



Effects of titanium impurity on alumina surface for the activity of Co/Ti–Al₂O₃ Fischer–Tropsch catalyst

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ABSTRACT

The surface impurity of titanium with a low concentration on alumina was investigated to elucidate the effects of titanium to catalytic performance on Co/Ti–Al₂O₃ catalysts during Fischer–Tropsch (FT) synthesis. Titanium impurity is possibly incorporated as an impurity in Al₂O₃ preparation process, and its content could alter the surface characters of Al₂O₃. The variation of surface characteristics also significantly alters the dispersion of Co₃O₄ clusters, reducibility and it consequently changes the catalytic activity. In the present study, titanium impurity with a composition of 0.2–0.5 wt% on γ-Al₂O₃ was found to be optimal to obtain a high catalytic performance with respect to CO conversion and C₅₊ selectivity. The enhanced catalytic activity on Ti-modified Co/Al₂O₃ catalyst was mainly attributed to the increased dispersion of cobalt clusters homogeneously with a suppression of cluster aggregation during FT reaction, and it is mainly resulted from the surface modification of alumina with a low content of titanium oxides by changing the surface acidity of γ-Al₂O₃.

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1. Introduction

Gas-to-liquids process has been considerably progressed as one of the promising processes to produce environmentally benign fuels with lower emission of pollutants [1]. Therefore, the cobalt-based catalyst for Fischer–Tropsch (FT) synthesis, which is inevitably required to produce synthetic fuels from syngas, have been widely investigated to improve its catalytic performance by designing the properly dispersed cobalt-based FT catalysts. To achieve these goals, commercially available inorganic supports such as Al₂O₃ [2,3], TiO₂ [4] and SiO₂ [5,6] have been modified with various metals such as Zr, La, Mg, TiO₂ and/or SiO₂ to enhance cobalt dispersion and mechanical strength [7]. Promoters, such as Ru, Re and Pt, combined with cobalt species have greatly enhanced catalytic performance by increasing reducibility of cobalt oxides and by forming small cobalt clusters [8]. Moderating the interaction of cobalt species and support can also achieve the higher activity and selectivity for C₅₊ selectivity during FT synthesis due to the ease of reduction of cobalt oxides and less formation of inactive cobalt

aluminates [2,3,7,9]. Stable catalytic activities for a long-term operation have been also obtained by modifying the physicochemical properties such as surface area, pore size and surface acidity of supports which concomitantly change the cobalt dispersion and reducibility and the extent of carbon deposition [8,9], for example, the higher C₅₊ selectivity and catalyst stability has been generally observed on the FT catalyst having a proper cobalt cluster size [1,3]. In addition, strong metal–support interaction (SMSI) may change the fraction of chemically inactive cobalt species during oxidation and/or reduction steps [9] which is varied according to the concentration of metal impurities on Al₂O₃ support [1]. Impurities such as La, Ti or Mg are usually present in commercially available γ-Al₂O₃ support, which could be generally originated from the impurities contained in aluminum and titanium precursors at large scale Al₂O₃ synthesis process. Small quantity of those impurities on γ-Al₂O₃ support could significantly alter a catalytic performance by changing the physicochemical properties of the support, and it consequently changes the surface properties of deposited cobalt oxides in a final FT catalyst.

The present investigation has been focused on the effects of the low concentration of titanium oxide on γ-Al₂O₃ surface, and its influence on cobalt-based FT catalysts by varying Ti/Al₂O₃ ratio from 0 to 1.0 wt% Ti impurity on γ-Al₂O₃ prepared by sol–gel synthetic method has been systematically studied. The impurity of titanium oxides which are one of the possible impurity of γ-Al₂O₃ is found to play as a modifier on a laboratory-made

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