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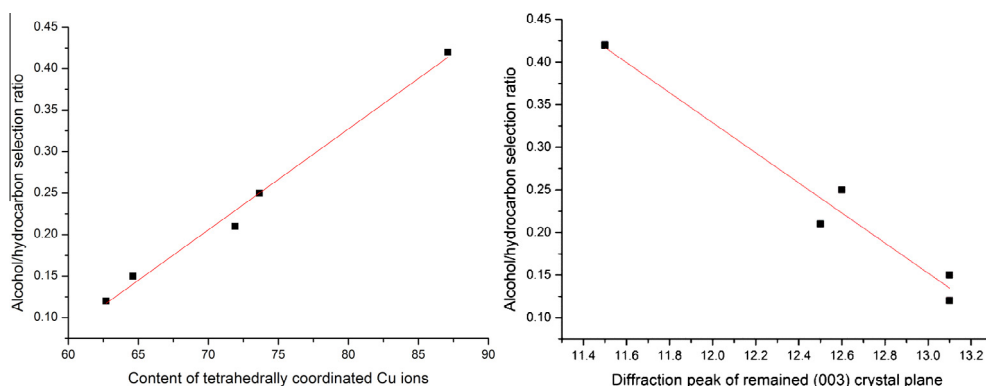
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Synthesis of higher alcohols over highly dispersed Cu–Fe based catalysts derived from layered double hydroxides

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GRAPHICAL ABSTRACT

Alcohols/hydrocarbons product ratios have a linear correlation with the contents of tetrahedrally coordinated Cu ions of the catalysts. Moreover, larger spacing of layers is favorable for the synthesis of alcohols.



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ABSTRACT

Highly dispersed Cu–Fe based catalysts with Fe/Cu molar ratios ranging from 0.2 to 1 were prepared via thermal decomposition of layered double hydroxides (LDHs) precursors and tested for higher alcohol synthesis (HAS) via CO hydrogenation. The catalysts were characterized using different techniques such as XRD, TEM, XPS, and H₂-TPR. It was demonstrated that the Cu and Fe ions were highly dispersed in the brucite-like layers of the LDHs. With increased Fe/Cu atomic ratio, the tetrahedrally coordinated Cu ion content, Cu reduction temperatures, and the spacing of layers initially increase until the Fe/Cu ratio reaches 0.5 and then decrease. In addition to the catalytic evaluation for CO hydrogenation and catalyst characterization, the relationships between the physical–chemical properties of the catalysts and their catalytic performances were also investigated. It was also found that the alcohols/hydrocarbons ratios correlate linearly with the tetrahedrally coordinated Cu ion content. Moreover, higher reduction temperatures of Cu species as well as larger spacing between the layers in the catalyst are favorable for the synthesis of alcohols. The incorporation of a suitable amount of Fe is beneficial for the production of higher alcohols, with the best catalytic performance (alcohol selectivity of 20.77% and C₂+ alcohol selectivity of 48.06%) obtained from a Fe/Cu atomic ratio of 0.5.

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1. Introduction

Fossil fuels have played an important role in the development of modern industry processes throughout the past century [1]. However, the depletion of crude oil due to increased consumption as well as the implementation of more stringent environmental regulations during recent years has led to a renewed interest in seeking out environmentally friendly alternative fuels and additives. Under these circumstances, the so-called Fischer–Tropsch (F–T) process has now become a promising solution for the synthesis of alternative liquid fuels from syngas derived from coal, natural gas, or renewable biomass. In addition to the hydrocarbons produce as the main product of the F–T reaction, by-products [2,3] such as alcohols, aldehydes, ketones, acids, esters, and other oxygenated chemicals are also produced. Out of these potential by-products, the higher alcohols (C1–C5) have a wide range of applications, including use as oxygenates for fuels, fuel additives, or intermediates for value-added chemical products such as medicines, cosmetics, lubricants, detergents, and polyesters [4]. Hence, higher alcohol synthesis (HAS) through the F–T process has become an active subject of research in the area of alternative clear fuel production [5].

Till now, various types of catalysts have been reported for use in HAS from syngas, such as alkali promoted Cu/ZnO [6–9], Cu-modified F–T catalysts [10–13], Rh-based catalysts [14,15], and Mo-based catalysts [16,17]. Among those catalytic systems available for HAS reaction, Cu-based catalysts containing active metal towards F–T synthesis (Fe, Co, or Ni), such as Cu–Fe based catalysts, are considered very promising catalysts [18,19]. According to previous studies [12,19,20], the synergistic effect between Cu and F–T elements plays an important role in HAS reactions because the production of C2+ alcohols requires a dual active site. Cu could be acting to facilitate the dissociative chemisorption of H₂ and the associative adsorption of CO, while F–T elements could induce the dissociative adsorption of CO as well as hydrogenation.

Many researchers have reported Cu–Fe based catalysts with relatively good catalytic performances through adding additives or loading active components onto supports [11,12,21]. However, the structure of these catalysts was usually amorphous or very complicated, making it difficult to elucidate the relationship between the catalytic structure and the performance of the reaction. Therefore, it would be highly useful to construct a model catalyst with regular structure in order to study the synergistic effects among the active components.

Recently, layered double hydroxides (LDHs) materials have gained wide interest for use as heterogeneous catalysts or supports due to their versatility in chemical composition and structural architecture. The Cu-containing LDHs materials have been shown to possess highly dispersed Cu ions [22,23], which implies a significant synergistic effect between Cu and Fe. In addition, the layered structure of the catalysts was retained after calcination [22]. Using multinuclear NMR spectroscopy, Grey et al. [24] further verified that the layered nature of LDHs created a homogeneous and regular structure, and also reduced negative impacts on synergistic effects through inhibiting the sintering of Cu at higher temperatures [25,26]. Moreover, the topotactic transformation of LDHs materials to metal oxides or metal–metal oxide composites could be of great significance for multi-metal catalysts. Therefore, the regular structure and the special physical chemical properties of the LDHs materials make them appropriate for use in order to study the synergistic effects between Cu and Fe in the HAS process. Herein, in this paper we designed and synthesized Cu–Fe based catalysts derived from LDHs precursors for use in the hydrogenation of CO to higher alcohols. Through the use of different characterization techniques such as N₂-physisorption, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM),

X-ray photoelectron spectroscopy (XPS), and H₂ temperature program reduction (H₂-TPR), we are able to discuss the influence of the Fe/Cu molar ratio on the LDHs structure, the relationships between the physical–chemical properties of the catalysts, and the catalytic performances of as-prepared catalysts.

2. Experimental

2.1. Catalysts preparation

Highly dispersed Cu–Fe based CF_x (*x* refers to the molar ratio of Fe/Cu: *x* = 0.2, 0.35, 0.5, 0.8, 1) catalysts were prepared according to the reported method [22] with some modifications. In a typical procedure, 1.21 g Cu(NO₃)₂·3H₂O, 0.505 g (0.707 g, 1.01 g, 1.616 g, 2.02 g) Fe(NO₃)₃·9H₂O, 12.8 g Mg(NO₃)₂·6H₂O, and 5 g Al(NO₃)₃·9H₂O [For CF1 catalyst, $n(\text{Cu}^{2+} + \text{Mg}^{2+})/n(\text{Fe}^{3+} + \text{Al}^{3+}) = 3$] were dissolved in 400 mL deionized water, referred to as solution A. Solution B was the mixture of 0.25 mol/L K₂CO₃ and 0.8 mol/L KOH. Solutions A and B were simultaneously added into a glass reactor under vigorous stirring at room temperature and a pH value of 9.5.

The slurry was then aged at 120 °C for 20 h, filtered, washed thoroughly with distilled water, and finally dried at 80 °C for 12 h. The samples with layered double structure were identified as CF_x-LDH (*x* = 0.2, 0.35, 0.5, 0.8, 1).

These CF_x-LDH precursors were then calcined at 350 °C in stationary air for 3 h and the obtained catalysts were identified as CF_x (*x* = 0.2, 0.35, 0.5, 0.8, 1). Certain amounts of the catalysts were reduced in a flow of syngas (H₂/CO ratio of 2:1, 40 mL min⁻¹) under atmospheric pressure at 573 K for 8 h. Then they were moved into a container full of fluid wax to protect the catalysts from oxygen and waited for further characterizations.

Typically, catalysts CF0 without Fe was prepared following the same procedure described above as comparison.

2.2. Characterizations

The specific surface areas and pore volumes of the samples were detected using N₂ adsorption–desorption isotherms (Micromeritics ASAP-2000). The bulk structures of the samples were measured by XRD (Rigaku D/max-RA, Cu K α radiation, $\lambda = 1.542 \text{ \AA}$). The morphologies of the samples were obtained using TEM (JEM-2010 FEF, 200 kV). XPS data were recorded on a Thermo VGESCALAB250 X-ray photoelectron spectrometer at a pressure of 2×10^{-9} Pa using an Al K α X-ray as the excitation source. H₂-TPR was carried out in a quartz reactor at atmospheric pressure. 0.03 g of the sample was loaded into the center of a reactor tube which had been purged with N₂ gas at 473 K for 1 h. Then a reductive gas (5% H₂/Ar) was introduced into the tube at a flow rate of 30 mL min⁻¹. The temperature of the reactor was increased linearly from 373 to 1273 K with a ramping speed of 10 K min⁻¹ using a temperature-programmed controller.

2.3. Catalytic evaluation

1.0 mL samples (40–60 mesh) diluted with an equivalent amount of quartz granules were evaluated in a pressured fixed-bed reactor at 533 K, 4.0 MPa, and GHSV of 5000 h⁻¹ with a H₂/CO ratio of 2:1. Prior to the reaction, the catalysts were reduced in situ in a flow of syngas (H₂/CO ratio of 2:1, 40 mL min⁻¹) under atmospheric pressure at 573 K for 8 h. Data was taken at steady-state after 24 h on-stream. The effluent gases were analyzed using a Carbosieve-packed column with a TCD and an Al₂O₃ column with a flame ionization detector (FID). Propake-Q columns with TCD and

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