

# Studies on accelerated deactivation of ruthenium-promoted alumina-supported alkalized cobalt Fischer-Tropsch synthesis catalyst

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## Abstract

Accelerated deactivation of ruthenium-promoted alumina-supported alkalized cobalt (K-Ru-Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) Fischer-Tropsch (FT) synthesis catalyst along the catalytic bed over 120 h of time-on-stream (TOS) was investigated. Catalytic bed was divided into three parts and structural changes of the spent catalysts collected from each catalytic bed after FT synthesis were studied using different techniques. Rapid deactivation was observed during the reaction due to high reaction temperature and low feed flow rates. The physico-chemical properties of the catalyst charged in the Bed #1 of the reactor did not change significantly. Interaction of cobalt with alumina and the formation of CoAl<sub>2</sub>O<sub>4</sub> increased along the catalytic bed. Reducibility percentage decreased by 4.5%, 7.5% and 12.9% for the catalysts in the Beds #1, #2 and #3, respectively. Dispersion decreased by 8.8%, 14.4% and 26.6% for the catalysts in the Beds #1, #2 and #3, respectively. Particle diameter increased by 0.6%, 2.4% and 10.4% for the catalysts in the Beds #1, #2 and #3, respectively, suggesting higher rate of sintering at the last catalytic bed. The amount of coke at the last catalytic bed was significantly higher than those of Beds #1 and #2.

## Key words

Fischer-Tropsch synthesis; cobalt; accelerated deactivation; sintering; coke formation

## 1. Introduction

Fischer-Tropsch synthesis (FTS) is a potentially promising option for environmentally friendly production of chemicals and fuels from biomass, coal and natural gas [1,2]. In industrial applications, a high-performance catalyst plays an essential role. In FTS process, the catalyst activity, selectivity and lifetime are influenced by the nature and structure of support, the nature of metal, metal dispersion, metal loading and catalyst preparation method [3,4]. Supported cobalt catalysts for the Fischer-Tropsch (FT) synthesis are receiving commercial applications for gas to liquid (GTL) technologies. Cobalt-based FT synthesis catalysts have more advantages than iron-based catalysts such as high conversion per pass, long lifetime, low water gas shift activity and high selectivity towards high hydrocarbons. However, cobalt-based catalysts used in FT synthesis are relatively expensive as compared with iron-based catalysts and require highly dispersed cobalt in conjunction with stable catalytic activity for an extended period of operation to remain economically attractive. The deactivation

of cobalt catalysts is mainly due to the oxidation of cobalt metal, cobalt-support interactions, the formation of inactive compounds (e.g., aluminate) resulted from metal migration into the support lattice, the aggregation and growth of metal cobalt on the surface of catalyst, refractory coke formation and the loss of metal cobalt because of attrition (especially for the three-phase slurry bed reactors) [4–11]. Water is the main FT by-product and accounts for ca. 50 wt% of all products. The amount of water depends on the synthesis gas conversion, reaction system and type of catalyst. When cobalt deactivates, it means metallic cobalt is converted into either CoO, Co<sub>3</sub>O<sub>4</sub> or mixed oxides in the forms of  $x\text{CoO}\cdot y\text{Al}_2\text{O}_3$  or CoAl<sub>2</sub>O<sub>4</sub>. This is not thermodynamically possible unless it is affected by water [12,13].

Though the deactivation of cobalt catalysts has been studied extensively, literature review reveals that the deactivation mechanism of cobalt catalyst along the reactor has rarely been studied. In other words, it is not well known whether factors such as coke formation, oxidation and sintering have their major influences on the deactivation of catalysts located at different parts in a fixed-bed reactor. This study focused on

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