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Rh-Mn/tungsten carbides for direct synthesis of mixed alcohols from syngas: Effects of tungsten carbide phases

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ABSTRACT

Effects of the crystalline tungsten carbide (WxC) phases on an ordered mesoporous bimetallic Rh-Mn/WxC, which were prepared by changing carbon source to tungsten (C/W) ratios of the WxC support using a hard-template of an ordered mesoporous SBA-15, were investigated for a direct synthesis of mixed alcohols by CO hydrogenation from syngas. The C/W ratios on the mesoporous Rh-Mn/WxC showed a significantly different catalytic activity, especially on the C_1 - C_3 alcohol productivity. The Rh-Mn/WxC prepared at C/W molar ratio of 10 having a metastable W_2C main phase (Rh-Mn/WxC(10)) revealed a higher CO conversion of 8.1% and selectivity to higher alcohols of 54.4% compared to other catalysts having a main crystalline phases of WO_3 or WC. The enhanced catalytic activity and selectivity to mixed alcohols on the Rh-Mn/WxC(10) were attributed to the largely exposed smaller active Rh nanoparticles with its stronger interactions with the metastable W_2C phases. The superior activity was originated from the intimate interactions of Rh nanoparticles with Mn promoter by maintaining proper oxidation states confirmed by surface ratios of the metallic Rh to oxidized Rh^{n+} species. The stable preservation of the ordered mesoporous structures of the W_2C phase in the amorphous carbon matrixes significantly altered the chemical states of the small Rh nanoparticles below 2 nm in size by preferentially existing on the outer surfaces of the W_2C support, which resulted in showing an enhanced productivity of higher C_1 –C_3 alcohols with 171.8 g/(kg_{cat}·h).

1. Introduction

Some efficient utilization technologies of renewable energy sources like biomass derivatives to develop environmentally benign chemical processes have been largely attracted for the productions of clean alternative fuels due to the limited reservoirs of crude oils [1]. The chemical transformation routes of syngas (mainly, CO and H_2), which can be derived from biomass gasification or reforming of many hydrocarbon sources, have a lot of potentials to produce valuable chemicals such as mixed alcohols (ethanol and butanol) or oxygenates as well as hydrocarbons by CO hydrogenation reaction. These value-added chemicals can be further used as fuel additives for an enhancement of octane or cetane number or as petrochemical intermediates as well [2–4]. Based on many previous researches related with the synthesis of mixed alcohols from syngas directly [5], the reported heterogeneous catalysts can be generally categorized such as Rh-based, Cu-based (modified methanol synthesis catalysts), modified Fischer-Tropsch synthesis (Fe-based catalysts), and Mo-based catalysts [2,5,6]. Among them, we focus on the precious novel Rh-based heterogeneous catalysts, since it has been well known to have a higher activity to form C_{2+} oxygenates such as ethanol, acetaldehyde and acetic acid from syngas selectively [2,7]. In addition, the active Rh metal nanoparticles has a potential to form various value-added products such as alcohols, hydrocarbons and oxygenates by properly adjusting reaction conditions. The Rh metal also has the proper characteristics for a selective formation of many oxygenates due to its intrinsic electronic characters in the periodic table between an easy dissociation of CO molecules on the Fe or Co metal to

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