

Carbon Dioxide Conversion to Valuable Products over Iron Catalyst: Temperature Effect

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Received February 24, 2020; Accepted April 30, 2020

Abstract

In this study, the γ -Al₂O₃-supported iron catalyst is prepared by the wet impregnation method. Catalyst composition was: 15Fe/3Cu/10Zn/72 γ -Al₂O₃. The BET, H₂-TPR, XRD, and SEM techniques were applied for catalyst characterization. The catalyst was tested in a fixed-bed reactor at pressure, temperature, H₂/CO₂ ratio, and GHSV of 20 atm, (270, 300, 330)°C, 3, 3 nL.h⁻¹.gCat⁻¹, respectively. The enhancing temperature increased methane selectivity to 34.5% and increased CO₂ conversion to 27.4%. It was observed that the increase in temperature enhances the CO₂ conversion and catalyst activity.

Keywords: Iron catalyst; CO₂ conversion; Temperature effect.

1. Introduction

The atmospheric CO₂ concentration has increased by 20 % in the past 50 years due to the burning of fossil fuels [1]. Carbon dioxide, as a main part of the greenhouse gases, causes detrimental effects such as global warming and acidification of the oceans. Selective conversion of CO₂ to methane depends on different parameters, including the method of catalyst preparation [2-4], loading of the metal [5-7], and the type of catalyst support [5-6].

Suslova *et al.* conducted an experimental study to evaluate the effects of size particle and Cobalt oxidation state. The results showed that the nature of the support affects the catalyst activity and selectivity in the hydrogenation of carbon dioxide [8]. Owing to the intrinsic activity of iron-based catalysts in the reverse water-gas shift (RWGS) reaction, they are usually preferred for converting carbon dioxide to hydrocarbons [9-10]. Many researchers have argued that catalytic hydrogenation of carbon dioxide to hydrocarbons is a pathway involving the carbon monoxide intermediate. It is noteworthy that the hydrogen to carbon monoxide ratio during the hydrogenation process of CO and CO₂ plays a pivotal role in different selectivity of the two processes [11-14]. Iglesia *et al.* showed that all the products were identical to the primary products of the FT and obtained from the desorption of the growing chain of hydrocarbons [15]. In this study, iron supported γ -Al₂O₃ catalyst was prepared via the wet impregnation method, and CO₂ hydrogenation over an iron-based catalyst was investigated at different temperatures.

2. Experimental

2.1. Catalyst preparation

The iron catalyst was prepared through the wet impregnation method by adding a water solution of Fe(NO₃)₃·9H₂O; Cu(NO₃)₂·4H₂O and Zn(NO₃)₂·4H₂O to γ -Al₂O₃-support. The catalyst was dried overnight at 110°C and subsequently calcined in air at 400°C for 4 h. The catalyst was pressed into pellets, crushed, and sieved to obtain particle sizes in the range of 16–30 mesh.

2.2. Catalyst characterization

Surface area, pore volume and mean pore size of the catalyst was determined by N_2 physisorption using a Micromeritics ASAP 3020 automated system. An XRD spectrum of the fresh catalyst was conducted with a Philips PW1840 X-ray diffractometer with monochromatized Cu (K α) radiation. Temperature - Programmed Reduction (TPR) profile of the calcined catalyst was recorded using a Micromeritics TPD-TPR 290 system. The morphology of the calcined catalyst was investigated by scanning electron microscopy (SEM).

2.3. Catalytic activity test

As shown in Fig. 1, the catalytic reaction was conducted in a fixed-bed stainless steel reactor. The catalyst (2 g) was loaded in the reactor and reduced by a 15% H_2 -85% N_2 flow gas and 400°C for 2 h. After the activation process, CO_2 hydrogenation was conducted at pressure of 20 atm., temperature of (270,300,330°C), H_2/CO_2 ratio of 3, GHSV of 3 $nL.h^{-1}.gCat^{-1}$. Gas and liquid products were analyzed by gas chromatography (Agilent 7890A).

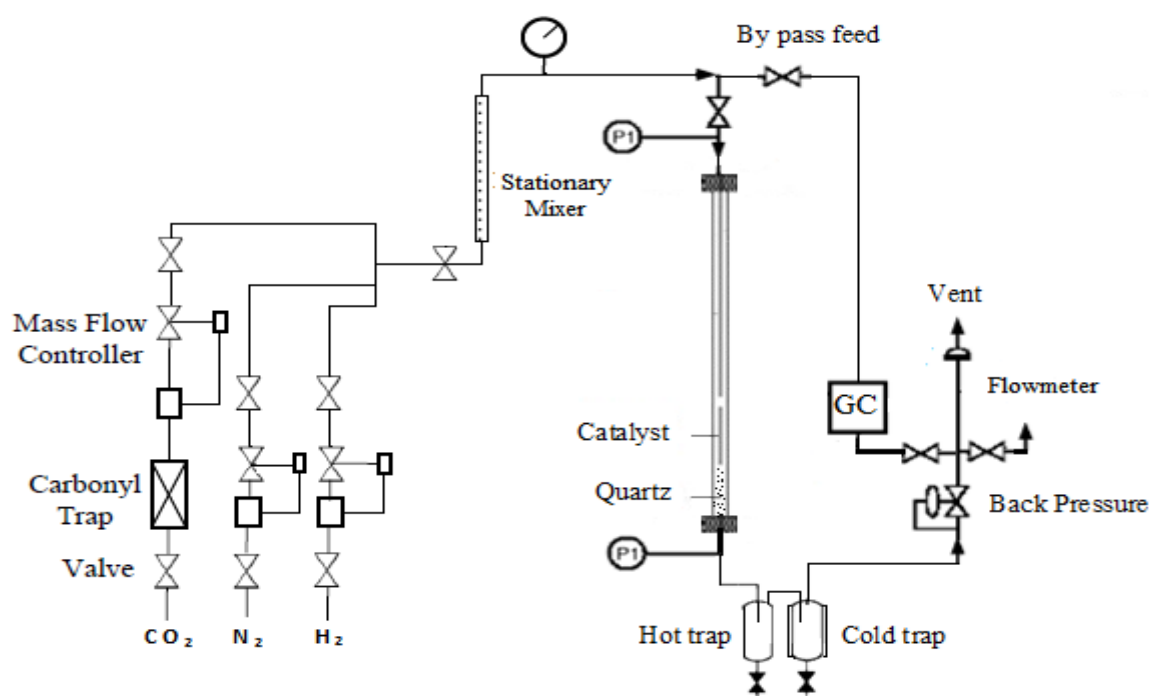


Figure 1. Catalytic test system

3. Result and discussion

Table.1 shows the result of the BET surface area, pore-volume, and mean pore size of the catalyst. By adding Fe, Cu, and Zn to the support, surface area, and pore volume decreased because of blocking the support pores.

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

Catalyst*	BET m^2/g	Pore volume cm^3/g	Average pore volume nm
$\gamma-Al_2O_3$ support	209.5	0.6919	12.73
15Fe/3Cu/10Zn/72 $\gamma-Al_2O_3$	124.5	0.3130	10.06

*Catalyst was degassed at 300°C for 2 h before N_2 adsorption

The catalyst was characterized by XRD after calcination. Fig. 2 shows the XRD pattern of the prepared catalyst. As shown in this figure, the characteristic peak at $2\theta = 33.3^\circ$ corresponding to the hematite. However, the XRD pattern is used to determine the catalyst phases.

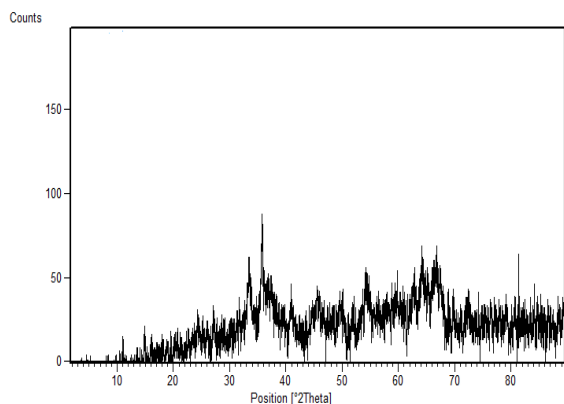


Figure 2. X-ray diffractions of the catalyst 15Fe/3Cu/10Zn/72 γ -Al₂O₃

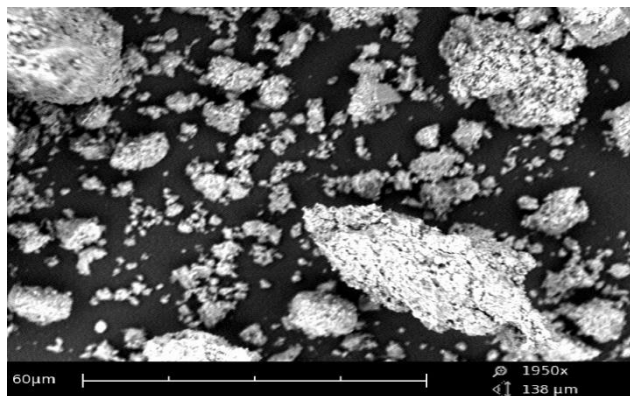
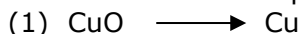


Figure 3. SEM image of 15Fe/3Cu/10Zn/72 γ -Al₂O₃

The SEM image of the catalyst is shown in Fig. 3. SEM image revealed the morphology of the catalyst. Figure 4 shows the profile of H₂-TPR. H₂-TPR shows the catalyst reduction temperature and the amount of hydrogen consumed. The first peak is the conversion of CuO to Cu.



The second peak is attributed to the transformation of Fe₂O₃ to Fe₃O₄, and the third peak represents the transformation of Fe₃O₄ to Fe [16].

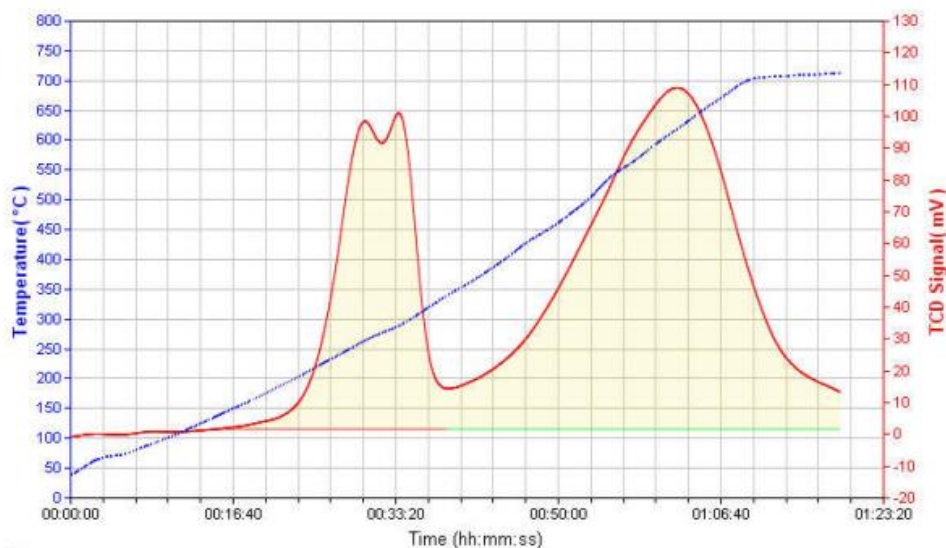
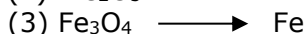
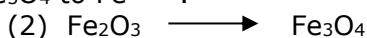
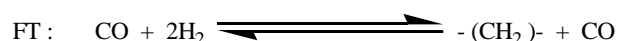
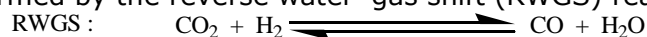


Figure 4. H₂-TPR profile of 15Fe/3Cu/10Zn/72 γ -Al₂O₃

3.1. CO₂ hydrogenation over iron supported γ -Al₂O₃ catalyst

CO₂ hydrogenation in Fischer-Tropsch synthesis is performed in two steps, with the CO intermediate being formed by the reverse water-gas shift (RWGS) reaction:



CO₂ conversion and products selectivity were calculated using the data collected at 8 h time on stream. Table 2 is indicated by products selectivity. It shows that with increasing temperature, the selectivity of light hydrocarbons (C₁-C₃) increased, and heavy hydrocarbons (C₄⁺) decreased.

Table 2. CO₂ conversion and products selectivity of the catalyst in different temperature

T	(°C)	290	310	330
X _{CO2}	(%ime)	16.8	19.9	27.4
S _{CO}	(%)	9.87	8.73	7.42
C ₁		22.66	29.29	39.04
C ₂		14.67	15.29	17.88
C ₃		11.35	12.37	13.24
C ₄ ⁺		41.45	34.32	22.42

where: X_{CO2}: CO₂ conversion; S_{CO}: CO selectivity; T = (290, 310, 330°C); P=20 atm, GHSV=three L.h⁻¹.gcat⁻¹, H₂/CO₂ = 3.

By increasing the temperature, CO₂ conversion, as well as the selectivity of light hydrocarbons (C₁-C₃), is enhanced.

4. Conclusion

Iron supported γ -Al₂O₃ catalyst was prepared wet impregnation method. The catalyst was conducted in a fixed-bed reactor. The activity of 15Fe/3Cu/10Zn/72 γ -Al₂O₃ catalyst was investigated in CO₂ hydrogenation at pressure, temperature, H₂/CO₂ ratio and GHSV of 20 atm, (270,300,330°C),3, 3 nL.h⁻¹.gCat⁻¹. respectively. The catalyst was active in CO₂ hydrogenation reaction with conversions of approximately 16.8–27.4%. The increasing temperature increased CO₂ conversion and improved hydrocarbon yield.

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