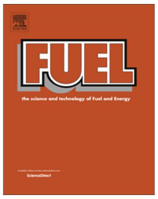
Fuel 136 (2014) 130–135

Contents lists available at ScienceDirect

Fuel

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



Fischer Tropsch synthesis from H_2-deficient biosyngas over Mn added Co/SiO_2 catalysts

Yuping Li [a,*], Xinxin Qin [a], Tiejun Wang [a,*], Longlong Ma [a], Lungang Chen [a], Noritatsu Tsubaki [b]

[a] *CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, 510640 Guangzhou, PR China*
[b] *Department of Applied Chemistry, School of Engineering, University of Toyama University, Gofuku 3190, Toyama 930-8555, Japan*

HIGHLIGHTS

- Adding 0.8 wt.% Mn to Co/SiO_2 increased the small-sized Co reduction.
- High CO conversion of 52.6% using H_2-deficient biosyngas over Co-(0.8%)Mn/SiO_2 was obtained.
- 7.0 vol% CO_2 in the feed gas inhabited CO_2 formation during FTS.
- Relatively slow CO_2 hydrogenation rate decreased its conversion, compared with CO conversion.
- FTS from H_2-deficient gas may be efficient, due to avoiding of gas composition adjustment steps.

ARTICLE INFO

Article history:
Received 10 November 2013
Received in revised form 9 June 2014
Accepted 19 June 2014
Available online 19 July 2014

Keywords:
Fischer Tropsch synthesis
H_2-deficient biosyngas
Co/SiO_2
Mn addition

ABSTRACT

Co/SiO_2 catalysts with 0.4–7.0 wt.% of Mn addition were prepared and evaluated for Fischer–Tropsch synthesis (FTS), using H_2-deficient biosyngas ($H_2/CO/CO_2/N_2 = 45/45/7/3$, vol%) as feed gas. 0.8 wt.% of Mn addition to Co/SiO_2 increased Co dispersion and weakened Co–Si interaction on Co–(0.8%)Mn/SiO_2 catalyst. Co reducibility was improved to 32.1% and 79.3% at 150–400 °C and 150–750 °C respectively by H_2-temperature programmed reduction (TPR), which resulted in CO conversion of 52.6% and C_{5+} yield of 43.6% at 24 h time on stream when H_2-deficient biosyngas was used as feed gas for FTS. Co was further dispersed with low reducibility at higher Mn addition amount, which decreased CO conversion and favored gaseous hydrocarbon synthesis over Co–(2.0%)Mn/SiO_2 and Co–(7.0%)Mn/SiO_2. The higher H_2/CO usage ratio was obtained over Co/SiO_2 using H_2-deficient biosyngas, compared with that using feed gas with H_2/CO ratio of 2.0 over the same catalyst. The existence of small amount of CO_2 (like 7.0 vol%) in biosyngas might be the main reason to inhibit water gas shift reaction and impel CO_2 conversion.

1. Introduction

Catalytic conversion of biomass-derived syngas to long-chain hydrocarbons by Fischer–Tropsch synthesis (FTS) is a promising process for the sustainable liquid fuel supply [1]. However the costly composition adjustment procedures of biosyngas such as H_2 adding, reforming and CO_2 removal, are usually needed because the raw gas after biomass gasification is H_2-deficinent and CO_2-rich, which does not fit the stoichiometric requirement of FTS [2]. Enormous efforts have been made to improve the gas utilization efficiency of these H_2-deficient biosyngas [3,4]. It was reported that H_2 content was increased by water-gas shift (WGS) reaction over Fe-based FTS catalysts [5–7], for the following FTS [8]. However the increased CO_2 content after WGS reaction and the low CO_2 hydrogenation rate decreased the carbon utilization efficiency of biosyngas [9,10].

Co-based catalyst, promoted by noble metal (Ru, Rh, Pt, et al) and metal oxide (ZrO_2, La_2O_3, MnO, et al) [11,12], seem to be an attractive option for H_2-deficient biosyngas conversion to hydrocarbons due to their high hydrogenation ability and C_5^+ selectivity [13,14]. As a promoter, Mn is promising because of its high H_2 bonding energy [15]. Although it is proved that FTS performance depends on catalyst composition, feed gas composition and reaction condition, due to the adsorption and hydrogenation difference of CO_2 and CO on the active catalyst surface [16,17], few concrete studies have been focused on the conversion characteristics of biosyngas [18,19]. In this work FTS was carried out over Mn-added Co/SiO_2 catalysts, using model biosyngas ($H_2/CO/CO_2/N_2 = 45/45/7/3$, vol%; $H_2/CO = 1.0$) as feed gas. Particular attention was paid

---

* Corresponding author.
E-mail addresses: liyp@ms.giec.ac.cn (Y. Li), wangtj@ms.giec.ac.cn (T. Wang).

http://dx.doi.org/10.1016/j.fuel.2014.06.048
0016-2361/

towards the influence of Mn addition amount, feed gas composition and catalyst stability on FTS performance to improve the utilization efficiency of H_2-deficient biosyngas.

2. Experimental

2.1. Catalyst preparation

20 wt.% of SiO_2 supported Co catalysts were prepared by incipient-wetness impregnating method (IWI). 1.0 mol/L cobalt nitrate aqueous solution was added to SiO_2 (BET surface area of 101 m^2/g, pore volume of 0.58 ml/g, pore diameter of 40 nm, NH_3 uptake of 0.02 mmol/g) at room temperature to completely wet the SiO_2 samples. The impregnated solid was dried at 120 °C for 12 h and calcined in air at the ramp rate of 2 °C/min to 400 °C with holding at 400 °C for 4 h. The impregnation of Co on SiO_2 was repeated until the total of 20 wt.% Co/SiO_2 was obtained. The sample was then used as the support material for IWI of 0.5 mol/L manganese nitrate aqueous solution, following the same drying and calcination procedures as mentioned above. The calcined sample was pressed under 15 MPa and sieved to the desired pellet size (20–40 mesh). The catalysts prepared were denoted as Co–(x%)Mn/SiO_2, where x referred to Mn amount (wt.%, 0.4, 0.8, 2.0,7.0 respectively).

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/max-rC using Cu Kα radiation source. The line broadenings of Co diffraction peaks localized at 36.8° and 44.6° were used to estimate Co crystallite sizes of the calcined and reduced catalysts respectively, according to Scherrer equation. Before H_2 chemisorption, 0.1 g samples were reduced at 400 °C under 30 ml/min of 5%H_2/95%N_2(vol) flow for 8 h and then purged with N_2 at 400 °C for 1 h. H_2 was then pulsed to the reduced catalysts at 100 °C, according to the reports that H_2 chemisorption at 100 °C is most reliable for silica-supported cobalt catalyst [20]. Co dispersion was estimated by the uptake amount of H_2 chemisorption at 100 °C.

In H_2-temperature programmed reduction (H_2-TPR), about 0.10 g calcined catalyst was placed in a quart tube reactor, then heated from room temperature to 900 °C at the ramp rate of 5 °C/min in 5%H_2/95%N_2(vol) flow at 30 ml/min. TCD detector was used to monitor H_2 consumption amount. The 5 Å molecular sieve trap was set after the reactor to remove the formed water before entering TCD detector. The catalyst reducibility at 150–750 °C were evaluated according to the hydrogen consumption amount from 150 °C to 750 °C, which was determined by comparing with the calibration areas of 5 vol% H_2 in N_2 and correlated to percentage of metal reduced during standard reduction processing (ramp 2 °C/min to 400 °C, hold for 8 h). And the TPR spectrum was integrated and normalized to unity for qualitative analysis of cobalt reducibility at 150–400 °C, which was calculated as: (Integrated area$_{150\text{-}400\,°C}$/Integrated area$_{150\text{–}750\,°C}$) × Reducibility$_{150\text{–}750\,°C}$.

2.3. FTS reaction

FTS reaction was carried out in a fixed-bed reactor under 2.0 MPa, 240 °C and gas hour space velocity (GHSV) of 1000 h^{-1}. The model H_2-deficient biosyngas ($H_2/CO/CO_2/N_2$ = 45/45/7/3, vol%; H_2/CO = 1.0) was used as feed gas to simulate the biosyngas, produced after O_2 gasification of biomass and CO_2 removal. In each FTS run, 1.00 g catalyst was reduced in situ at 400 °C under 5%H_2/95%N_2(vol) flow for 8 h. After that, the catalyst was cooled to 180 °C and reheated to the reaction temperature under feed gas flow. The pressure was increased to 2.0 MPa with a back-pressure regulator. The tail gas was analyzed by two online gas chromatographs at intervals of 2 h. CO, N_2, CH_4 and CO_2 were analyzed by carbon-sieve column (3 m × 3 mm i.d., 100 °C) with TCD detector. Gaseous hydrocarbons (C_1–C_5) were analyzed by Porapak Q column (3 m × 3 mm i.d., 110 °C) with FID detector. The liquid product in the traps was collected at intervals of 24 h, which separated into two phases of water and oil. The oil phase was analyzed by a FID GC equipped with SE-30 capillary column, heated from 40 °C to 280 °C at the ramp rate of 5 °C/min with holding at 280 °C for 30mins. Formation of few waxy materials was observed in the traps, which was collected with the initial oil product. N_2 in the feed gas was used as internal standard to calculate conversion and hydrocarbon selectivity. The hydrocarbon selectivity distributions were calculated on the basis of carbon number.

The reactant conversion and hydrocarbon selectivity (mol%) were calculated by the following formulas:

$$X_{reactant}(\%) = [(\text{moles of reactant}_{in} - \text{moles of reactant}_{\text{out}})/\text{moles of reactant}_{\text{in}}] \times 100\%,\ \text{reactant}—\text{CO}, \text{CO}_2, \text{H}_2;$$

$$\text{S}_{Cn}(\%) = [n \times \text{moles of Cn}_{\text{produced}}/(\text{moles of }(\text{CO}+\text{CO}_2)_{\text{in}}\text{-moles of}(\text{CO}+\text{CO}_2)_{\text{out}})] \times 100\%,\ \text{Cn}—\text{the hydrocarbon product with carbon number of } n;$$

$$\text{H}_2/\text{CO usage ratio} = X_{\text{H}_2}/\text{X}_{\text{co}};$$

$$\text{S}_{\text{CO}_2} = [(\text{moles of}_{\text{CO}_2\ \text{out}} - \text{moles of}_{\text{CO}_2\ \text{in}})/(\text{moles of CO}_{\text{in}}\text{-moles of CO}_{\text{out}})] \times 100\%(\text{in the cases that CO}_2\text{ was produced});$$

$$\text{Yield}_{\text{C5+}}(\%) = \text{X}_{\text{CO}} \times (1 - \text{S}_{\text{CH}_4} - \text{S}_{\text{C}_2-\text{C}_4} - \text{S}_{\text{co}_2}) \times 100\%;$$

The total carbon balance for the majority of the experiments was within 100 ± 10%. Because in most cases, the selectivity to heavier wax (>C_{28}), alcohols and acetones was less than 3%, their values were ignored in the selectivity calculation.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1(A) and (B) illustrate the XRD patterns of the calcined and reduced Co–Mn/SiO_2, which exhibit the phase of Co_3O_4 and cubic metallic Co, respectively. Yet the existence of weak CoO diffraction line for the reduced catalyst in Fig. 1(B) was the result of the reoxidation of metal Co under atmosphere condition during XRD analysis. No peaks corresponding to MnO or Mn-support species were displayed, even for Co–(7.0%)Mn/SiO_2 with 7.0wt.%Mn addition, probably because of the high dispersion of Mn species. But the existence of Co–Mn mixed species could be deduced by the slightly smaller 2θ values of Co_3O_4 reflections in Mn-promoted catalysts in Fig. 1(A), resulted from the decrease in the cell parameters of Mn^{3+} incorporation into the Co_3O_4 lattice [21].

XRD patterns of the calcined and reduced Co–Mn/SiO_2 catalysts shows the wider diffraction peaks at 36.8° of Co_3O_4 and 44.6° of Co° respectively, with the increase of Mn addition amount. The particle size calculated by Scherrer's equation is not completely accurate, because of the neglected contribution of crystallite strain to the diffraction line broadening. However, the differences in Co particle sizes indicate that Mn addition affects the size and crystallinity of Co_3O_4 particles, as a result of a physicochemical interaction between these compounds during calcination treatment.

The most intensive peaks of Co_3O_4 and Co° in XRD pattern of Co/SiO_2 resulted in the largest Co^0 particle size of 11.3 nm and 16.5 nm for the calcined and reduced catalysts respectively in Table 1. For Co–Mn/SiO_2 catalysts, the decrease of Co° size with