



Effects of surface modification with zirconium phosphate on Ru/Co/SiO₂ Fischer–Tropsch catalysts analyzed by XPS and TEM analyses

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ARTICLE INFO

Article history:

Received 9 July 2012

Received in revised form 2 September 2012

Accepted 3 October 2012

Available online 8 November 2012

Keywords:

Fischer–Tropsch synthesis

Cobalt

Zirconium phosphate

Aggregation

SiO₂

Catalytic stability

ABSTRACT

The effects of surface modification with zirconium phosphate on cobalt-based Fischer–Tropsch synthesis (FTS) catalyst to the enhanced catalytic stabilities were explained with the help of the surface sensitive X-ray photoelectron spectroscopy (XPS) and transmission electron spectroscopy (TEM) on the reacted catalysts at three different periods of reaction duration such as 10, 30 and 70 h on stream. The catalyst deactivation was significantly attributed to the aggregation of cobalt clusters at the very beginning of reaction, and the modification of SiO₂ surface with the proper amount of zirconium phosphate largely suppressed cobalt aggregation during the reaction period of 70 h. The enhanced catalytic stability is attributed to the homogeneous distribution of cobalt clusters with a low mobility by being confined in the thermally stable zirconium phosphate matrices on SiO₂ surface. The roles of zirconium phosphate on catalytic stability are mainly explained by analyzing the relative dispersion of zirconium phosphate as well as cobalt clusters on SiO₂ surface with time on stream.

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1. Introduction

Fischer–Tropsch synthesis (FTS) has been attracted as a promising alternative process to convert coal or natural gas to environmentally benign fuels via syngas with a low emission of pollutants [1,2]. The cobalt-based FTS catalyst is widely investigated in order to obtain a high catalytic activity and to selectively produce high molecular weight hydrocarbons. The proper interaction of cobalt clusters with supports is one of the important properties to get a high catalytic performance since it is strongly related with the reducibility of cobalt oxides [3–5]. The surface properties of Co/SiO₂ catalyst are also influenced by the nature of cobalt precursors and preparation methods which result in a variation of metal–support interaction [6,7]. The modification of SiO₂ support with some metals like zirconium is usually employed to prevent a strong metal–support interaction and to enhance the selectivity to higher molecular weight hydrocarbons on cobalt-based catalysts. In addition, zirconium species also plays an important role in enhancing the turnover frequency (TOF) by decreasing the strong metal–support interaction [4,6]. In the case

of phosphorous-containing catalysts, aluminum phosphate has also been receiving a great attention as a support for various catalytic reactions [8,9] such as hydrotreating catalysts. The positive effect of phosphorous are mainly related with the stabilization of active species by forming M–P oxo-species (M = Co, Mo, Ni), and resulted in suppressing metal–support interaction due to strong affinity between aluminum and phosphorous species [10]. Although phosphorous modified cobalt-based FTS catalyst generally revealed a low productivity due to the possible formation of non-active and hardly reducible cobalt phosphates [11], zirconium phosphate has recently received much attention due to its wide range of applications such as dehydration, dehydrogenation or methanol conversion reactions [12,13]. The phase of zirconium phosphate has been generally known as a hydrogen phosphate (Zr(H₂PO₄)₂) species and H₂PO₄[−] species which are stable up to a temperature of 750 °C.

In the present paper, the influence of zirconium phosphate formation on SiO₂ surface in terms of cobalt aggregation and catalytic stability has been further investigated based on the results of our previous works [14,15] by employing surface sensitive X-ray photoelectron spectroscopy (XPS) and transmission electron spectroscopy (TEM) on the FTS catalysts sampled at three different reaction time during 70 h. The aim of this investigation is to elucidate the effects of zirconium phosphate modification on SiO₂

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