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FISCHER-TROPSCH SYNTHESIS OVER NANO-SIZED IRON-BASED CATALYSTS : INVESTIGATION OF PROMOTER AND TEMPERATURE EFFECTS ON PRODUCTS DISTRIBUTION

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Abstract

Carbon monoxide hydrogenation to higher hydrocarbon was investigated over nanoparticles iron-based catalyst. Fe/Cu catalysts incorporated with the Mg promoter and without promoter were prepared by the micro-emulsion method. The composition of the final nano-sized iron catalysts, in term of the atomic ratio contain as : 100Fe/4Cu , and 100Fe/4Cu/2Mg. XRD , BET , TEM and TPR techniques were used to study phase, structure, morphology and reduction temperature of catalysts. Test of reaction was performed in a fixed bed reactor at pressure, temperature, H_2/CO ratio and GHSV of 17 bar, 270-310°C, 1, 2.5 nl.h^{-1}.gCat^{-1}., respectively. Mg-promoted nano iron catalyst increased CO conversion and C_5^+ selectivity to 73% and 48% ,respectively. The increasing of temperature from 270 to 310 increased CO conversion and light hydrocarbons.

Keywords : Nano-sized iron catalyst; CO hydrogenation; Mg Promoter; Temperature effect.

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1. Introduction

Fischer–Tropsch Synthesis (FTS) is an efficient technology to synthesize liquid transportation fuel as well as other valuable chemicals. FTS is hydrogenation of carbon monoxide in presence of transition metal catalyst. The active metals used in FTS are Fe, Co, and Ru [1-5]. Among these metals, Ru is the most active catalyst for CO hydrogenation, and is capable of producing long-chain hydrocarbons [4], but only iron and cobalt based catalysts are industrial scale economically. Because the reserves of coal and natural gas are in abundance compared to crude oil, FTS can supply liquid fuels for the world for extended period of time compared to petroleum refining [6-9].

Except low cost and availability, the high water-gas shift (WGS) activity makes Fe-based catalysts more suitable for the conversion of low H_2/CO ratio syngas. Nano materials have different morphology and enhanced surface area that, in theory, should yield better reaction rates as a result of increase in available catalyst sites [10-11]. In this paper, nano-sized iron catalyst was prepared by microemulsion method. The catalyst was tested in a fixed-bed stainless steel reactor in different temperature in FTS conditions and Mg promoter effect was investigated in FTS too.

2. Experimental

2.1. Catalyst preparation

Nanostructure iron catalyst was prepared by microemulsion method [11-13]. Addition water solution of a metal precursor, $FeCl_3 \cdot 6H_2O$, to a mixture of an oil phase containing 1-butanol 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 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 copper oxide and magnesium oxide were prepared similarly. In the subsequent step, the nanoparticles of Fe_2O_3, CuO, and MgO were mixed together. The promoted catalyst was dried at 120°C for 20 h and calcined at 400°C for 3 h in air. The catalysts were pressed into pellet, crushed, and sieved to obtain particle sizes in the range of 30–40 mesh.

2.2. Catalyst characterization

BET surface area and pore volume were determined by N_2 physisorption using a Micromeritics ASAP 3020 automated system. A 0.3 g catalyst sample was degassed in the system at 100°C for 1 h and then at 300°C for 2 h prior to analysis. Average particle size of the calcined powders was measured by LEO 912AB TEM. The XRD pattern of fresh catalyst was conducted with a Philips PW1840 X-ray diffractometer with monochromatized Cu (*Ka*) radiation. Temperature- programmed reduction (TPR) profile of the calcined catalyst was recorded using a Micromeritics TPD-TPR 290 system. The TPR of 50 mg of each sample was performed in 5% H_2-95% Ar gas mixture. The sample was heated from 50 to 900°C at 10°C/min.

2.3. Catalytic activity

As shown in Fig. 1, the catalytic reaction experiment was conducted in a fixed-bed stainless steel reactor. The catalyst (1.5 g) was loaded in the reactor and reduced by a 10% H_2-90% N_2 flow gas for 3 h. The catalyst activation was followed in a stream of synthesis gas with $H_2/CO = 1$ and space velocity of 2 NL/(h·g) for 24 h at 270°C in atmospheric pressure. After the activation process, the reactor pressure and temperature raised to 17 bar and 290°C, respectively. The reaction was initiated in synthesis gas stream with $H_2/CO = 1$ and GHSV of 2.5 NL/(h·g). The products were analyzed by a gas chromatography (Varian CP 3800) [14-15]. The activities and product selectivities were assessed after 60 h from initial time.

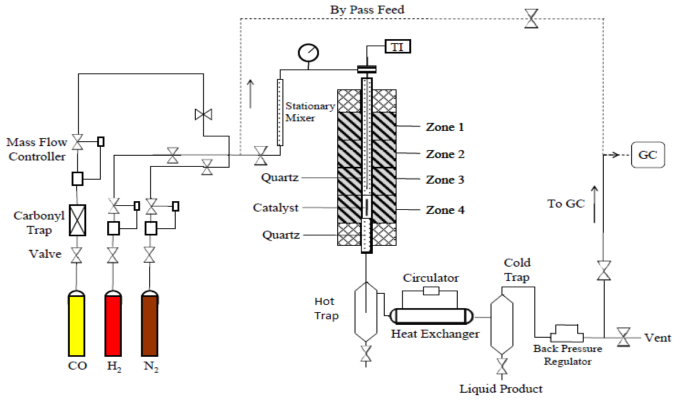

Fig. 1. Catalyst test system

3. Results and discussion

3.1. Characterization of nanoparticle iron-based catalyst

The TEM image of the catalyst is illustrated in Fig. 2. The TEM micrograph of the catalyst revealed that the nanoparticle size was in the range of 20-40 nm.

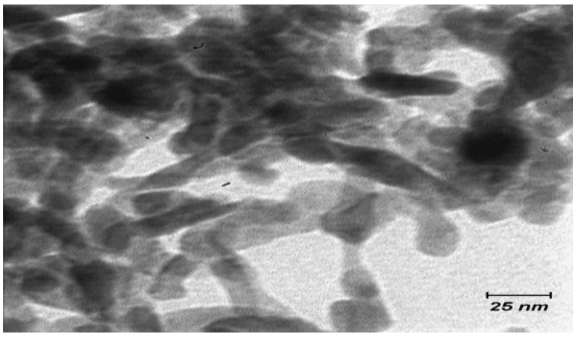

Fig. 2. TEM image of the 100Fe/4Cu/2Mg catalyst.

The BET surface area, pore volume and pore size of the catalysts are shown in table 1. *Mg*-promoted Fe catalyst showed lower average pore sizes and BET surface area than unpromoted catalyst.

Table 1 Surface area and pore volume of the catalysts

Catalyst	BET Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore size (nm)
100Fe/4Cu	59.2	0.193	15.87
100Fe/4Cu/2Mg	56.4	0.171	17.31

Temperature programmed reduction(TPR) pattern of nano-sized iron catalyst presents three main reduction peaks at about 250, 370 and 630°C. It is seems that the first peak corresponds to the reduction of CuO to Cu and the second peak may be related to reduction of Fe_2O_3 to Fe_3O_4. The third stage corresponds to subsequent reduction of Fe_3O_4 to metallic iron [11].

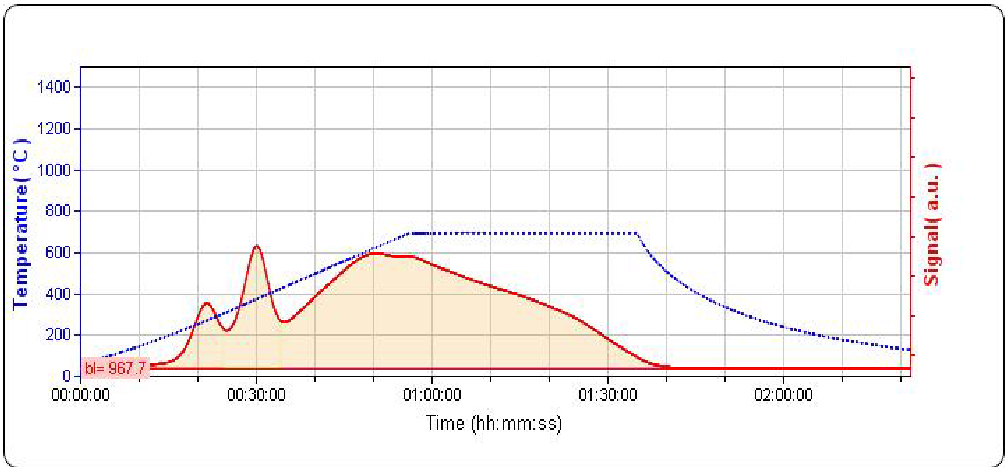

Fig.3. H_2-TPR profiles of the 100Fe/4Cu/2Mg catalyst

Figure 4 shows the XRD pattern of the prepared catalyst. The only detectable phase identified in the diffraction pattern of the catalyst is hematite (Fe_2O_3), which has characteristic peaks at 2θ values of 24.2, 33.1, 35.6, 40.8, 49.52, 54.0 and 57.6.

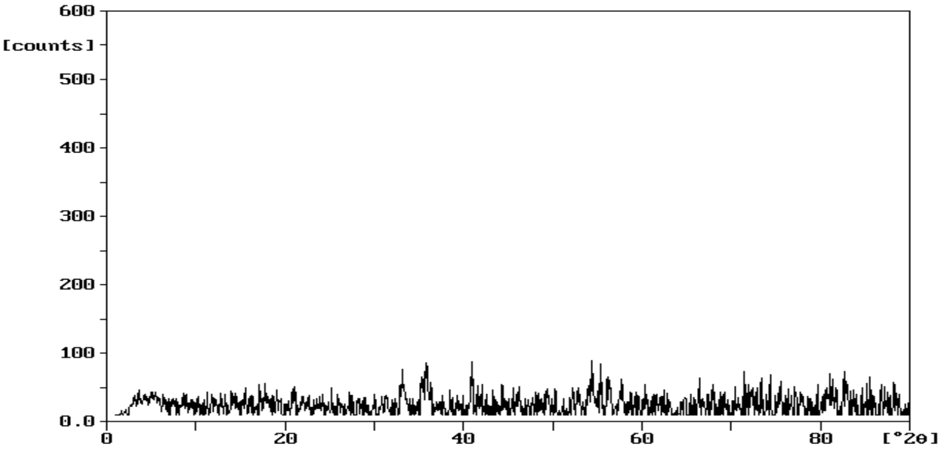

Fig. 4. XRD pattern of the fresh 100Fe/4Cu/2Mg catalyst.

3.2. Product selectivity

The changes of methane, high-molecular-weight hydrocarbons (C_5^+) selectivities and feed conversion are shown in Fig. 5. It can be seen that the selectivity to methane slowly decreases while the selectivity to C_5^+ increase with increasing promoter for the catalyst.

Comparing unpromoted catalyst, the Mg promoted catalyst produce more C_5^+ hydrocarbons while the methane selectivity is affected by the presence of Mg.

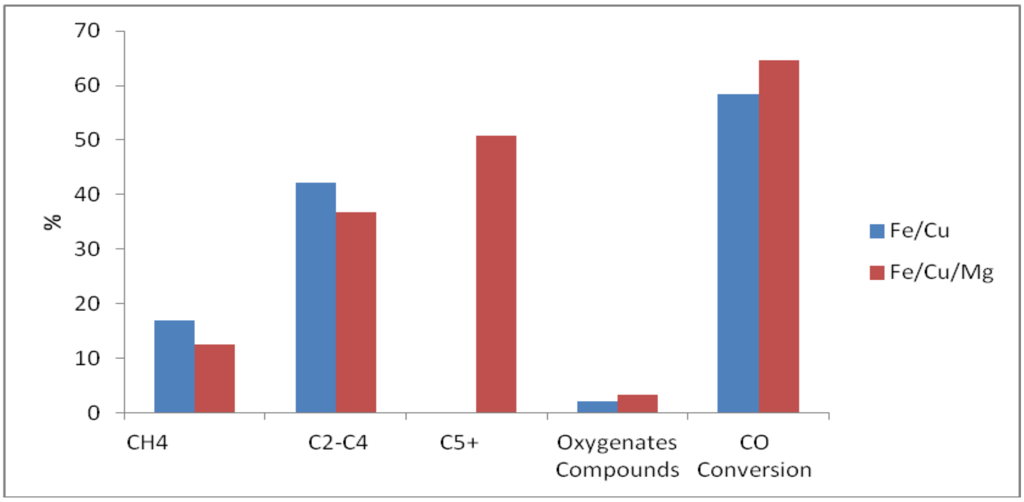

Fig 5. Feed conversion and products selectivity of the catalysts

The process conditions as well as the catalyst influence the product selectivity. The influence of temperature on CO conversion and the products selectivity was investigated. An increase of temperature results in a shift toward products with a lower carbon number on Mg promoted iron – based catalyst. Fig 6 was shown temperature effect on methane, C_2-C_4 and C_5^+ selectivity on nano-sized iron based catalyst at 270 - 310°C, 17 bar, $H_2/CO = 1$, and 2.5 $Nl.h^{-1}.gCat^{-1}$ GHSV after 60h.

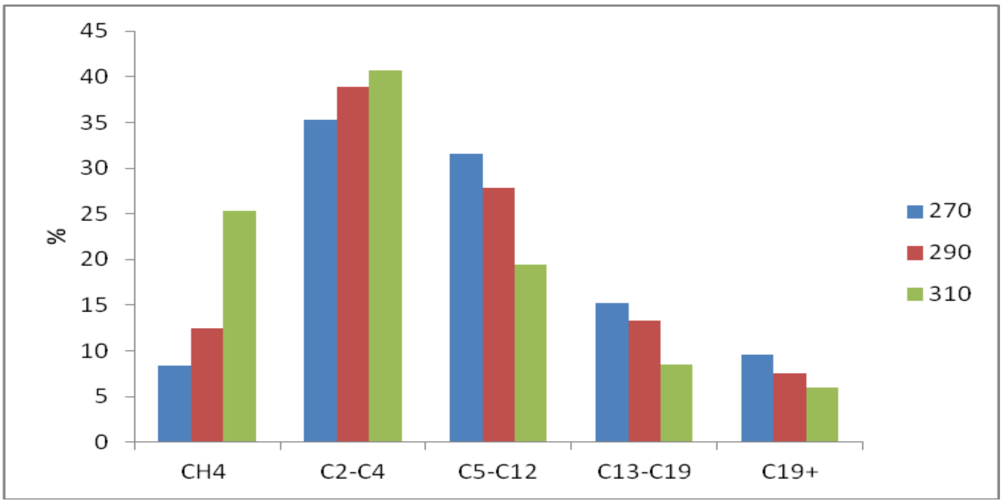

Fig 6. Products selectivity of the 100Fe/4Cu/2Mg catalyst in different temperatures.

4. Conclusion

In this study, nano-structured iron catalyst was prepared by micro-emulsion method. By adding Mg promoter into nano-sized iron catalyst, it influence on the catalytic activity during the Fischer-Tropsch synthesis. The improvement of the catalytic performances can be attributed to the effect of the promoter on H_2 and CO adsorption, which further significantly affects the FTS performance of the catalyst. Mg promoter improves the FTS and WGS activities. The increasing of temperature from 270 to 310°C improve the FTS activity of iron based catalyst. CO conversion and light hydrocarbons enhanced due to increasing of temperature.

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