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Effect of the porous structure of the support on hydrocarbon distribution in the Fischer–Tropsch reaction

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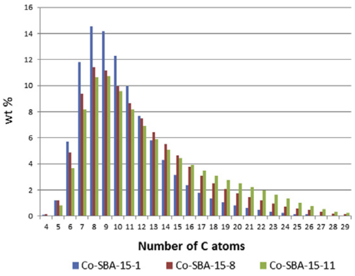
HIGHLIGHTS

- We synthesize and evaluate catalysts to produce diesel fraction components in FTS.
- Pore diameter significantly influences the liquid products distribution.
- The catalyst with smaller pore size showed a deviation from the ASF mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

Emissions standards are increasingly stringent due mainly to its impact on the environment. Although the diesel engine is an attractive solution for carbon dioxide reduction, a challenge remains to simultaneously control nitrogen oxides and matter particulate emissions to accepted levels. On engine tests, it has been observed that Fischer–Tropsch diesel significantly reduces CO, HC, PAHs and particulate emissions compared to oil derived diesel. However, selectivity control in Fischer Tropsch Synthesis is still a key challenge due the Anderson-Schultz-Flory polymerization mechanism followed by hydrocarbon distribution. In this work we are presenting the first steps towards a new strategy that can tune, in one step, the selectivity to desired products by taking advantage of the shape selectivity properties of SBA-15 mesoporous silica used as support.

Co-SBA-15 (30%wt) catalysts with different pore size were prepared by excess solution impregnation. Our results show that pore diameter not only affects the size and reducibility of Co particles but it also significantly influence the liquid products distribution, with the high molecular weight hydrocarbon fraction increasing on large pores, attributed to the existence of a shape selectivity effect induced by the textural properties of the catalyst namely its pore size and pore volume.

1. Introduction

The production of clean fuels, particularly diesel, by means of Fischer–Tropsch synthesis (FTS) has sparked renewed interest in recent years both in industry and academia. The predominantly linear paraffinic hydrocarbons produced in the FTS, along with virtually no contaminants such as sulfur, nitrogen and aromatics, produce FT diesel with higher cetane number (≥75) [1] and lower pollutant emission levels than a refinery diesel. Due to the typical

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Anderson-Schultz-Flory (ASF) polymerization mechanism [2], it is possible to obtain in a single step, high selectivity to hydrocarbons with a very narrow boiling point range. Because of this, FT processes aiming to produce synthetic diesel, uses catalysts that have a high selectivity to high molecular weight (waxes) linear alkanes which, subjected to a subsequent mild hydrocracking process, maximize diesel production, while their properties are further improved by isomerization of the linear alkanes.

Several excellent reviews have been published on the Fischer Tropsch Synthesis and some concepts have been established [3–6]. Most existing catalysts designed to obtain a high selectivity to waxes in the FTS use cobalt as main active metal supported on a porous inorganic oxide (SiO_2, Al_2O_3, TiO_2), together with one or more promoters. The activity of these catalysts is proportional to the concentration of Co surface, which depends essentially on two parameters: the reduction degree (RD) of cobalt oxide reached during the catalyst reduction step prior to the FTS and the dispersion of the reduced cobalt. These two parameters are generally related to each other and are largely determined by the Co-support interaction. Thus, when TiO_2 is used as support, the strong interaction between Co and TiO_2, favors a high metal dispersion but results in the formation of low reducibility of Co species, giving rise to a low concentration of active sites. In contrast, the weak interaction between Co–SiO_2 favors Co particles reduction. However, they tend to agglomerate leading to relatively low dispersions. The behavior of Co supported on Al_2O_3 is generally intermediate between that shown by Co on TiO_2 and SiO_2. It has also been established that the efficiency of this reaction can be greatly improved by designing new thermally stable catalysts with good mechanical and heat transfer properties, minimizing hot spots developed in the catalyst bed, which promote metal particle sintering.

In the last decade, several authors have explored the possibility of employing mesoporous silicas as an alternative for Co based F-T conventional supports [7–16]. In particular the high surface area ordered mesoporous materials ($>800\ m^2\ g^{-1}$) and its regular porous structure, with narrow pore diameter distribution, allows for a higher Co dispersion even at high metal loadings and can exerts control on the metal particle size distribution, which influence their catalytic properties.

However, the effect of the porous structure of the support on hydrocarbon distribution in the FT reaction remains not well understood and is still subject of controversy. All these studies have suggested that the pore size distribution could significantly affect the Fischer–Tropsch Synthesis reaction rate and hydrocarbon selectivity but the way it occurs remains unclear. Okabe et al. [7] reported that wide pore catalysts are preferable for higher conversion and higher C5+ selectivity because of the higher reducibility of large cobalt particles in wide pores over the pore size range from 4 to 10 nm. In an early study, Anderson et al. [8] reported that the FTS activity and selectivity of cobalt based catalyst could be affected by their pore sizes. The observed increase in methane selectivity with decreasing average pore size was attributed to mass transport phenomenon. However, Lapszewicz et al. [9] years later reported that the variation of product distribution as a function of catalyst pore diameter was a result of the change of adsorption patterns of hydrogen and carbon monoxide rather than mass transfer phenomena. The analysis of Lapszewicz data seems to suggest that this change of adsorption patterns is related to the particle size which in turn relates very well with pore diameter. Ernst et al. [10] studied the FT activity and selectivity of Co/SiO_2 prepared by a sol–gel technique in acid and base media. It was found that the activity for FT increased with the specific surface area, and the selectivity for higher molecular weight hydrocarbon was favored when the pore diameter was lower than 4 nm. Khodakov et al. [11] investigated the pore size effects on Fischer–Tropsch reaction rates and selectivities over cobalt catalysts using periodic (SBA-15 and MCM-41) and commercial mesoporous silicas as supports. They found that the Fischer–Tropsch reaction rates and C5+ selectivity were much higher on cobalt catalysts with the support pore diameter exceeding 3 nm than on the narrower pore catalysts. Iglesia et al. [12] reported that hydrocarbon product selectivity depends on a complex interplay between diffusion, reaction and convection processes occurring within the catalyst pellets and reactors. A structural parameter χ, which includes parameters such as pellet radius, pellet porosity, mean pore radius of support and active metal distribution on support, seems to play a vital role in determining the Fischer–-Tropsch activity and selectivity. Feller et al. [13] and Saib et al. [14] showed evidence of the role of pore diameter on cobalt cluster size stressing on the fact that with increasing cluster size, a strong increase in the extent of secondary reactions occurs i.e. olefin readsorption. According to Saib et al. [14], activity of the supported cobalt catalysts in the Fischer–Tropsch synthesis seems to be a function of the metal dispersion and the extent of deactivation during the Fischer–Tropsch synthesis while the C5+-selectivity could be described using the reactant transport model proposed by Iglesia et al. [12] and is a function of conversion. Xiong et al. [15] studying the role of pore size in Co/SBA-15 catalysts also concluded that catalysts with larger pores led to larger cobalt cluster size, lower dispersion and higher reducibility and gave rise to more bridge type CO adsorbed on FTS. They also stated that catalysts with larger cobalt cluster size showed higher C5+ selectivity in the FTS. The reported results are very solid and clear evidences have been shown in all cases supporting the author claims. However, we believe that an additional factor i.e. shape selectivity also plays a role.

We previously reported [16] on the possibility of a shape selectivity effect of mesoporous structures (namely HMS) on the shaping of the liquid product distribution in the FTS reaction. The present work deals with the study of the behavior of cobalt on SBA-15 mesoporous silica, which will support our previous findings since its pore size could easily be changed by means of using a swelling agent and controlling synthesis conditions.

A mixture of a triblock copolymer: polyethylene oxide/polypropylene oxide/polyethylene oxide (EO/PO/EO), was used as surfactant in SBA-15 molecular sieve synthesis with different pore size, possessing two kinds of moieties, i.e. the hydrophilic EO block and the hydrophobic PO block. The micellization of the triblock copolymers are driven by the hydrophobic polyethylene oxide (PO) block with a core consisting of PO blocks and a corona of EO blocks [7]. SBA-15 pore size is mainly determined by the hydrophobic part of the micelles and can be changed by controlling synthesis conditions.

2. Experimental

2.1. Supports synthesis and characterization

SBA-15 mesoporous silica with different pore sizes were synthesized using Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, $M_{AV} = 5800$, BASF) and tetraethyl orthosilicate (TEOS) under acidic conditions, following the methodology proposed by Wang et al. [17]. 10 g of P123 were added to 350 mL of 2 M HCl solution at 35 °C to obtain a clear solution. Then 21 g of TEOS were added drop wise under vigorously stirring for 48 h. The obtained white solid was recovered by vacuum filtration, washed several times with distilled water and air-dried overnight at 80 °C. Organic molecules occluded in the mesopores were removed by direct calcination at 500 °C with air flow for 6 h. The small pore size silica support (SBA-15-1) was synthesized without any hydrothermal treatment. In order to