Comparison of Cobalt based catalysts supported on MWCNT and SBA-15 supporters for Fischer-Tropsch Synthesis by using autoclave type reactor

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Abstract. 10 and 40 wt% Co/Multiwall Carbon Nanotubes (MWCNT) and 10 and 40 wt% Co/Santa Barbara Amorphous-15 (SBA-15) catalysts were prepared via incipient wetness impregnation method. It was characterized by Scanning Electron Microscopy, BET, X-ray Diffractometry (XRD), Transmission Electron Microscopy (TEM), Temperature-Programmed Reduction and H_2 Desorption. A 200 ml hastelloy autoclave reactor was implemented to see the performance of the catalysts. It was observed that the performance of 40 wt% Co/SBA-15 was higher that other catalysts in terms of production of longer chain paraffins.

Introduction

Fischer-Tropsch Synthesis (FTS) is the heart of Gas to Liquid (GTL) technologies. The FTS process is carried out in the presence of heterogeneous cobalt or iron catalysts. The advantages of the Co catalysts are the milder reaction conditions and higher activity when the feedstock was natural gas [1, 2]. The catalysts consist of metal promoted cobalt and iron supported on high-surface-area binders or supports such as silica, alumina, or zeolites. Commonly, FTS reactions are carried out in multi-tubular fixed bed and fluidized bed reactors operated at about 30 bars and at temperature 200 – 350 °C [3, 4]. Depending on process conditions and the type of the catalyst, the high quality fuels and valuable chemicals are produced [5].

The first cobalt catalyst used at Mülheim was a 100 Co/18 ThO2/100 Kieselguhr catalyst [6-7]. Cobalt based catalysts are only used in Low Temperature Fischer-Tropsch (LTFT) process, since at high temperature the yield of CH_4 increased, which is unwanted commercially. Because of the high price of Co, it is desirable to minimize the amount used but to maximise the available surface area of the metal. To achieve this, different carriers (supports) such as alumina (0.5 – 600 m^2g^{-1}), silica (300 – 400 $m^2g^{-1)}$) and titania (25 – 100 m^2g^{-1}) are used [8]. A drawback for these supports is their reactivity towards Co metal which could lead to formation of mixed oxides (aluminate or silicate) [2]. The reduction of these mixed compounds is only reducible at high reduction temperatures [9, 10]. Insufficient reduction of Co species on the support surface causes decrease the number of active cites, and this degrades the catalytic properties of the catalyst [11].

Use of carbon nanotubes as a support material for heterogeneous catalysis has been explored by several researchers [12, 13]. Studies comparing the catalytic activity of metal catalysts supported on various oxides, amorphous carbon and CNTs showed that catalytic performance was generally excellent on CNTs. The use of mesoporous silica such as SBA-15 (8 g of pluronic 123, 240 ml of HCL, 18.2 ml of TEOS, 60 ml of deionized water) as support for preparing Co-based catalysts has been recently explored [14]. SBA-15 possesses a high surface area (600 – 1000 m^2/g) and is formed by a hexagonal array of uniform tubular channels with pore diameters ranging from 5 to 30 nm.

Also SBA-15 possesses thicker pore walls. In their work D. Zhao et al [15] identified that thicker walls lead to the greater hydrothermal stability. After calcination in 500 °C images of SEM showed a similar particle morphology which reflects the thermal stability of the macroscopic structure [15]. Also in analysis conducted on SBA-15 which is calcined in 500 °C, the same number of peaks before and after calcination was observed in XRD, confirming that hexagonal SBA-15 is thermally stable. At the same time high surface area gives high metal dispersions at high cobalt loadings which were observed by the group of researchers in the head of Y. Wang [16]. In their work they found that hexagonal mesoscopic organization of the SBA-15 with pore diameter 5.5 nm is almost retained even after edition of 20 mass% Co.

Experimental method

Multiwall Carbon Nanotubes were commercially obtained and characterized. Another support material which is SBA-15 was synthesised using Pluronic P123 ($EO_{20}PO_{70}EO_{20}$ Aldrich) which is dissolved in hydrochloric acid. Tetraethyl orthosilicate (TEOS) was added and the mixture was stirred for 24 hours in 35 – 38 °C. After 24 hours the temperature was raised to 80 °C and stirred for 48 hours until white precipitate mixture was formed. The precipitate was further dried overnight and calcined at 550 °C for 4 hours [15]. Cobalt catalysts supported on raw MWCNT and SBA-15 were prepared via incipient wetness impregnation method [17] with different cobalt loadings (labeled as 10%Co/MWCNTx and 40 % Co/MWCNTx, 10 % Co/SBA-15 and 40 % Co/SBA-15). $Co(NO_3)_2*6H_2O$ was used as a cobalt precursor. After impregnation procedure, CNT based cobalt catalyst precursors were dried at 120 °C for 6 hours and calcined at 350 °C for 3 hours. Also, SBA-15 based cobalt catalyst precursors were dried at 120 °C for 12 hours and calcined at 400 °C for 5 hours. Overall scheme of the preparation is shown in Fig. 1.
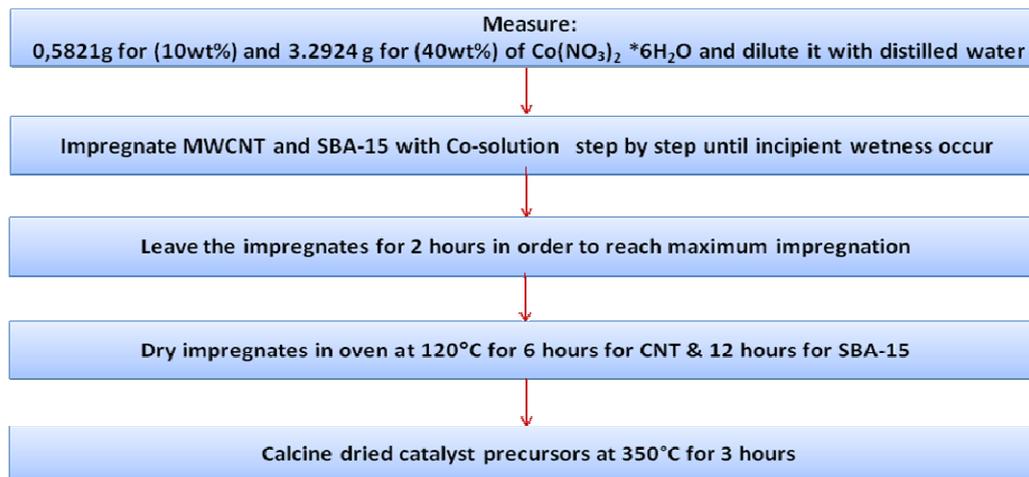

Fig. 1, Flowchart of catalyst preparation diagram

Characterization of catalyst precursors were performed in several techniques such as SEM, XRD, TPDR/O and TEM. Samples running at SEM were done at different magnifications. The magnifications were 20,000 and 100,000. X-ray diffraction measurements were carried out to identify surface elements of calcined cobalt precursor. In TPR, each catalyst samples were first purged in a flow of argon at 400 °C for 1 hour, to remove absorbed water, and then cooled to 40 °C. In each case 0.025 g catalyst was loaded in the quartz tube reactor and TPR performed using 5 % hydrogen in nitrogen gas (Mox) mixture with a flow rate of 40 ml min^{-1}.

Result and Discussions

Fig. 1 collects representative SEM images of two catalyst precursors which are 10 % CoMWCNTx (a) and 10 % Co/SBA-15 (b). Micrograph of calcined catalyst prepared with cobalt nitrate in Fig. 1a shows objects on top of MWCNT which may refer to loaded cobalt species. In micrograph of 10 % Co/SBA-15 (fig 1b) obviously can be seen the microstructure of SBA-15 which represents unique "necklace" type structure.
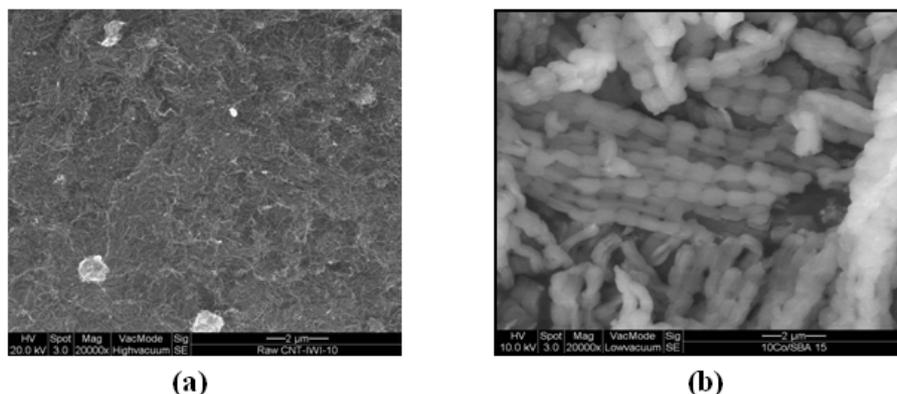

(a)   (b)

Fig. 1, SEM images of 10 % CoMWCNTx (a) and 10 % Co/SBA-15 (b) catalyst precursor

After calcination of both MWCNT and SBA-15 based catalysts XRD analysis was carried out in order to identify the surface species of the catalyst precursor. XRD results of 10Co/MWCNT showed that peaks from the XRD pattern match the ICDD Card #65-3103 for Co_3O_4.
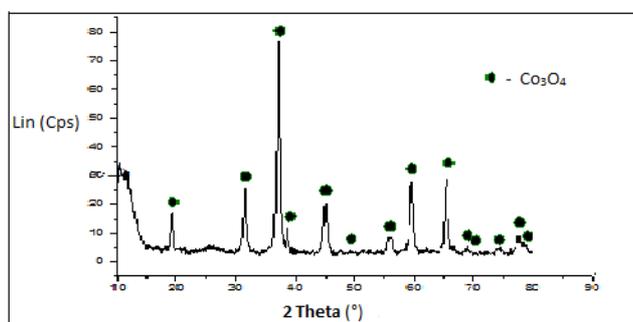

Fig. 2, XRD results of 10Co/MWCNT

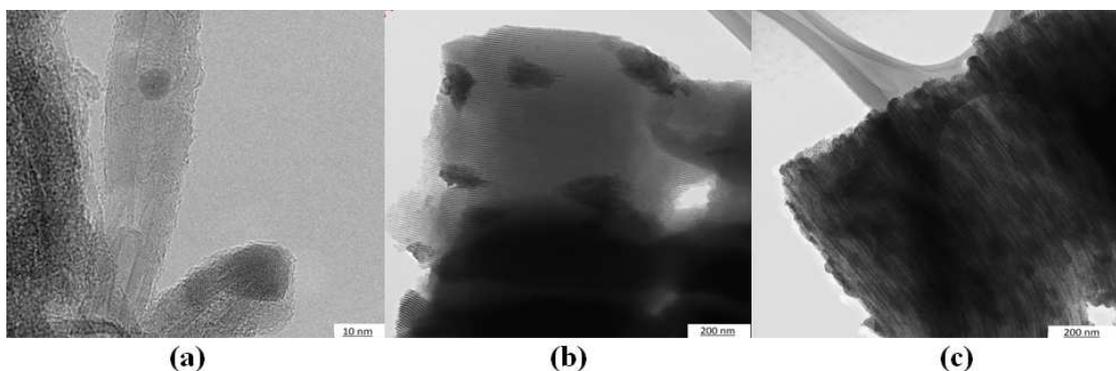(a)   (b)   (c)

Fig. 3, TEM images of a) 10Co/MWCNTx, b) 10Co/SBA-15 and c) 40CoSBA-15.

From TEM images can be seen that Co particles are present on the surface of catalyst supports.

Catalyst evaluation in autoclave reactor: Catalyst evaluation was carried out in 200 ml stirred tank hastelloy Autoclave reactor under 220 °C, 20 bar. In each reaction the ratio of the catalyst towards the solvent was 1 gm 50 ml^{-1} and the ratio of hydrogen to carbon monoxide was 2 to 1 [1, 18, 19]. Flow rate of the supplied gas was 1800 ml h^{-1} and was measured by a rotameter and bubble meter which was set at the outlet system of the reactor setup. The reactor was modified in order to make it suitable for Fischer-Tropsch reaction. The general schematic model of the modified reactor is shown in Fig. 4.
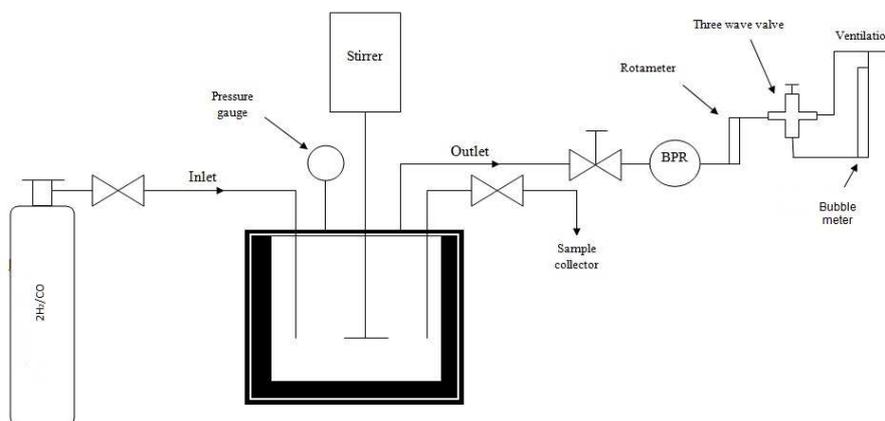

Fig. 4, Schematic model of the reactor

Before reaction, catalysts were reduced to active Co^0 metal form [2] by 5 % H$_2$/Argon in self designed fixed bed system in 400 °C, 2.5 bars for 10 hours (Fig. 5). Flow rate of 5 % hydrogen in argon was 1800 ml h^{-1} and regulated by back pressure regulator and rotameter.
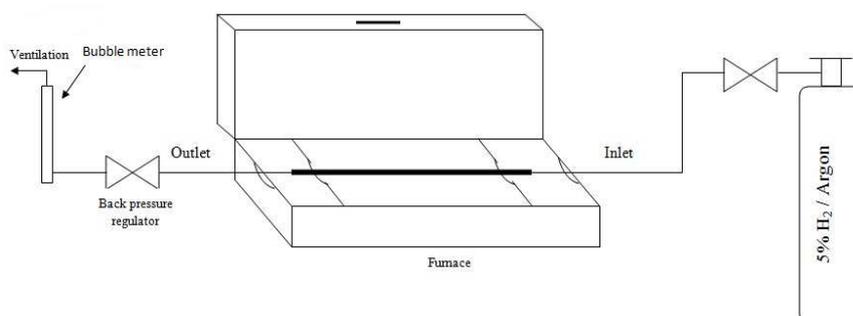

Fig. 5, Catalyst reduction system

After reduction procedure, catalysts were transferred to autoclave vessel and suspended there with hexadecane [18, 20]. Among all 4 catalysts, performance of 40Co/SBA-15 catalyst was significantly better towards production of longer chain hydrocarbon wax which was collected after reaction from the surface of the catalyst. Liquid products of the reaction were analysed in GCMS Agilent 7890/5975N GCMSD. Both 10 % Co/MWCNT and 10 % Co/SBA-15 did not generate significant product. Obtained products from 40Co/MWCNT and form 40Co/SBA-15 catalysts are shown in Figs. 6 and 7 respectively.
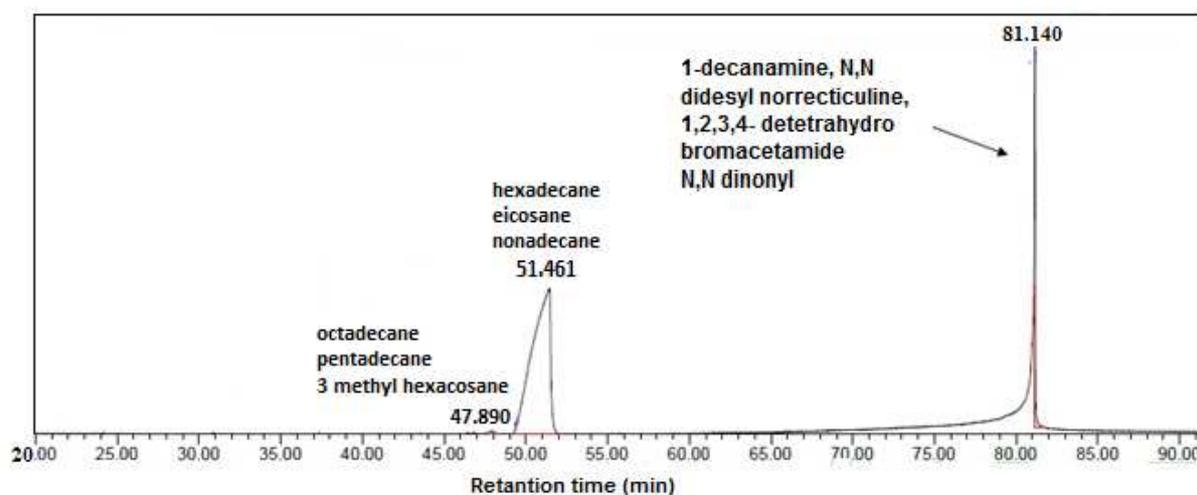
Fig. 6, GCMS results for 40Co/MWCNT catalyst

From Fig. 6 can be seen that generated products were not so broad. Only octadecane ($C_{18}H_{38}$), nonadecane ($C_{19}H_{40}$), eicosane ($C_{20}H_{42}$) and hexacosane ($C_{26}H_{54}$) was produced. Among them hexacosane is the longest chain hydrocarbon which usually appears in the form of white solid.
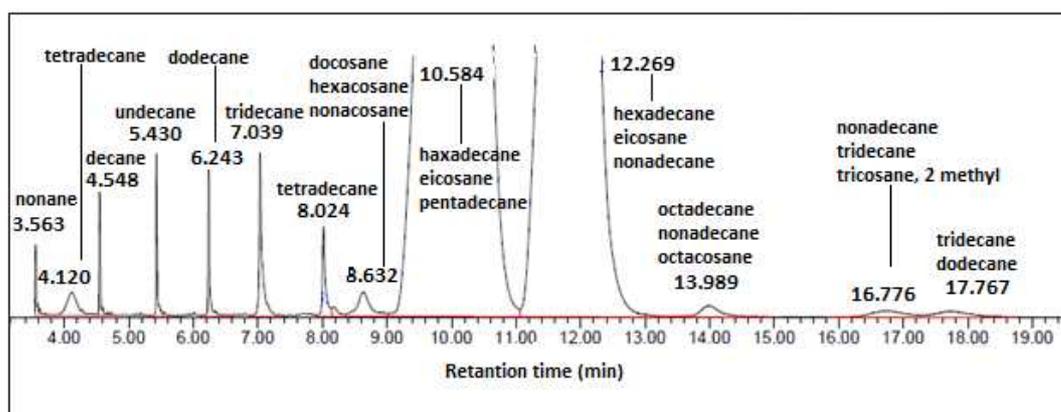

Fig. 7, GCMS results for 40Co/SBA-15 catalyst

Fig. 7 represents performance of 40Co/SBA-15 catalyst. After reaction, it was observed that C_{5+} chain growth in this catalyst was much high comparing to other catalysts. Hydrocarbon in the solid form (white solid) was collected from the top of catalyst. Liquid hydrocarbon product was collected, separated and analyzed in aforementioned GSMS system. From GSMS data it was found that straight chain hydrocarbon (paraffin) starting from nonane (C_9H_{18}) was produced.

Conclusion

2 types of Co catalysts for Fischer-Tropsch synthesis, supported on MWCNT and SBA-15 were synthesized and tested in 200 ml autoclave reactor. Based on the data generated from all involved equipments in the process, the conclusions are summarized as follows:
1. GCMS analysis showed that the performance of 40 % Co/SBA-15 catalyst was significantly higher than performance of 40 % Co/MWCNT based cobalt catalyst. 10 % Co/MWCNT and 10 % Co/SBA-15 catalysts did not perform well.
2. Based on GCMS analysis 10 % Co/MWCNT and 10 % Co/SBA-15 did not work in autoclave slurry system.
3. Distribution of cobalt metal throughout the support material was better on SBA-15 carrier rather than on MWCNT which can be seen from TEM images of the catalyst precursors.

4. Incipient wetness impregnation method which was applied for the catalyst preparation was successful from analysis by XRD and SEM results.
5. Fischer-Tropsch synthesis on SBA-15 based catalyst was successfully applied in slurry phase reactor.
6. Based on the performance of SBA-15 can be concluded that this material is perspective in the field of catalysis as a promising catalyst support.

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