

PROMOTION OF NANO STRUCTURE IRON CATALYST WITH ZIRCONIUM FOR FISCHER-TROPSCH SYNTHESIS

Yahya Zamani^{1*}, Mohammad Irani¹, Sohrab Taghipoor¹, Rahman Shakibaei Lalehloo², Amir Sepehrianazar³

¹ Research Institute of Petroleum Industry (RIPI), National Iranian Oil Company; West Blvd., Near Azadi Sports Complex P.O. BOX 14665-137, Tehran, Iran

² Department of Chemistry, Karaj Branch, Islamic Azad University, Karaj, Iran

³ Polymer Engineering Group, Ahar Branch, Islamic Azad University, Ahar, Iran

Received December 19, 2017; Accepted February 15, 2017

Abstract

The effect of zirconium on nano-structure iron catalysts were compared to the unpromoted nano-structure iron catalyst for Fischer-Tropsch Synthesis. The catalysts were prepared by micro-emulsion method. The composition of the final nano-sized iron catalysts, in term of the atomic ratio contain as: 100Fe/5Cu, 100Fe/5Cu/2Zr. XRD, BET, H₂-TPR and TEM techniques were utilized to assess the catalysts phase, structure and morphology. The promoted catalyst compare to the unpromoted catalyst, has higher FT rate and CO₂ production. Zr promoter has the best performance than unpromoted iron catalyst.

Keywords: Nanoparticles iron catalyst; Microemulsion; Fischer-Tropsch Synthesis; Zr Promoter.

1. Introduction

The Fischer-Tropsch Synthesis (FTS) is a heterogeneous surface catalyzed polymerization process. During this process, CH_x monomers formed via hydrogenation of adsorbed CO on transition metals produce hydrocarbons and oxygenates with a broad range of chain lengths and functional groups. FTS is an important step in the manufacture of hydrocarbon fuels from coal or syngas. Although several metals are active for the FTS, only iron and cobalt catalysts are economically feasible on an industrial scale. The use of iron-based catalysts is suitable not only for their low cost and availability, but also their high water-gas shift activity makes it possible to use these catalysts with low H₂/CO ratios [1-7].

Among promoters, potassium has been used as a promoter for iron catalysts. Potassium can also increase the catalytic activity for FTS and WGS reactions. Copper is normally added to Fe-based FTS catalysts as a chemical promoter. It is added to enhance hematite reducibility [8-10]. A positive effect of other transition metals, such as Mo, Ta, V, and La, on the iron based catalyst activity for both CO hydrogenation and WGS activity also has been reported [11-14]. Although the studies on the Fe-based FT catalysts are extensive, the investigations on the effect of Zr on the catalyst is scarce. In this study, a micro-emulsion method has been developed to prepare two nano-sized iron catalysts by preparing nano-size iron with copper and zirconium oxide separately from their solutions. Effect of Zr promoter was investigated on catalyst morphology, activity and product selectivity in FTS. The catalysts were tested in a fixed-bed reactor at FTS conditions.

2. Experimental

2.1. Catalyst preparation

Nano-structure iron catalysts were prepared by water-in-oil microemulsion method. A water solution of metal precursors, FeCl₃·6H₂O and Cu(NO₃)₂·4H₂O were added to a mixture of an oil

phase containing 1-propanol and chloroform and sodium dodecyl sulfate (SDS) as a surfactant. Hydrazine in the aqueous phase was added as precipitating agent and stirred for 3 hour. The obtained mixture was left to decant overnight. 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 390°C for 3 h. Nanostructured zirconium oxide was prepared like nanostructured iron and copper. At the next step, they were mixed together. The promoted catalysts were dried at 120°C for 20 h and calcined at 390°C for 3 h in air [12]. The catalyst compositions were designated in terms of the atomic ratios as: 100Fe/5Cu, 100Fe/5Cu/2Zr. All samples were pressed into pellets, crushed and sieved to obtain particles with 16-30 mesh.

2.2. Catalyst characterization

BET surface area, pore volume and average pore size distribution of the catalysts were determined by N₂ physisorption using a Micromeritics ASAP 3020 automated system. A 0.2 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. The analysis was done using N₂ adsorption at -196°C. XRD spectra of fresh catalyst were conducted with a Philips PW1840 X-ray diffractometer with monochromatized Cu (K α) radiation for determining of iron phases. Temperature programmed reduction (TPR) profiles of the calcined catalysts were recorded using a Micromeritics TPD-TPR 290 system. The TPR of 50 mg of each sample was performed in 5% hydrogen/argon gas mixture. The H₂ reduction process illustrated three stages in the temperature range between 200-800°C. Average particle size of the calcined powders was measured by LEO 912AB TEM. The composition of catalysts was determined using atomic absorption instrument (Perkin-Elmer model 2380).

2.3. Cata-test system and operation procedure

The catalytic experiments were conducted in a fixed-bed stainless steel reactor. The reactor was loaded by 1.5g catalyst. The catalyst was reduced in a %10 H₂/N₂ flow at 400°C for 2h. The catalyst activation was followed in a stream of synthesis gas with H₂/CO=1 and SV= 2NL.h⁻¹.gCat⁻¹ for 24 h in atmospheric pressure and temperature of 270°C. Following the activation process, the reactor pressure and temperature raised to 20 bar and 290°C, respectively and the reaction initiated in synthesis gas stream with H₂/CO =1 and GHSV= 2.8 NL.h⁻¹.gCat⁻¹.

The products were analyzed by a gas chromatograph (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 attached to a flame ionization detector (FID) for analyzing organic liquid products [9,15]. The activities and product selectivities were assessed after 60 h from initial time.

3. Results and discussion

Transition elements are used as promoters because they can modify the adsorption pattern of the reactants (H₂ and CO) on the active sites. The effect of Zr promoter on the behavior of the iron-based FTS catalysts; namely, CO chemisorptions enhancement has been justified as a consequence of the iron tendency to withdraw electronic density from zirconium. Therefore the strength of the Fe-CO bond was enhanced [12]. Elemental analysis was performed to determine the composition of elements in the nano-sized iron catalysts. Table.1 shows results of catalysts surface area.

Table 1. Textural properties of the catalysts

Catalyst	BET surface area (m ² /g)	Pore volume, (cm ³ /g)	Average pore size (nm)
100Fe/5Cu	46.3	0.25	15.2
100Fe/5Cu/2Zr	43.2	0.23	13.4

By adding of zirconium, the BET surface area, pore volume and average pore size in the catalysts decrease as it promotes the aggregation of the catalyst crystallites and blocks up the pore volume of the catalyst.

Nanostructured iron catalysts were characterized by X-ray diffraction (XRD) after calcinations. Fig. 1 shows the XRD patterns of the catalysts prepared by the microemulsion method. The addition of Zr did not cause any obvious change, and no phase containing metals above were detected. All the catalysts showed the Fe_2O_3 crystalline phase. The characteristic peak at $2\theta = 33.3^\circ$ corresponds to the hematite 104 plane .

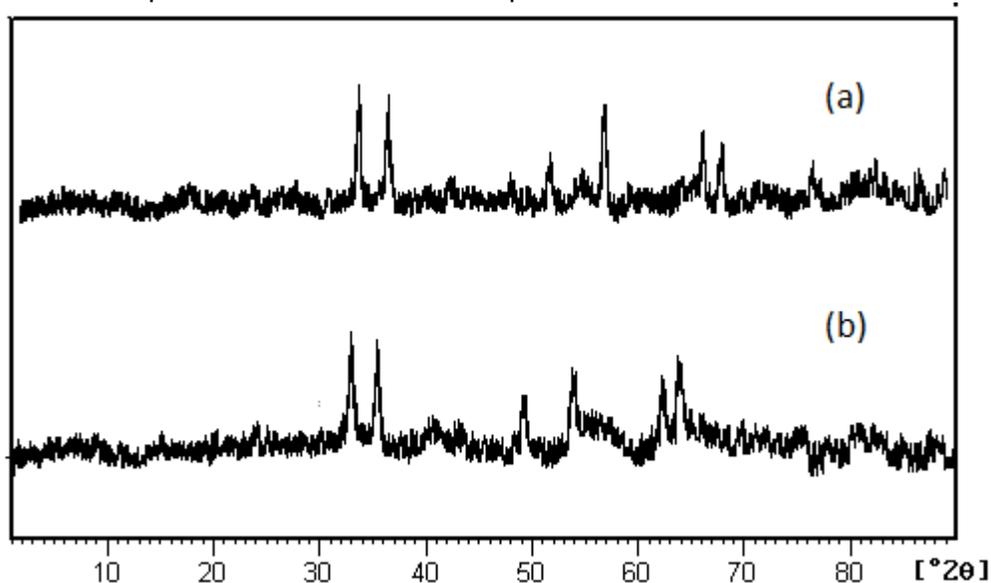


Fig. 1. XRD spectra of the fresh catalysts; (a) 100Fe/5Cu (b) 100Fe/5Cu/2Zr

The morphology of the catalyst was illustrated by TEM images as shown in Fig. 2. TEM revealed that the nanoparticles diameter was in the range of 10–30 nm.

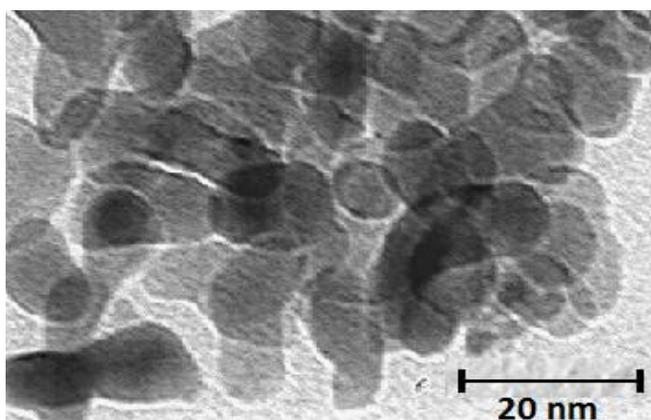


Fig 2. TEM micrograph of 100Fe/5Cu/2Zr catalyst

Fig. 3 shows the H_2 -TPR profiles of the nano-sized iron catalysts. H_2 -TPR determined reduction behavior of the catalysts. The first stage is ascribed to the transformations of CuO to Cu , the second stage is attributed to the transformation of Fe_2O_3 to Fe_3O_4 whereas the third stage represents the transformation of Fe_3O_4 to Fe .

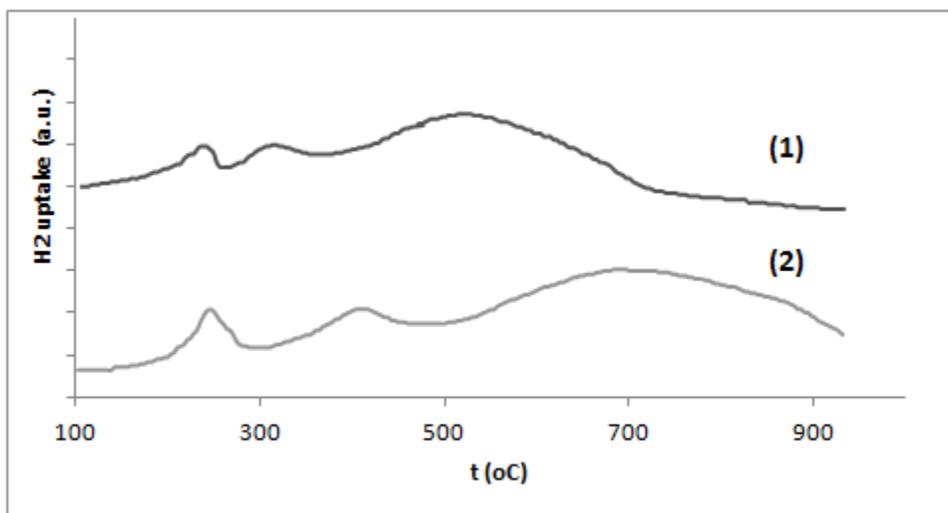


Fig.3. H₂-TPR profiles of the catalysts; (1) 100Fe/5Cu (2) 100Fe/5Cu/2Zr

Addition of promoter increased reduction temperature and reaction time. The promoter increases the catalyst activity. The addition of copper accelerates the deactivation of the catalyst, whereas the addition of Zr improve the FTS activity of iron-based catalysts. Fig.4 shows FTS rate and Water Gas Shift (WGS) rate. During FTS process, one part of H₂O produced by FTS reaction is a by WGS reaction.

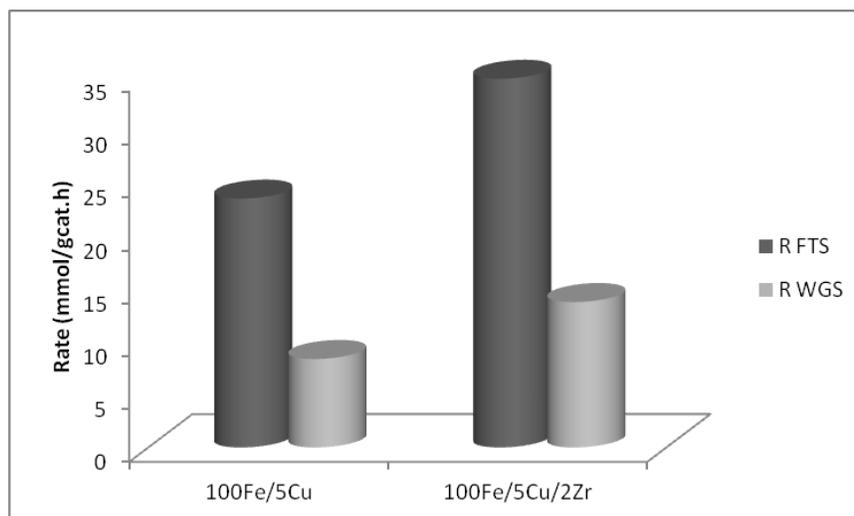
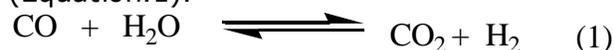


Fig. 4. R_{FTS} and R_{WGS} of the catalysts

Zr promoter into iron-based catalyst can promote CO adsorption, increases the concentration of CO species, shifts WGS reaction to right and thus improves WGS activity (Equation.1).



The high WGS activity decreases the H₂O pressure and stabilizes the iron carbides. Zr promoted iron catalyst has higher CO conversion than unpromoted catalyst. Products selectivity of the catalysts shows in fig.5. It shows selectivities to gaseous and light hydrocarbons (methane and C₂-C₄) and heavy hydrocarbons (C₅⁺). All of these results imply that the chain growth reaction is increased and the hydrogenation reaction is decreased while Zr was added in the catalyst. Both the amount of the promoters and the reaction conditions influence the product selectivity.

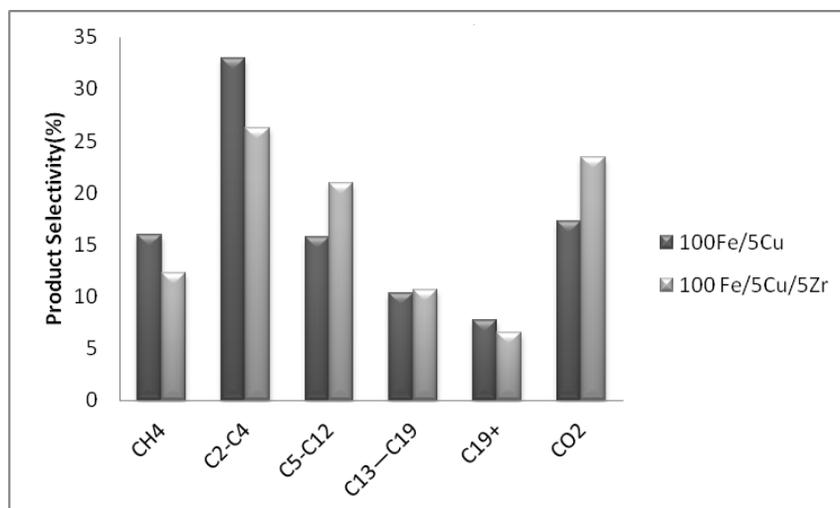


Fig 5. Products selectivity of the catalysts; Reaction condition: Time on Stream 60 h, 290 °C, 20MPa, H₂/CO = 1 and SV= 2.8nl.gCat⁻¹. h⁻¹.^a Selectivity to oxygenates was negligible (<3%) in all cases

In this work, addition of Zr promoter facilitates the CO dissociative adsorption, leading to a higher coverage of carbon species on the surface and thus promotes the chain growth reaction.

4. Conclusions

Nano-structured iron catalysts were prepared by microemulsion method. Effect of the zirconium into nanoparticles iron catalyst was investigated on the performance of the CO hydrogenation. Zr promoter into nano-sized iron catalyst has significant influences on the catalytic performances during Fischer-Tropsch synthesis. The changes in the catalytic performances can be attributed to the effect of promoter on H₂ and CO adsorption, which further significantly affects the FTS performances of the catalysts. Zr promoter significantly improve the FTS and WGS activities.

Acknowledgements

We are grateful to the Research Institute of Petroleum Industry (RIPI) for financial support. We also express our thanks to Central laboratory of Ferdowsi University of Mashhad for recording TEM micrographs.

References

- [1] Abdulbaset A, Mclroy DN, Armando GM. Effect of synthesis and activation methods on the catalytic properties of silica nanospring (NS)-supported iron catalyst for Fischer-Tropsch synthesis, *Fuel Proces. Technol.*, 2018; 169: 132-141.
- Lisheng G, Jian S, Jian W, Zhiyong W. Fischer-Tropsch synthesis over iron catalysts with corncob-derived promoters. *J. Energy Chem.*, 2017; 26(4): 632-638.
- [3] Steen EV, Claeys M, Möller KP, Nabaho D. Comparing a cobalt-based catalyst with iron-based catalysts for the Fischer-Tropsch XTL-process operating at high conversion, *Appl. Catal. A: Gen.*, 2018; 549: 51-59.
- [4] Mingyue D, Yong Y, Baoshan W, Yongwang L, Longlong M. Study on reduction and carburization behaviors of iron phases for iron-based Fischer-Tropsch synthesis catalyst. *Appl. Energy*, 2015; 160: 982-989.
- [5] van der Laan GP, Beenackers AAC. Kinetics and selectivity of the Fischer-Tropsch synthesis: A literature review. *Catal. Rev. Sci. Eng.*, 1999; 41 : 255-318.
- [6] Bukur DB, Mukesh D, Patal SA. Promoter effects on precipitated iron catalysts for Fischer-Tropsch synthesis. *Ind. Eng. Chem. Res.*, 1990; 29: 194-204.
- [7] Zamani Y, Bakavoli M, Rahimizadeh M, Mohajeri A, Seyed, SM. Study of Ce Promoter on Nano Structure Iron Catalyst in Fischer-Tropsch Synthesis. *Chem. Eng. Trans.*, 2012; 29:847-852.

- [8] Sarkari M, Fazlollahi F, Ajamein H, Atashi H, Larry LB. Catalytic performance of an iron-based catalyst in Fischer-Tropsch synthesis. *Fuel Proces. Technol.*, 2014; 127: 163-170.
- [9] Zamani Y. Fischer-Tropsch synthesis over nano-sized iron-based catalysts : Investigation of promoter and temperature effects on products distribution. *Pet Coal*, 2015; 57(1): 71-75.
- [10] Cheng K, Ordonsky VV, Virginie M, Legras B, Chernavskii PA, Kazak VO, Cordier C, Paul S, Wang Ye, Khodakov AY. Support effects in high temperature Fischer-Tropsch synthesis on iron catalysts. *Appl. Catal. A: Gen.*, 2014; 488:66-77.
- [11] Zamani Y. Effect of Mn promoter on nano-sized iron catalyst for Fischer-Tropsch Synthesis. *Pet Coal*, 2016; 58(4): 444-449.
- [12] Zamani Y, Bakavoli M, Rahimizadeh M, Mohajeri A, Seyedi SM. Synergetic Effect of La and Ba Promoters on Nanostructured Iron Catalyst in Fischer-Tropsch Synthesis. *Chin. J. Catal.*, 2012; 33: 1119-1124.
- [13] Pour AN, Kamali S SM, Bozorgzadeh HR, Zamani Y, Tavasoli A, Ahmadi MM. Effect of Mg, La and Ca promoters on the structure and catalytic behavior of iron-based catalysts in Fischer-Tropsch synthesis. *Appl Catal A: Gen*, 2008; 348: 201-208.
- [14] Feyzi M, Jafari F. Study on iron-manganese catalysts for Fischer-Tropsch synthesis. *J. Fuel Chem. Technol.*, 2012; 40(5): 550-557.
- [15] Bakavoli M, Zamani Y, Akbar ZM. Study on the carbon dioxide hydrogenation to hydrocarbons over nanoparticles iron-based catalyst. *Pet Coal*, 2014; 56(5): 480-486.

To whom correspondence should be addressed: Dr. Yahya Zamani, Research Institute of Petroleum Industry (RIPI), National Iranian Oil Company; West Blvd., Near Azadi Sports Complex P.O.BOX 14665-137, Tehran, Iran,