Preparation and Characterization of CoMn/TiO$_2$ Catalysts for Production of Light Olefins

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ABSTRACT: *A series of x(Co, Mn)/TiO$_2$ catalysts (x=2–12wt.%) containing 25%Co and 75%Mn were prepared by the co-impregnation method. All prepared catalysts have been tested in Fischer-Tropsch synthesis for production of C$_2$-C$_4$ olefins. It was found that the catalyst containing 8wt.%(Co,Mn)/TiO$_2$ is an optimal catalyst for production of C$_2$-C$_4$ olefins. The effect of operation conditions such as the H$_2$/CO molar feed ratios, temperature, Gas Hourly Space Velocity (GHSV) and total reaction pressure on the catalytic performance of optimal catalyst was investigated. Characterizations of both precursors and catalysts were carried out using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) specific surface area measurement, Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).*

KEY WORDS: *Co-impregnation, Fischer-Tropsch synthesis, Operation conditions, Catalytic performance.*

INTRODUCTION

The production of fuels substituting the natural petroleum is an interesting way of the Fischer-Tropsch Synthesis (FTS). An approach to improve the selectivity in this process for conversion of synthesis gas to hydrocarbons involves the use of a bimetallic catalyst system containing metals catalyst combined with a support [1]. There has been renewed interest in recent years in FTS, especially for the selective production of petrochemical feedstocks such as ethylene, propylene and butylene (C$_2$-C$_4$ olefins) directly from synthesis gas [2-3]. The FTS reaction with cobalt-based catalysts has been studied by many investigators and it has been shown that cobalt based catalysts, in general, are superior to similarly prepared iron-based catalysts with respect to especially catalyst life [4-7]. Modification of the traditional

FTS catalysts (Mn, Ni, Co, Ru) by promoters and supports has provided one means of manipulating the FTS products spectrum [8]. Due to the thermodynamic and kinetic limitations of the reaction, few catalysts are able to amplify the C$_2$-C$_4$ hydrocarbons fraction. However some examples are reported in the literature and these are Mn and Co based catalysts on partially reducible oxide supports such as MnO$_2$, V$_2$O$_5$ and TiO$_2$ instead of the conventional inert supports like SiO$_2$ and Al$_2$O$_3$ were used in FTS [9-11]. Co-Mn catalysts have been investigated intensively for its higher selectivity to lower molecular weight olefins [12-14], but these studies have focused mainly on the characterization of catalyst and improvement of preparation method. There has been considerable interest for the modification of cobalt with

manganese oxide and it has shown that a Co/MnO catalyst with Co/Mn molar ratio of unity can give decreased methane yields together with enhanced propylene formation [15-18], at atmospheric pressure and at low conversion. However, the works of *Iglesia et al.* [19] at higher pressure and at high conversion indicate that the influence of the support on the specific activity of the methane and C_5^+ hydrocarbons selectivity can be neglected.

In one of our previous work [20], we used the co-precipitation method to investigate the effect of a range of precipitation variables such as, precipitate aging time, the [Co]/[Mn] ratios and the catalyst calcination temperatures on the structure of a precipitated cobalt-manganese catalyst. Our work showed that the optimum catalyst has a molar [Co]/[Mn] ratio of 25%Co/75%Mn and is supported by 30 wt%.%TiO_2 based on the total catalyst weight. In the present research work, the catalysts containing 25%Co/75%Mn which is supported by TiO_2 were prepared using co-impregnation method. We attempted to investigate influence the metals loading, calcination conditions and operational conditions on the catalytic performance. Characterization of both precursors and calcined catalysts were carried out by powder X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area measurement and thermal analysis methods such as Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

EXPERIMENTAL SECTION
Catalyst preparation

All the tested catalysts in this study were prepared using the following the co-impregnation method. At first, TiO_2 (anatase, 120.0 m^2g^{-1} surface area and 0.38 cm^3g^{-1} pore volume) was heated at 500 ºC for 6 h. Then TiO_2 was co-impregnated with mixed aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2.4H_2O$ containing 25%Co and 75%Mn to generate a series of x (Co,Mn)/TiO_2 catalysts (x=2–12wt.%). The catalyst precursors were dried at 120 °C for 16 h after each co-impregnation step and then calcined at 500 ºC for 16 h after the final co-impregnation step.

Catalyst characterization
X-Ray Diffraction (XRD)

XRD measurements were performed using a Bruker axs Company, D8 Advance diffractometer (Germany). Scans were taken with a 2θ step size of 0.02 from 4 to 70º and a counting time of 1.0 s using CuK_α radiation source generated at 40 kV and 30 mA.

BET specific area measurements

The BET surface area were measured using a N_2 adsorption-desorption isotherm at liquid nitrogen temperature (-196ºC), using a NOVA 2000 instrument (Quantachrome, USA).

Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The TGA and DSC were carried out using simultaneous thermal analyzer apparatus of Rheometric Scientific Company (STA 1500+ Model, England) under a flow of dry air. The temperature was raised from 25 ˚C to 650 ˚C using a linear programmer at a heating rate 5 ˚C min^{-1}.

Scanning Electron Microscopy (SEM)

The morphology of catalysts and their precursors was observed by means of an S-360 Oxford Eng scanning electron microscopy (made in USA).

Catalyst Testing

The catalyst tests were carried out in a fixed bed stainless steel micro reactor at different operation conditions (Fig. 1). All gas lines to the reactor bed were made from 1/4" stainless steel tubing. Three mass flow controllers (Brooks, Model 5850E) equipped with a four-channel control panel (Brooks 0154) were used to adjust automatically the flow rate of the inlet gases (CO, H_2, and N_2 with purity of 99.999%). The mixed gases passed into the reactor tube, which was placed inside a tubular furnace (Atbin, Model ATU 150-15) capable of producing temperature up to 1300ºC and controlled by a digital programmable controller (DPC). The reactor tube was constructed from 0.9" stainless steel tubing; internal diameter of 1.0 cm, with the catalyst bed situated in the middle of the reactor. The reaction temperature was controlled by a thermocouple inserted into catalyst bed and visually monitored by a computer equipped with software. The meshed catalyst (1.0 g) was held in the middle of the reactor with 90 cm length using quartz wool. The reactor was equipped with an electronic back pressure regulator (TESCOM model, USA) with the
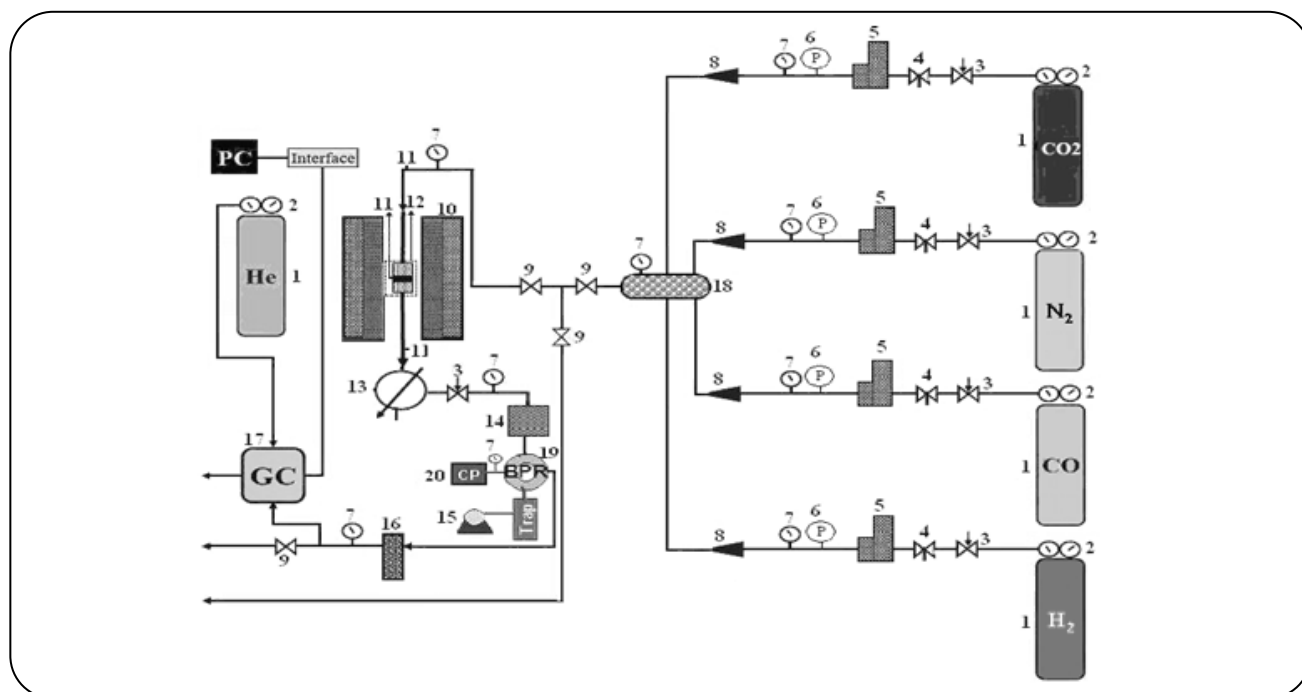
Fig. 1: Schematic representation of the reactor in a flow diagram used. 1-Gas cylinders, 2-Pressure regulators, 3-Needle valves, 4-Valves, 5-Mass Flow Controllers (MFC), 6-Digital pressure controllers, 7-Pressure Gauges, 8-Non return valves, 9-Ball valves, 10-Tubular Furnace, 11-Temperature indicators, 12-Tubular reactor and catalyst bed, 13-Condenser, 14-Trap, 15-Air pump, 16-Silica gel column, 17-Gas Chromatograph (GC), 18-Mixing chamber, 19-BPR: Back Pressure Regulator (Electronically type), 20-CP (Control panel).

ability of controlling of total pressure between atmospheric to 100 bar. The catalyst was pre-reduced *in situ* atmospheric pressure in a flowing H_2 stream (flow rate =30 mlmin^{-1}) at 400 ℃ for 16 h before synthesis gas exposure. The FTS was carried out at 250-340 ℃ (P=1-10 bar, H_2/CO=1/1-3/1, GHSV= 1200-2200 h^{-1}). Reactant and product streams were analyzed on-line using a gas chromatograph (Varian, Model 3400 Series) equipped with a 10-port sampling valve (Supelco company, USA, Visi Model), a sample loop, Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD). The contents of sample loop were injected automatically into a packed column (Hayesep DB, Altech Company, USA, 1/8" OD, 10 meters long, and particle mesh 100/120). Helium was employed as a carrier gas for optimum sensitivity (flow rate=30 mlmin^{-1}). The results in terms of CO conversion, selectivity and yield of products are given at each space velocity. The CO conversion (%) was calculated according to the normalization method (Eq. (1)):

$$CO\ conversion(\%) = \frac{(Moles\ CO_{in}) - (Moles\ CO_{out})}{Moles\ CO_{in}} \times 100 \quad (1)$$

The catalyst selectivity was calculated according to Eq. (2):

$$Selectivity\ of\ j\ product\ (\%) = \quad (2)$$

$$\frac{Moles\ of\ j\ prduct \times n}{(Moles\ CO_{in}) - (Moles\ CO_{out})} \times 100$$

n is the carbon number in j product.

The carbon balance (%) was calculated as the percentage of the carbon amount of the effluent and extracted products in the carbon amount of the inlet feed gas and is defined as Eq. (3):

$$Carbon\ balance\ (\%) = \quad (3)$$

$$\frac{Moles\ of\ carbon_{in} - Moles\ of\ carbon_{out}}{Moles\ of\ carbon_{in}} \times 100$$
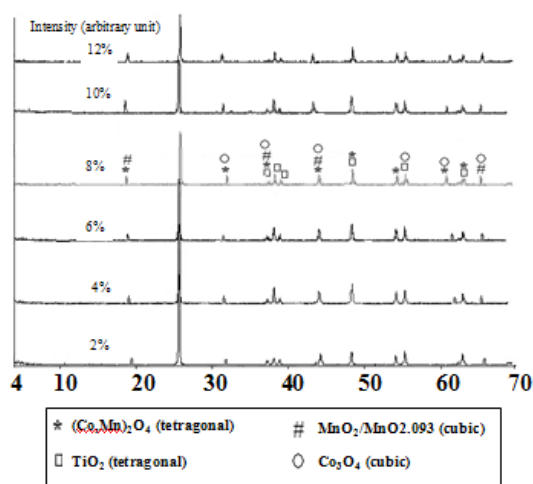
RESULTS AND DISCUSSION
Effect of preparation conditions

The effect of a range of co-impregnated $x(Co,Mn)/TiO_2$ catalysts preparation variables at the precursor stage of these materials has been investigated.

Table 1: Catalytic performance of $x(Co,Mn)/TiO_2$ (x=2, 4, 6, 8, 10 and 12 wt.%).

x wt.%		2	4	6	8	10	12
CO conversion (%)		28.1	30.5	33.8	36.0	42.0	44.2
Product selectivity (%)	CH_4	12.4	9.7	9.8	8.6	10.7	15.2
	C_2H_6	5.6	4.1	4.4	3.3	11.3	13.6
	C_2H_4	6.3	8.6	6.8	10.2	7.6	7.3
	C_3H_8	11.1	13.9	14.3	16.5	16.9	16.4
	C_3H_6	32.1	33.7	34.3	36.3	28.9	25.1
	C_4H_{10}	0.9	1.3	1.3	0.7	0.7	9.8
	C_4H_8	1.3	1.5	1.9	1.9	1.4	1.9
	CO_2	12.7	12.2	10.3	8.6	10.2	13.6
	C_5^+	17.5	16.7	16.9	16.1	11.4	10.5

Fig. 2: XRD patterns for x wt%(Co,Mn)/TiO₂ of calcined catalysts.

Subsequently, the morphological and structural effects on the activity of the final calcined catalysts were studied. The optimum preparation conditions are identified with respect to the catalytic activity for the conversion of synthesis gas to light olefins.

Effect of catalyst loading

All tested catalysts in this section evaluated under the same reaction conditions ($H_2/CO=2/1$, GHSV=1800 h^{-1}, P=1 bar at 280 ºC). The catalysts were prepared with loadings of x (x=2, 4, 6, 8, 10 and 12 wt.%). The catalytic performances of $x(Co,Mn)/TiO_2$ catalysts are shown in Table 1. It can be seen that the CO conversion increases with increasing the amount of x wt.%. According to the
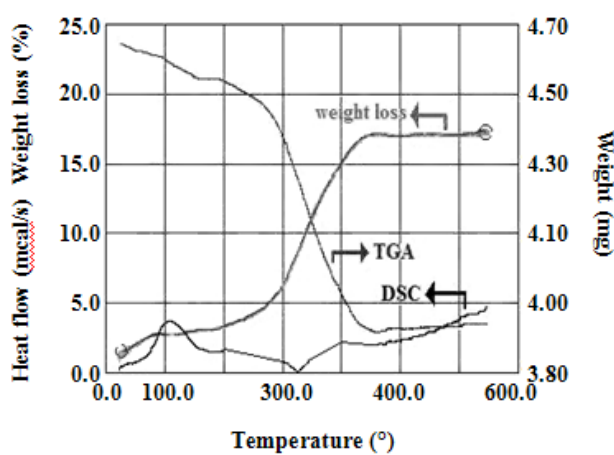
obtained results, the catalyst containing 8wt% $(Co,Mn)/TiO_2$ has shown the best catalytic performance than other tested catalysts. This catalyst has highest selectivity towards C_2-C_4 olefins and also lowest selectivity to methane and CO_2 in comparison with the other tested catalysts. So, this catalyst was chosen as the optimal catalyst with respect to the conversion of synthesis gas to light olefins.

Characterization studies were carried out using different techniques for the calcined catalysts with loadings of x wt.% of (Co,Mn). The activity increased steadily as x were increased and similar phases were identified by XRD for the calcined catalysts, although the relative diffracted intensities of these phases for all catalysts were different (Fig 2); these phases were $MnO_2/MnO_{1.937}$ (cubic), Co_3O_4 (cubic), $(Co,Mn)(Co,Mn)_2O_4$ (tetragonal) and TiO_2 (tetragonal). The catalyst containing 8wt% $(Co,Mn)/TiO_2$ showed the best catalytic performance than the other prepared catalysts. In order to identify the phase changes of this catalyst during the FTS reactions, the catalyst after reaction was characterized by XRD. The XRD phases of the tested catalyst were found to be in form of Co_3O_4 (cubic), CoO (cubic), MnO (cubic), TiO_2 (Tetragonal), Co_2C (orthorhombic). As shown, the tested catalyst has oxidic and cobalt carbide phases, both of which are active phases in the FTS catalysts. Oxidic phases are highly selective for the production of olefins, and carbide phases are active in the hydrogenation of CO [21,22].

Characterization of the 8wt% $(Co,Mn)/TiO_2$ catalyst precursor was also carried out to measure the losses of weight as the temperature of the sample is increased.

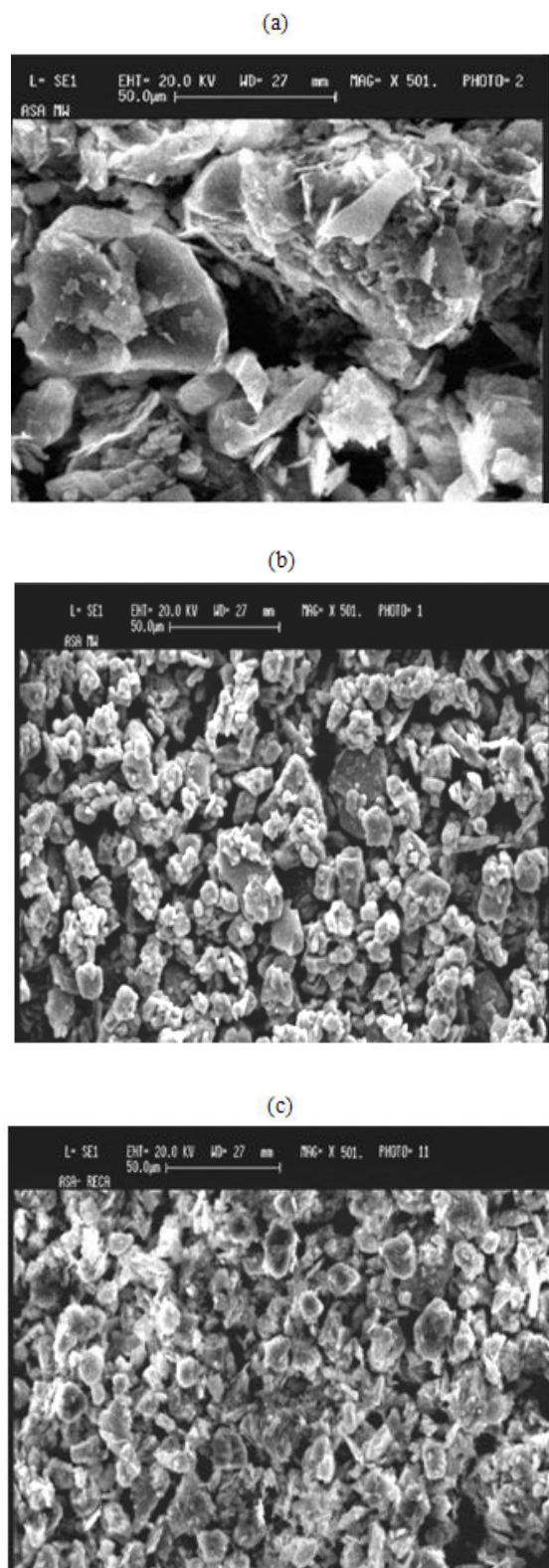*Table 2: BET results for the x(Co,Mn)/TiO₂ (x=2, 4, 6, 8, 10 and 12 wt.%) precursors and catalysts.*

x wt.%		Specific surface area (m²g⁻¹)	
	Precursor	Calcined catalyst (before reaction)	Calcined catalyst (after reaction)
2	65.3	68.4	66.8
4	67.6	71.1	68.6
6	71.7	74.3	72.4
8	78.4	83.7	82.4
10	79.9	85.3	81.2
12	81.5	86.9	82.5

Fig. 3: TGA and DSC curves for 8wt%(Co,Mn)/TiO₂ catalyst precursor.

The TGA/DSC curves for this catalyst precursor are shown in Fig. 3. The weight losses found from TGA measurements were agree fairly well with those expected for the decomposition of nitrate compounds to oxides. For this catalyst precursor, the thermogravimetric curve seems to indicate two–stage decomposition. The first-stage is considered to be due to the removal of adsorbed and dehydration (40-160 °C) and the second stage (190-480 °C) is due to the decomposition of nitrate compound to cobalt and manganese oxides phases (Co_3O_4 and $(Co,Mn)(Co,Mn)_2O_4$) that were identified by XRD technique. The TGA curve is involved with a total overall weight loss of ca. 17.4 wt%. DSC measurement was preformed in order to provide further evidence for the presence of the various species and evaluates their thermal behavior. As it shown in Fig. 3, the endothermic peak at lower temperature (40-160 °C) represents the removal of the physically adsorbed and dehydration from

the catalyst precursor. The endothermic peaks at around 300-410 °C is due to the decomposition of cobalt and manganese nitrates. The BET specific surface area results for all precursors and calcined catalysts (before and after reaction) are given in Table 2. According to the obtained results, the BET surface areas for prepared catalysts are dependent on the weight percent of x. However, the specific surface area of catalysts precursor and calcined catalysts (before reaction) for each catalyst, were found to be nearly similar. Besides, the BET specific surface areas of the catalysts before and after reaction are different. The results in Table 2, also show that the calcined catalysts (before the reaction) have higher specific surface areas than their precursors. As it shown the calcined catalyst containing 8wt% (Co,Mn)/TiO₂ has the high specific surface area. In the other hand, as it can be seen on Table 2, the BET specific surface area for the optimal catalyst after the test show a lower decreasing in comparison with other tested catalysts, this might be a reason why the 8wt% (Co,Mn)/TiO₂ catalyst shows a better catalytic performance than the other tested catalysts.

SEM observations have shown differences in morphology of precursor and calcined optimal catalysts (before and after the reaction), the electron micrograph obtained from catalyst precursor depicts several larger agglomerations of particles (Fig. 4a) and shows that this material has a less dense and homogeneous morphology. After the calcination at 500 °C for 16 h, the morphological features are different with the precursor sample and shows that the agglomerate size is greatly reduced in comparison with the precursor (Fig. 4b). It may be due to this reason that the calcined catalyst surface is covered with small crystallite of cobalt and

Fig. 4: The SEM images of calcined catalyst containing of 8wt%(Co,Mn)/TiO₂; (a) precursor, (b) calcined catalyst before reaction, (c) calcined catalyst after reaction.

manganese oxide, in agreement with XRD results. However, the size of these grains grew larger by agglomeration in the tested catalyst (Fig. 4c), which may be due to the sintering after reactions.

Effect of calcination conditions

Two samples of precursors containing 8wt% $(Co,Mn)/TiO_2$ was calcined in air and nitrogen atmospheres separately (Fig.5). The obtained CO conversion and products selectivity (T=280ºC, $H_2/CO=2/1$, P=1 bar and GHSV=1800h^{-1}) are summarized in Fig. 6. A comparison of the results in this figure indicated that the calcined catalyst in air (500 ºC for 16 h and heating rate 1.0 ºC min^{-1}) has the highest CO conversion and highest selectivity with respect to C_2-C_4 light olefins. Taking these results into consideration, the air was chosen as an optimum calcination atmosphere for the 8wt%(Co,Mn)/TiO$_2$ catalyst that prepared using co-impregnation method. Characterization of both catalysts that calcined in air and nitrogen atmospheres was carried out using BET specific surface area and the results indicated that the catalyst calcined in air had a higher specific surface area (58.1 m^{2}g^{-1}) than the catalyst calcined in nitrogen atmosphere (47.3 m^{2}g^{-1}).
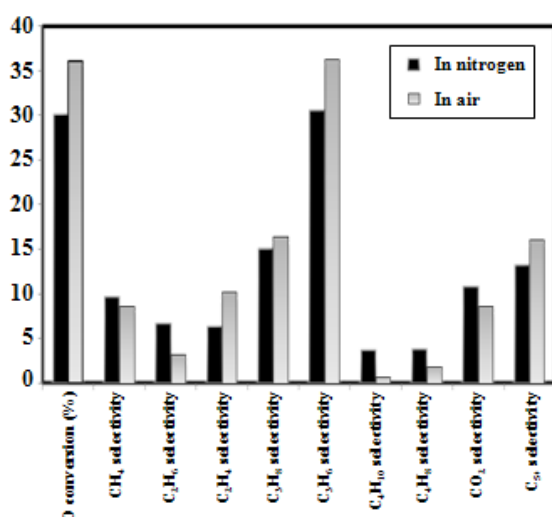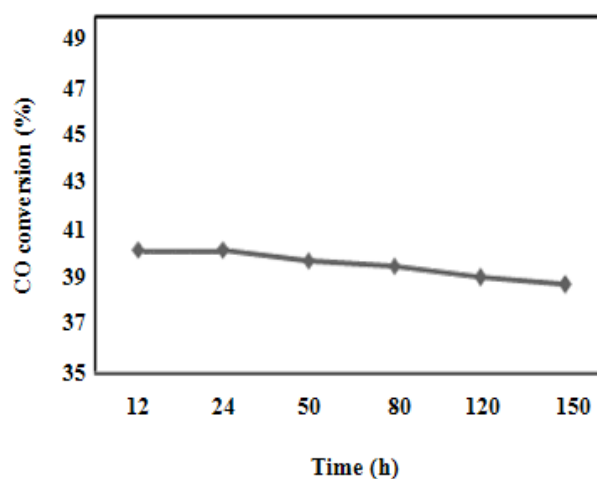
In order to study the effect of calcination heating rate on the catalytic performance, a series of precursors containing 8wt% (Co,Mn)/TiO$_2$ were calcined (500 ºC for 16 h) at various heating rates in air atmospher and tested for FTS. The heating rate was varied between 1.0-6.0 ºC min^{-1}. The CO conversion and light olefins products selectivity percent are shown in Table 3 (T=280 ºC, $H_2/CO=2/1$, P=1 bar and GHSV=1800 h^{-1}). It can be seen that heating rates up to about 4.0 ºC min^{-1} did not exert a major effect on the catalytic performance of the catalyst, while the heating rates over 4.0 ºC min^{-1} resulted in a significant decrease in the CO conversion and olefin selectivity.

Therefore, in this study, heating rate of 4.0 ºC min^{-1} is considered to be the optimum heating rate for calcination of the 8wt% (Co,Mn)/TiO$_2$ catalyst in air atmosphere. The BET specific surface area results for the calcined catalysts at different heating rates are shown that the specific surface area values obtained for the calcined catalyst in air at heating rate 4.0 ºC min^{-1} (83.7 m^{2}g^{-1}) is relatively higher than that observed for those calcined catalysts at 2.0 ºC min^{-1} (63.1 m^{2}g^{-1}), 3.0 ºC min^{-1} (68.4 m^{2}g^{-1}),

Table 3: Effect of calcination heating rate on the catalytic performance 8wt.%(Co,Mn)/TiO$_2$ catalyst.

Heating rate (°C min^{-1})		1.0	2.0	3.0	4.0	5.0	6.0
CO conversion (%)		34.7	36.0	38.4	41.0	34.5	31.2
Product selectivity (%)	CH$_4$	9.6	8.6	7.2	6.6	6.9	8.6
	C$_2$H$_6$	3.1	3.3	3.8	3.3	3.7	3.2
	C$_2$H$_4$	8.6	10.2	11.9	12.2	14.7	15.5
	C$_3$H$_8$	13.5	16.5	15.9	16.5	13.1	12.3
	C$_3$H$_6$	33.2	36.3	35.8	38.3	34.2	31.1
	C$_4$H$_{10}$	1.8	0.7	1.9	0.5	1.8	2.6
	C$_4$H$_8$	2.9	1.9	1.4	1.8	1.9	2.3
	CO$_2$	9.8	8.6	8.2	7.9	8.5	11.8
	C$_5^+$	17.5	16.1	13.9	15.1	15.2	12.6

Fig. 5: Effect of different calcination atmosphere on the catalytic performance.

Fig. 6: CO conversion versus time during the stability test.

5.0 °C min^{-1} (76.4 m^{2}g^{-1}) and 6.0 °C min^{-1} (73.5 m^{2}g^{-1}). As it mentioned before, the calcined catalyst in air at 500 °C for 16 h, with heating rate of 4.0 °C min^{-1} showed a higher selectivity toward light olefins. So, one of the major reasons of the higher activity of catalyst calcined at 4.0 °C min^{-1} may be due to its higher BET surface area.

Effect of operational conditions

One of the other major factors which have a marked effect on the catalytic performance of a catalyst is the operational conditions. For optimizing of the reaction conditions in this study, the effects of operational conditions such as H$_2$/CO feed molar ratios, GHSV, reaction temperatures and reactor total pressures were examined to investigate the catalyst stability and its performance for the FTS.

Effect of H$_2$/CO molar feed ratio

The influence of the H$_2$/CO molar feed ratio on the catalytic performance of the catalyst containing 8wt% (Co,Mn)/TiO$_2$ for the FTS reaction at 280 °C under atmospheric pressure was investigated. The CO conversion and light olefins products selectivity percents are shown in Table 4. The results showed that with variation in H$_2$/CO molar feed ratios from 1/1 to 3/1, the different selectivities with respect to C$_2$-C$_4$ light olefins

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Table 4: Effect of different H₂/CO feed ratio on the catalytic performance of 8wt.%(Co,Mn)/TiO₂ catalyst.

H_2 /Co molar ratio		1/1	2/1	3/2	3/1
CO conversion (%)		19.4	41	33.4	39.6
Product selectivity (%)	CH_4	6.6	6.6	8.6	9.3
	C_2H_6	3.7	3.3	6.1	8.2
	C_2H_4	4.8	12.2	7.2	5.9
	C_3H_8	20.8	16.5	25.1	22.6
	C_3H_6	33.6	38.3	31.3	26.2
	C_4H_{10}	3.1	0.5	0.9	2.1
	C_4H_8	2.1	1.8	1.6	1.1
	CO_2	8.8	7.9	6.1	8.2
	C_5^+	16.5	15.1	13.1	18.7

Table 5: Effect of different GHSV on the catalytic performance of 8wt.%(Co,Mn)/TiO₂ catalyst.

GHSV(h^{-1})		1200	1400	1600	1800	2000	2200
CO conversion (%)		42.2	41.6	41.0	40.0	39.7	37.2
Product selectivity (%)	CH_4	6.9	6.5	6.6	7.0	7.1	8.4
	C_2H_6	2.6	3.0	3.3	3.5	3.6	4.7
	C_2H_4	10.4	10.7	12.2	11.4	11.7	13.5
	C_3H_8	15.3	15.1	16.5	16.4	16.9	17.9
	C_3H_6	30.4	33.7	38.3	35.1	35.1	32.6
	C_4H_{10}	4.6	3.7	0.5	1.4	0.8	1.2
	C_4H_8	3.7	3.6	1.8	2.4	1.4	1.7
	CO_2	8.4	8.4	7.9	8.3	8.8	8.5
	C_5^+	17.7	15.3	15.1	14.5	14.6	11.5

were obtained. However, in the case of the H₂/CO=2/1 (GHSV=1800 h⁻¹), the total selectivity of C_2-C_4 light olefins products was higher and the CH₄ and CO₂ selectivity was lower than the other H₂/CO molar feed ratios under the same reaction temperature and pressure. Therefore, the H₂/CO=2/1 ratio was chosen as the optimum molar feed ratio for conversion of synthesis gas to C_2-C_4 olefins over this catalyst. The actual phases identified in the tested catalyst at the H₂/CO=2/1 molar feed ratio were Co₃O₄ (cubic), CoO (cubic), MnO(cubic), TiO₂ (Tetragonal) and Co₂C(orthorhombic).

Effect of GHSV

To obtain a better understanding of the factors affecting the catalytic performance of 8wt% (Co,Mn)/TiO₂ catalyst, a series of experiments were carried out at different GHSV from 1200 to 2200 h⁻¹ under the optimal reaction conditions (H₂/CO=2/1, P=1 bar at 280 ℃) and the results are presented in the Table 5. Comparing the obtained results leads to the conclusion that in GHSV=1600 h⁻¹ the selectivity with respect to C_2-C_4 hydrocarbons especially light olefins was increased. Therefore, in this study, the GHSV of 1600 h⁻¹ is considered to be the optimum GHSV. At this GHSV, in addition to a high CO conversion and total selectivity of light olefins products, a low CH₄ and also high olefin/paraffin ratio (C_2-C_4) was observed. These results indicate that the GHSV is a parameter of crucial importance on the catalytic performance of iron-nickel catalysts for hydrogenation of CO.

Table 6: Effect of different reaction temperatures on the catalytic performance of 8wt.% (Co,Mn)/TiO₂ catalyst.

Temperature (ºC)		250	260	270	280	290	300	310	320	330	340
CO conversion (%)		28.0	29.0	29.9	33.3	40.7	41.0	42.5	43.7	45.0	46.2
Product selectivity (%)	CH_4	6.3	6.4	6.4	6.6	6.3	6.6	6.9	9.3	8.4	9.7
	C_2H_6	4.8	5.4	5.4	4.2	2.5	3.3	4.6	10.7	11.1	12.0
	C_2H_4	4.4	5.3	5.6	5.9	12.1	12.2	10.1	7.4	7.2	7.4
	C_3H_8	14.5	14.1	13.1	12.2	10.2	16.5	15.7	6.3	7.1	7.1
	C_3H_6	35	36	36.1	40.5	42.2	38.3	36.2	30.8	31.9	29.6
	C_4H_{10}	5.4	4.6	4.4	3.2	2.1	0.5	1.1	3.4	4.2	4.1
	C_4H_8	6.8	5.9	6.2	4.6	3.1	1.8	1.7	3.1	2.3	2.6
	CO_2	7.6	7.6	7.3	7.3	7.1	7.9	8.1	10.3	11.1	15.9
	C_5^+	14.2	15.2	15.1	15.1	12.2	15.1	15.6	18.7	16.7	13.1

Effect of reaction temperature

The effect of reaction temperature on the catalytic performance of the optimal catalyst was studied at a range of temperatures between 250-340 ºC under the same reaction conditions (P=1 bar, H₂/CO=2/1 and GHSV=1600 h⁻¹). The results are presented in the Table 6 and show that with increasing the reaction temperature the CO conversion was increased. In addition, for the reaction temperature at 290 ºC, the total selectivity of light olefin products was higher than the total selectivity of these products obtained at the other reaction temperature. In general, an increase in the reaction temperature leads to an increase in the catalytic activity; furthermore, it has shown that the reaction temperature should not be too low [23]. At low reaction temperatures, the conversion percentage of CO is low and so it causes a low catalytic performance. On the other hand, increasing the reaction temperature leads to the formation of amounts of coke as an unwanted product. Since at 290 ºC, a high CO conversion, total selectivity of light olefins products, low CH₄ and CO₂ selectivity was observed, so this temperature is considered to be the optimum operational temperature. The actual phases identified in the tested catalyst at the 290 ºC were Co₃O₄ (cubic), CoO (cubic), MnO(cubic), Co₂C (orthorhombic) and TiO₂ (Tetragonal).

Effects of total pressure

An increase in total pressure would generally result in condensation of hydrocarbons, which are normally in the gaseous state at atmospheric pressure. Higher pressures and higher carbon monoxide conversions would probably lead to saturation of catalyst pores by liquid reaction products [24]. A different composition of the liquid phase in catalyst pores at high syngas pressures could affect the rate of elementary steps and carbon monoxide and hydrogen concentrations. A series of experiments were carried out to investigate the performance of catalyst containing 8wt% (Co,Mn)/TiO₂ during variation of total pressure in the range of 1-10 bar, at the optimal reaction conditions of H₂/CO=2/1 and 290 ºC (Table 7). The results indicate that at the total pressure of 1 bar, the optimal catalyst showed a total selectivity of 57.4% with respect to C₂-C₄ light olefins. It is also apparent that increasing in total pressure in the ranges of 2-10 bar significantly increases the C₅⁺ selectivity and leads to an increase to 38.3% at the pressure of 10 bar. On the other hand, as it can be seen on Table 7, at the ranges of 1-3 bar total pressures, no significant decreasing on CO conversion was observed, however, the methane and CO₂ products selectivity were decreased and the results indicate that at the total pressure of 3 bar, the optimal catalyst showed the high total selectivity of 56.5% with respect to C₂-C₄ light olefins and also led to 15.2% total of selectivity towards the C₅⁺ products. The results also indicate that the CO conversion and the total selectivity with respect to C₂-C₄ light olefins were decreased as the total pressures are increased from 4 bar to 10 bar. Hence, because of high CO conversion, low CH₄ and CO₂ selectivity and also higher total selectivity with respect to

Table 7: Effect of different total reaction pressures on the catalytic performance of 8wt.% (Co,Mn)/TiO2 catalyst.

Pressure (bar)		1	2	3	4	5	6	7	8	9	10
CO conversion (%)		40.7	40.5	40.5	39.3	39.2	38.7	38.7	36.3	35.2	33.4
Product selectivity (%)	CH_4	6.3	6.2	5.6	5.2	4.8	4.8	4.8	4.5	4.5	4.5
	C_2H_6	2.5	2.9	4.6	7.7	1.9	1.9	2.3	2.6	2.6	2.9
	C_2H_4	12.1	10.4	9.5	4.2	4.3	4.3	4.3	5.1	5.1	5.1
	C_3H_8	10.2	11.6	12.1	12.3	15.2	12.2	11.3	10.1	10.6	11.2
	C_3H_6	42.2	44.8	45.5	39.2	31.2	31.2	30.1	30.3	27.6	27.4
	C_4H_{10}	2.1	1.1	1.4	1.2	3.8	5.2	6.3	6.3	5.1	4.2
	C_4H_8	3.1	1.6	1.5	0.7	3.1	2.8	2.9	3.1	3.4	2.9
	CO_2	7.1	6.7	4.6	5.1	3.7	3.7	3.6	3.6	3.5	3.5
	C_5^+	12.2	14.7	15.2	24.4	33	33.9	34.4	34.4	36.6	38.3

Table 8: Catalytic performance of the 8wt.%((Co,Mn)/TiO2 catalyst during the life time test.

Time (h)		12	24	50	80	120	150
CO conversion (%)		40.5	40.5	39.7	39.5	39.0	38.7
Product selectivity (%)	CH_4	5.6	5.5	5.5	5.7	5.8	5.8
	C_2H_6	4.6	4.9	4.7	4.9	4.9	5.2
	C_2H_4	9.5	9.3	9.1	8.7	9.1	8.7
	C_3H_8	12.1	11.9	12.5	12.3	11.9	11.7
	C_3H_6	45.5	45.7	45.1	44.2	42.5	40.2
	C_4H_{10}	1.4	1.8	1.9	3.1	3.3	4.0
	C_4H_8	1.5	2.0	3.5	3.7	4.1	4.8
	CO_2	4.6	4.6	4.6	5.1	4.3	4.3
	C_5^+	15.2	14.1	13.2	12.4	12.9	13.2
Carbon balance (%)		90.3	90.1	89.8	90.2	90.0	90.3

C_2-C_4 olefins at the total pressure of 3 bar, this pressure was chosen as the optimum pressure.

Optimal catalyst life testing

In order to study the stability of the optimal catalyst containing 8wt% (Co,Mn)/TiO$_2$, it was initially tested for 12 h under 3 bar total pressure (H$_2$/CO=2/1) at 290 ℃ and it found that over 12 h, no loose in activity or selectivity of this catalyst was observed. This time on stream was extended to 150 h to test the long term stability of the catalyst. The obtained results in Table 8 indicate that during the FTS a stable trend for this catalyst

was observed and it does not loose activity considerable during 150 h. The selectivity toward light olefins and C_5^+ and also the activity remained constant around 98% during the FTS reaction (Fig. 6). Since the activity and selectivity remained unchanged, it was assumed that the catalyst did not deactivate (the CO conversion reached the steady state after about 12 h on stream). For comparing the usual tested catalyst for 12 h and the tested catalyst for long term stability of 150 h, both of these catalysts were characterized by XRD and BET methods to study their phases and also measure their specific surface areas. The BET specific surface area of
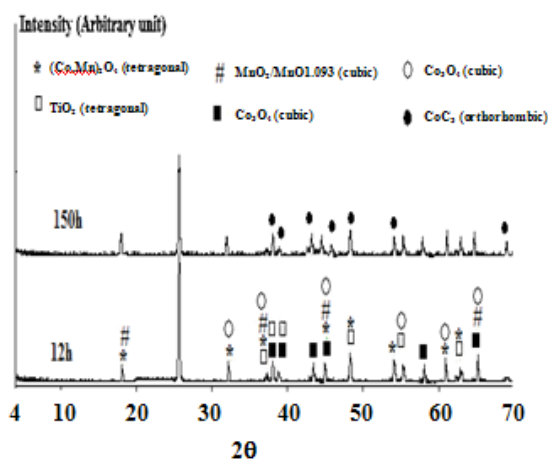
Fig. 6: CO conversion versus time during the stability test.

the optimal catalyst after 150 h was found to be 80.2 $m^2 g^{-1}$, which in comparison with the BET results of the tested catalyst for 12 h (82.4 $m^2 g^{-1}$), no significant change in the specific surface area was observed. The XRD pattern of the tested catalyst after 150 h is similar to the XRD pattern of the usual tested catalyst for 12 h (Fig. 7). However the XRD pattern of the tested catalyst after 150 h presents evidence for the presence of Co_3C (orthorombic), in addition to the other common phases of Co_3O_4 (cubic), CoO (cubic), MnO (cubic), TiO_2 (Tetragonal) and Co_2C (orthorhombic) with the usual tested catalyst for 12 h. As it can be seen, the XRD pattern of calcined catalyst after life time test showed the oxidic and cobalt carbide phases which both of them are active phases in the FTS. In our present study, we found that there is a relationship between the stream on time, FTS activity and the phase composition of the catalyst and with additional stream on time, the formation of cobalt carbides is necessary for high FTS activity.

CONCLUSIONS

x(Co,Mn)/TiO₂ catalysts (x=2–12wt.%) catalysts were prepared by the co-impregnation method and tested for the conversion of synthesis gas to light olefins. It was found that the catalyst containing 8wt% (Co,Mn)/TiO₂ is an optimal catalyst. The results are shown that the calcination conditions have significant influences on the catalytic performance of optimal catalyst. The best calcination conditions were found to be air atmosphere at 500 ºC for 16 h with a heating rate of 4.0 ºC min^{-1}. The catalytic performance of 8wt% (Co,Mn)/TiO₂ catalyst

has been studied under different operational conditions including H₂/CO molar feed ratios, reaction temperatures, different GHSV and reaction pressures. The optimum operational conditions were found to be 290 ºC with molar feed ratio of H₂/CO=2/1 and GHSV=1600 h^{-1} under the total pressure of 3 bar. The results are shown that this catalyst was highly stable and had retained its activity and selectivity for 150 h.

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