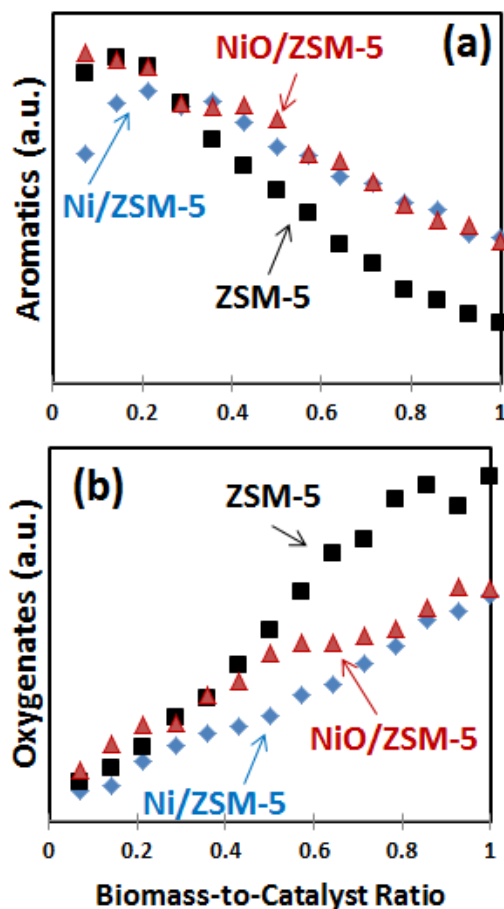


Figure 1. Production of (a) aromatic hydrocarbons and (b) oxygenates during upgrading of pine pyrolysis vapors over (■) ZSM-5, (◆) Ni/ZSM-5, and (▲) NiO/ZSM-5.

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