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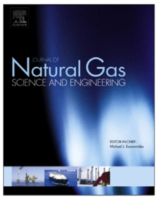

Effects of mass transfer on Fischer-Tropsch kinetics over mesoporous silica-supported Co–Mn–Ce nano catalysts in a fixed-bed reactor

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ABSTRACT

An impregnated ternary mixed oxide (Co–Mn–Ce) on nano silica support was applied, as a novel Fischer-Tropsch catalyst, in a fixed-bed reactor. Using catalysts of various pellet sizes, the Thiele modulus was determined to quantify regions of pore diffusion resistance and surface reaction. Mechanistic studies were conducted via intrinsic kinetic experiments under no pore diffusion conditions (i.e. Thiele modulus<0.4) as follows: $T = 483.15–583.15$ k, $P = 2–6$ bar, $H_2/CO = 1–2$, and $GHSV = 4500\ hr^{-1}$. Based on Langmuir–Hinshelwood–Hougen–Watson (LHHW) approach, the optimum mechanism was found to be associative adsorption of CO and H_2 with the irreversible associative hydrogen, with the carbon monoxide adsorption determined as the rate-controlling step. For the optimum model, intrinsic activation energy, R-squared value, and mean absolute relative residual were obtained as 62 kj/mol, 0.97 and 10.41%, respectively. Finally, a promising graphical approach was proposed to predict effective reaction rate, considering the effects of internal mass transfer in catalyst beads.

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1. Introduction

Heterogeneous catalyzed hydrogenation of CO is a commonly used, promising method for producing a wide spectrum of hydrocarbons, especially olefins (C_2–C_4) and clean fuels (Mirzaei et al., 2013a; Hanaoka et al., 2015). Due to the complicated nature of Fischer-Tropsch synthesis (FTS), its mechanistic kinetic study deems very important for an industrial process design, simulation and optimization over each catalytic system. While different parameters such as operating conditions are also noticeable, catalyst composition is the major determinant of Fischer-Tropsch performance (Akın and Önsan, 1997). An appropriate catalyst is to predominantly promote specific reactions towards obtaining desired products. Among the group VIII metals, iron and cobalt are known as the most popular and reliable Fischer-Tropsch catalysts (FTCs) (Dry, 2002; Yu et al., 2006). Exhibiting high Fischer-Tropsch activity and selectivity towards heavier hydrocarbons, cobalt activity towards water-gas shift reaction is low (Shimizu et al., 2015; Mirzaei et al., 2011). As such, it is widely applied in such FTS systems as those employed in GTL technology where the syngas is obtained from natural gas (Nakhaei Pour et al., 2014). Adding certain active metals to cobalt-based catalysts, one can change their activity and selectivity by modifying their geometric or electronic structure (Eisenacher and Adesina, 2000). Modification of cobalt with the same molar ratio of manganese oxide enhances the formation of light alkenes while suppressing methane yield at low conversion and atmospheric pressure (Colley et al., 1988; Hutchings et al., 1995; Arsalanfar et al., 2012a). Manganese usually improves the stability of both iron (Dad et al., 2015) and cobalt (Liu et al., 2009) in FTS. Adding cerium to FTC minimizes carbon deposition during FTS (Eisenacher and Adesina, 2000) and lowers the reduction temperature of cobalt catalysts (Ernst et al., 1997). Cerium also indicates dispersing effects on cobalt, especially over silica supports (Ernst et al., 1999). Moreover, cobalt-cerium matrix is essentially selective towards olefin formation (Arsalanfar et al., 2012b), so that it plays a synergistic role in the chemisorptions of reactant (Bruce et al., 1993). Among the wealth of information been recently presented in the literature about the kinetics of cobalt-based FTC (Todic et al., 2013; Botes et al., 2009), just a few emphasized on the kinetics of bimetallic cobalt-manganese (Atashi et al., 2010; Keyser et al., 2000) and cobalt-cerium catalysts (Mansouri et al., 2013a).

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Further, performed in fixed-bed micro-reactors, these studies have only dealt with intrinsic kinetic models presented via a LHHW approach. Consequently, there is a need for investigating simultaneous effects of manganese and cerium on the mechanism and kinetics of Co-based FTC.

It is well-established that cobalt catalysts have their dispersion and reducibility influenced by surface properties and support texture (Arsalanfar et al., 2014). Moreover, with the sizes of impregnated cobalt clusters on silica support depended on the average pore diameter of SiO_2, FTC is subject to significant changes in reducibility, selectivity and Fischer-Tropsch activity (Saib et al., 2002; Song and Li, 2006; Li et al., 2006), i.e., FTC performance depends on the active metal cluster size which can be tuned by the support structure.

The size of catalyst pellet also influences kinetic rate and product distribution (Borg et al., 2008; Rytter et al., 2007). Depending on the catalyst size, intrinsic reaction rate may be affected by internal mass transfer limitations (Vervloet et al., 2012; Hallac et al., 2015). So, the Thiele modulus and effective kinetic rate are necessary to be considered in the presence of intraparticle diffusion (Brunner et al., 2015).

In this paper, effects of catalyst pellet size on kinetic rate and pore diffusion resistance are investigated based on the Thiele modulus. Then, the intrinsic kinetics and reaction mechanism are illustrated in a fixed-bed reactor over mesoporous silica supported Co–Mn–Ce nano catalyst. Finally, a useful graphical method is introduced to predict an effective (apparent) rate for each catalyst size, based upon the intrinsic kinetics.

2. Experimental

2.1. Support (nano-silica) preparation

In the present research, so-called Sol-gel method was employed to fabricate a nano-silica support. A solution of sodium silicate (12 wt %) was prepared using cold deionized water (277.15 k). The solution was then stirred at 500 rpm and titrated by hydrochloric acid (normality = 10) for 60 min. Once the gel was formed, it was heated up to 313.15 k, to lower the viscosity. The obtained gel was washed, nine times, with 9 L of distilled water before being filtered to have such impurities as Na^+ ions removed. Finally, the precipitate was dried at 353.15 k for 24 h and then calcined at 673.15 k for 6 h.

2.2. Catalyst preparation

Catalysts were prepared using incipient wetness impregnation method. Aqueous solutions of $Co(NO_3)_2.6H_2O$ (99% Merck) (10 wt %), $Mn(NO_3)_2.4H_2O$ (99% Merck) (10 wt%), and $Ce(NO_3)_2.6H_2O$ (99% Merck) (5 wt%) were prepared and mixed with pre-calcined (673.15 K for 4 h) nano silica support (75 wt %). The resulting mixture was heated to 353.15 k in a rotary-evaporator for 4 h. The precipitate was dried in an oven (353.15 k, 12 h) and calcined (673.15 k, 6 h) to give the final catalyst. The catalyst pellets of different mesh sizes were prepared to study the effects of mass transfer and effective kinetics.

2.3. Catalyst characterization

Scanning electron microscopy (Cambridge S-360) was applied to observe the morphology of the synthesized support, precursor, and catalysts (fresh and used). Gold-coating the samples for 80 s (in 20 s-intervals), charging problems were inhibited.

In conjunction with SEM, elemental analysis of the fresh catalyst was carried out using energy-dispersive X-ray spectroscopy (EDX) (Cambridge S-360) wherein energy intensity was set to range within 0–20 kev.

In order to measure BET surface area of the support and the catalysts (before and after the test), the samples were first degassed under nitrogen atmosphere (573.15 k, 3 h) and evacuated at 77.15 k for 66 min. Then, N_2 physisorption was performed on a Nova 2000 (Quantachrome Instruments).

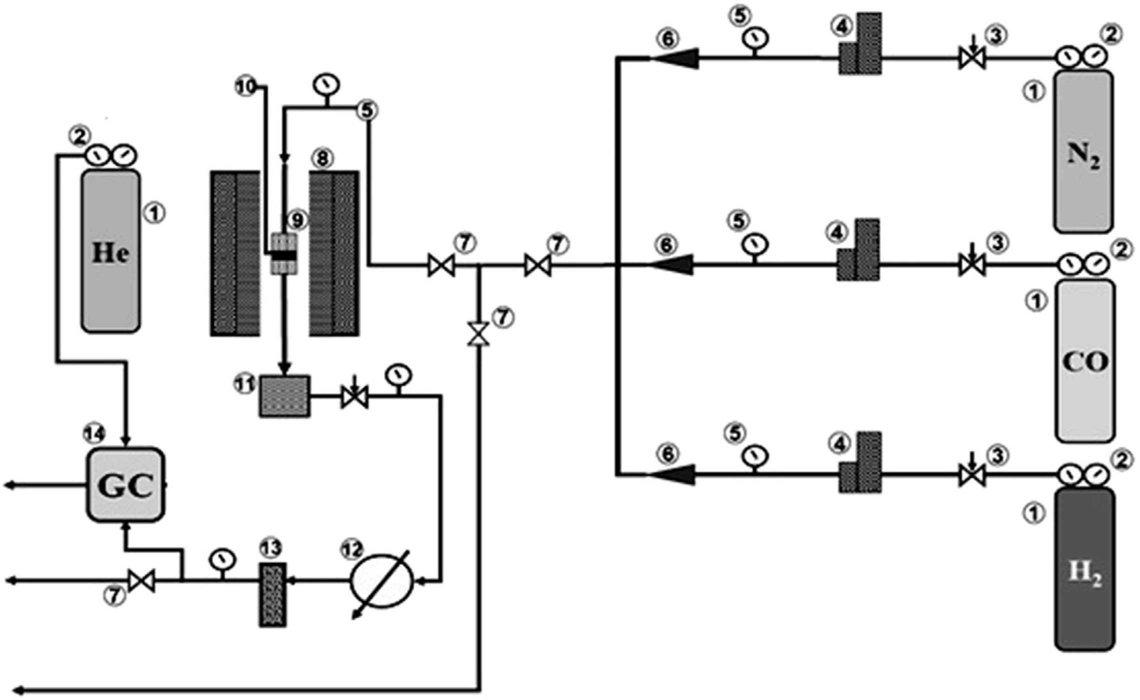

Fig. 1. Sketch of the reactor in the flow diagram: 1-gas cylinders, 2-pressure regulators, 3-needle valves, 4- mass flow controller (MFC), 5-pressure gage, 6-check valves, 7-ball valves, 8-tabular furnace, 9-reactor, 10-catalyst bed, 11-trap, 12-condenser, 13-silica-gel column, 14-gas chromatograph (GC).

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