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Effect of Operation Conditions on the Catalytic Performance of the Co/Mn/TiO$_2$ Catalyst for Conversion of Synthesis Gas to Light Olefins

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Abstract. *The effect of operation variables, such as the H_2/CO molar feed ratio, gas hourly space velocity (GHSV), temperature, and pressure, on the catalytic performance of the Co/Mn/TiO$_2$ catalyst prepared at the Research Institute of the Petroleum Industry (RIPI) was investigated, and optimum reactor conditions were obtained to produce the maximum amount of light olefins. The catalyst was prepared by co-precipitation of Co and Mn phases in the presence of commercial TiO$_2$ with maximum selectivity for ethylene and propylene production. It was found that the $[H_2]/[CO]=2/1$, space velocity (GHSV) of 1800 h^{-1}, 280° C temperature and 4 bar pressure were optimum operating conditions for the modified catalyst for the conversion of Synthesis Gas(SG) to light olefins. The results were interpreted in terms of the structure of the catalyst. Characterizations of catalysts were carried out using XRD, SEM and BET specific surface area.*

Keywords: *Operation condition; Co-precipitation; Cobalt manganese oxide catalyst; Fischer-Tropsch synthesis; Light olefins.*

INTRODUCTION

An increasing demand for clean fuels and chemicals is expected to lead to an important shift from crude oil to natural gas as feedstock for chemical industries. This will certainly involve the use of Fischer-Tropsch (FT) technology, which is usually defined as a type of surface catalyzed polymerization reaction in which hydrocarbons are produced according to the ASF (Anderson-Schulz-Flory) distribution [1-3], thus limiting the yield of light olefins (C_2-C_4). In recent years, researchers have become interested in making light olefins (C_2-C_4) from Syn-Gas via FT synthesis, rather than the more conventional methods of catalytic cracking of naphtha and dehydrogenation of alkanes [4]. The catalysts of iron and cobalt mixed with Manganese used for conversion of Synthesis Gas to hydrocarbons, have been extensively studied because of their characteristics, such as selective formation of light olefins in the C_2-C_4 range [1,5-11], particularly propylene [10] with a suppressed C_1 product on deviating from the ASF distribution [12]. It was further found that Manganese Oxide in these two types of catalyst acted as a structural promoter that was difficult to reduce, thus leading to an increase in the specific surface area [13]. Mn has been widely used as one of the promoters of unsupported Fe-based FT catalysts, particularly in promoting the production of C_2-C_4 olefins [14]. Numerous studies have been reported on hydrocarbon product distribution from Fischer-Tropsch synthesis on cobalt catalysts, but most of them have not taken into account the reactor operating characteristics, such as H_2/CO ratio, reactor temperature and pressure [15,16]. Furthermore, reports from industrial pilot plants or commercial reactors usually lack information on catalyst composition and operating conditions. Some investigators have reported the effect of operation parameters on product distribution from cobalt-based catalysts [7,17] and showed that the olefin contents of the product spectrum decreased with increasing

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pressure, which was consistent with previous investigations [6,18,19].

In this work, we attempt to extensively report the influence of operating variables, such as H_2/CO molar feed ratio, reaction temperature, pressure, and gas hourly space velocity (GHSV), on the catalytic performance of the recently developed RIPI-Co/Mn/TiO_2 catalyst with optimum selectivity for olefins and propylene in particular. We also characterized the catalyst precursor, as well as the catalysts, using various techniques including powder X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and BET surface area measurement.

EXPERIMENTAL

Catalyst Preparation

The catalysts tested in this study were prepared using a co-precipitation procedure. Aqueous solutions of $Co(NO_3)_2$-$6H_2O$ (1.0 mol/l) and $Mn(NO_3)_2$-$6H_2O$ (1.0 mol/l) were pre-mixed in a round-bottomed flask fitted with a condenser and the resulting solution heated. Aqueous Na_2CO_3 (1.0 mol/l) was added drop wise to the mixed nitrate solution, which was continuously stirred, whilst the temperature was 70°C. The final pH achieved was 8 ± 0.1. This procedure took approximately 10 minutes to complete. The resulting precipitate was then left in this medium for 30 mins. The aged precipitate was first filtered and then washed several times with warm distilled water (100°C) until no further Na^+ was observed in the washings, tested by flame atomic absorption. The precipitate was then dried at 120°C for 16 h to give a material denoted as the catalyst precursor, which was subsequently calcined in static air in the furnace (500°C, 16 h) to give the final catalyst. For preparation of the supported catalyst, TiO_2 (anatase) support has been added to the mixed solution of cobalt and manganese nitrates.

Catalyst Characterization

X-Ray Diffraction (XRD)

Powder X-Ray diffraction (XRD) measurements were performed using a Bruker Axs Company, D8 Advance diffractometer (Germany). Scans were taken with a 2θ step size of 0.02° and a counting time of 1.0 s using a CuK_α radiation source generated at 40 kV and 30 mA. Specimens for XRD were prepared by compacting it into a glass-backed aluminum sample holder. Data was collected over a 2θ range from 4° to 70° and phases were identified by matching experimental patterns to entries in the Diffrac$^{\text{plus}}$ Version 6.0 indexing software.

BET Measurements

The BET surface area were measured using a N_2 adsorption-desorption isotherm at liquid nitrogen temperature (-196°C), using a NOVA 2000 instrument (Quantachrome, USA). Prior to the adsorption-desorption measurements, all the samples (precursors and catalysts) were degassed at 200°C in a N_2 flow for 3 h to remove the moisture and other adsorbents.

Scanning Electron Microscopy

The morphology of catalysts and their precursors were observed by means of a Cam scan MV2300 scanning electron microscopy.

Catalyst Testing

The catalyst tests were carried out in a fixed bed stainless steel micro reactor under various operating conditions (Figure 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 the flow rate of the inlet gases (CO, H_2 and N_2 with purity of 99.99%) automatically. 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 1300°C, and controlled by a digital programmable controller (DPC). The reactor tube was constructed from 1/2″ stainless steel tubing with an internal diameter of 9 mm. The catalyst bed is located at the middle of the reactor. The reaction temperature was controlled by a computer based on the temperature measurement obtained by a thermocouple inserted into the catalyst bed. The meshed catalyst (1.0 g catalyst with particle size of 250-500 μm) was held in the middle of the reactor. The tube length of the reactor is 110 cm. The quartz bed of the catalyst is in the middle of the tube, which was packed with granules of quartz, and the catalyst was held over the reactor bed in the middle of the tube. The reactor tube is equated to three thermocouples that can control the temperature of the mixture before and after the reaction and also the catalyst bed reactor (during the reaction).

The studied system consists of an electronic back pressure regulator that can control the total pressure of the desired process. The catalyst was pre-reduced in situ atmospheric pressure in a flowing H_2 stream (flow rate = 30 ml/min) at 400°C for 16 h before synthesis gas exposure. The Fischer-Tropsch reactions were carried out under different conditions of $T = 220 - 400$°C, $P = 1 - 8$ bar, $H_2/CO = 1/1$-$3/1$ and GHSV=1200-2400 h^{-1}. Reactant and product streams were analyzed in an on-line manner using a gas chromatograph (Varian, Model 3400 Series) equipped with a 10-port sampling valve (Supelco company, USA,

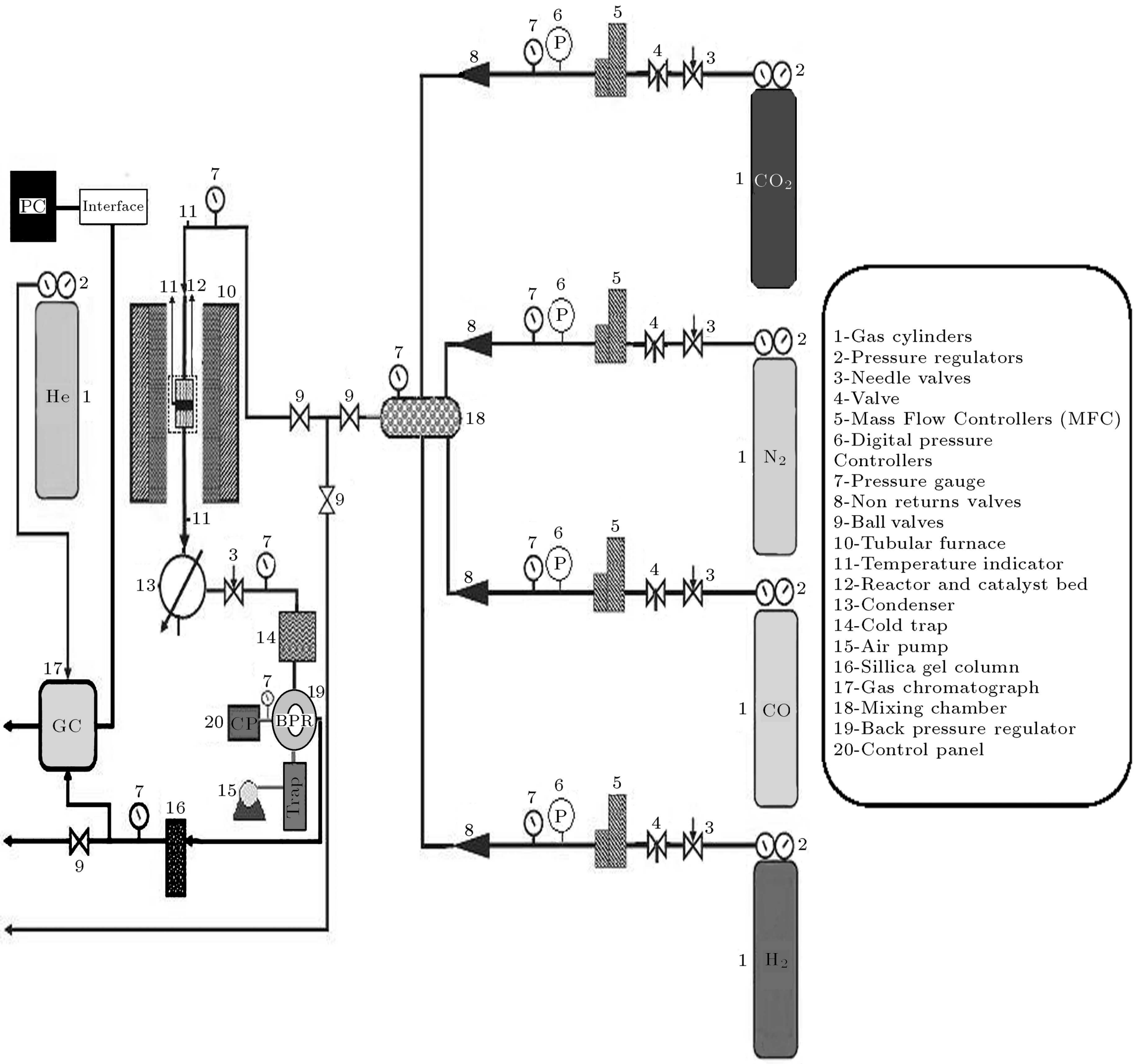


Figure 1. Schematic representation of the experimental set-up.

Visi Model), a sample loop and Thermal Conductivity Detector (TCD). The contents of the 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 ml/min). The calibration was carried out using various calibration mixtures and pure compounds obtained from the American Matheson Gas Company (USA). GC controlling and collection of all chromatograms were done via an IF-2000 single channel data interface (TG Co, Tehran, Iran) in a windows® environment. The calibrations were carried out for mixtures of olefins, C_2-C_4 as well as alkanes and pure preeminent gases (Co, H_2, N_2, O_2, Co_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_{10}) obtained from the American Matheson Gas Company (USA). The molecular weight of C_{5+} was measured using a Petrocoal-DH column and the composition of C_{5+} was obtained using a Carbone balance between input and output gas flow rate. The results, in terms of CO conversion, selectivity, and yield of product, were obtained at each space velocity. The CO conversion (%) was calculated according to the normalization method:

$$m\text{CO conversion}(\%) =$$

$$\frac{(\text{Moles CO}_{\text{in}}) - (\text{Moles CO}_{\text{out}})}{\text{Moles CO}_{\text{in}}} \times 100.$$

The selectivity (%) towards the individual components on a carbon-basis was calculated according to the same principle:

$$\text{Selectivity to product} - j(\%) =$$

$$\frac{\text{Moles of product}j}{(\text{Moles CO}_{\text{in}}) - (\text{Moles CO}_{\text{out}})} \times 100.$$

RESULTS AND DISCUSSION

Effect of Operation Conditions

The effects of a range of operation variables, such as H_2/CO feed gas molar ratios, space velocities (GHSV), reaction temperatures and reactor total pressures, on the catalytic performance of a co-precipitated $Co/Mn/TiO_2$ catalyst prepared on RIPI, have been investigated to identify and optimize the operating conditions and, also, to examine the catalyst stability for the conversion of synthesis gas to C_2-C_4 light olefins on the Fischer-Tropsch synthesis.

Effect of H_2/CO Molar Feed Ratio

The influence of the H_2/CO molar feed ratio on the steady state performance of the cobalt manganese oxide catalyst for the Fischer-Tropsch reaction at 280°C under atmospheric pressure was investigated, and the CO conversion and light olefins product selectivity for different H_2/CO molar feed ratios are presented in Figure 2. The results show that with variation in the H_2/CO feed ratio from 1/1 to 3/1, different values for selectivity with respect to light olefins were obtained. However, in the case of the $H_2/CO=2/1$ (GHSV=1800 h^{-1}), the total selectivity for light olefins was higher, and the CH_4 selectivity was lower than those obtained for other H_2/CO molar feed ratios under the same temperature and pressure. It is also apparent that, for all H_2/CO feed molar ratios, the RIPI catalyst shows a high selectivity toward propylene. Keyser et al. [7] have also indicated that for the Fischer-Tropsch synthesis over the Cobalt Manganese oxide catalyst, with increasing H_2/CO feed molar ratio, the content of C_2 and C_4 olefin is decreased, while the propylene content is increased. Therefore, the $H_2/CO=2/1$ ratio was chosen as the optimum ratio for conversion of synthesis gas to light olefins over cobalt manganese catalysts.

Effect of Space Velocity (GHSV)

To obtain a better understanding of the factors affecting the catalytic performance of the RIPI catalyst, a series of experiments were carried out for GHSV from 450 to 2700 h^{-1} under identical reaction conditions of 1 bar and 280°C, and a H_2/CO ratio of 2. Figure 3 shows the CO conversions and product selectivity's percents as a function of GHSV. It can be noticed from Figure 3 that by increasing the GHSV to 1800 h^{-1}, the selectivity for both C_2 and C_3 olefins increased. The ethylene selectivity increased slightly with further increases in the space velocity. In the case of propylene, however, the maximum selectivity was obtained at GHSV of 1800 h^{-1}. As can be seen from Figure 3, the C_5^+ products selectivity decreased with increasing GHSV. The GHSV of 1800 h^{-1} was considered to be the optimum GHSV due to high CO conversion, high selectivity for light olefins, and low selectivity for CH_4 and CO_2.

Effect of Reaction Temperature

The Co-based catalyst is generally not considered at high temperatures in Fischer-Tropsch synthesis, so an extensive range of temperature was studied in order to make a transition from low temperature Fischer-Tropsch (LTFT) to high temperature Fischer-Tropsch (HTFT).The effect of reaction temperature on the performance of the RIPI catalyst was studied at a temperature range of 220 to 400°C under identical conditions of $H_2/CO=2/1$, space velocity (GHSV) of 1800 h^{-1} and 1 bar pressure. The results, presented in Figure 4, indicated that by increasing the operating temperature, the CO conversion increased. In addition, the maximum total selectivity for light olefins was obtained at 280°C in CO conversion. In general, an increase in the reaction temperature leads to enhanced selectivity for CH_4 and CO_2 , as well as the formation of large amounts of coke as an unwanted by product [20].

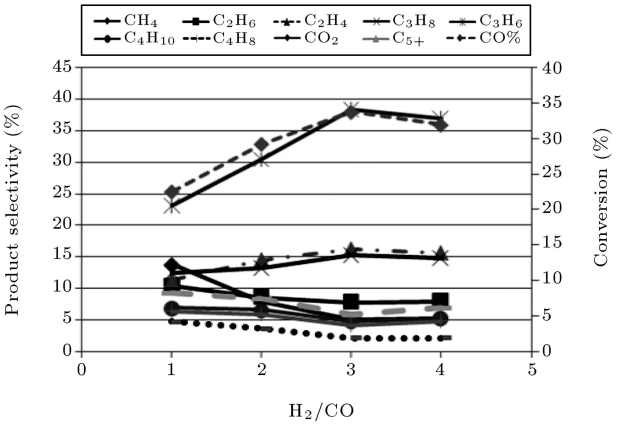


Figure 2. Effect of H_2/CO feed ratio on the performance of the RIPI catalyst, $T = 280°C$, $P = 1$ atm, GHSV=1800 h^{-1}.

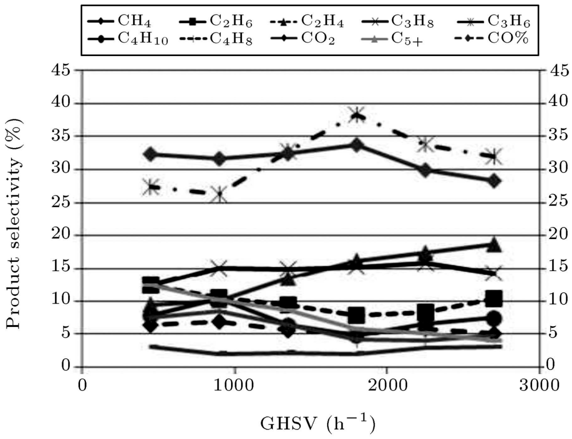


Figure 3. Effect of GHSV on the performance of the RIPI catalyst, $T = 280°C$, $P = 1$ atm , H_2/CO =2/1.

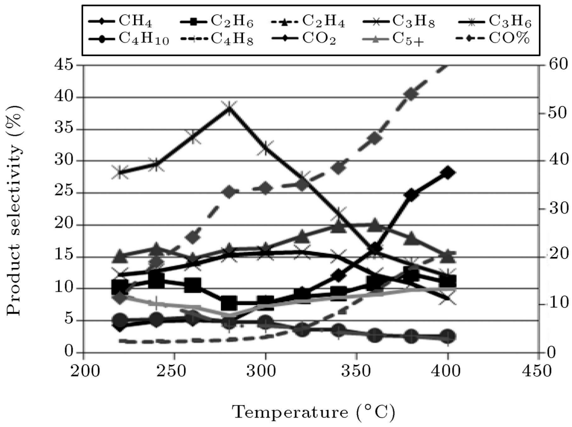


Figure 4. Effect of reaction temperature on the performance of the RIPI catalyst, $P = 1$ atm, GHSV = 1800 h^{-1}, $H_2/CO=2/1$.

Therefore, in this study, 280°C was considered to be the optimum operating temperature due to the high total selectivity for light olefins, low CH_4 production and lack of coke formation.

The actual phases identified in the XRD pattern of the catalyst at 280°C were Co_3O_4 (cubic), CoO (cubic), $(Co,Mn)(Co,Mn)_2O_4$ (tetragonal), MnO_2 (tetragonal and orthorhombic), $CoMnO_3$ (cubic), MnO (cubic), Co_2C (orthorhombic) and Co_3C (orthorhombic), as shown in Figure 5. The tested catalyst has oxidic and Cobalt carbide phases both of which are active phases in the catalyst. Oxidic phases are highly selective for the conversion of synthesis gas to olefins, and carbide phases are active in the hydrogenation of CO [21,22].

The SEM observations have shown differences in the morphology of precursor and optimum calcinated catalysts (before and after the Fischer-Tropsch reaction). The electron micrograph obtained from the catalyst precursor depicts several larger agglomerations of particles (Figure 6a) and shows that this material has a less dense and heterogeneous morphology. After calcination at 500°C, the morphological features are different from the precursor sample, and this shows that the agglomerate size is greatly reduced, compared with the precursor (Figure 6b). It may be due to this reason that the calcinated catalyst surface is covered with small crystallites of cobalt and manganese oxide, which seems to be in agreement with XRD results. However, the size of these grains grew larger by agglomeration in the spent catalyst of the Fischer-Tropsch synthesis at 280°C (Figure 6c), which may be due to the sintering during reactions. In order to distinguish the influence of reaction temperature on the specific surface area of the RIPI catalyst, all the tested catalysts at different temperatures were characterized by BET specific surface area measurements whose results are shown in Figure 7 (with 5% accuracy). The calcinated catalyst before the test showed a higher specific surface area (136.8 m^2g^{-1}) than those of the catalysts after the test at different temperatures. This means that the specific surface area slightly decreases with increasing reaction temperature for the tested catalysts, which could be due to an increase in sintering that leads to the particles agglomeration. This shows that the reaction temperature should not be too high. At high reaction temperatures, a lot of coke may be formed, and also the specific surface area of the catalyst will be reduced. The results obtained from BET measurements are in agreement with the SEM study, which showed that the size of grains grew larger

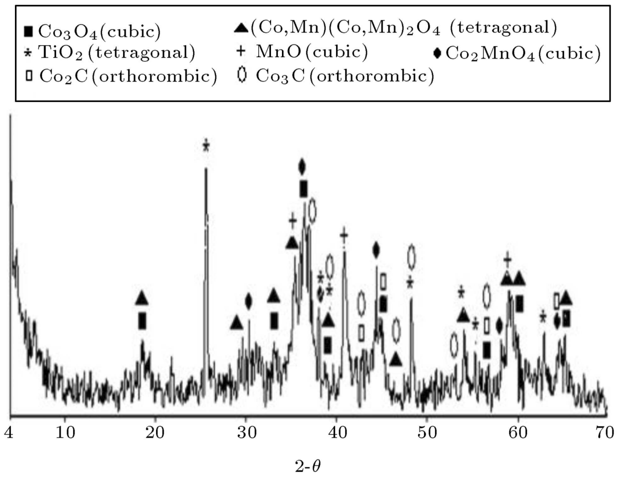
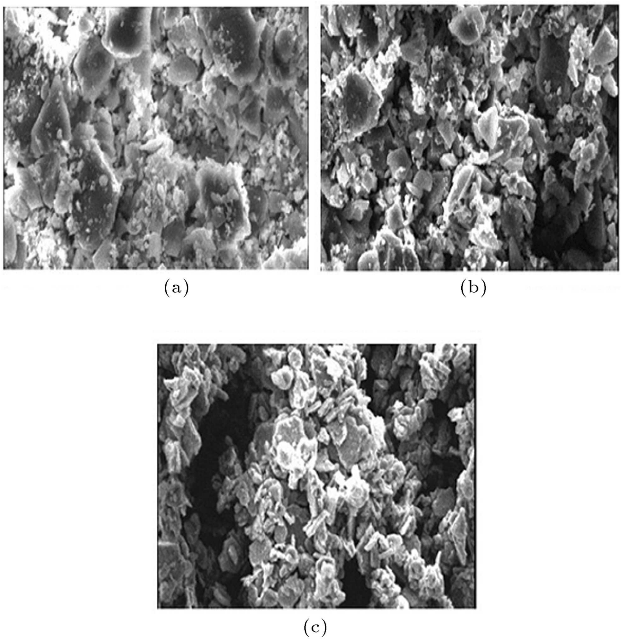


Figure 5. XRD patterns of RIPI catalyst after reaction at 280°C.


(a) (b)

(c)

Figure 6. The SEM images of calcinated RIPI catalyst. (a) Precursor. (b) Calcinated catalyst before reaction. (c) Calcinated catalyst after reaction.

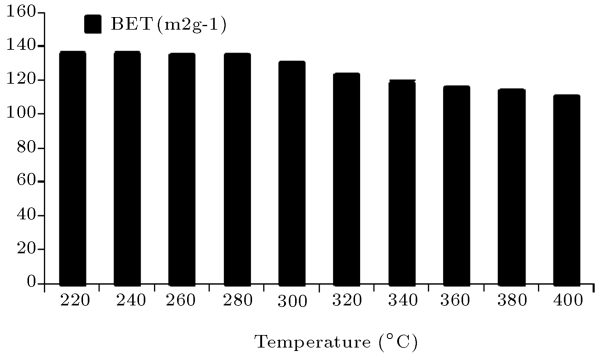


Figure 7. BET results for RIPI catalysts after reaction at various temperatures.

by agglomeration in the spent catalyst, leading to a decrease in the BET specific surface area.

Effect of Total Pressure

Pressure is an important parameter for the Fischer-Tropsch synthesis, which is supposed to be operated under high pressure. An increase in total pressure would generally result in the condensation of hydrocarbons, which are normally at the gaseous state at atmospheric pressure. Higher pressures and higher carbon monoxide conversions would probably lead to the saturation of catalyst pores by liquid reaction products [23]. A different composition of the liquid phase in catalyst pores at high Syn-Gas partial 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 the RIPI catalyst at various total pressures in the range of 1-8 bar, under optimum reaction conditions of H_2/CO=2/1, GHSV of 1800 h^{-1}, and temperature of 280°C. The effect of pressure on reaction performance is presented in Figure 8. The results indicated that at the total pressure of 1 bar, the RIPI catalyst showed a total selectivity of 58.7% for C_2-C_4 olefin and 5.8% for C_5^+. It is also seen from Figure 8 that increasing total pressure in the ranges of 4 to 8 bars would significantly increase the selectivity for C_5^+ up to 23% at the pressure of 8 bars. On the other hand, as can be noticed from Figure 8, for pressures in the range of 1 to 4 bars, no significant decrease in CO conversion was observed, while the selectivity for light olefins was increased, indicating that the total pressure of 4 bar lead to the optimum performance of the catalyst at which the highest selectivity of 58.9% for C_2-C_4 light olefins was obtained. It should be noted that the selectivity of C_5^+ under this condition was about 7.2%. The results also indicated that CO conversion and total selectivity for C_2-C_4 olefins decreased as the total pressure was increased from 5 to 8 bar. Hence, due to high CO conversion, low CH_4 selectivity and selectivity for high C_2-C_4 olefins, 4 bar pressure seems to be the optimum operating pressure.

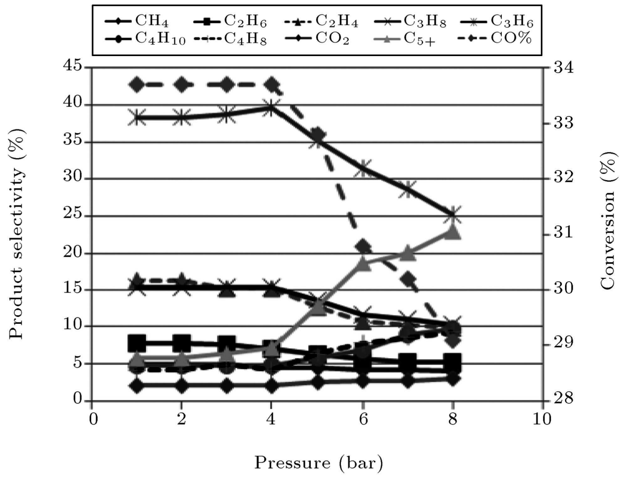


Figure 8. Effect of total pressure on the performance of the RIPI catalyst, $T = 280°C$, GHSV = 1800 h^{-1}, $H_2/CO = 2/1$.

Optimum Catalyst Life Testing

In order to study the stability of the RIPI catalyst, it was initially tested for 24h under 4 bar Syn-Gas pressure (H_2/CO=2/1) at 280°C for which it was found that over a period of 24h, no loss in activity or light olefins selectivity was observed. In order to test the long term stability of the catalyst, the time interval was extended to 150h. The obtained results shown in Figure 9 indicate that during the Fischer-Tropsch synthesis, a stable trend for the catalyst was observed in a 150 h time interval. The activity of the catalyst remained constant during the Fischer-Tropsch synthesis reaction. Since the activity remained unchanged, it was concluded that the structure of the catalyst was stable. For comparing the structure of the catalyst tested for 8h and the catalyst tested for long term stability of 150h, both of these catalysts were characterized by XRD, SEM and BET methods to study their phases and morphological features and also to measure their specific surface areas. The BET specific surface area of the RIPI catalyst after 150h was found to be 133.5 m^2g^{-1} and that of the tested

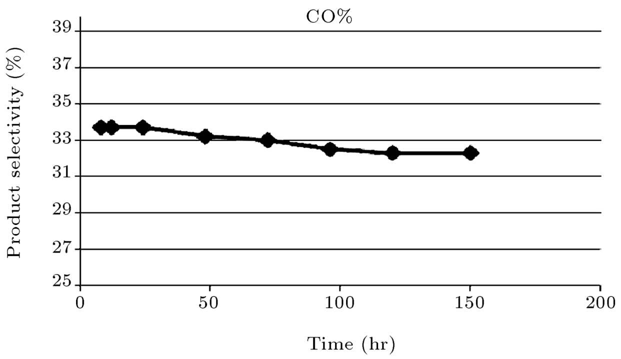


Figure 9. Effect of Time-On-Stream (TOS) on catalyst conversion.

catalyst for 8h was found to be 135.2 m^2g^{-1}. These results indented that no significant changes occurred in the specific surface area of the catalyst. Figure 10 shows that the XRD pattern of the catalyst having undergone a 150 hr test is almost similar to the XRD pattern of the catalyst having undergone an 8 hr test. The only difference between the structures of these two catalysts after undergoing their corresponding test periods is the presence of Co_3C (hexagonal), in addition to the other common phases of Co_3O_4 (cubic), $(Co,Mn)(Co,Mn)_2O_4$ (tetragonal), CoO (cubic), MnO (cubic), TiO_2 (tetragonal), Co_2C (orthorhombic) and Co_3C (orthorhombic) for the catalyst tested for 8hr. As can be seen, the XRD patterns of the calcinated catalyst after life time tests showed that the Cobalt oxide phase is an active phase in the Fischer-Tropsch synthesis. The characteristic morphological features of both calcinated catalysts having undergone short term and long term stability tests are presented in Figure 11. There was no significant change in morphology between the two samples; 8h (Figure 11a) and 150 h (Figure 11b), however, as can be seen, for the tested catalyst after 150 h, there is a slight increase in agglomerate size. It, therefore, appears that longer test time enhances agglomerate size growth during reaction conditions, which may be due to the possibility of the bulk Cobalt carbides presence in Co_3C (hexagonal), Co_2C (orthorhombic) and Co_3C (orthorhombic) forms, as detected by the XRD pattern. The existing catalyst phase strongly depends on the structure of the catalyst and the activation procedure employed. The presence of Mn enhances the carbon monoxide conversion rate and hydrocarbon selectivity, simultaneously [24-27]. Zhang et al. [28] found that the presence of Mn improved dispersion of Cobalt active phases and facilitates the formation of bridged type adsorbed CO. The presence of Manganese generally led to the formation of larger cobalt agglomerates (∼8-15 nm). Then, catalysts with larger Co particles (∼> 5 nm) and lower Co reduction displayed a higher intrinsic hydrogenation activity and a longer catalyst lifetime [29]. A significant effect of Mn was observed on Titania-supported catalysts prepared by Morales and Weckhuysen [26]. STEM-EELS showed [30] that the oxidized catalysts contained Co_3O_4 and MnO_2 monometallic particles, while in the deposition-precipitation sample, Mn cations were incorporated into the Co_3O_4 structure, resulting in the $Mn_xCo_3-xO_4$ mixed oxide phase. These mixed phases, however, could be reduced, which would give rise to a cobalt metal phase and migration of MnO particles toward the TiO_2. The presence of MnO resulted in lower cobalt reducibility [25].

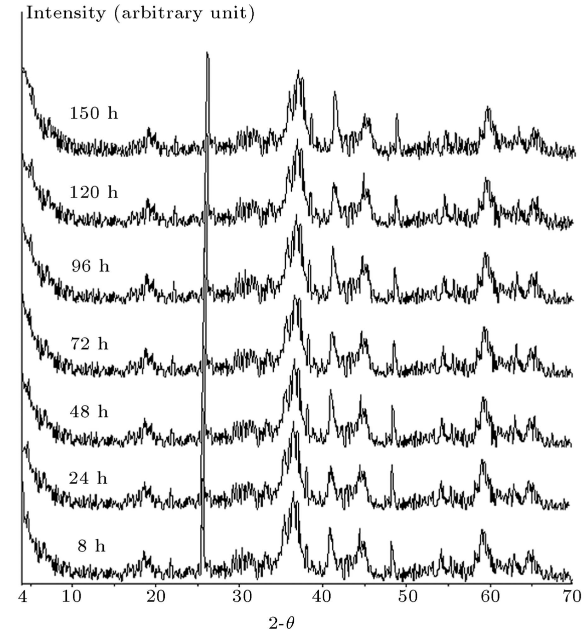


Figure 10. XRD patterns of RIPI catalyst after reaction for 8 h and 150 h time intervals.

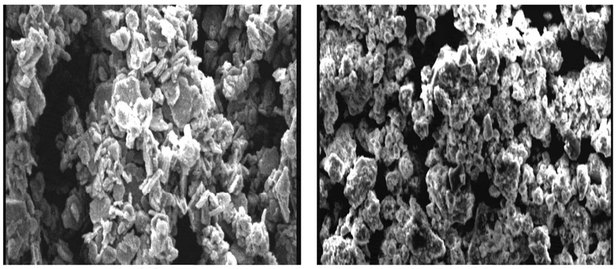

(a) (b)

Figure 11. The SEM images of RIPI catalyst. (a) Tested for 8 h. (b) Tested for 150 h.

CONCLUSION

A titania supported cobalt manganese oxide catalyst, RIPI catalyst, which has been prepared using a co-precipitation procedure, was tested under different reaction conditions, and it was found that operating conditions have a great effect on the structure and catalytic performance of the catalyst. The effect of various factors, such as reaction temperature, reaction pressure, H_2/CO molar feed ratio and space velocity (GHSV), were examined on the catalytic performance of the RIPI catalyst. The optimum operating conditions for the production of highest selectivity toward light olefins were found to be at the temperature of 280°C with molar feed ratio of $H_2/CO=2/1$ under the total pressure of 4 bar and at the GHSV of 1800 h^{-1}. The characterization of precursor and calcinated catalysts (before and after the test) was performed by powder XRD, SEM and BET surface area measurement. These results also showed that the catalyst is sensitive to operating conditions. The suggested optimum operating parameters should be incorporated in order to achieve the highest selectivity toward light olefins from the TiO_2 supported cobalt manganese oxide catalyst, prepared using a coprecipitation procedure.

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