Journal of Molecular Catalysis A: Chemical 425 (2016) 190–198

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Research Paper

Production of high-calorie synthetic natural gas using copper-impregnated iron catalysts

Yong Hee Lee[a], Dae-Won Lee[b,**], Kwan-Young Lee[a,c,*]

[a] Department of Chemical and Biological Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 02841, Republic of Korea
[b] Department of Chemical Engineering, Kangwon National University, 1 Kangwondaehak-gil, Chuncheon-si, Gangwon-do 24341, Republic of Korea
[c] KU-KIST School of Converging Science and Technology, Korea University, Anam-dong, Seongbuk-gu, Seoul 02841, Republic of Korea

ARTICLE INFO

Article history:
Received 26 July 2016
Received in revised form 6 October 2016
Accepted 9 October 2016
Available online 12 October 2016

Keywords:
High-calorie synthetic natural gas
Fe-Cu catalyst
Heating value

ABSTRACT

Fe-Cu catalysts were applied in the production of high-calorie synthetic natural gas (HC-SNG), wherein a proper level of C_2–C_4 hydrocarbon selectivity must be secured. The Fe-Cu catalysts were activated by reduction under diluted CO gas before the reaction, and their catalytically active Fe phases changed according to the reduction temperature: Fe_3O_4 formed when reduced at 300 °C, carbon-deficient FeC_x at 400 °C and Fe_3C at 500 °C. Iron carbide catalysts achieved stronger CO adsorption and higher BET surface area than Fe_3O_4 catalysts, which resulted in higher CO conversion. The carbon-deficient FeC_x was metal-like in its electron structure due to the low number of bonded carbons, and it was attributed to the highest CO and H_2 conversion of FC15-400R by providing H_2 activation ability. The C_n ($n \geq 2$) selectivity or carbon chain growth of the hydrocarbons increased as the carburization degree of the active Fe phase increased, which was associated with an increase in the CO chemisorption strength. The impregnated Cu exerted little influence on the product selectivity, but it promoted hydrogen adsorption, thereby improving the paraffin-to-olefin ratio of the produced hydrocarbons.

1. Introduction

Natural gas is still regarded as the most promising alternative fossil fuel resource for petroleum. It is estimated that the global production of natural gas will increase from 632 billion m^3 in 2013 to 1667 billion m^3 in 2040 [1]. The reserves-to-production ratio (R/P), which indicates the remaining time (or amount) to depletion for a fossil fuel resource, is estimated to be 54.1 years for conventional natural gas [2]. However, as unconventional resources such as shale gas, tight gas, coalbed methane, and methane hydrate are discovered, the R/P value of natural gas is extended, making it one of the most important issues in energy industry. In addition, the use of natural gas is recommended because it has environmental advantages over the use of other fossil fuel resources. Because methane has the highest H/C atomic ratio (= 4) among hydrocarbons, the combustion of natural gas releases the least amount of carbon dioxide (CO_2) per production of unit energy (50.1 g CO_2/kJ) than the combustion of other fossil fuels (88.0–97.8 g CO_2/kJ for coal and 67.3 g CO_2/kJ for gasoline) [3]. As a result, natural gas is proposed as the only realistic solution for alleviating the carbon dioxide emissions of fossil-fuel-based power stations [4]. Other environmental benefits of natural gas combustion are the relatively low emissions of carbon monoxide, particulate matter, sulfur oxides and nitrogen oxides. Now it is widely recognized that "a Golden Age of the Gas" will begin in near future [5].

Natural gas is transported by ships or pipeline. To be transported by ships, natural gas should be liquefied under high-pressure compression, which is called liquefied natural gas (LNG). The natural gas which is transported in a gas state through pipeline is called pipeline natural gas (PNG). In general, LNG has a much higher heating value (approximately 41–42 MJ/Nm^3 [6]) than that of PNG (33.8–38.8 MJ/Nm^3) [7–9] because LNG contains more C_{2+} hydrocarbons than PNG does. South Korea and Japan import LNG by ships because they are surrounded by sea, separated from the main continent. Thus, the standard heating value of natural gas distributed in these countries is established at high values over 42.7 MJ/Nm^3. However, the average heating value of LNG in the worldwide market is on the continuous decrease because LNG suppliers tactically lower the heating value of LNG by separating C_{2+} hydrocarbons. Their purpose is first to respond to the increasing number of PNG customers by standardizing the heating values downward toward

---

* Corresponding author at: Department of Chemical and Biological Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 02841, Republic of Korea.
** Co-corresponding author.
E-mail addresses: stayheavy@kangwon.ac.kr (D.-W. Lee), kylee@korea.ac.kr (K.-Y. Lee).

http://dx.doi.org/10.1016/j.molcata.2016.10.013
1381-1169/

the level of PNG and second, to make more profit by selling C_{2+} hydrocarbon gas [10]. Due to the continuous decrease in the heating value of LNG, the rate by which municipal gas distribution is measured in South Korea was recently changed from a volume-based rate to the heat-based rate. However, this practice results in an increase in the total volume consumption to meet the demanded heating values, which causes other problems, such as an increase in the cost for transport and storage.

Synthesizing high-calorie natural gas has been suggested as a solution for the problem of low-calorie natural gas. To state the obvious, the production of high-calorie gas should be based on inexpensive carbon resources, such as coal or biomass. Most existing technologies for synthetic natural gas (SNG) synthesize pure methane (*i.e.*, methanation) from coal-based synthesis gas (syngas). On the basis of the commercial SNG (methanation) processes [11], the production of high-calorie synthetic natural gas (HC-SNG) may be divided into a three-step process: (1) a coal gasifier, where coal is converted into syngas, (2) a water-gas shift (WGS) reactor to increase the H_2/CO proportion to 3, which is the stoichiometric ratio of the methanation reaction, and (3) a series of '*high-calorie SNG production*' reactors to convert the syngas into a methane and C_{2+} hydrocarbon gas mixture. The heating value of SNG can be enhanced by increasing the fraction of C_2–C_4 hydrocarbons because the heating value of individual hydrocarbons simply increases as the carbon number increases (the heating values of ethane, propane and *n*-butane are 64.3, 92.2 and 121.3 MJ/Nm^3, respectively [12]). Thus, the activity of the catalysts for the production of high-calorie SNG should be based on methanation, but at the same time, the catalyst should possess a short-chain (C_2–C_4) Fisher-Tropsch (FT) activity.

The four group VIII metals, Fe, Co, Ni and Ru, are well known to be the most active for hydrogenation of carbon monoxide to hydrocarbons [13]. Because Ni catalysts are highly selective for methane [13,14], they are not suitable for the production of high-calorie SNG. Inui et al. studied the Co-based catalyst to convert coke oven gas into high-calorie SNGs [15,16]. However, the Co-Mn-Ru/Al_2O_3 catalysts are limited in securing high C_2–C_4 selectivity. Ru has been reported to provide a strong H_2 spillover effect on the active Co phase, which resulted in increases in the CO conversion and CH_4 selectivity but also caused a decrease in the carbon chain growth [17,18]. The SNG produced using Co-Mn-Ru/Al_2O_3 contained 12.8 *vol.%* of C_2–C_4 hydrocarbons (24.6% in selectivity) to result in a heating value of 43.8 MJ/Nm^3 [18], which narrowly satisfied the required standard heating value (>42.7 MJ/Nm^3). However, this heating value is not considered high enough to mix with other low-calorie gases to increase their heating values.

Hence, we focused on Fe-based catalysts, which are known to be especially active for the production of C_2–C_4 hydrocarbons (olefins) [19–29] in FT synthesis. It was reported that a commercial Fe-based, high-temperature Fischer-Tropsch (HTFT) process produces 49 wt.% C_2–C_4 hydrocarbons with 36 wt.% gasoline and diesel [30]. Therefore, the short-chain FT activity can be regarded as an advantage of Fe when it is used as an active component of the catalyst for the production of high-calorie SNG.

The FT activity of Fe catalysts is dependent on the type of active species. Magnetite (Fe_3O_4) and various types of iron carbides (FeC_x) are known to be catalytically active in FT synthesis. Most recent studies (published in the years 2005–2015) claimed that FeC_x has higher FT activities than that of Fe_3O_4 [31–34]. However, the active phases of Fe catalysts are frequently observed to be a mixture of Fe_3O_4 and FeC_x (especially χ-Fe_5C_2). As a promoter component for Fe, Cu is a promising candidate because Cu promotes the dissociation of hydrogen (reactant) to improve the reducibility of the Fe species [35,36]. At the same time, it could act as a structural promoter to stabilize the magnetite and iron carbide phases against thermal degradation or agglomeration [37,38]. As mentioned above, Fe catalysts usually produce high olefin-to-paraffin ratio products compared to Co [39]. This is mostly due to the hydrogenation activity of Fe, which is the lowest among the first period of group VIII metals [40]. The low hydrogenation activity of Fe is <u>*not*</u> a disadvantage in Fischer-Tropsch applications because an otherwise high hydrogenation activity rather leads to an increase in the methane selectivity, which is unfavorable from the standpoint of FT synthesis. On the contrary, the low hydrogenation activity of the catalyst could be a disadvantage in the production of high-calorie SNG. First, it results in an increase in the olefin selectivity. It is desirable for the catalysts of the production of high-calorie SNG to maintain low olefin selectivity because an olefin has lower heating value than its analogous paraffin. Second, if a catalyst is not properly active for hydrogenation, the carbon chain growth of hydrocarbons can extend beyond an acceptable level. In SNG production, the formation of hydrocarbons longer than C_5 must be prohibited because they are condensable and cause many problems during the transportation of HC-SNG. Thus, unlike for Fischer-Tropsch catalysts, a proper level of hydrogenation activity is a type of prerequisite for the catalysts for the production of high-calorie SNG. In Fe-based catalysts, the promotion by Cu can be a way to augment the poor hydrogenation activity of Fe.

In this work, Fe-Cu catalysts were applied to the production of high-calorie SNG. The Fe-Cu catalysts were prepared by impregnating the precipitated α-Fe_2O_3 with Cu in a wide range of Fe/Cu compositions. We anticipated that CO would be activated to grow into C_2–C_4 hydrocarbons over the Fe sites, while Cu would provide the hydrogenation sites required to suppress the carbon chain growth into undesirably high hydrocarbons ($\geq C_5$) and to promote the formation of paraffin. The catalysts were activated *via* CO reduction at various temperatures, by which different types of active Fe phases were obtained, and their activities were tested in the production of high-calorie SNG. The activities were evaluated in terms of CO conversion, C_2–C_4 selectivity, chain growth probability (α), heating value (MJ/Nm^3) based on the produced hydrocarbons, *etc.* The promoting effect of Cu was examined especially in terms of the paraffin-to-olefin ratio in hydrocarbon products. Characterization techniques based on X-ray spectroscopy and temperature-programmed reduction/desorption were applied to explain the activity of the tested catalysts.

2. Materials and methods

2.1. Catalyst preparation

Fe-Cu catalysts were prepared by impregnating α-Fe_2O_3 with Cu. First, α-Fe_2O_3 was synthesized by the precipitation method as follows: 100 mL of deionized water was poured into a 500 mL three-neck flask with three necks. The water temperature was adjusted to 80 °C, and the pH was adjusted to 7 using a 1 M aqueous solution of $(NH_4)_2CO_3$ (Aldrich). Then, 60 mL of an aqueous $Fe(NO_3)_3{\cdot}9H_2O$ (Sigma-Aldrich) solution (Fe metal concentration = 1 M) was dropped into the flask at a rate of 2 mL/min. Iron hydroxides were precipitated by adding a precipitating agent, $(NH_4)_2CO_3$ (*aq*., 1 M). The pH was maintained at 7 ± 0.03 while the precipitation continued. The precipitates were aged at 80 °C for 2 h and then washed sufficiently using 6 L of deionized water. The washed precipitates were dried at 110 °C overnight and then oxidized to α-Fe_2O_3 at 550 °C under static air for 1 h. The α-Fe_2O_3 was impregnated with Cu by the incipient wetness method using aqueous solutions of $Cu(NO_3)_2{\cdot}2.5H_2O$ (Sigma-Aldrich). The impregnated samples were dried at 110 °C overnight and calcined at 550 °C for 5 h. For convenience, Fe–Cu catalysts are abbreviated to FC catalysts, and are denoted as FC*x*-*y*R, where *x* and *y* represent the Fe/Cu ratio (x = 40, 15, 6) and reduction temperature (y = 300, 400,