Indian Journal of Chemical Technology
Vol. 26, July 2019, pp. 337-341

Role of Mn on reducibility and acidity of Cu-Zn promoted Co-Fe based bimetallic Fischer–Tropsch (F–T) catalysts

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Received 7 November 2017; accepted 24 June 2019

The effect of Mn is studied on Cu-Zn promoted alumina supported bimetallic (Co-Fe) FT catalyst. The catalysts have been prepared by wet impregnation technique on alumina with the respective metal nitrate solutions. Characterization of the catalysts have been carried out with XRD, H_2-TPR, NH_3-TPD and BET surface area. The results indicate that small addition of Mn enhances reducibility and minimizes the acidity of catalysts. This study will help to understand the contribution Mn for the development of efficient catalysts for Fischer-Tropsch synthesis.

Keywords: Fischer-Tropsch synthesis, Wet impregnation, Reducibility, Acidity

Fischer–Tropsch synthesis is a catalytic process in which syngas (mixture of CO + H_2) is converted to hydrocarbon of variable molecular weight[1]. Interest in F–T synthesis technology is growing rapidly, not because of the abundant coal and natural gas in the globe, but because of the global demand for fuel supplies and environmental policies on the quality of fuel emitted to the environment. Through Fischer–Tropsch synthesis, coal and remotely located natural gas can be utilized to synthesize liquid products[2]. As F–T process involves a catalytic chemical reaction, so catalyst is indispensable. The development of novel catalysts with high activity and selectivity is desirable as it leads to improved quality and value of F–T synthesis products. F–T catalysts are typically based on Gr VIII metals such as Fe, Co, Ni and Ru. However, Co and Fe based catalysts are pivotal for F–T synthesis. Besides the active metals, promoters such as Ru, Cu, Mn and Zn are supported on Al_2O_3, SiO_2 and TiO_2. In F–T synthesis process, high-performance catalyst plays an essential role in industrial applications[3]. Some researchers prefer Fe-based catalyst not only because of the lower cost, higher availability, higher selectivity to C_2-C_4 and higher resistance to contaminants from a commercial perspective, but also because of the higher water-gas shift activity to enhance the H_2 composition and thus to enable the in-situ adjustment of H_2 /CO ratio[4-6]. Some researchers prefer Co-based catalysts for FTS in order to focus on current interest because of higher productivity for synthesis of long-chain hydrocarbons C_{5+}, as source for ultra-clean synthetic diesel and special lubricants[7-9]. Some researchers have argued that the bimetallic catalyst obtained from Co-Fe may have some special advantages in CO hydrogenation[10]. In these circumstances, optimizing the usage of high price cobalt and enhancing the physico-chemical properties of the supported cobalt catalyst, is a challenging task. As a promoter Cu, Zn, Mg and Mn have effect on Fe and/or Co based catalysts. The aim of the present study is to prepare Cu, Mn and Zn promoted Co-Fe based bimetallic catalysts and to understand the effect of Mn on the reducibility and acidity of the catalysts[11, 12].

Experimental Section

Material

All chemicals are of commercial grade and used without further purification: Cobalt (II) nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$, Loba Chemie], Ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$,Merck], Copper (II) nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$, Merck], Manganese nitrate tetrahydrate [$Mn(NO_3)_2 \cdot 4H_2O$, Qualigens], Zinc nitrate tetrahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, Merck], and Cetyl trimethyl ammonium bromide [CTAB, ($C_{19}H_{42}BrN$, Sigma-Aldrich], Aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$, Merck].

Preparation of mesoporous alumina

Mesoporous alumina was synthesized through hydrothermal technique with molar compositions: 1.0

Al: 0.5 CTAB: 5.28 urea : $70H_2O$[13]. In a typical synthesis process, 74.0 g of $Al(NO_3)_3.9H_2O$ and 62.15 g of urea were dissolved in 550 mL of de-ionized water under vigorous stirring at 35°C for 30 min. Then, a certain amount (35.75 g) of CTAB was added into the solution and remained at 35°C under vigorous stirring until homogeneous solution was formed. The mixture was then poured into a Teflon bottle and hydrothermally treated at 120°C for 24 h. Finally, the white precipitate was filtered, washed with de-ionized water, dried at 120°C in air oven over night and then calcined at 750°C in air with ramps 30°C to 200°C at 2°C /min for 10 min, 200°C to 400°C at 2°C /min for 30 min, 400°C to 750°C at 5°C /min for 120 min.

Preparation of Cu and Zn promoted Co-Fe catalyst with different Mn loading

A series of four catalysts were synthesized with different composition of manganese through the wet impregnation method Fig. 1. The support material is impregnated with the active metals from the respective aqueous solution of the active metal salts. In this procedure, the active metal with weight percentage compositions: 13Co:5Fe:2Zn:2Cu:xMn (where x=2,4,6,8) were taken. First prepared solution of respective precursor and impregnated on alumina (2g). After impregnation, samples were kept overnight in air oven at 100°C. Afterwards dried sample was calcined at 750°C for 2 h in furnace with heating ramps of 30°C to 200°C at 2°C /min for 10 min, 200°C to 400°C at 2°C /min for 30 min, 400°C to 750°C at 5°C /min for 120 min. The details of the catalysts are given in Table 1.

Characterizations

BET surface area

The N_2-adsorption desorption isotherms of the catalysts were measured at liquid nitrogen temperature with Micromeritics TriStar 3000 surface area analyzer. The surface areas of the catalysts were calculated by Brauner-Emmett-Teller (BET) equation and pore size distributions were determined by BJH (Barrett-Joyner-Halenda) method.

TPR and TPD

The temperature programmed reduction (TPR) and temperature programmed desorption (TPD) profiles of the catalysts were measured by using Chemisorb 2720 (Make: Micrometrics, USA) instrument equipped with a TCD detector. The H_2-TPR profiles were measured in a mixture gas of 10% H_2 in Ar at a flow rate of 20 mL/min and the temperature was linearly increased from room temperature to 1000°C at a rate of 10°C/min. The NH_3-TPD of the catalysts were measured by flowing NH_3 (0.4 % NH_3 in balance He) at room temperature and then the adsorbed gas was desorbed in the flow of He at a flow rate of 20 mL/min and the temperature was increased from room temperature to 1000°C at a rate of 10°C/min.

XRD

X-ray powder diffraction patterns were recorded using a Rigaku Ultima IV instrument. The crystallite size was determined from the XRD pattern using Scherrer formula: d = 0.9 λ /β Cos θ

where, d is the average crystallite size, λ is the wavelength of the X-ray, β is the line broadening at FWHM and θ is the position of strongest Bragg profile in the diffractogram.

Results and Discussions

XRD

The X-ray power diffraction (XRD) profiles of the calcined catalysts are shown in Fig. 2. In all the

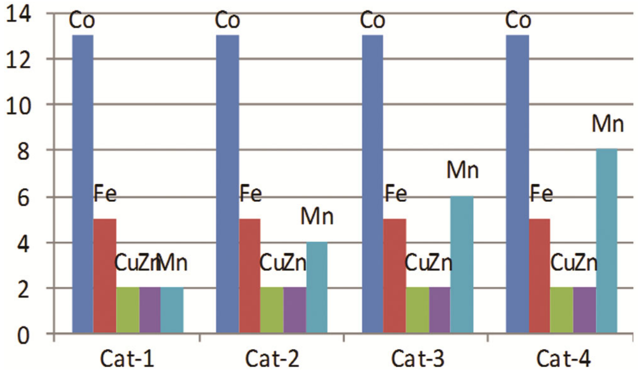

Fig. 1 — Schematic representation of catalyst composition

Table 1 — Catalyst composition and nomenclature

Catalyst component	Composition (wt%)	Catalyst name
Cobalt, Iron, Copper, Zinc, Manganese	13,5,2, 2	Cat-1
Cobalt, Iron, Copper, Zinc, Manganese	13,5,2, 4	Cat-2
Cobalt, Iron, Copper, Zinc, Manganese	13,5,2, 6	Cat-3
Cobalt, Iron, Copper, Zinc, Manganese	13,5,2, 8	Cat-4

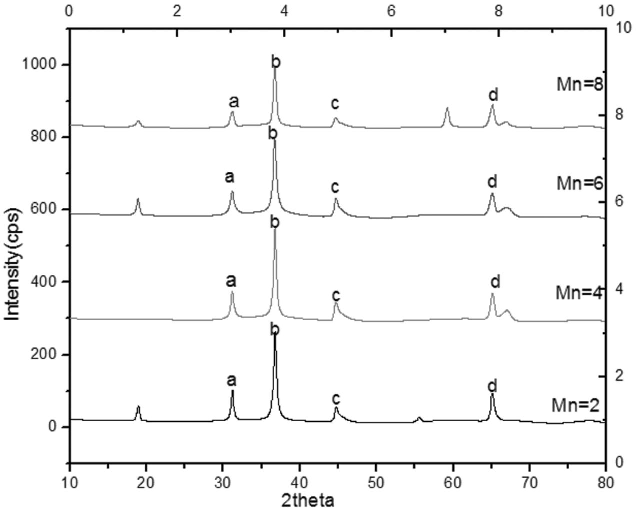

Fig. 2 — XRD spectra of catalysts

Table 2 — Co_3O_4 crystallite size from XRD analysis

Catalyst	Crystallite size(nm)
Cat-1	24
Cat-2	22
Cat-3	19
Cat-4	17

Table 3 — Physical properties of catalysts obtained from N_2 adsorption/desorption (BET analysis)

Catalyst	Pore volume	Pore diameter	Surface area(m^2/g)
Cat-1	0.24	9.5	102
Cat-2	0.24	11.14	87
Cat-3	0.27	12.40	87
Cat-4	1.04	40	85

profiles, only peaks of Co_3O_4 crystallites of appear at 31.2°, 36.7°, 59.3° and 65.2° indicated as a, b, c and d (14). But, crystallite size estimated from Scherrer equation at 36.7, it was observed that increasing loading of Mn favors the decrease in crystallites. It can be observed from the Table 2 that the Co_3O_4 crystallite size decreases with increase in Mn loading which suggests that lower particle size will improve dispersion of Co on the support surface.

BET Surface area

BET surface areas of the catalysts are given in Table 3. BET surface area of the catalysts decreases with increase in Mn loading on the alumina support. The results for average pore size and specific pore volume were determined using the Barrett-Joyner-Halenda (BJH) desorption method, as shown in Table 3**.**

N_2 physisorption isotherms of all the catalysts (Fig. 3) correspond to type IV[15]. The nitrogen adsorption at $p/p_0 < 0.4$ shows that none of the materials have significant microporosity. At higher p/p_0 relative pressure confirms a broader pore size distribution of the catalyst[16]. In summary, significant amount of Mn addition is needed for improvement of structure property.

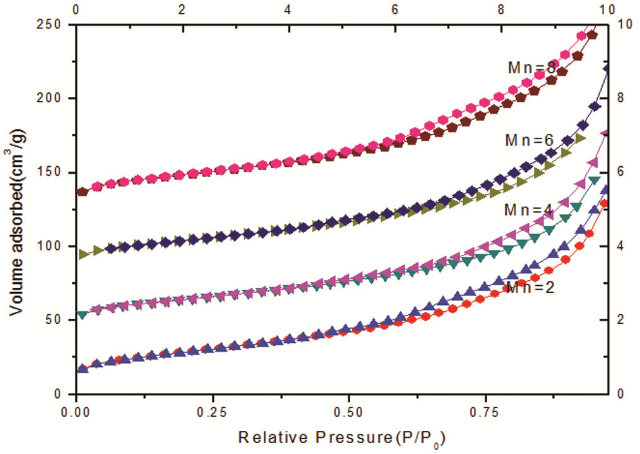

Fig 3 — Nitrogen adsorption-desorption isotherms of catalysts

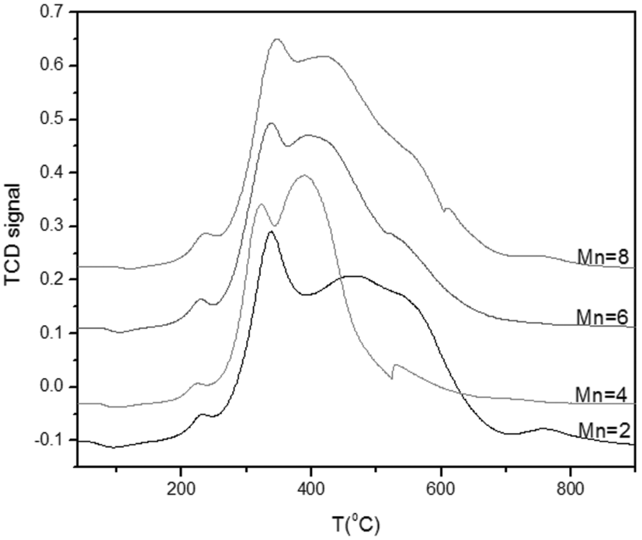

Fig. 4 — Temperature programmed reduction profile

TPR

H_2-TPR was carried out to elucidate the reduction behavior of the catalysts. Figure 4 shows H_2-TPR profiles of all catalysts, i.e. H_2 consumed during different reduction stages. The low temperature peak region of 227–377°C is attributed to reduction of Co_3O_4 to CoO and second peak region of 310 – 480°C is due to reduction of CoO to metallic Co (17). It is observed that the reduction peaks shifted to lower temperature due to increase in Mn loading from 2.0 wt. % to 4.0 wt. %. Afterward reduction peaks

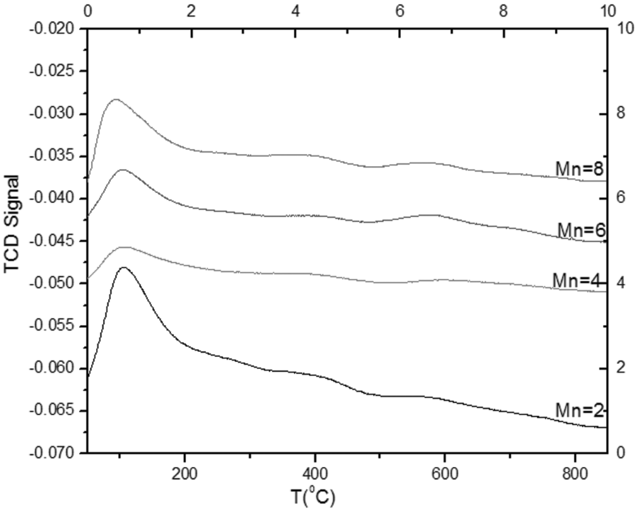

Fig 5 — Temperature programmed desorption profile

Table 4 — Surface acidity of catalysts as measured by NH_3 TPD

Catalyst	Temperature(^{0}C)	NH_3(adsorbed, μmol/g)
Mn=2	105	2.95
Mn=4	107	2.14
Mn=6	106	1.60
Mn=8	91	1.43

shift towards higher temperature with further increase in Mn. With reference to previous studies the small peaks which were observed between 500 – 600°C can be assigned to Fe_2O_3 to Fe_3O_4 and Fe_2O_3 to FeO. Very small peak were also observed between 750°C in Cat-1 and Cat-4 which refers to presence of iron-cobalt alloy or support-metal compound[17, 18].

TPD

The NH_3-TPD profiles of the catalysts with different Mn loading in the temperature range of 100 – 700°C are presented in Fig. 5. The corresponding acid site concentration expressed in micro mol (µmol) of NH_3/g catalyst is summarized in Table 4. The increase of loading of Mn decreases the adsorption of ammonia signifying the decrease of acid sites of the catalysts. Cat-4 catalyst depicted high basicity, which is observed at 176°C. It has been shown that FT synthesis is favored at weak acidic sites because CO is adsorbed at weak acidic site to carry out CO-hydrogenation reaction[19]. The result indicates that the amount of the strong basic sites is increased with the incorporated Mn promoter[20]. The present study corroborates that Mn influences on the cobalt dispersion by preventing the agglomeration of the Co particles[21] which is evident from the decrease of particle size of Co_3O_4 due to Mn loading.

Conclusion

In the present study, H_2 – TPR, NH_3 – TPD, BET surface area and XRD studies are carried out to understand the effect of Mn on Cu-Zn promoted alumina supported Co-Fe based bimetallic catalyst with increased addition of Mn. Reducibility of catalyst also improved with optimum loading of Mn. It is observed that up to optimum amount of Mn improves the physico-chemical properties of catalyst. Characterization results show that the optimization of Mn composition is utmost important during catalyst preparation. This study will also contribute to the development of efficient catalysts for production of hydrocarbons from syngas.

Acknowledgement

The authors are thankful to Director, CSIR-Central Institute of Mining & Fuel Research, Dhanbad for allow to publish this paper.

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