Exploiting the effects of catalyst geometric properties to boost the formation of light olefins in Fischer-Tropsch synthesis: Statistical approach for simultaneous optimization

Hossein Zohdi-Fasaei [a], Hossein Atashi [a, *], Farshad Farshchi Tabrizi [b, a], Ali Akbar Mirzaei [c]

[a] Department of Chemical Engineering, Faculty of Engineering, University of Sistan and Baluchestan, P.O. Box 98164-161, Zahedan, Iran
[b] Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran
[c] Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran

ABSTRACT

A statistical study was carried out to investigate simultaneous effects of different geometrical properties of the catalyst on the extent of light olefins in Fischer-Tropsch synthesis. Applying Taguchi design of experiment, a total of nine impregnated Co–Mn–Ce/SiO$_2$ catalysts were prepared and tested in a fixed-bed reactor under the following operating conditions: T = 533.15 K, 558.15 K and 583.15 K, P = 2 bar, H$_2$/CO = 2 and GHSV = 4500 hr^{-1}. Specific surface area, pore diameter, pore volume, and pore structure (pore size distribution) were considered as the main geometrical factors which were controlled by tuning such sol-gel parameters in silica synthesis as Reynolds (*Re*) and Froude (*Fr*) dimensionless numbers as well as acid dripping time (ϴ), and acid normality (N). Analysis of variance demonstrated that, both of specific surface area and pore volume imposed significant effects on the production of lower olefins. Statistical analysis indicated that, the mesoporous catalyst with a wide pore size distribution and large specific surface area and pore volume favored (i.e. maximized) the production of light olefins. These optimum geometries were achieved by setting the silica synthesis parameters to *Re* = 250,000, *Fr* = 0.213, ϴ = 30 min, and N = 6.

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1. Introduction

Fluctuating oil prices together with increasing energy demands have given rise to serious environmental and energy concerns, encouraging governments to invest on novel and clean technologies for the exploitation of fossil reservoirs (Das et al., 2013). The most abundant yet ecologically clean fossil fuel is natural gas whose relatively low density makes it expensive to transmit through a pipeline (Hall, 2005). In order to solve the problem, alternatives such as gas-to-liquid (GTL) technology have been developed to produce valuable chemicals (Rahimpour and Bahmanpour, 2011). Fischer-Tropsch synthesis (FTS) is regarded as the chemical heart of GTL technology in which a wide spectrum of hydrocarbons (e.g. light olefins and ultra-clean fuels with zero sulfur and low aromatic content) are produced from synthesis gas, i.e. a mixture of H$_2$ and

CO, via catalytic reactions (Ding et al., 2013, 2015). Hence, researchers have been interested in developing selective catalysts to obtain specific products via the process. Among the group VIII materials, only iron and cobalt represent reliable and cost-effective active metals for industrial FTS applications (Atashi et al., 2010). While syngas is derived from natural gas (e.g. using GTL technology (Nakhaei Pour et al., 2014)), cobalt-based catalysts are widely employed in FTS due to their high activity in the FTS, long lifetime, and low activity of the water-gas shift reaction (Shimizu et al., 2015; Mirzaei et al., 2011).

As the current demand for the light olefins, as building blocks of petrochemical industries, is increasing, studies on the development of Fischer-Tropsch catalysts to produce olefins of higher relative selectivity have recently received considerable deals of attention (Mirzaei et al., 2013; Kang et al., 2009). Several literature have studied the effects of catalyst compositional characteristics such as active metals (Mirzaei et al., 2005, 2006), support type and percentage (Xu et al., 1994; Arsalanfar et al., 2014), diverse promoters (Das et al., 1997; Yang et al., 2004), and synthesis parameters on the selectivity of lower olefins. For instance, it was demonstrated that,

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* Corresponding author.
  E-mail addresses: zohdi@pgs.usb.ac.ir, Hossein.zohdi@gmail.com (H. Zohdi-Fasaei), h.ateshy@hamoon.usb.ac.ir (H. Atashi).

introducing one or more active metals (e.g. manganese or cerium) into cobalt-based catalysts, one can end up with synergic effects that enhance the production of light olefins (Hutchings et al., 1995; Arsalanfar et al., 2012).

In addition to catalyst composition, catalytic geometrical properties such as pellet size, specific surface area, and pore structure further contribute to the FTS performance (Abbaslou et al., 2010; Prieto et al., 2009; Trépanier et al., 2010). For a catalyst with various sizes of pellets, complex interactions between such phenomena as molecular diffusion, Fischer-Tropsch reaction and convection in either of catalyst or reactor affect the selectivity of hydrocarbons (Saib et al., 2002). Furthermore, pore structure may influence metal size (Saib et al., 2002), active site dispersion (Witoon et al., 2011; Khobragade et al., 2012), and particle size distribution at the catalyst support, which would change the obtained mass transfer rates of components or the extent of reduction (Abbaslou et al., 2010). Provided the reducibility of active metals is not limited by metal-support interactions, blocking, pore diffusion, or ion-exchange, increasing the specific surface area of supported catalyst would enhance both the metal dispersion and Fischer-Tropsch activity (Bessell, 1993).

Consequently, there are unclear and complex relations between catalyst geometry and Fischer-Tropsch performance; the relations should be investigated for each particular supported catalyst (Song and Li, 2006).

Recent literature have shown that, either of large pore diameter or relatively low specific surface area tends to favor (i.e. maximize) the production of C_{5+} hydrocarbons over silica-supported cobalt-based catalysts (Kababji et al., 2009; Khodakov et al., 2002). In these works, contribution from only one characteristic (e.g. specific surface area or pore diameter) was studied at a time.

Reports on optimum geometric conditions (e.g. pore volume) for the production of light olefins over a cobalt-based catalyst are still very limited. In the present work, the L_9 Taguchi design of experiment and statistical analysis were employed to explain simultaneous effects of catalytic geometrical parameters such as specific surface area, pore diameter, pore volume, and pore structure on the yield of light olefins in Fischer-Tropsch process over a ternary cobalt-based catalyst. Furthermore, optimal values of the parameters along with sol-gel mixing conditions (when preparing the silica support) were presented to maximize selectivity of light olefins; to the best of our knowledge, a report on the subject is yet to be released.

2. Experimental

2.1. Experimental design (Taguchi method)

In this study, several catalytic geometrical properties, including specific surface area, pore diameter, pore volume, and pore structure, were considered as the main factors. However, setting the factors to specified levels according to an orthogonal array is not directly possible. Since the catalyst geometry is well affected by the support properties, the main factors can be controlled by tuning the synthesis parameters of the support. In this work, calculated as follows, silica sol-gel mixing parameters such as Reynolds (Re) and Froude (Fr) dimensionless numbers as well as acid dripping time (Θ) and normality (N) were considered as the primary controlling factors:

$$Re = \frac{n\rho D^2}{\mu} \qquad (1)$$

$$Fr = \frac{Dn^2}{g} \qquad (2)$$

where, n, D, ρ, μ and g are stirring speed, stirrer diameter, water-glass solution density, water-glass solution viscosity, and gravitational acceleration, respectively. Re is the ratio of inertial force to viscous force and Fr is the ratio of inertial force to gravitational force (Paul et al., 2004).

For each of the four controlling factors (Table 1), three levels were suggested by the L_9 orthogonal array in the Taguchi method, so as to prepare supports and catalysts of diverse geometries. The responses were taken as the main factors for the subsequent Fischer-Tropsch tests to statistically study how the catalyst geometrical properties would influence the production of light olefins in FTS. Catalytic experiments were performed in triplicate following a random approach to avoid unknown nuisance variables. Average selectivity of the obtained light olefins over each catalyst was considered as a response.

2.2. Synthesis of silica supports

Deionized water, sodium silicate solution, hydrochloric acid and hexamine (as a surfactant) were the materials used to prepare silica supports via sol-gel method. Initially dissolved in 1 L of deionized water, 1 g of hexamine was used to prepare determinant concentrations of hydrochloric acid and sodium silicate solutions. The solution was homogenized under stirring, before adding acid in a drop-wise fashion at the ambient temperature. The mixture was heated up to 343.15 K during gel formation and stirred continuously to reach the equivalence point (pH = 7). In each experiment, the levels of controlling factors were adjusted according to the L_9 orthogonal array (Table 2). The precipitates were several times-washed with 5 L of distilled water before being filtered to eliminate impurities. Finally, all of the samples were dried (at 393.15 K for 4 h) and calcined (at 873.15 K for 16 h) under the same conditions to give the final silica supports.

2.3. Preparation of Co—Mn—Ce ternary catalysts

Ternary catalysts of the formula $10Co—10Mn—5Ce/75SiO_2$ (weight basis) were prepared using incipient wetness impregnation method. For this purpose, calculated amounts of $Co(NO_3)_2 \cdot 6H_2O$ (99% Merck), $Mn(NO_3)_2 \cdot 4H_2O$ (99% Merck) and $Ce(NO_3)_2 \cdot 6H_2O$ (99% Merck) were separately dissolved in deionized water. The precursor solutions were well-impregnated on pre-calcined (at 673.15 K for 4 h) sol-gel silica supports in a rotary evaporator at 353.15 K for 4 h. Then the precipitates were dried (at 353.15 K for 12 h) and calcined (at 673.15 K for 6 h) to give the final catalysts.

The BET specific surface area and pore structures of the supports and catalysts were determined utilizing a N_2 adsorption-desorption analyzer (BELSORP-mini, BEL Co., Japan). Prior to measurements, the samples were degassed under N_2 atmosphere (at 393.15 K for 15 h) and evacuated at 77.15 K for 66 min. The pore size distribution and micropore characteristics (pore volume and pore diameter)

Table 1
Three levels of mixing controlling factors.

Controlling factors	Level 1	Level 2	Level 3
Re	2500	25,000	250,000
Fr	0.034	0.213	0.688
Θ (min)	30	45	60
N	10	8	6