G Model
JIEC 4039 No. of Pages 8

ARTICLE IN PRESS

Journal of Industrial and Engineering Chemistry xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Fe–Co/alumina catalysts for production of high calorific synthetic natural gas: Effect of Fe/Co ratio

Ji-Yong Lee[a,b], Ki-Won Jun[a,b,*], Seok Chang Kang[b], Chundong Zhang[b], Geunjae Kwak[b], Jin-Mo Park[c], Hyung-Sik Kim[c]

[a] Advanced Materials and Chemical Engineering, School of Science, Korea University of Science and Technology (UST), Yuseong, Daejeon, 305-333, Republic of Korea
[b] C1 Gas Conversion Research Group, Carbon Resources Institute, Korea Research Institute of Chemical Technology (KRICT), Yuseong, Daejeon, 34114, Republic of Korea
[c] New Energy Technology Research Center, Korea Gas Corporation (KOGAS), 1248, Suin-Ro, Sangnok-Gu, Ansan City, Kyunggi-do, 426-790, Republic of Korea

ARTICLE INFO

Article history:
Received 14 February 2018
Received in revised form 6 June 2018
Accepted 7 June 2018
Available online xxx

Keywords:
Fe–Co/alumina catalysts
Co-precipitation
Methanation
Fischer–Tropsch synthesis
High calorific synthetic natural gas

ABSTRACT

The effect of the Fe/Co ratio on the catalytic performance of Fe–Co/alumina catalysts has been investigated in the production of high-calorific synthetic natural gas (SNG) from syngas. Fe–Co/alumina catalysts with different Fe/Co molar ratios were synthesized by the co-precipitation method and characterized using XRD, BET, H_2-TPR, Raman, XAS, and XPS. At higher Fe/Co ratios ($\geq$2), the calcined Fe–Co/alumina catalysts were mainly composed of α-Fe_2O_3 and $CoFe_2O_4$. The presence of Co improved the dispersion of iron oxides and the catalyst reducibility under H_2 atmosphere. The Fe–Co/alumina catalysts partially formed FeCo alloys when they were reduced at 350 °C under H_2. The formation of FeCo alloy destabilized the iron carbide phase and suppressed the carbon chain growth. These Fe–Co/alumina catalysts were efficient in producing high calorific SNG with a heating value of over 60 MJ/Nm^3.

Introduction

Coal is one of the most important energy sources available to mankind. Its price per calorie is relatively low and it is distributed in various regions all over the world, which is advantageous in terms of energy security [1]. However, the biggest constraint on the use of coal as a fuel is the relatively high emission of CO_2, NO_x, SO_x, and particulate matter per unit calorific value. In contrast, the demand for natural gas as a clean fuel is continually increasing because it is mainly composed of CH_4, which generates significantly less air pollutants during combustion. However, the distribution of natural gas is concentrated in specific areas, resulting in additional costs in transport and storage [2].

Owing to these characteristics, countries that have abundant coal but lack natural gas have a keen interest in synthetic natural gas (SNG). For example, by 2013, China had invested in nine large-scale SNG power plants with an annual capacity of 37.1 billion m^3, which utilized coal to produce natural gas [3]. The use of the SNG process can reduce the costs associated with the transportation and storage of natural gas in addition to reducing the dependence on natural gas imports. It also has the advantage of less emissions of air pollutants compared to burning coal directly [4–7].

Unlike the US and Europe where natural gas can be supplied through pipelines, Northeast Asian countries are forced to import natural gas in the form of liquefied natural gas (LNG) because of limited gas resources and geographical constraints [8]. Although the calorific value of imported natural gas is steadily decreasing because natural gas is supplied after separating C_2–C_4 light hydrocarbons, Northeast Asian countries such as Korea and Japan still use the town gas that has a relatively high calorific value (41–46 MJ/Nm^3) [9]. It is worth noting that the conventional SNG process mainly produces methane, which has a very low calorific value (below 41.84 MJ/Nm^3) [10]. Therefore, it is necessary to develop catalysts and a process methodology that produces high calorific SNG with high selectivity toward C_2–C_4 paraffin gases.

In the traditional SNG process, synthetic natural gas is produced from syngas using a methanation catalyst [11]. Since the introduction of a Ni catalyst by Sabatier and Senderens in 1902, methanation catalysts have been mainly selected from group VIII. Among the active metals of group VIII, Ni is mainly used because of

---

* Corresponding author at: C1 Gas Conversion Research Group, Carbon Resources Institute, Korea Research Institute of Chemical Technology (KRICT), Yuseong, Daejeon, 34114.
E-mail address: kwjun@krict.re.kr (K.-W. Jun).

https://doi.org/10.1016/j.jiec.2018.06.006
1226-086X/

Please cite this article in press as: J.-Y. Lee, et al., Fe–Co/alumina catalysts for production of high calorific synthetic natural gas: Effect of Fe/Co ratio, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.06.006

its relatively high activity and low cost. Furthermore, it has low WGS activity and leads to a high yield of methane yield [12–14].

In order to produce SNG comprising methane and light hydrocarbon gases, the carbon chain growth by Fischer–Tropsch reaction is necessary to some extent as well as the methanation reaction. Typical catalytic components of Fischer–Tropsch synthesis (FTS) are iron and cobalt [15]. Although the active phase of the Fe catalyst in FTS is not clearly understood, it is agreed that the activity of the catalyst changes depending on the composition of the iron catalyst, which is composed of a mixture of iron oxide, iron metal, and iron carbide [16,17]. Co metal is known to be active in FTS, Co catalysts have been reported to have a very high methane selectivity in the case of incompletely reducing or forming Co_3O_4 particles [11].

Additionally, it is important to increase paraffin selectivity and maximize the C_2–C_4 selectivity in the high calorific SNG synthesis reaction. Paraffin is not only high in calorific value as compared to olefins but also easy to transport in the gas supply lines. In FTS, it is generally known that cobalt catalysts produce more paraffin than iron-based catalysts [9,18,19].

It is worth noting that Fe–Co catalysts have been previously investigated for FTS reaction [20–23] and are not typically expected to produce SNG with a high heating value. In this study, Fe–Co/alumina catalysts were designed to synthesize high calorific SNG composed of methane and C_2–C_4 paraffin gases from syngas. These catalysts were prepared with varying Fe/Co ratios and their activities were compared with that of Fe/alumina, Co/alumina, and a physical mixture of Fe/alumina and Co/alumina.

Experimental

Catalyst preparation

The Fe–Co/alumina catalysts were prepared by co-precipitation of the components from solutions of the corresponding metal nitrates. $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, and $Al(NO_3)_3{\cdot}9H_2O$ were dissolved in deionized water, and the total metal precursor concentration was 1 M. The mixed nitrate solution was added into 1 M K_2O_3 solution with stirring until a pH of 7–8 was reached to precipitate all metal ions. The value of the Fe/Co ratio was estimated by ICP (Table 1) and the analytical results were in good agreement with the nominal value. The precipitate was aged for 2 h at 80 °C, washed with 5 L of deionized water, and subsequently dried overnight at 110 °C. The dried precipitate was calcined at 550 °C for 5 h under static air. In this report, the Fe–Co/alumina catalysts have been denoted as FC-X, where X represents the Fe/Co ratio. The prepared catalysts and their compositions are listed in Table 1. Fe/alumina and Co/alumina catalysts were also prepared by the same precipitation method and $CoFe_2O_4$ (Aldrich, $\geq$99.9) was used to compare the catalytic properties with the FC-X catalysts.

Table 1
Notation and Fe/Co atomic ratios of the Prepared Fe–Co/alumina catalysts[a].

Catalyst code	Atomic ratio (Fe/Co)	
	Nominal	Measured[b]
FC-20	20	20.8
FC-9	9	9.4
FC-4	4	4.2
FC-2.5	2.5	2.6
FC-1.5	1.5	1.6
FC-1	1	1.1

[a] A constant molar ratio of Al/(Fe + Co) was kept at 0.3 for all the catalysts.
[b] The concentration of each component was measured by ICP-AES.

Catalyst characterization

Powder X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (Rigaku, D/Max-RC) equipped with Cu/Kα radiation operating at 40 kV in the range $2\theta = 5$–$80°$ to identify the phase change of the Fe–Co/alumina catalysts. The reducibility of the Fe–Co/alumina catalysts was investigated by temperature programming reduction (TPR) conducted with a Micromeritics instrument (Autochem II). In this experiment, 0.1 g of the sample was preheated in a quartz reactor under argon at 200 °C for 2 h and then cooled to 50 °C. The catalyst was heated again under a flow rate of 50 mL/min of 10% H_2/Ar at a rate of 10 °C/min from 50 to 1100 °C. The surface area of the catalyst was estimated from the N_2 desorption isotherms obtained at 77 K using a constant volume adsorbent (Micromeritics, ASAP 2420). FT-IR spectra were recorded on a Vertex80 v (Bruker) spectrometer over the range of 400–2000 cm^{-1}. Raman spectra of the samples were collected on a LabRAM HR Evolution Visible-NIR (HORIBA) spectrophotometer at 514 nm from an Ar ion laser. X-ray absorption spectroscopy (XAS) measurements of the K-edge of the sample powders were carried out in the transmission mode at the 8C nano XAFS beamline of the Pohang Light Source (PLS) in the 3.0 GeV storage ring, with a ring current of 70–100 mA. A Si(111) double-crystal was used to monochromatize the X-ray photon energy. XAS data reduction and fitting were carried out using Athena software, and X-ray absorption near edge structure (XANES) spectra were obtained by normalization. Extended X-ray absorption fine structure (EXAFS) data was obtained by performing a Fourier transform from the *k*-space to the R-space. The surface Fe species after calcination were characterized by XPS (AXIS NOBA). During these experiments, the Al Kα monochromatized line (1486.6 eV) was adopted and the vacuum level was around 10^{-8} Pa. The calcined powder sample was previously pressed into a thin pellet and the binding energy (BE) were corrected with the reference BE of O 1s (530.1 eV).

Activity test

The activity test of the catalysts was carried out using 0.5 g of the catalyst in a continuous fixed bed reactor. Each catalyst was reduced with hydrogen at 350 °C for 6 h before the reaction. Reactant gas was the mixed gas of $CO:H_2:Ar = 24:72:4$ (mole ratio) and the space velocity was 6000 $mL\,g_{cat}^{-1}\,h^{-1}$. The reaction pressure was controlled at 30 bar using a back-pressure regulator and the reaction temperature was maintained at 350 °C. The feed and product gases were analyzed by gas chromatography (GC, Yeonglin Instrument). Ar was used as an internal standard to calculate product selectivity of CO conversions. Ar, CO_2, CO, and CH_4 were analyzed using a thermal conductivity detector (TCD) equipped with packed columns (Porapak Q and molecular sieve), and the hydrocarbons (C_1–C_4, C_{5+}) were analyzed with a FID equipped with a capillary column (GS-GASPRO).

The conversions of carbon monoxide and the selectivity toward hydrocarbons were calculated using Eqs. (1) and (2). Here, $n_{co(in)}$ refers to the number of moles of CO in the feed and the $n_{co(out)}$ is the number of moles of CO that were not consumed. In this case, selectivity is defined as the percentage of CO moles converted to a C_n product (hydrocarbon, CO_2) and normalized to the amount of CO consumed. The calorific value of the product was calculated from Eq. (3) and based on the heat of combustion determined from the NIST Chemistry WebBook data. The calorific value was calculated with the exception of non-hydrocarbon species (CO, H_2, H_2O).

$$\text{Conversion} = 100 \times \frac{n_{co(in)} - n_{co(out)}}{n_{co(in)}} \tag{1}$$

Please cite this article in press as: J.-Y. Lee, et al., Fe–Co/alumina catalysts for production of high calorific synthetic natural gas: Effect of Fe/Co ratio, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.06.006