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A durable nanocatalyst of potassium-doped iron-carbide/alumina for significant production of linear alpha olefins via Fischer-Tropsch synthesis

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ABSTRACT

Improvement of activity, selectivity, and stability of the catalyst used in Fischer-Tropsch synthesis (FTS) to produce targeted hydrocarbon products has been a major challenge. In this work, the potassium-doped iron-carbide/alumina (K-Fe₅C₂/Al₂O₃), as a durable nanocatalyst containing small iron-carbide particles (~ 10 nm), was applied to high-temperature Fischer-Tropsch synthesis (HT-FTS) to optimize the production of linear alpha olefins. The catalyst, suitable under high space velocity reaction conditions (14–36 N L_{gcat}⁻¹ h⁻¹) based on the well-dispersed potassium as an efficient base promoter on the active iron-carbide surface, shows very high CO conversion (up to ~90%) with extremely high activity (1.41 mmol_{CO} g_{Fe}⁻¹ s⁻¹) and selectivity for C₅–C₁₃ linear alpha olefins.

1. Introduction

The linear alpha olefins (LAOs) obtained by oligomerization of ethylene or by Fischer-Tropsch synthesis (FTS), are very important chemical intermediates used in such as detergents, plasticizers, synthetic lubricants, and polymers (polyethylene) [1,2]. Because a wide variety of customer demands involve the LAO market, high profits can be expected if LAO production can be increased [3].

The process of oligomerization of ethylene to LAOs is well-known, but the FTS process for effective LAO production is not well studied [4,5]. Liu et al. reported the use of pretreated CoMn/SiO₂ as a selective catalyst for alpha olefins [6]. Recently, bio-promoted iron-carbide catalysts to convert carbon dioxide to LAOs directly were developed, but the long term stability of the catalysts was not discussed [7].

Commercially, gasoline and lower-olefin products can be obtained efficiently using the high-temperature FTS (HT-FTS) process. This process is conducted at temperatures of 300–350 °C using an iron-based catalyst [8–10]. However, conventional HT-FTS catalysts remain inadequate for production of significant quantities of LAO [11]. Typically, iron-based-support catalysts (e.g., Fe/α-Al₂O₃, Fe/CNT, Fe/SiO₂, Fe@C,

and Fe/zeolite) have been used in HT-FTS reactions to produce a variety of hydrocarbon products [12–18]. In recent years, more selective and efficient ways for production of high value-added hydrocarbons have been developed for FTS. For example, high selectivity (~60%) for C₂–C₄ lower olefins was achieved using Fe/α-Al₂O₃ and Fe/carbon-nanofiber (CNF) catalysts [19].

Gamma-phase alumina provides a robust support for the high-temperature catalytic reactions. Its use led to high metal dispersion based on strong metal-support interaction, which resulted in more active and stable sites [20,21]. In addition, alkali metals used as a base-additive donated electrons to active sites. These were also exploited to enhance the FTS catalyst [22–25]. For instance, potassium (K) and cesium (Cs) showed dramatic effects in HT-FTS by facilitating CO dissociation and increasing the growth of carbon chains [26–29]. The doped-K in Fe catalysts also enhanced alkene production [30].

On the other hand, elaborate control of the reaction conditions could also affect FTS products. For instance, increasing the space velocity in FTS is one effective way to achieve selective formation of the alkene products that result from reduced secondary reactions [31]. The hydrocarbon products spend less time in contact with the catalyst and

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