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Catalytic conversion of syngas to mixed alcohols over Zn-Mn promoted Cu-Fe based catalyst

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ABSTRACT

Zn-Mn promoted Cu-Fe based catalyst was synthesized by the co-precipitation method. Mixed alcohols synthesis from syngas was studied in a half-inch tubular reactor system after the catalyst was reduced. Zn-Mn promoted Cu-Fe based catalyst was characterized by SEM-EDS, TEM, XRD, and XPS. The liquid phase products (alcohol phase and hydrocarbon phase) were analyzed by GC–MS and the gas phase products were analyzed by GC. The results showed that Zn-Mn promoted Cu-Fe based catalyst had high catalytic activity and high alcohol selectivity. The maximal CO conversion rate was 72%, and the yield of alcohol and hydrocarbons were also very high. Cu (1 1 1) was the active site for mixed alcohols synthesis, Fe_2C (1 0 1) was the active site for olefin and paraffin synthesis. The reaction mechanism of mixed alcohols synthesis from syngas over Zn-Mn promoted Cu-Fe based catalyst was proposed. Zn-Mn promoted Cu-Fe based catalyst can be regarded as a potential candidate for catalytic conversion of biomass-derived syngas to mixed alcohols.

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1. Introduction

The world today largely relies on fossil fuel for energy demand. The petroleum energy sources are finite and will be depleted one day. Currently, several important problems need to be resolved worldwide, such as high need for energy, high depletion of non-renewable energy resources, high local and global environmental pollution. Biofuels [1] (biomass-derived fuels, including gasoline, diesel, jet fuel, mixed alcohols, etc.) produced from renewable resources or lignocellulosic biomass (woodchip, switchgrass, corn stover, etc.) can be used as an alternative to fossil fuel. The utilization of biofuels can mitigate global warming, and minimize the fossil fuel burning and CO_2 production. The two main utilization options of lignocellulosic biomass to produce useful and high-value fuel products are biochemical processes (biocatalytic hydrolysis) and thermochemical processes. The thermochemical processes mainly consist of gasifying biomass through gasification technology (thermal treatment), liquefying biomass (chemocatalytic hydrolysis), and pyrolysis technology [2,3].

Mixed alcohols synthesis from syngas (synthesis gas: $CO + H_2$) or biomass-derived syngas [3] (producing from gasifier that consists of CO, H_2, CO_2, N_2, CH_4 and some small alkanes) is an important process for the production of oxygenates fuels, fuel additives and other intermediates for value-added chemical feedstock such as medicine, cosmetic, lubricants, detergents, and polyester [4,5]. There are two types of heterogeneous catalysts used for mixed alcohols synthesis from syngas [5]: noble metal-based and non-noble metal-based catalysts. The noble metal-based catalysts, mainly Rh-based catalysts [6–9], show good catalytic performance but are too expensive for commercial application. The major non-noble metal-based catalysts available for mixed alcohols synthesis from syngas include Cu-based catalysts and Mo-based catalysts. Mo-based catalysts (MoS_2, Mo_2C, etc.) [10–12] are sulfur resistant and less sensitive to CO_2, but these catalysts must be carried out at high pressures and temperatures. Above all, Cu-based catalysts containing metal active toward Fischer–Tropsch synthesis (Fe, Co), such as Cu-Fe [4,13] or Cu-Co [14–18] based catalysts, are considered as the most promising catalysts for mixed alcohols synthesis from syngas. However, Cu-Co based catalyst is not available for large-scale industrial application due to the poor stabilization with long-term run and the low total alcohol selectivity [5]. Cu-Fe based catalyst can be regarded as one of the potential candidate catalysts for mixed alcohols synthesis via catalytic conversion of biomass-derived syngas. Lin et al. [4] found that in co-precipitated Cu-Fe catalysts, zinc could be used as electrical/chemical promoter, and manganese could be used as structural promoter. Lin et al. [4] also observed that there

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