

STUDY ON THE CARBON DIOXIDE HYDROGENATION TO HYDROCARBONS OVER NANOPARTICLES IRON-BASED CATALYST

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Abstract

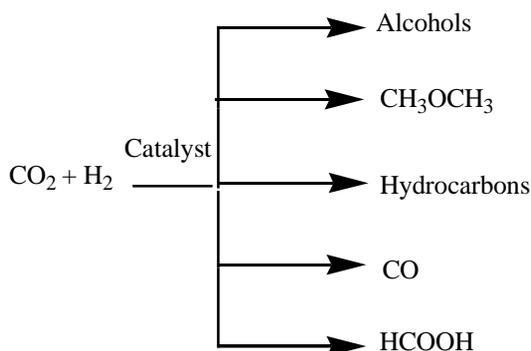
In this study, synthesis of hydrocarbons from carbon dioxide hydrogenation was investigated over nanoparticles Fe-Cu-Zn catalyst. Catalyst composition in atomic ratio was: 100Fe/4Cu/10Zn. The phase, structure, and morphology of the catalyst was characterized by X-ray diffraction, N₂ adsorption, transmission electron microscopy, and temperature-programmed reduction. Test of reaction was performed in a fixed bed reactor at pressure, temperature, H₂/CO₂ ratio and GHSV of 16 atm, 295°C, 3, 2.3 nl.h⁻¹.gCat⁻¹, respectively. Zn-promoted nano iron catalyst improved the Fischer-Tropsch synthesis activity and decreased methane selectivity to 16.6% and increased CO₂ conversion to 24.6%.

Keywords : Nano Fe-Cu-Zn catalyst; CO₂ hydrogenation; Products selectivity.

1. Introduction

The Fischers-Tropsch synthesis (FTS) has been extensively investigated since the discovery of methane production over nickel in 1902. In the past three decades, the hydrogenation of carbon monoxide was actively studied all over the world because it was an important step in the utilization of coal and natural gas as typical carbon sources. Production of hydrocarbons from CO₂ hydrogenation is essentially a modification of FTS, where CO₂ is used instead of CO. Catalyst compositions for CO₂ hydrogenation are analogous to that for FT synthesis but is amended to maximize the production of hydrocarbons. The concentration of carbon dioxide in atmosphere has consequently risen from 280 ppm before the industrial revolution to 390 ppm in 2010, which is further predicted to be 570 ppm by the end of the century [1]. However, the hydrogenation of CO₂ received much less attention, partially due to unfavourable thermodynamic consideration. In recent years, global warming caused by CO₂ emissions had been recognized as an urgent problem. As a solution, the chemical fixation of CO₂ has gained attention as one of the effective carbon dioxide utilizing technologies. The main problem in CO₂ hydrogenation is that its products are not valuable [2]. The main products of CO₂ hydrogenation can fall into two categories- fuels and chemicals (Scheme 1). Indeed, the need of fossil fuels is ever increasing with growing energy consumption. However, the resources of fossil fuels are being diminished and fuel prices have undergone strong fluctuation in recent years. Therefore, it would be highly desirable to develop alternative fuels from non-fossil fuel sources and processes. The products of CO₂ hydrogenation such as

methanol, dimethyl ether, and hydrocarbons, are excellent fuels in internal combustion engines, and also are easy for storage and transportation [3].



Scheme 1 Products from CO_2 hydrogenation

For the fixation of CO_2 emitted from industrial sources, various chemical processes for converting CO_2 into valuable chemical compounds have been considered. One such process is to convert carbon dioxide into linear hydrocarbons; this reaction has already been thoroughly studied [4]. Many investigations have focused on direct synthesis of hydrocarbons from CO_2 , catalytic synthesis of methanol from CO_2 , and methanol to olefin processes [5]. Zhao *et al.* reported direct synthesis of diethyl carbonate at supercritical conditions using nickel acetate [6]. CO_2 hydrogenation on metal catalysts is occurred through a consecutive mechanism in which CO_2 is first converted to CO by the reverse water gas shift (RWGS) reaction, and then CO is hydrogenated to hydrocarbons [7-8]. Therefore, the chain growth mechanism of hydrocarbon synthesis from carbon dioxide is similar to that of the FT reaction. Iglesia *et al.* [9-10] proposed that all products formed by desorption from chain growth site were primary FT synthesis products. In this study, nanosized iron based catalyst was prepared via micro emulsion method and CO_2 hydrogenation over Fe-Cu-Zn catalyst was investigated at different time on stream.

2. Experimental

2.1. Catalyst Preparation

Nano-sized iron catalyst was prepared through water-in-oil micro emulsion method by adding water solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to a mixture of an oil phase containing 2-propanol and chloroform, and sodium dodecyl sulfate (SDS) as a surfactant. NaOH (aq) was added as precipitating agent and the solution was stirred for 3 h. The resulting mixture was left aside to decant overnight. The solid was recovered by centrifugation and washed thoroughly with distilled water and acetone. Finally, the sample was dried overnight at 120°C and subsequently calcined in air at 400°C for 3 h. Nanostructured ZnO was prepared similarly. In the subsequent step, the three oxides were mixed together. The promoted catalyst was dried at 120°C for 24 h and calcined at 400°C for 3 h in air [11].

2.2. Catalyst characterization

BET Surface area and pore volume of the catalyst was determined by N_2 physisorption using a Micromeritics ASAP 3020 automated system. An XRD spectrum of fresh catalyst was conducted with a Philips PW1840 X-ray diffractometer with monochromatized Cu (K α) radiation to determine the

catalyst phase. Temperature - Programmed Reduction (TPR) profile of the calcined catalyst was recorded using a Micromeritics TPD-TPR 290 system. Average particle size of the calcined powders was measured by LEO 912AB TEM.

2.3. Catalytic activity test

As shown in Fig. 1, the catalytic reaction was conducted in a fixed-bed stainless steel reactor. Flow rate of inlet gases and reactor pressure were controlled by electronic mass flow and pressure controllers, respectively. The catalyst (1 g) was loaded in the reactor and reduced by a 20% H₂-80% N₂ flow gas for 4 h. The catalyst activation was followed in a stream of synthesis gas with H₂/CO = 1 and space velocity of 2 NL/(h·g) for 24 h at 270°C in atmospheric pressure. After the activation process, CO₂ hydrogenation was done at pressure, temperature, H₂/CO₂ ratio and GHSV of 16 atm, 295°C, 3, 2.3 NL·h⁻¹·gCat⁻¹ respectively. The products were analyzed by a gas chromatography (Varian CP 3800) equipped with three subsequent connected columns. Two packed columns connected to two thermal conductivity detectors (TCD), which used for analyzing H₂, CO, CO₂, CH₄, and other non-condensable gases. A Petrocol Tm DH100 fused silica capillary column was attached to a flame ionization detector (FID) for analyzing organic liquid products [12-15].

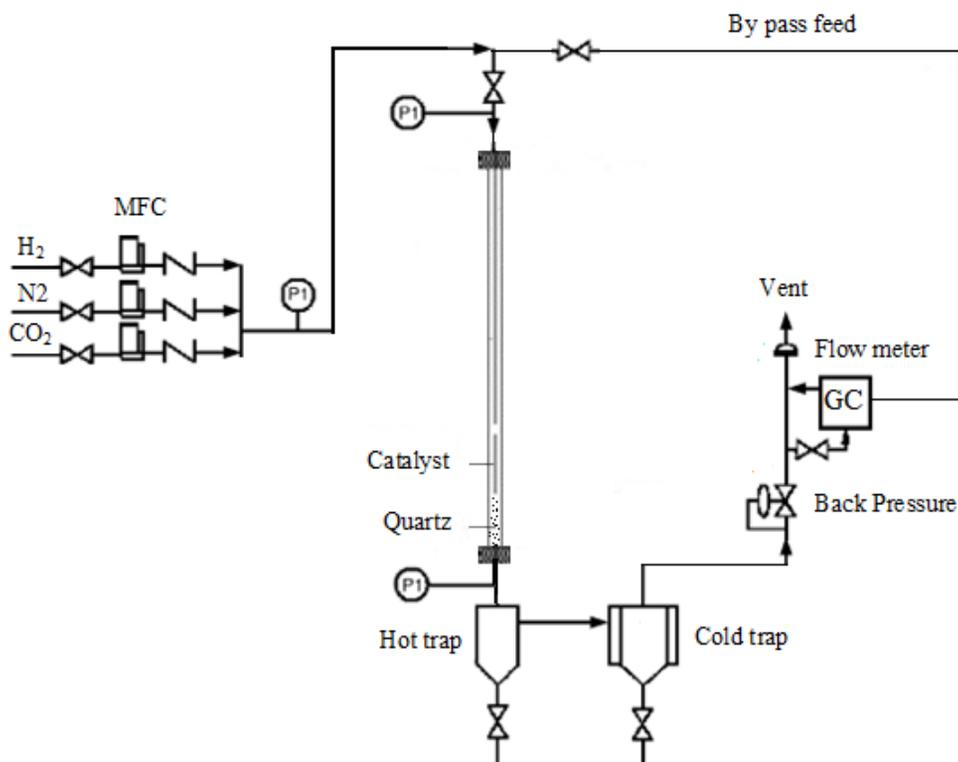


Figure 1. Catalyst test system

3. Results and discussion

3.1. Characterization of nanoparticle iron-based catalyst

Table.1 shows the result of the BET surface area, pore volume, and pore size of the catalyst. By adding Zn to the catalyst, the BET surface area and pore volume decreased. Furthermore, it might promote the aggregation of the catalyst crystallites and block up the pores.

Table 1. BET surface area ,pore volume and pore diameter of the catalysts

Catalysts*	BET (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
100Fe/4Cu	59.148	0.174	16.168
100/4Cu/10Zn	53.253	0.165	18.235

*Catalyst was degased at 300°C for 2 h before N₂ adsorption.

The catalyst was characterized by XRD after calcination. Fig. 2 shows the XRD pattern of the prepared catalyst. As shown in this figure, no new phase was detected when Zn was added. The catalyst showed cubic hematite crystal structure according to the JCPDS database. The characteristic peak at $2\theta = 33.30$ corresponding to the hematite (104) plane was used to calculate the average metal particle size by the Scherrer equation [11].

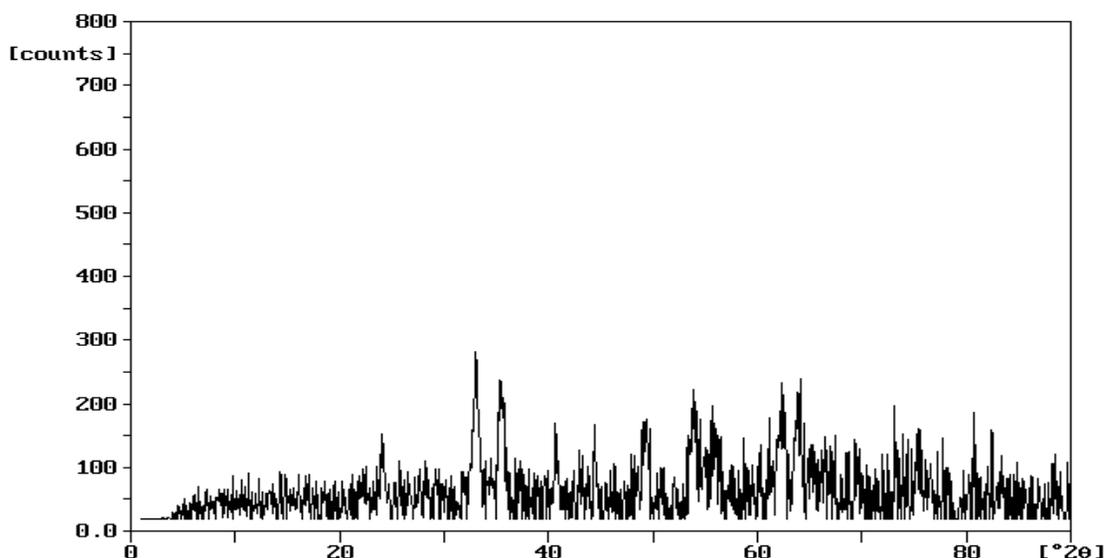


Fig. 2. X-ray diffractions of the catalyst.

The TEM image of the catalyst is illustrated in Fig. 3. TEM image revealed that the nanoparticle size was in the range of 20–50 nm.

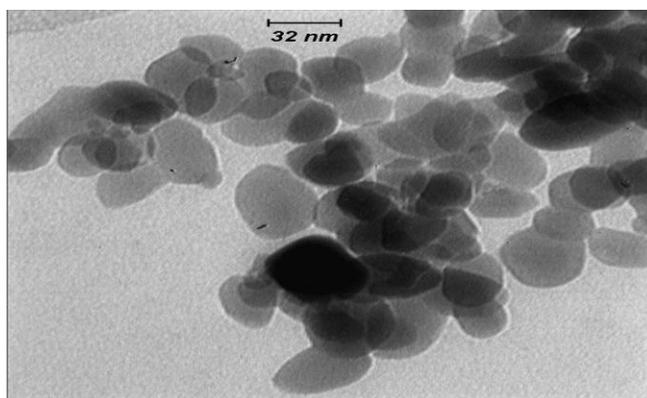


Fig. 3. TEM image of the catalyst.

Fig. 4 shows the H₂-TPR profile of the catalyst. H₂-TPR determines the reduction behavior of the catalyst. The first stage is ascribed to the transformations of CuO to Cu. The second stage is attributed to the transformation of Fe₂O₃ to Fe₃O₄, and the third stage represents the transformation of Fe₃O₄ to Fe [13].

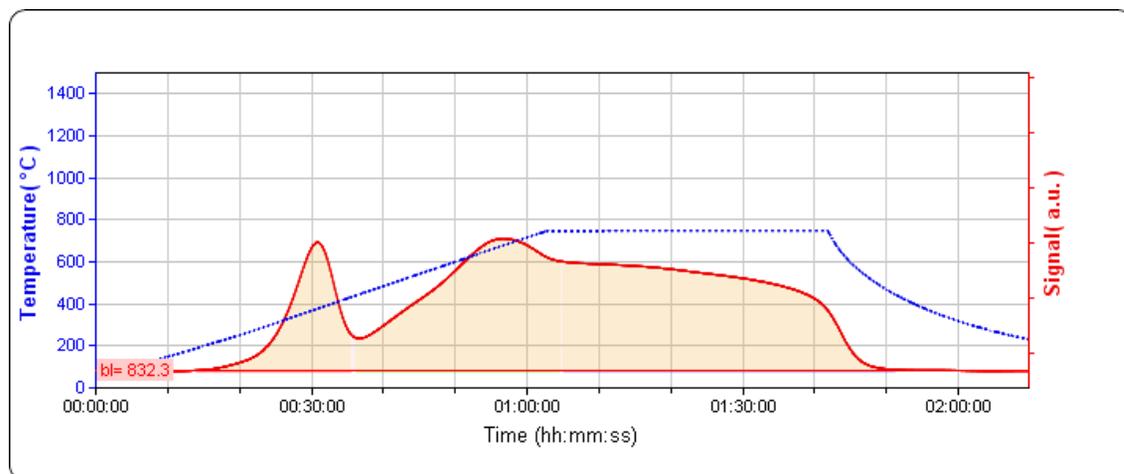
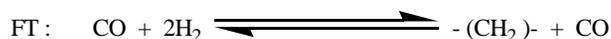


Figure 4. H₂-TPR profile of the catalyst

3.2. CO₂ hydrogenation over nanoparticles iron-based catalyst

CO₂ hydrogenation in Fischer–Tropsch synthesis is performed in two steps with the CO intermediate being formed by the reverse water–gas shift reaction:



Products selectivity are indicated in Table 2. It shows the selectivity for light hydrocarbons (methane and C₂–C₄), and heavy hydrocarbons (C₅⁺).

Table 2 The activity and selectivity of the catalysts

Time(h)	24	48
X _{CO2} (%)	19.7	24.6
S _{CO} (%)	10.8	11.2
C ₁	17.9	16.6
C ₂	11.2	11.6
C ₃	14.1	13.2
C ₄	11.6	12.1
C ₅ ⁺	45.2	46.3

X_{CO2}: CO₂ conversion, S_{CO}: CO selectivity

Reaction conditions: T = 295 K, P = 16 atm, GHSV = 2.3 NL.h⁻¹.gcat⁻¹, H₂/CO₂ = 3.

Fig. 5 shows CO₂ conversion at different time on stream. CO₂ conversion was reached about 25% after elapse time of 48 hours.

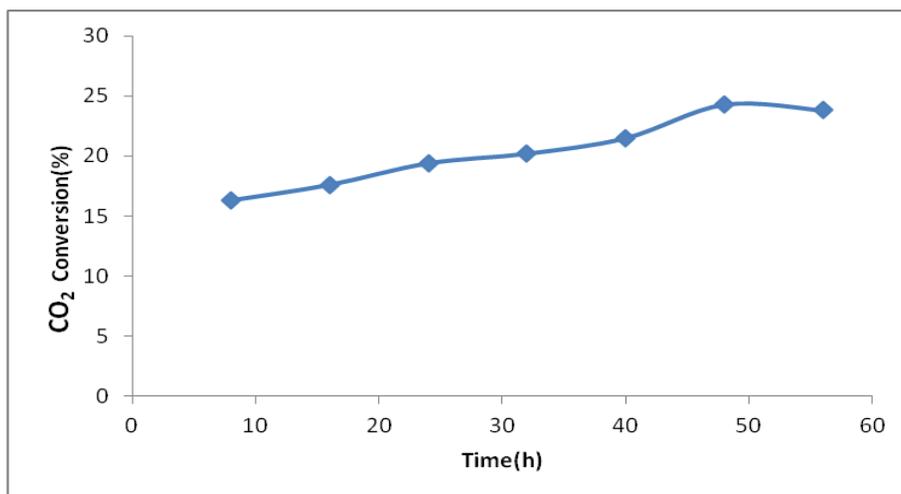


Fig 3. Catalytic activity of CO₂ hydrogenation. Reaction conditions:

T=295 K,P=16 atm,GHSV=2.3 NL.h⁻¹.gcat⁻¹, H₂/CO₂ = 3.

4. Conclusion

Zn-promoted nano iron based catalyst was prepared microemulsion method. The catalyst tested in a fixed-bed reactor. The activity of 100Fe/4Cu/10Zn catalyst was investigated in CO₂ hydrogenation at pressure, temperature, H₂/CO₂ ratio and GHSV of 16 atm., 295°C, 3, 2.3 nl.h⁻¹.gCat⁻¹ respectively. The catalyst was active in CO₂ hydrogenation reaction with conversions of approximately 19–24.6%. Zn-promoted nano iron catalyst improved hydrocarbon yield.

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