EFFECT OF Mn PROMOTER ON NANO-SIZED IRON CATALYST FOR FISCHER-TROPSCH SYNTHESIS

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Abstract

A series of nanoparticle-sized iron catalysts incorporated with Mn promoter were prepared by microemulsion method. The catalysts were investigated using BET, H_2-TPR, XRD and TEM techniques. An appropriate amount of this promoter in atomic ratio X/Fe = 0.02 (X =Mn) can promote Fischer–Tropsch synthesis. Effect of Mn addition on the performance of nano-sized iron catalyst was studied in a fixed – bed reactor at 290ºC, 17 atm, 3 NL/(h.gcat) and H_2 to CO ratio of 1. The results indicate that this promoter can improve the CO conversion and water-Gas Shift reaction, suppress the formation of methane, enhance the selectivities to olefin and lower molecular weight products.

Keywords: Fischer–Tropsch Synthesis; Nano-sized iron-based catalyst; Mn promoter; Products distribution.

1. Introduction

Fischer–Tropsch synthesis (FTS) is a route for upgrading natural gas, coal, and biomass to liquid fuels and other chemical products. Fe and Co catalysts are currently used in industrial scale [1-3]. Although Fe catalysts are not as active as Co-based catalysts, they show high water–gas shift (WGS) activity, which makes Fe catalysts more suitable for the conversion of low H_2/CO ratio syngas derived from coal or biomass [4-6]. In order to obtain excellent performances of iron catalyst, chemical promoters, such as K, Cu, Mg, Zn, *etc.*, are often added into iron-based catalyst [7-12]. Lohitharn and Goodwin reported that Cr or Zr promotion of a precipitated Cu-promoted Fe catalyst significantly improves its catalytic activity [13]. Wen-Sheng Ning *et.al.* investigated that the Fe catalysts co-promoted by K, Cu, Zn and Al showed increasing CO conversion with time on stream [14]. Bukur *et al.* [15] studied the effects of K and Cu promoters on the activity and selectivity of precipitated iron-based catalysts for FTS. Their results showed that K and Cu promoters improved the FTS activity and WGS activity. Pour *et.al.* [16] investigated the effect of Ca, Mg and La promoters on iron-zeolite catalyst that these promoters increased both primary and secondary reactions for CO_2 production and decreased the primary and secondary reactions for water production [16]. Previous work, I investigated the effect of Mg promoter on nano-sized iron catalyst that this promoter increased both primary and secondary reactions for CO_2 production and decreased reactions for water production [17]. In this paper, two catalysts (100Fe/4Cu, 100Fe/4Cu/2Mn) were prepared by using micro-emulsion method to investigate the effect of Mn promoter on catalyst morphology, activity and product selectivity in FTS.

2. Experimental

2.1. Catalyst preparation

Iron nanostructured catalysts were prepared by coprecipitation in a water-in-oil microemulsion [18]. All the chemicals were analytically pure and used without purifying further. A water solution

of metal precursors, $FeCl_3 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 4H_2O$ was added to a mixture of an oil phase containing 2-propanol and chloroform with a ratio of 50 to 50 and sodium dodecyl sulfate (SDS) as surfactant was added to a solution. After stirring, a transparent mixture, which was stable for at least 24 h was obtained. A similar microemulsion containing hydrazine in the aqueous phase was used as the precipitating agent. The solid was recovered by centrifugation and washed thoroughly with distilled water, ethanol and acetone. Finally, the samples were dried overnight at 120°C, and subsequently calcined in air at 350°C for 4 h. Manganese promoter was added by wetness impregnation. The prepared catalysts were dried at 120°C for 16 h and calcined at 350°C for 4 h in air. The catalyst compositions were designated in terms of the atomic ratios as: 100Fe/4Cu; 100Fe/4Cu/2Mn. All samples were pressed into pellets, crushed and sieved to obtain 100−180 μm.

2.2. Catalyst characterization

BET surface area and mean pore diameter were determined using an ASAP 3020 instrument of Micromeritics. The samples were degassed under vacuum at 120°C for 3 h before measurement. H_2-TPR experiments were performed in a quartz reactor using a mixture gas of 5% H_2/95%Ar (v/v) as the reductant. About 0.5 g catalyst was packed in the quartz reactor. The catalyst sample was heated from room temperature to 800°C at a heating rate of 5°C/min. The flow rate of mixture gas was 50 ml/min. The hydrogen consumption was monitored by the change of thermal conductivity of the effluent gas stream. Catalysts morphologies for the synthesized catalysts observed using LEO 912AB TEM. XRD spectra of fresh catalyst was conducted with a Philips PW1840 X-ray diffractometer with monochromatized Cu (Kα) radiation for determining of iron phases.

2.3. Cata-test system and analyzing instrument

Catalytic reaction runs were conducted in a fixed-bed stainless steel reactor. Gas flow rates and reactor pressures were controlled by electronic mass flow and pressure controllers. Four heating zone equipped with temperature controller and indicator supplied the required reaction heat. 1.5 g of catalyst was loaded to the reactor. The catalyst was first pre-reduced by using a flow of %10H_2/N_2. Activation was followed in a stream of synthesis gas with H_2/CO =1 and GHSV= 1.5nl.h^{-1}.gFe^{-1} for 24h in atmospheric pressure and 270°C. Following reduction, the reactor pressure raised to 17 bar and temperature to 290°C and reaction started in a stream of synthesis gas with H_2/CO =1 and GHSV= 3NL.h^{-1}.gCat^{-1}. The products were analyzed by gas chromatographs (Varian CP 3800) [18].

3. Results and discussion

3.1. BET Technique

The surface area and pore size distribution of the fresh catalysts are shown in table.1. It is apparent that Mn promoter influences the surface area, pore volume and pore size distribution. Addition of this promoter decreases the BET surface area and pore volume on catalysts as compared with Fe/Cu catalyst. It may be that the addition of Mn promoter promotes the aggregation of the catalyst crystallites and blocks up the pore volume of the catalyst.

Table 1. The composition and textural properties of the catalysts

Catalyst	BET surface area (m²/g)	Pore volume (cm³/g)	Pore size (nm)
100Fe/4Cu	57.3	0.26	15.56
100Fe/4Cu/2Mn	53.8	0.21	17.54

3.2. XRD

The phase composition of the fresh catalysts is determined by XRD analyses. Nanostructured iron catalysts were characterized by X-ray diffraction (XRD) after calcinations. Fig. 1 shows the XRD patterns of the catalysts. The addition of Mn did not cause any obvious change, and

no phase containing metals above were detected. All the catalysts showed the Fe_2O_3 crystalline phase, whoever their structure seems to be like cubic hematite structured Fe_2O_3 crystal in JCPDS database. The characteristic peak at $2\theta = 33.3°$ corresponds to the hematite.
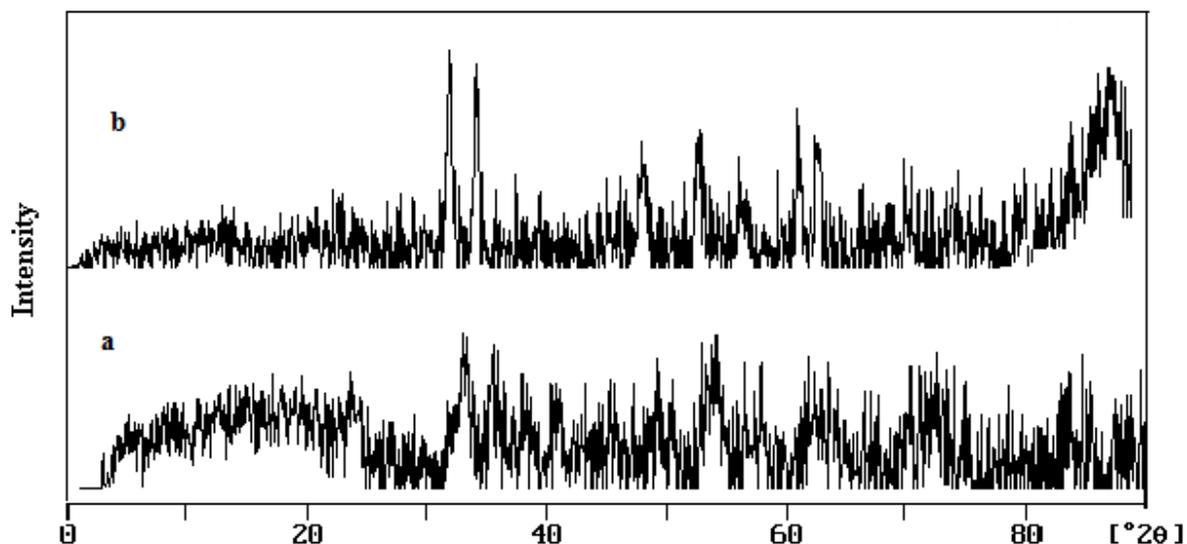

Fig 1. XRD spectra of the fresh catalysts. (a) 100Fe/4Cu (b) 100Fe/4Cu/2Mn

3.3. TEM

In general, catalysts were faceted and irregular shaped with some uneven surfaces. TEM revealed that the diameters of the catalysts were in the range of 20–40 nm (Fig. 2).
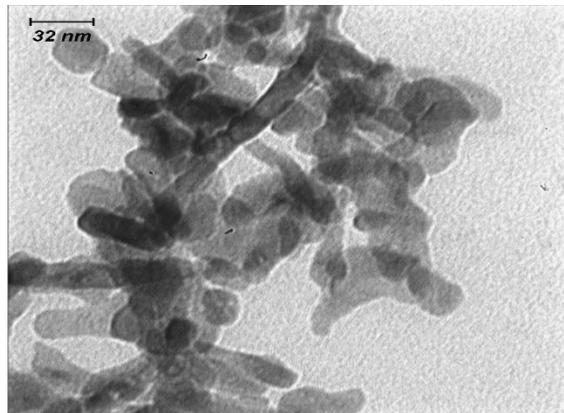

Fig 2. TEM micrograph of the catalyst 100Fe/4Cu/2Mn

3.4. H$_2$-TPR

H_2-TPR was used to investigate in the reduction behavior of the catalysts. As shown in Fig. 3, the reduction process of the catalysts occurs in three distinct stages. The first stage is ascribed to the transformations of CuO to Cu and Fe_2O_3 to Fe_3O_4, whereas the second stage represents the transformation of Fe_3O_4 to FeO. The third stage is related FeO to Fe [18]. The H_2-TPR profiles indicated that the addition of Cu significantly promotes the reduction of the two stages, whereas the addition Mn promoter suppresses the reduction of nano-sized iron-based catalyst.
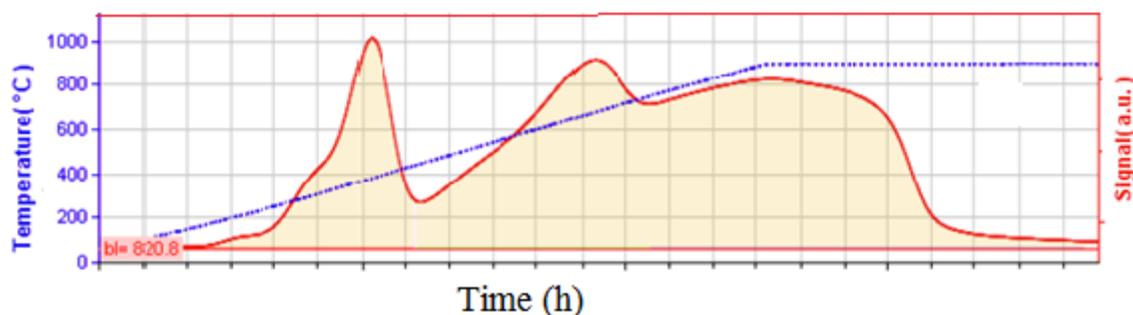
Fig 3. H_2-TPR profiles of 100Fe/4Cu/2Mn catalyst.

3.5. Reactor system and evaluation of FTS performances

FTS performances of the catalysts were measured in a fixed-bed reactor under conditions of 290°C, 1.7 MPa, 3NL.gr Fe $^{-1}$. h^{-1} and H_2/CO = 1 (v/v). The activities and product selectivities were tested over a period of 194 h steady-state runs. Fe/Cu catalyst has lower initial activity and deactivates slowly with time on stream, whereas the CO conversion of promoted iron catalyst is higher and deactivates quickly. The CO conversions of Fe/Cu and Fe/Cu/X(X=Mn) catalysts reach a maximum and then dropped. The addition of Mn increased the catalyst activity, but also improve the catalyst stability.

3.6. Product selectivity

Hydrocarbon product distribution of the catalysts is shown in table 2. It shows that Fe/Cu/Mn catalyst has the highest selectivities to gaseous and light hydrocarbons (methane and C_2–C_4) and the lowest selectivities to heavy hydrocarbons (C_5^+). The chain growth reaction is restrained and the hydrogenation reaction is enhanced on the catalyst incorporated with Cu promoter, whereas the addition of Mn promoter does not promote the chain growth reaction. Both the promoter and the reaction conditions influence the product selectivity.

Table 2. The activity and selectivity of the catalysts

Catalysts	100Fe/4Cu	100Fe/4Cu/2Mn
CO conversion (%)	56.2	63.5
Hydrocarbons selectivities (%mol.)		
CH_4	12.3	13.3
C_2-C_4	28.8	33.9
C_5-C_{12}	18.6	13.5
C_{13}—C_{19}	12.3	11.4
C_{19}^+	8.3	6.8
CO_2[a] selectivity (%)	19.7	21.1
Olefins to Paraffins molar ratio (C_2-$C_4^=$/C_2-C_4)	0.96	1.47
α[b]	0.67	0.56

Reaction condition: Time on Stream 70 h, 290°C, 1.7MPa; H_2/CO = 1 and SV= 3 NL.g Cat $^{-1}$. h^{-1}.
[a] Selectivity to oxygenates was negligible (<3%) in all cases; α[b] = chain growth probability

Figure 4 shows the promoter effect on CO conversion versus time on stream. The results show that the promoter facilitates the H_2 dissociative adsorption, leading to a lower coverage of carbon species on the surface and thus reduces the chain growth reaction.
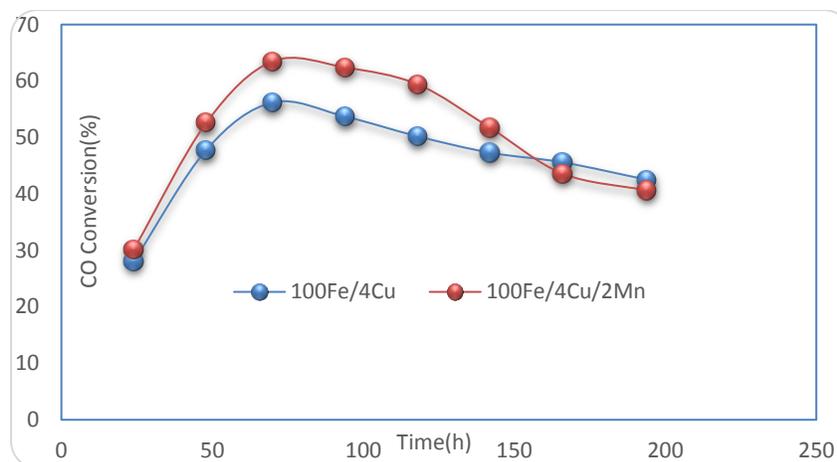
Fig4. Promoter effect on CO conversion versus time on stream

The results were shown that promoted iron catalyst should have the higher selectivities to gaseous, light hydrocarbons and olefins and the lower selectivities to heavy hydrocarbons.

Iron-based FTS catalyst consist of nanometresized Fe_2O_3 crystallites to which often promoters are added to improve the catalyst performance. A typical catalyst contains promoters like copper to enhance catalyst reducibility, Mn to improve FTS and WGS reactions.

4. Conclusion

The changes in the catalytic performances can be primarily attributed to the effects of (Cu and Mn) promoters on the H_2 adsorption and CO adsorption, which further significantly affects the FTS performances of the catalysts. The addition of Mn promoter improves the FTS activity and WGS reaction activity. As compared with individual promotion of Cu, the double promotions of Cu and Mn keep excellent stability and significantly improve the FTS and WGS activities. Addition of Mn promoter significantly improves production of light olefins.

Acknowledgement

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