



Crucial factors for catalyst aggregation and deactivation on Co/Al₂O₃ in a slurry-phase Fischer–Tropsch synthesis

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ARTICLE INFO

Article history:

Received 12 June 2011

Received in revised form

26 September 2011

Accepted 17 November 2011

Available online 26 November 2011

Keywords:

Fischer–Tropsch synthesis

Deactivation

Aggregation

Hydrophilicity

Cobalt

Phosphorous-modification

Alumina

ABSTRACT

The different behaviors for catalyst deactivation by forming aggregated catalyst lumps were investigated on the phosphorous-modified Co/P–Al₂O₃ and the unmodified Co/Al₂O₃ Fischer–Tropsch synthesis (FTS) catalysts in a slurry-phase continuous stirred tank reactor. The lower catalytic activity at steady-state with a fast deactivation rate was observed on the phosphorous-unmodified Co/Al₂O₃ catalyst due to the facile formation of aggregated catalyst lump with a high hydrophilic property of support and a significant hydrocarbon deposition on catalyst surface. The amount of adsorbed water and the deposited hydrocarbons are strongly related with aggregated catalyst lump formation. The adsorbed water could possibly transform the local γ -Al₂O₃ surface to pseudo-boehmite (Bronsted acidic Al₂OH sites) material which is characterized as a low attrition resistance and accelerates the formation of fine powders during FTS reaction. The formed fine powder during FTS reaction could be easily aggregated and it is resulted in catalyst deactivation due to the difficult intraparticle diffusion of reactants. The possible mechanisms of phase transformation of γ -Al₂O₃ to pseudo-boehmite and formation of aggregated catalyst lump were suggested by measuring the deposited hydrocarbons and the concentration of adsorbed water on catalyst surface with the help of the characterizations such as X-ray photoelectron spectroscopy, temperature-programmed surface reaction, diffuse reflectance infrared Fourier transform and water-sorption method.

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1. Introduction

Cobalt-based Fischer–Tropsch synthesis (FTS) catalyst has been intensively investigated since its high catalytic activity, stability and excellent selectivity to desired hydrocarbons with a low water-gas shift (WGS) activity [1]. In addition, gas-to-liquids (GTL) process using cobalt-based FTS catalyst has been recognized as an important alternative process to convert natural gas to environmentally benign fuels and useful chemicals [1]. The catalytic activity on cobalt-based FTS catalyst has been reported to be mainly affected by cobalt particle size, its reducibility and the nature of the supporting materials. With the addition of noble metal promoters like Ru, Re and Pt in a combination with active cobalt component, a remarkable enhancement of the catalyst performance could be obtained

because of the enhanced reducibility and dispersion of cobalt particles [2,3].

The catalytic deactivation of cobalt-based FTS catalyst is also frequently observed during pretreatment and FTS reaction, and it is a main topic to develop a robust GTL process by employing stable industrial catalysts. The possible reasons for catalyst deactivation on cobalt supported Al₂O₃ catalysts are generally categorized as an oxidation of metallic cobalt by water generated, agglomeration of cobalt particles, strong Co–Al₂O₃ interaction to form an inactive cobalt aluminate phase and blockage of pore or active metal surface by hydrocarbon deposition and so on [1,4,5]. The water generated during FTS reaction also affects catalytic performance by possible changing the oxidation states of supported cobalt particles according to the partial pressure of water and by altering the transport coefficients of reactants such as CO and H₂ and hydrocarbons produced [2,5]. In particular, the effects of water on cobalt-based catalysts to catalytic activity have been reported controversially as negative [6,7] or positive [8] according to the nature of supports and their pore size [9], and particle size of supported cobalt species [5,10,11]. In general, the catalyst possessing a wide pore

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