



## Full Length Article

# Characterizations and product distribution of Co-based Fischer-Tropsch catalysts: A comparison of the incorporation manner

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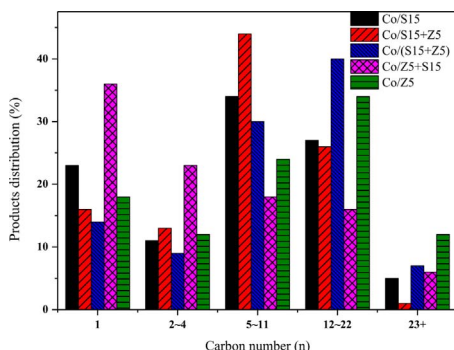
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## GRAPHICAL ABSTRACT

The consecutive hydrocracking of Co/SBA-15 primary hydrocarbons facilitated the formation of C<sub>5</sub>–C<sub>11</sub> on the Co/S15 + Z5 catalyst with medium acid site, accordingly the selectivity of the C<sub>5</sub>–C<sub>11</sub> hydrocarbons was enhanced from 34% to 44%. The optimum dispersion of Co<sub>3</sub>O<sub>4</sub> and Co<sup>2+</sup>/Co<sup>3+</sup> ratio on the Co/(S15 + Z5) catalyst facilitated the selective hydrogenolysis and the product distributions shifting to C<sub>12</sub>–C<sub>22</sub> with the increased selectivity from 27% to 40%.



## ARTICLE INFO

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## ABSTRACT

Co-based catalysts supported on SBA-15 and ZSM-5 were prepared by various incorporation manners and evaluated for the Fischer-Tropsch synthesis (FTS). The weight ratio of SBA-15 and ZSM-5 were 1:1 and Co had a constant loading of 15 wt% in all of the finished catalysts. Their physicochemical properties and catalytic performance were investigated by the N<sub>2</sub> adsorption–desorption, XRD, TEM, XPS, NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR, H<sub>2</sub>-O<sub>2</sub> titration, H<sub>2</sub>-chemisorption and in a high pressure fixed-bed reactor, respectively. Characterizations indicated that the main cobalt species was Co<sub>3</sub>O<sub>4</sub> with small crystal size and high dispersion on the catalysts with SBA-15 as support, while the CoO with strong interaction with the support, as well as large particle size and low dispersion of Co<sub>3</sub>O<sub>4</sub> was observed on the ZSM-5 supported catalyst. It was found that the catalysts with SBA-15 as main support displayed superior CO conversion (85–90%) than the catalysts with Co species mostly deposited on the ZSM-5 support (~70%), which was arise from the easy reduction of Co<sub>3</sub>O<sub>4</sub> with weak interaction with SBA-15 support. The consecutive hydrocracking of Co/SBA-15 primary hydrocarbons facilitated the formation of C<sub>5</sub>–C<sub>11</sub> on the Co/S15 + Z5 catalyst with medium acid site, accordingly the selectivity of the C<sub>5</sub>–C<sub>11</sub> hydrocarbons was enhanced from 34% to 44%. The optimum dispersion of Co<sub>3</sub>O<sub>4</sub> and Co<sup>2+</sup>/Co<sup>3+</sup> ratio on the Co/(S15 + Z5) catalyst facilitated the product distributions shifting to C<sub>12</sub>–C<sub>22</sub> with the increased

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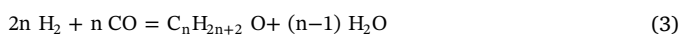
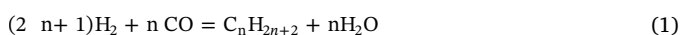
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selectivity from 41% to 52%. Furthermore, The superior catalytic stability for Co/(S15 + Z5) could be attributed to the synergistic effect of hydrogenolysis and cracking, which suppressed the coke deposition.

## 1. Introduction

The increasingly stringent environmental regulations and depletion of crude oil have renewed the interest of using non-petroleum resources, such as natural gas, coal-bed gas, landfill gas, coal or biomass, as a potential source for the liquid fuels and chemicals. It is generally accepted that the syngas (CO and H<sub>2</sub>) can be produced by steam reforming or gasification of non-petroleum resources. Fischer–Tropsch synthesis (FTS) is a heterogeneous catalytic reaction, which converts the syngas into clean liquid fuels or valuable chemicals [1,2]. The reactions in the FTS are included as follows:



Furthermore, the predominantly linear paraffinic hydrocarbons produced in the FTS and virtually no contaminants such as sulphur, nitrogen and aromatics together with a high cetane number are more environmentally friendly than conventional petroleum-based liquid fuels [2]. The wide and unselective products distribution, however, is one of the most difficult challenges in the FTS. It is generally accepted that it arises from the chain growth mechanism of hydrogenation of CO, which can be described by the Anderson-Schulz-Flory (ASF) model [3]:

$$W_n/n = (1-\alpha)^2\alpha^{n-1} \quad (5)$$

$W_n$  is the weight fraction of hydrocarbons containing  $n$  carbon atoms and  $\alpha$  is the chain growth probability determined by the catalyst and the specific process conditions.

A variety of metal catalysts, typically including the Ru, Co and Fe catalysts, have proven to be active catalysts for the FTS [4,5]. Among these metals, the Fe-based catalysts can be used for the production of light alkenes or oxygenates, which are important chemical feedstock. Moreover, the Co represents the optimal choice for the production of long-chain linear hydrocarbons (wax, diesel fuel or gasoline) due to the higher selectivity of hydrocarbons, well stability, less oxygenates, lower water–gas shift (WGS) activity and commercial availability [6]. The development of novel ZnCrOx or Zr-Zn binary oxides catalyst with high selectivity is one of the main focuses in the recently academic community, and considerable progress has been made in the direct syngas conversion to light olefins [7,8].

Generally, the chemical state of active components, the nature of promoters and supports are main catalyst factors affecting the products distribution and CO conversion for the FTS. Several reviews and recent publications have devoted to the influence of the chemical state of active components and the promoters on the FTS activity and products distribution [9–13]. Meanwhile, many studies have attempted to clarify the effects of supports' porosity and surface properties on the catalytic performance of supported Co catalysts [14–16].

The use of periodic mesoporous materials, especially mesoporous silicas (MCM-41 and SBA-15) or acidic zeolites (micropores or hierarchical ZSM-5) as supports for preparing Co-based FTS catalysts has been explored [1,17–21]. The presence of a high surface area (~500 m<sup>2</sup>) and uniform porous channels with controllable pore diameters and pore lengths should allow, in principle, for a better control on the cobalt particle size and the catalytic properties. Moreover, the mesopores in which the active metal particles are located may function as a nanoreactor to control the chain growth by shape selectivity or by enhancing the re-adsorption of  $\alpha$ -olefin intermediates [9]. Several

research groups have clarified that the cobalt loaded on the SBA-15 with a pore diameter of roughly 9 nm and the use of cobalt nitrate or the mixture of nitrate and acetate as cobalt precursor demonstrated a higher C<sub>10</sub>–C<sub>20</sub> hydrocarbons [21–23]. The acidity of the zeolites is beneficial to adjustment of the FT product distributions in the gasoline range via the secondary cracking, isomerization and aromatization reactions. It has been demonstrated that the direct deposition of FT components on the zeolite results in the low CO conversion and high CH<sub>4</sub> selectivity due to the strong interactions between the metal cations and the anionic zeolite framework [24]. The combination of zeolite and a FT component by typically physical mixing or by constructing core-shell catalysts increased the selectivity to gasoline range hydrocarbons but with rapid deactivation due to the poisoning of the acid sites by coke deposition [25–28]. In our previous report, the combination of ZSM-5 and SBA-15 as composite supports for Co-based catalysts were shown to have much improved selectivity of C<sub>5</sub><sup>+</sup> hydrocarbons over the respective single material supported catalysts [6].

Herein, we report our recent investigation on the product distributions and catalytic stability of FTS with the combination of ZSM-5 zeolite and SBA-15 (periodic mesoporous silicas) in different incorporation manners. The characterizations of the textural, structural and acidic properties of the catalysts, the dispersion and reducibility of the cobalt species were correlated with the product distributions to make clear of the incorporation manner-catalytic performance relationships.

## 2. Experimental

### 2.1. Catalyst preparation

SBA-15 was synthesized following the methodology reported by Zhao et al. [29]. In brief, P123 (EO20PO70EO20, MAV = 5800, Aldrich) was dissolved in 2 M HCl under stirring. Then the required amount of TEOS (Aldrich) was gradually added into the above solution with continuous stirring for 24 h. The gel mixture was transferred into a Teflon-lined autoclave to crystallize at 110 °C for 2 days followed by filtering, exhaustive washing and drying at 80 °C. Finally, the dried solid was calcined in a flow of air at 550 °C for 6 h to remove the organic template.

Zeolite ZSM-5 with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 40 was purchased from Qilu Huaxin Industry Co. Ltd.

The supported Co-based catalysts were prepared by incipient wet impregnation method. The supports were completely wetted with H<sub>2</sub>O to estimate the total volume. Then, cobalt(II) nitrate was dissolved into the required amount of H<sub>2</sub>O to impregnate the supports followed by drying at 80 °C for 24 h and calcination at 400 °C for 4 h. The loading of Co in the final catalysts was kept constant at 15 wt%.

The final catalysts were prepared in different ways, i.e., by supporting the Co metal on a SBA-15 (denoted as Co/S15), by supporting the Co metal on a ZSM-5 zeolite (denoted as Co/Z5), by physically mixing the Co/SBA-15 catalyst and ZSM-5 zeolite (denoted as Co/S15 + Z5), by supporting the Co metal on the hybrid of SBA-15 and ZSM-5 support (SBA-15 and ZSM-5 were mechanically mixed with the weight ratio of 1:1, denoted as Co/(S15 + Z5)) and by physically mixing the Co/Z5 catalyst and SBA-15 (denoted as Co/Z5 + S15). For instance, 2 g ZSM-5 was firstly impregnated with the solution of 2.96 g Co(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, then the calcined Co/Z5 catalyst was mechanically mixed with 2 g SBA-15 to prepare the Co/Z5 + S15 catalyst.

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