Optimum High-Quality Ceramic Support like SiC, Al₂O₃ & TiO₂ for Cobalt as a Very Active Metal for Fisher-Tropsch-Synthesis in a Fixed Bed Reactor Configuration

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Abstract: A series of experiments were performed on indigenously synthesized catalyst pellets of cobalt as a very active metal on ceramic support like SiC, Al₂O₃ & TiO₂ in a fixed bed reactor configuration with an aim to study the catalyst activity & selectivity, chemical kinetics, design flexibility, temperature, pressure by characteristics diffusion distance. Catalyst pellets were prepared and then characterized by N₂ adsorption, X-ray Diffraction, Scanning Electron Microscope, and Temperature Programmed Reduction. The results showed the Brunauer, Emmett and Teller area of SiC was the lowest among the three supports prepared for testing. However, its reducibility showed improvement with use of cobalt acetate, as a precursor, rather than cobalt nitrates. Mechanical strength and behavior was checked by the hardness testing machine. Fischer Tropsch (FT) synthesis experiments were performed in the fixed bed reactor set at 450-500 K and 2.3-2.5 MPa using synthetic gas having H₂/CO ratio = 2.0. FT synthesis showed that cobalt/silicon carbide catalyst gives high CO conversion and lower methane selectivity, compared to Co/Al₂O₃ and Co/TiO₂, as well as high C₅⁺ selectivity of almost 90%. Moreover, its stability was enhanced by the addition of ZrO₂, as without this addition, the Co/SiC interactions are weaker and can cause carbon sintering, and thus, the deactivation rate to increase.

Key words: Fischer-Tropsch-synthesis, clean coal, alternate liquid fuel, metallic catalysts & syngas.

1. Introduction

Fischer-Tropsch synthesis is for conversion of synthesis gas, a mixture of carbon monoxide and hydrogen into wide range of long chain hydrocarbons and oxygenates. In general, it provides a practical way for the chemical liquefaction of solid or gaseous carbon resources. The liquefaction of these carbon sources via the Fischer-Tropsch synthesis provides an alternative route for production of transportation fuels and petrochemical feedstock. The interest in

Fischer-Tropsch technology is increasing based on four criteria: world reserves of carbon containing resources; geographic resources; feedstock; and reduction of CO₂ emissions. The reserves of coal and natural gas are much larger than the reserves of crude oil around world. At the end of 1999, the reserves of crude oil were 140×10^9 t. The proven reserves of natural gas were $146 \times 1,012$ m³ which is equivalent to 132×10^9 t of oil and the reserves of coal were 984×10^9 t which is 656×10^9 t of equivalent oil [1]. The Fischer-Tropsch synthesis is becoming an important process to meet the future energy demand due to its wide range of advantages: abundant coal reserves available as feedstock; produces ultralow, high cetane diesel; less cost than direct coal liquefaction; deep

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geological sequestration offers solutions for CO₂ emissions; gas to liquid offers reduced CO₂ generation; Biomass to liquid offers zero carbon footprints; The synthetic fuel is much cleaner and produces less pollution during combustion.

The ideal gasoline, one having a high octane rating as well as being environmentally acceptable, would consist of highly branched alkanes. The RON (road octane number) of iso-octane (2, 2, 4-methyl pentane) is 100. On the other hand, the ideal diesel fuel, one having a high cetane number, would consist of essentially linear alkanes. The cetane number of n-hexadecane is 100. In practice, however, virtually all engine fuels are produced from crude oil which can contain large amounts of aromatics as well as unacceptable levels of organic sulfur and nitrogen compounds. Although environmentally undesirable, aromatics increase the octane rating of the gasoline, however, they decrease the cetane number of the diesel fraction and this cut therefore requires severe hydro treatment to convert the aromatics to naphthenes and to lower the S and N contents. Despite this, the cetane number of the final product is still much lower than that of linear alkanes. An approximate estimate of the recoverable crude oil reserves is about $2,000 \times 10^9$ bbl. (barrels) which at the current consumption rate could last for another 40-50 years. In addition, the tar sands reserves are estimated at about 2 trillion barrel and the shale oil reserves at about $2,500 \times 10^9$ bbl. oil equivalent [2]. Nowadays, GTL (gas to liquid) is given importance in Fischer-Tropsch synthesis process. Natural gas along with coal is a promising feedstock if available in enough quantity to produce synthetic fuel which has characteristics similar to conventional fuels but are very efficient, cleaner and environmental friendly. The process has become competitive to petroleum due to its increased demand and improved quality. The basic chemistry involved in this process is given below:

Hydrocarbons + Oxygenated compounds + H₂O

The product obtained by this method is usually olefinic in nature, i.e., about 70%-80% while the remaining is paraffins. Oxygenated products are also formed in very small fraction which is mostly neglected whereas rings like compounds or aromatics are formed if temperature goes above 300 °C. These aromatics are good for use by thermally decomposing them to produce fuel with good anti-knocking properties. Since mostly 70%-80% product is olefinic, so the chemistry involved is:

Presently among all the fossil fuels, natural gas and petroleum are the only fossil fuels that are being used to fulfill the need of transportation fuel but due to exhaustion of this is being done from long time ago and this fuel is depleting with the passage of every new day, so there is a need of alternate methods by which synthetic fuel can be prepared which will fulfill the future need and overcome the crisis. Apart from the need, this fuel is virtually sulfur free and clean from contaminants and has less environmental impact than the traditional fossil fuel. Due to its high activity and long life, cobalt-based Fischer-Tropsch catalyst is currently the catalyst of choice for conversion of syngas to liquid fuels. The exothermic nature of the Fischer-Tropsch reaction combined with the high activity of cobalt catalyst makes the removal of heat from the reactor of critical importance. In the case of a tubular fixed bed reactor, this becomes even more problematic due to the inherent temperature profiles inside the tube. This problem can be controlled by finding the balance between the tube diameter and the usage of a “quench” medium such as the recycle of inert. Due to the good mixing and heat transfer characteristics of a slurry phase reactor, the temperature control in such a reactor is much less of a problem than in a tubular fixed bed reactor. Care must, however, be taken in the design of such a reactor that, during normal operating conditions and also during the shutdown of the reactor, no stagnant zones with

poor mixing occur which may result in localized hot spots. If the catalyst is exposed to very high temperature, carbon will be formed, which may damage the structural integrity of the catalyst. Another critical design aspect of a slurry phase reactor is the separation of the catalyst from the wax. Sasol was successful in the development of a very efficient catalyst/wax separation system. By matching the characteristics of the catalyst with those of the separation system, the loss of catalyst can be restricted to a few ppm (parts per million) of catalyst in the wax produced by the Fischer-Tropsch process. Production of renewable fuels such as gasoline, diesel and jet fuel can be produced by various types of feedstock. Necessary operations are carried out to produce syngas which is then cleaned to remove particulate matter and impurities before they are subjected to Fischer-Tropsch synthesis. The feedstock for Fischer-Tropsch plants should have higher sources of carbon that must be converted first into gaseous reactants, i.e., CO, H₂. This conversion is called gasification and the product is called synthesis gas or syngas. Syngas is inserted into the Fischer-Tropsch reactor in the presence of various metal catalyst, i.e., cobalt, iron, ruthenium, nickel. In case of natural gas used as feed stock, cobalt catalyst is the best to use. FT reactors are operated at high temperature ranges, i.e., 150-300 °C. High temperatures are favorable in FT reactions because they lead to faster reactions and higher conversion [3]. FTS can be conducted with very low temperature range between 563 and 583K within a wide range of CO conversion using saturated water as coolant. By using saturated water, reactor exhibited good isothermal condition under most simulated conditions [4].

2. Materials and Experimental Methods for Preparation of FT Catalyst by Impregnation

Different procedures are commonly used for the preparation and synthesis of solid phase catalysts which may affect the quality and specific application.

Quality of raw materials used for synthesis of heterogeneous catalysts depends upon every steps of preparation method. The choice of a laboratory method for preparing a given catalyst depends on physical and chemical characteristics desired in the final composition. It is easily understood that the preparation methods are also dependent on the choice of the base materials and experience shows that several ways of preparation can be considered, even for a given selection of the base material. This variety of possibilities might seem to confirm that making a catalyst is a “black art”. In the recent past, however, some generalities have become discernible in catalyst preparation and it may now be claimed that a catalyst preparation science is being built. A general way for preparation of catalyst involves various unit operations that consist of: chemical and physical transformations which are implied. The scientific laws which govern such transformations based on fundamental inorganic chemistry; the operation variables such as temperature, pressure, pH, time, concentration; the general characteristics of the products of the operation. Most catalyst formulations involve a combination of some or even all these operations. However, even though the preparation procedures differ considerably from one catalyst to another, three broad categories can be introduced to classify the catalysts with respect to the preparation procedure: bulk catalysts and supports; impregnated catalysts; mixed-agglomerated catalysts. Various unit operations used in catalyst preparation are crushing, grinding, mixing, washing, solubility, filtration, drying, calcination, precipitation, and stirring. Cobalt-supported catalysts for FT synthesis are very often prepared by impregnation. Impregnation is a method of cobalt deposition on porous support in which a dry support is contacted with a solution containing dissolved cobalt precursors. In this section, we discuss impregnation techniques which involve solutions of cobalt salts and cobalt carbonyls [5].

The actual solid phase catalyst commonly used in

powder form having an active metal like cobalt or iron supported on ceramic support to enhance the surface area. Some ceramic supports are silicon carbide, silica, alumina, titania for the conversion of carbon monoxide and hydrogen mixtures to high quality liquid fuel, pharmaceutical wax and light oil fraction. One of the most peculiar and relevant requirements for a solid catalyst to be of practical use is an appropriate dispersion of the active species. A high dispersion is usually desired because it corresponds to a greater utilization of the active species since the catalytic phenomena occur at the surface of the solid. Thus porous solids with a high internal surface area are often necessary in order to reach reasonable values of activity. The porous texture is the result of the preparation unit operations for the unsupported catalysts or it will be supplied by the support itself in the case of supported catalysts. By increasing the pore volume of the catalyst, the BET (Brunauer, Emmett and Teller) surface area will increase for high dispersion of active metal but the mechanical properties are adversely affected. Several unit operations must be performed carefully to control the pore volume of the catalyst during synthesis.

In general, the experimental method for impregnation of active metal on ceramic supports (e.g., silicon carbide, alumina, silica, silica-alumina, or combination of any one) followed the given one scheme:

(1) Calcinate the required amount of support powder (SiC, Al₂O₃, TiO₂) at 600-650 °C for 6-8 h in muffle furnace or box furnace under air or inert gas atmosphere;

(2) Dissolve the required amount of active metal precursor (cobalt nitrate, cobalt acetate) in 50-60 mL of distilled/deionized water until complete solubility even to certain temperature range;

(3) Pour the calcinated support powder in the prepared solution of active metal precursor;

(4) Stir the solution containing support powder for 30-45 min vigorously for uniform mixing;

(5) After stirring, set the evaporation temperature between 80 °C and 100 °C for drying the samples;

(6) After complete evaporation, grind it to fine powder form;

(7) Dry the samples in vented oven for 12-16 h at 120-140 °C;

(8) Calcinate the samples at 550 °C for 5-6 h and sieve in proper grade to be used in fix bed reactor.

By means of characterization like XRD (X-ray diffraction), SEM (scanning electron microscope), BET area, FTIR (fourier transform infrared spectroscopy), Simultaneous TG (thermo-gravimetric) and DTA (differential thermal analysis) and particle size analyzer provides significant evidence about the activity/structure/porous structure of active metal FT catalysts and various promoters like K, Ru, Pt, Pd, Au, Zn. It enables us about identification of the active sites of metallic catalysts and exposes possible ways for optimization of catalyst structure. A wide range of physical and chemical techniques has been used. In many cases, catalyst structure could be investigated during different pretreatments and catalytic reaction under certain conditions. A novel meso crystalline ceramic-supported metallic catalyst is prepared in-house, to conduct hydrogenation of carbon monoxide in highly active and sufficiently selective FT synthesis. SEM reveals a meso porous structure, whilst the XRD fingerprints an orthorhombic crystalline structure. Actual FT runs were performed using a single 28 mm ID (internal diameter) tube. On a positive note, the system pressure drop remained within acceptable limits, i.e., 0.03 MPa/m, in spite of the nano size. Gainfully, the diesel produced is a clean fuel, though with a higher proportion of wax in the product stream. The latter fraction is not considered to be a negative baggage anymore. Wax fetches more prices in the international market, however, clashes with the primary aim of producing liquid fuel. Cracking of the wax is therefore the preferred route in so far as the present research is concerned. For heterogeneous catalysts, aqueous/ethanol

impregnation can control the porous structure and formation of unwanted mixed oxides which are not active in FT reactions at high temperature. As very low ratio of catalyst and reactor volume, micro-reactor has a similarly low productivity per unit of reactor volume as the fixed-bed reactor [6].

3. Results and Discussion with Experimental Setup and Catalyst Characterization

In present research work, cobalt supported on various ceramic supports like alumina, silica, titania, silicon carbide with promoter like potassium, sulfur, phosphorus is utilized. High temperature is not favored for Co based catalysts because of unwanted large quantity of methane production [7]. An assembly of Fischer Tropsch bench scale facility having two single tube fixed bed bench-scale reactor was used with internal diameter of 9 mm and tube length of 0.3 m along with two separator units and online gas chromatograph is connected with the whole facility to find out the composition of reacting gases mixture and leaving gases mixture. The rest of the reactor was packed with ceramic balls and special type of cloth material. CO, H₂ flow was controlled through separate mass flow controllers (Sevenstar D07 MFC). Prior to the synthesis, the catalyst went under reduction in H₂ for 16 h at 350 °C at 0.4 bar. Then the reactor was cooled down to 180 °C and pressurized to 1 bar. The synthesis gas from the gasifier can be fed to this facility because gasifier is not available. We used bottle gases like CO, H₂ and N₂ to make syngas mixture as required. The synthesis was started at 200 °C with H₂/CO ratio of 2. A run time of 12 h for three runs with different gas composition was conducted under constant pressure and temperature. After leaving the reactor, the products pass through two traps, one hot and one cold. The hot and cold traps separate the heavy and light hydrocarbons from the product stream respectively. The composition of

synthesis gas is in the range of syngas expected to be produced from underground coal gasification of Thar coal reserves. Suspended solids are separated from the synthesis gas (syngas). Thus, no solids are assumed to be present in all downstream units, simplifying the model since only two fluid phases, liquid and vapor, are considered. The samples from each run were collected from the manual valves situated beneath the traps. Schematic diagram showing the flow and control of the gases and product is described in Fig. 1. Sample analysis was done on an offline gas chromatograph and mass spectrometer. Temperature of the reactor was controlled by placing one thermocouple near the wall and the other in the catalyst bed. Pressure was controlled using a back-flow regulator. The main Fischer Tropsch reaction rate based on Co/TiO₂/K catalyst, since the catalyst used was cobalt, no water-gas shift reaction is taken into account due to cobalt catalyst's negligible in-situ WGS activity and the H₂/CO ratio taken in this study being 2. Design parameters of the reactor and the appropriate FT synthesis conditions control the production of liquid or solid hydrocarbons [8].

Cobalt supported on titania along with potassium as a promoter catalyst was placed in the middle of the reactor and flow of gases controlled by mass flow controller. The quantitative analysis and SEM image done by Joel-SEM (JED2300) is given in Table 1 and Fig. 2. Fig. 3 describes the EDS (energy-dispersive X-ray spectroscopy) of the catalyst. Structure of supported cobalt oxide, surface sites and the nature of intermediates reaction can be forecast by means of FTIR analysis. Calcined metallic cobalt oxide Co₃O₄ detected at band 1,124 cm⁻¹ with tetrahedral and octahedral sites of cobalt is shown in FTIR Fig. 4, FTIR of Co/TiO₂/K catalyst. Presence of cobalt oxide can be identified by experience to analyze the spectrum of Co₃O₄ and Co₃O₄ with CoO as impurities.

Fig. 1 Schematic diagram of bench scale fixed-bed reactor.

4. Results and Conclusion

Considering exhaustible oil reserves and current hike in crude oil prices, there is a growing interest for preparation of hydrocarbon fuels from municipal solid waste, coal or biomass. From the available routes, gasification of coal to synthesis gas and thence to gasoline or diesel via Fischer-Tropsch is quite promising from the standpoint of utilization of huge coal reserves present in Pakistan. The conversion of coal to alternative fuels could offer more environmentally acceptable process for energy production. Coal gasification refers to a process that breaks down coal into its components, by subjecting it to pressure and high temperature in addition to the use of steam and air/oxygen. This leads to the production of synthesis gas, which is mainly a mixture of carbon monoxide, hydrogen and traces of carbon dioxide,

methane, and some other compounds depending upon quality of coal. Gasification is a vital process for the production of syngas (CO + H₂) chemical composition depends upon feedstock properties like volatile matter, fixed carbon, moisture.

To create an efficient technology pathway of syngas production through gasification which will provide an alternative to preserve natural gas for domestic consumption and as a raw material for higher value added products like fertilizers, synthetic fuel, pharmaceutical wax, electric power and petrochemical industry. On long term basis, this facility has a potential to produce a clean source of hydrogen for commercial applications. Coal gasifier capable of using enormous source of untapped energy in local coal will promote a phenomenal share to shrink the energy challenges of our industries. Clearly, the abundance and availability of coal make it such a

Table. 1 Quantitative Analysis of Catalyst.

ZAF Method Standard less Quantitative Analysis of Catalyst
Fitting Coefficient: 0.6609

Element	(keV)	Mass (%)	Error (%)	Atom (%)	Compound	Mass (%)	Cation	K
O K	0.525	35.72	3.28	62.98				14.2548
K K	3.312	2.04	0.59	1.47				3.2542
Ti K	4.508	52.13	0.88	30.71				70.0994
Co K	6.924	10.11	2.15	4.84				12.3916
Total		100.0		100.0

Fig. 2 SEM image of Co/TiO₂/K catalyst.

Fig. 3 EDS image of Co/TiO₂/K catalyst.

Fig. 4 FTIR of Co/TiO₂/K catalyst.

promising alternative energy source over natural gas or other fossil fuels. It is notable that abundantly available black gold is not being utilized properly up to present time to meet energy demands of Pakistan. The gasification of MSW (municipal solid waste)/coal/biomass coupled with FTS (fischer tropsch synthesis) processing leads to liquid fuels of different grades and compositions for commercial applications. The catalyst developed in-house shows adequate selectivity for the targeted diesel fuel fraction in the product stream. Developing indigenous R & D (research and development) capabilities for adopting various advanced coal technologies to suit local conditions are the key purposes of this catalyst synthesis for FT synthesis technology.

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