

# A REVIEW OF FISCHER-TROPSCH SYNTHESIS ON THE COBALT BASED CATALYSTS

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## ABSTRACT

*Fischer-Tropsch synthesis is a promising route for production of light olefins via CO hydrogenation over transition metals. Co is one of the most active metals for Fischer-Tropsch synthesis. Some different variables such as preparation parameters and operational factors can strongly affect the selectivity of Fischer-Tropsch synthesis toward the special products. In the case of preparation variables, several parameters such as catalyst preparation method, effect of different supports, and influence of promoters have been studied. Also, some operational factors including pretreatment conditions and experimental parameters such as temperature, pressure, and H<sub>2</sub>/CO ratio have been investigated. In addition, the stability of the Co-based catalyst is one of the most important characteristics. Therefore, catalyst deactivation is the main phenomenon and should be considered and controlled during the CO hydrogenation over the Co-based catalysts. Several factors such as poisoning, sintering, etc., lead to catalyst deactivation. The effects of the promoters on the catalyst structure were examined by XRD, SEM, TPD, BET and TEM measurements. The results of the catalytic tests showed that the addition of promoters altered the product selectivities when compared to the unprompted catalyst. According to the above-mentioned parameters and variables, we present here a review of Fischer-Tropsch synthesis for production of light olefins over the Co-based catalyst in a fixed-bed reactor.*

**Keywords :** Fischer Tropsch Synthesis, Co catalyst, synthesis of catalyst.

## I. INTRODUCTION

### 1.1 History of Fischer-Tropsch Synthesis

The synthesis of hydrocarbons from CO hydrogenation over transition metal catalysts was discovered in 1902 when Sabatier and Senderens produced CH<sub>4</sub> from H<sub>2</sub> and CO mixture passed over Ni, Fe and Co catalysts. In 1922, Hans Fischer and Franz Tropsch proposed the synthol process. Succeeding these initial discoveries, considerable effort went into developing catalysts for this process. The first catalyst that produced higher hydrocarbons at atmospheric[1-8]pressure was reported by Franz Fischer in 1925. This catalyst contained iron oxide and zinc oxide, but later Fischer found that a mixture of cobalt oxide and chromic oxide was more active. In 1935, Ruhrchemie started the first pilot-plant. The standard catalyst in this, and other commercial plants was built during the next years contained a mixture of Co, ThO<sub>2</sub>, MgO and Kieselguhr. In 1980s, expensive investments in the FT research and development programs picked up again in major petroleum companies. The global resurgence of interest in FT synthesis has been primarily driven by the problems of utilization of standard gas, diversification of sources of fossil fuels, and environmental concerns. Synthetic liquid fuels generally have

a very low content of sulfur and aromatic compounds to gasoline and desired from crude oil. FT synthesis is considered as a part of gas to liquids (GTL) technology; in this process natural and associated gases were converted to desirable products. Today, the research is systematically directed towards three main aspects: Catalysts, reactor design and process development.[13]

A comprehensive study of FT synthesis in literature, including journal and conference articles, book, reports and patents can be found in the FT Archive at [www.Fischer-tropsch.org](http://www.Fischer-tropsch.org). This website is sponsored by Syntroleum Corporation in cooperation with Dr. Anthony Stranges, professor of History at Texas A&M University and contains more than 7500 references and citations. This site has collected record of the documents from 1920's through 1970's, which are important for researching the history and development of FT synthesis and related processes as well as up-to-date listing of the latest publications in this field[11-15]

## 1.2 Fischer-Tropsch Process

Coal and natural gas were utilized as feedstock of the transportation fuels market and the chemical industry. The natural gas conversion to hydrocarbons (Gas to Liquids route) is one of the most promising subjects in the energy industry due to economic utilization of remote natural gas to environmentally clean fuels, specialty chemicals and waxes. The resources of coal and natural gas are very large,[25] and both of them can be converted into syngas (a mixture of CO and H<sub>2</sub>) by either partial oxidation or steam reforming processes. Possible reactions of Fischer Tropsch Process are shown in Fig. 1.2. Reforming of natural gas with either steam or carbon dioxide (CO<sub>2</sub>), or by partial oxidation produces synthesis gas.

The most important reactions are as :

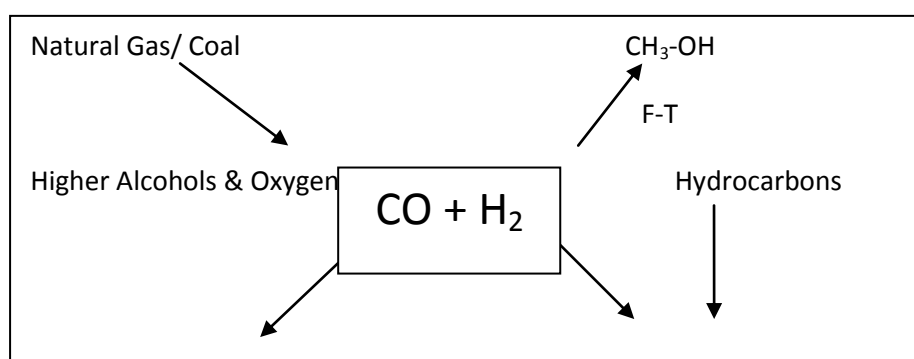
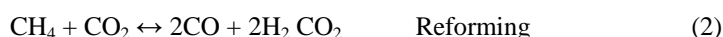
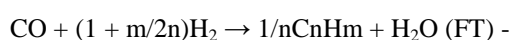


Fig. 1.2 . Possible reactions of Fischer Tropsch Process



$$\Delta\text{HFT} = 165 \text{ kJ mol}^{-1} \quad (5)$$



$$\Delta\text{HWGS} = 41.3 \text{ kJ mol}^{-1} \quad (6)$$

Where, n is the average carbon number

m is the average number of hydrogen atoms of the hydrocarbon products.

Water is a primary product of the FT reaction, and CO<sub>2</sub> can be produced by the WGS reaction.

Figure 1.2.1 shows a block diagram of the overall FT process configuration. The commercial process involves four main steps to producing FT products: syngas generation, gas purification, FT synthesis and product upgrading.

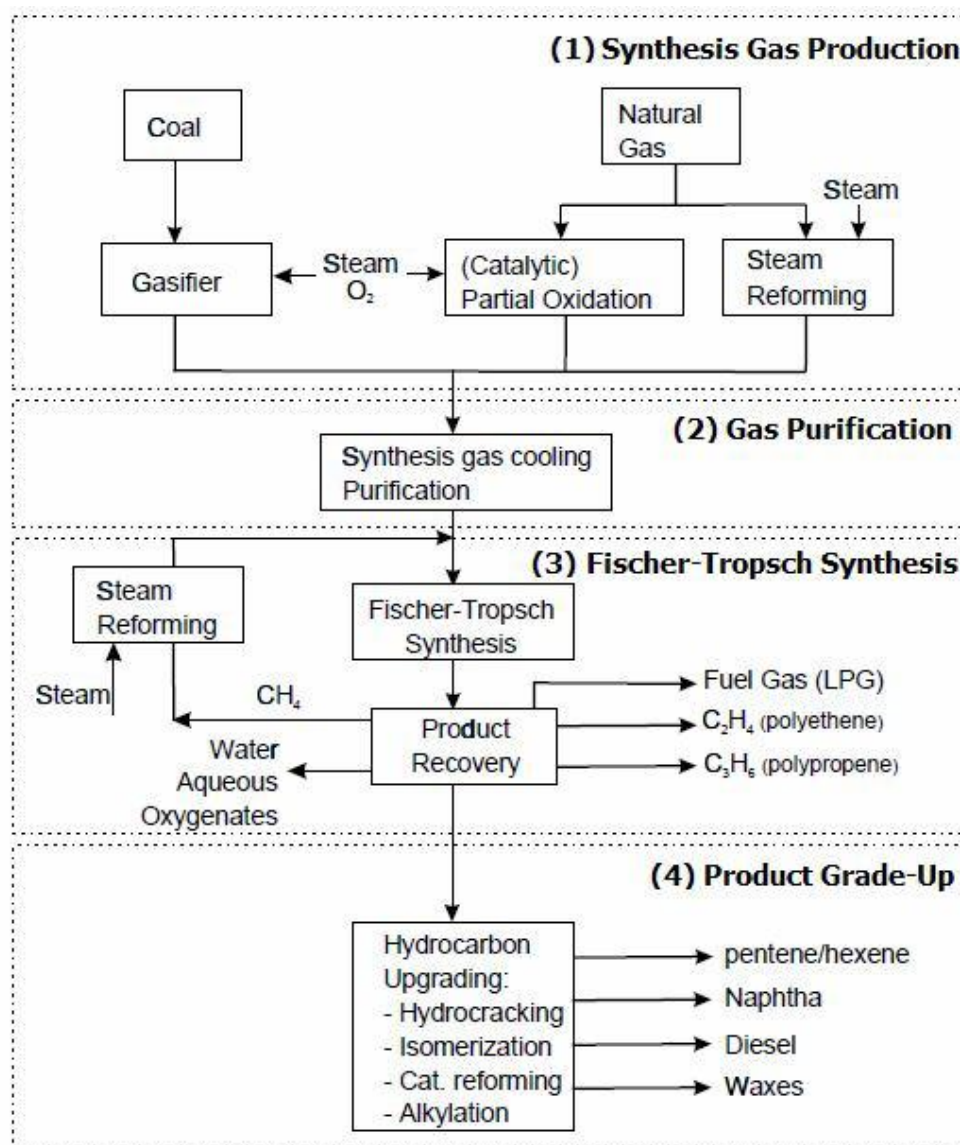


Figure 1.2.1 shows a block diagram of the overall FT process configuration

### 1.3 Chemistry of Fischer-Tropsch Synthesis

FT synthesis has been recognized as a polymerization reaction with the following steps:

1. Adsorption of reactant (CO) over the catalyst surface.
2. Chain initiation: dissociation of CO followed by hydrogenation.
3. Chain growth: insertion of additional CO molecules followed by hydrogenation.
4. Chain termination.
5. Desorption of products from the catalyst surface.

Dissociation of absorbed CO molecules and stepwise addition of hydrogen atoms produces the chemisorbed methyl species. By further hydrogenation of these methyl species methane was formed or these hydrogenated methyl species act as initiators for chain growth. Chain growth is carried out *via* sequential addition of CH<sub>2</sub> groups while the growing alkyl chain remains chemisorbed to the metal surface at the terminal methylene group[21-25]-. Chain termination is carried out at any time during the chain growth step to yield either  $\alpha$ -olefin or n-paraffin once the product desorbs. The hydrogenation of CO in FT synthesis consists of many complex serial parallel reactions. The main products of FT synthesis, with cobalt or iron based catalyst, are hydrocarbons ranging from methane to high boiling point paraffins.

The following is the FT synthesis reaction:

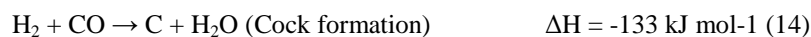
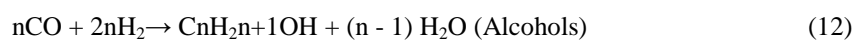
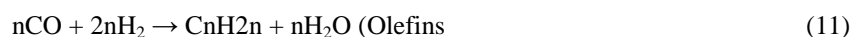
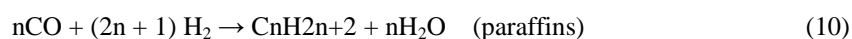
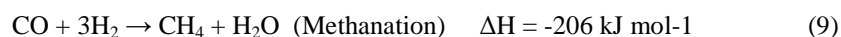


The water gas shift (WGS) reaction is a secondary reaction that readily occurs when Fe catalysts are used.

Combining reaction one (above) with reaction six (in previous section) gives the net reaction for Fe catalyzed FT synthesis (reaction 8).



Specific FT synthesis products are synthesized according to the following reactions:



Carbon deposition on the catalyst surface causes catalyst deactivation.

#### 1.4 Product Distribution in Fischer Tropsch Reaction

FT synthesis is kinetically controlled and the intrinsic kinetics is a stepwise chain growth, in effect the polymerization of CH<sub>2</sub> groups on a catalyst surface. Selectivity of FT synthesis products are determined by the ability of the catalyst to catalyze chain propagation *vs.* chain termination reactions. The polymerization rates, and therefore kinetics, are independent of the products formed.[27-31] The probability of chain growth and chain termination is independent of chain length. Therefore, selectivity of various hydrocarbons can be predicted based on simple statistical distributions calculated from chain growth probability and carbon number. The chain polymerization kinetics model known as the Anderson-Shulz-Flory (ASF) model is represented by the following equation:

$$\ln(W_n/n) = n \ln \alpha + \ln[(1 - \alpha)^2/\alpha] \quad (15)$$

W<sub>n</sub>: weight fraction of the product of carbon number;

n: number of carbon atoms;

$\alpha$ : probability of chain growth;

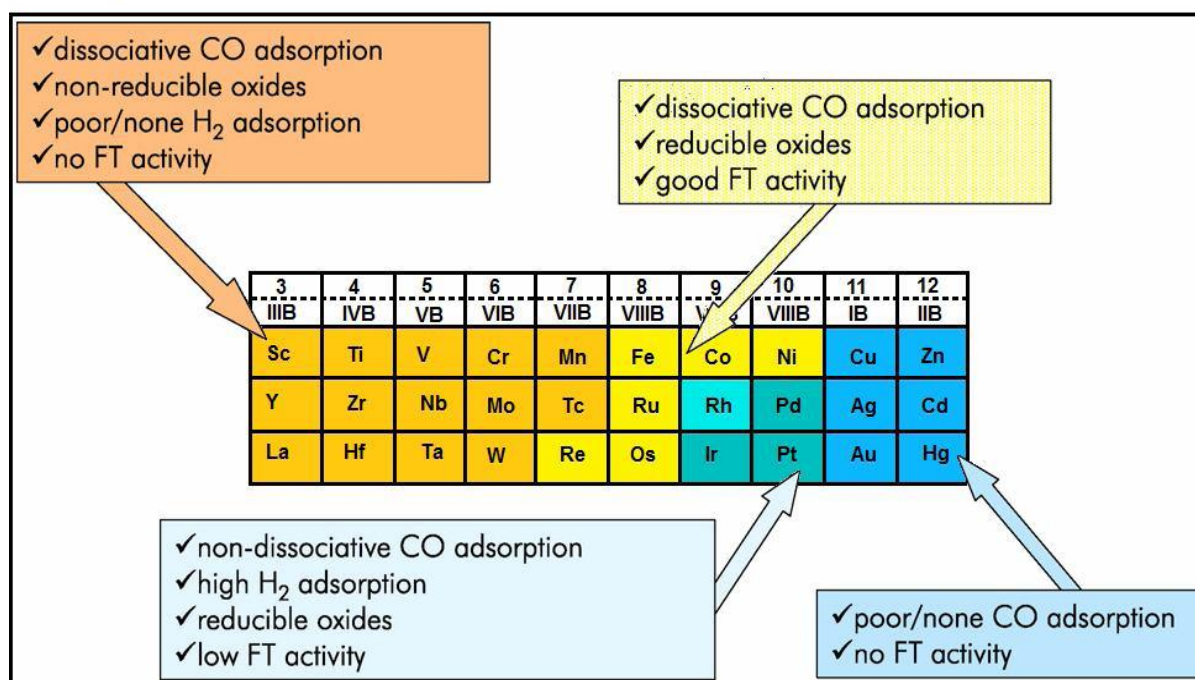
(1 -  $\alpha$ ): probability of chain termination.

The main parameters that influence the distribution of products are: pressure, reactor temperature, catalyst type, feed gas composition, and promoters.

### **1.5 Active Metals for Fischer-Tropsch Reaction :**

The first supposition, reported, was proposed by Fischer and Tropsch in 1926 [14]. They assumed the dissociative adsorption of the carbon monoxide on the metal atom, with formation of a carbide species. Few metals show activity on FT reaction: the main required characteristics are dissociative CO adsorption, good H<sub>2</sub> adsorption and at the same time, easy reducibility[30]

of the metal oxide. From the point of view of the mechanism, FT reaction can be conceived as a sort of polymerization, with an adsorption step, chain initiation, chain propagation and chain growth termination. The growing alkyl chain desorbs from the metal by hydrogenation, forming paraffins olefins. After this first supposition, several different mechanistic pathways have been elaborated. On the basis of these considerations, the transition metals belonging to the third, fourth, fifth and sixth group are not good catalysts for FT synthesis, because, despite of their favorable dissociative CO adsorption, they form very stable oxide that are not reducible under FT conditions. On the other hand, iridium, platinum, palladium and the metals belonging to the groups 11 and 12, are characterized as a non-dissociative adsorption of carbon monoxide, and for this reason they are not active in FT synthesis. Behavior of transition metals for FT synthesis is shown in Fig.1.4 VIII transition metal oxides are generally regarded as good CO hydrogenation catalysts. The specific activity of various metals used for CO hydrogenation was investigated, and their order correspondent to activity in CO hydrogenation is displayed in Fig. As it can be observed, Fe, Co, Ru, Ni and Rh exhibit higher activities than the other metals. Ru is one of the most active catalysts for FT, but it is too prohibitive and poorly available to be used to develop an industrial process. Nickel has shown high hydrogenation activity, so its selectivity to methane is too high for FT.



1.4 Active Metals for Fischer-Tropsch Reaction

## II. CATALYST PREPARATION PROCEDURES FOR FISCHER-TROPSCH REACTION

Cobalt and iron are the only two metals of choice for industrial applications. Co catalysts produce mainly **straight** chain hydrocarbons (no oxygenates like Fe) in FT synthesis.

Both Co and Fe catalysts have been used in the industry for hydrocarbon synthesis; to select cobalt or iron, an important parameter is also the carbon feedstock. Iron has a high water gas shift activity, and for this reason is particularly suitable for hydrogen-poor feed stocks, as those obtained from coal or biomass. Cobalt performs better with an almost stoichiometric ratio of hydrogen and carbon monoxide, so it is preferred when the carbon feedstock is a natural gas.

### 2.1 Catalyst Preparation Procedure

The catalytic performance of FT catalysts strongly depends on the methods of catalyst preparation. Preparation of cobalt supported catalysts involves several important steps: choice of appropriate method for deposition of active phase, choice of suitable support, promoter and determination of the optimum treatment for production of the final Co catalyst.[1-8] The FT activity of the Co catalyst is also strongly affected by the calcination and reduction pretreatment. In this section, we attempt to discuss three different preparation methods for production of FT catalyst including: co-precipitation, impregnation and sol-gel procedures.[11-18]

#### [a] Co-Precipitation Procedure

The preparation of catalysts by co-precipitation is technically very important. Co-precipitation is appropriate for the production of a homogeneous catalyst components distribution.

The total free energy change due to agglomeration,  $\Delta G$ , is determined by

$$\Delta G = \Delta G_{\text{bulk}} + \Delta G_{\text{interface}} + \Delta G_{\text{others}} \quad (16)$$

$\Delta G_{\text{bulk}}$ : the difference of the free energy between solution and solid species.

$\Delta G_{\text{interface}}$ : the free energy change related to the formation of the interface

$\Delta G_{\text{others}}$ : summarizes all other contributions.

The coprecipitation method has been generally used for preparation of Fe catalyst and few papers have been published for preparation of Co catalyst for CO hydrogenation *via* FT synthesis by using co-precipitation method [18-28]. The obtained precipitate was dried and calcined to obtaine final catalyst. The schematic representation of catalyst preparation *via* co-precipitation procedure used in our research works is displayed in fig.

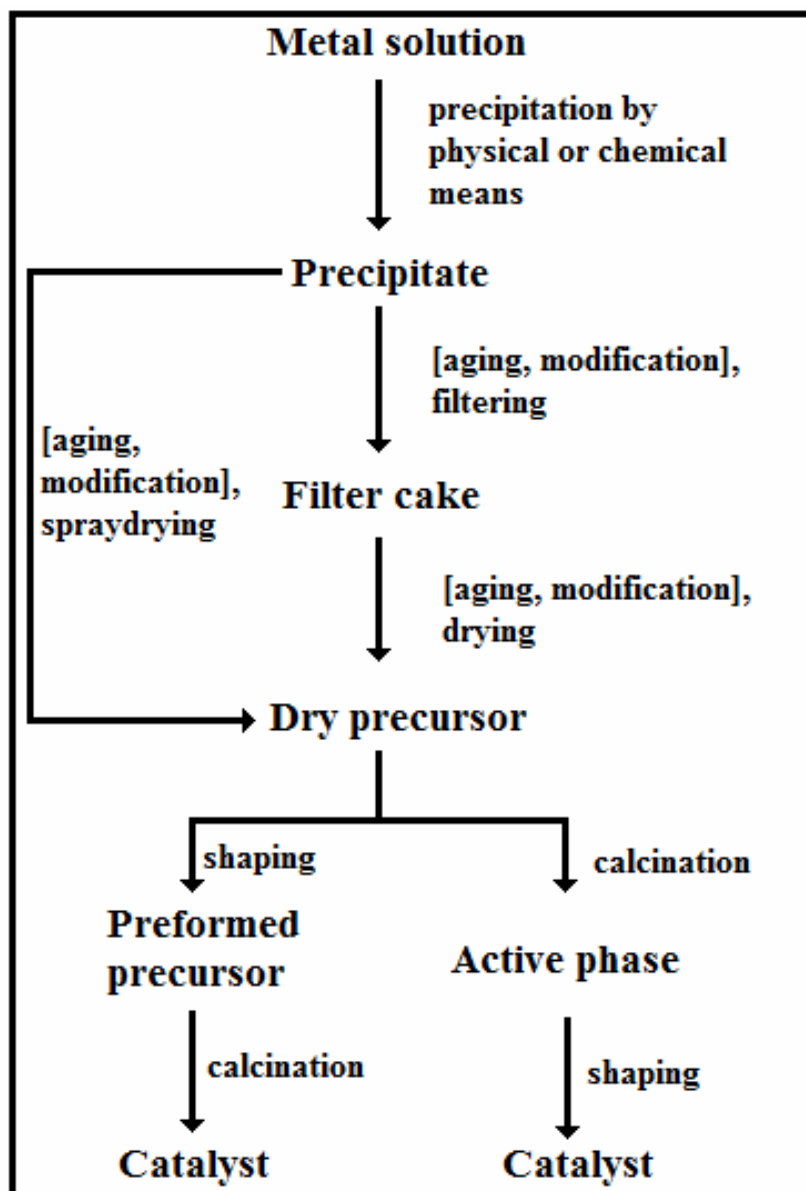


Fig.: [a] Co-Precipitation Procedure

### [b] Sol-Gel Method

Sol-gel is another technique to prepare catalysts for FT synthesis [43-51]. The sol-gel process includes the generation of a sol followed by that of a gel. A sol (a liquid suspension of solid particles ranging 1 nm to 1 micron) can be obtained through hydrolysis and partial condensation of a precursor such as an inorganic salt or a metal alkoxide.[18] The most important advantages of sol-gel preparation are:

- (1) The ability to change compositional homogeneity at a molecular level.
- (2) The ability to represent various components in a single step.
- (3) The ability to confect samples at low temperature.
- (4) The ability to change physical specifications such as pore size distribution and pore volume.

Figure b shows the four main steps in taking a precursor to a particular product form *via* sol-gel preparation including: formation of a gel, aging of a gel, removal of solvent and heat treatment.

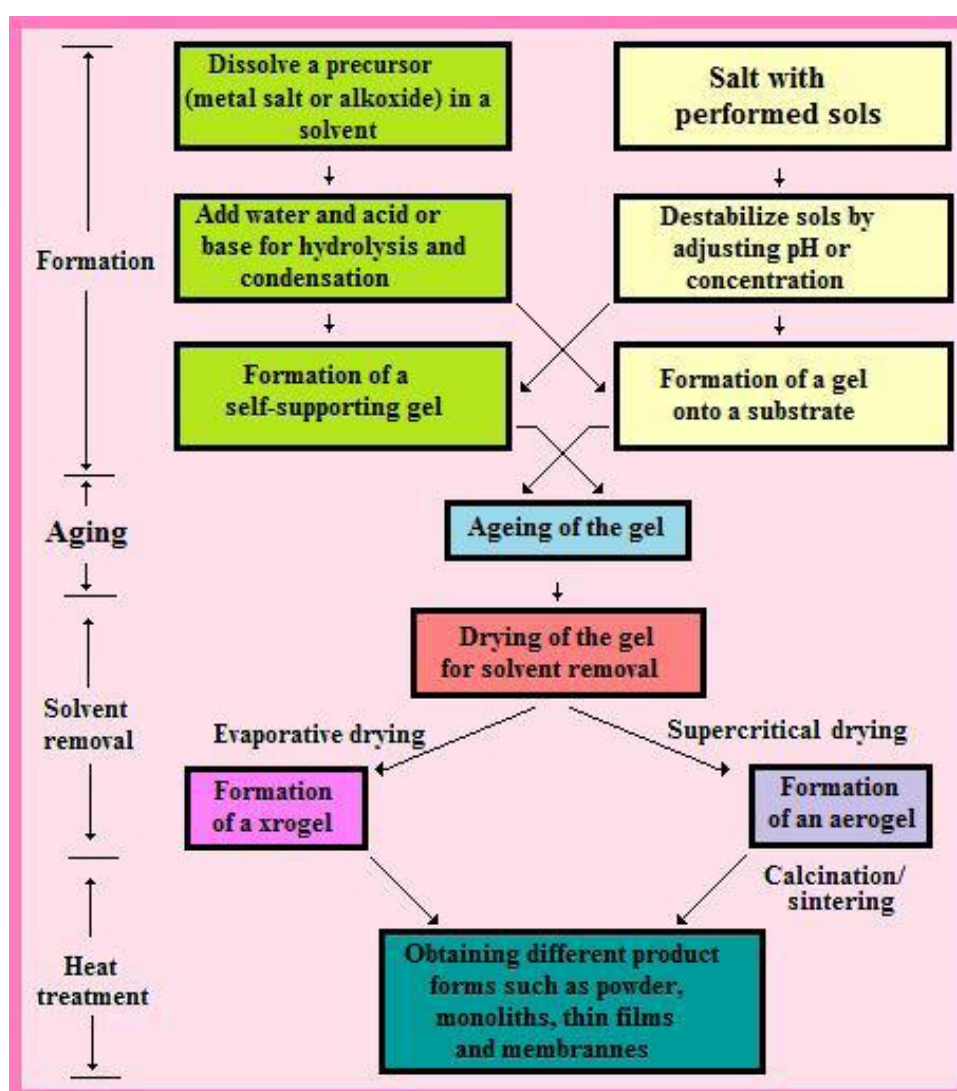


Fig . [b] Sol-Gel Procedure

**Formation.** The precursor in a sol-gel preparation can either be a metal salt/alkoxide dissolved in an appropriate solvent or a stable colloidal suspension of preformed sols. At its simplest level, sol-gel chemistry with metal alkoxides can be described in terms of two classes of reactions:



Hydrolysis:  $-M-OR + H_2O \rightarrow -M-OH + ROH$

Condensation:  $-M-OH + XO-M \rightarrow M-O-M + XOH$

where X can either be H or R (an alkyl group).

**Aging.** Aging represents the time between the formation of a gel and the removal of solvent. As long as the pure liquid remains in a matrix, a gel is not static and can undergo many transformations [52]. For alkoxide-derived gels, condensation between surface functional groups

continues to occur after the gel point. This process can actually be desirable because it leads to a more cross-linked network that is mechanically stronger and easier to handle. Parameters that affect the aging process include temperature, time and pH of the pure liquid.

**Drying.** As the pure liquid is evaporated from gel network, the capillary pressure associated with the liquid vapor interface within a pore can become very large for small pores. Similar to aging, a gel is not static during drying and, for that reason, drying can be viewed as part of the overall aging process. The properties of a product are thus dependent on the drying method and even with a single method, the drying conditions.

**Calcination.** After the removal of pure liquid, further heat treatment is necessary. Often, heating is done in the presence of a reactive gas (e.g. flowing air, oxygen or hydrogen) in order to burn off any residual organics or to oxidize (or reduce) the sample. Exposing the sample to a high temperature over an extended period of time leads to sintering, consequently a decrease in surface area.

### III. OPERATIONAL PARAMETERS

One of the main factors effect on the catalytic performance of the catalysts for FT synthesis is the operational conditions. These operational parameters are included two main groups of:

(1) the pretreatment conditions and (2) experimental conditions

#### Pretreatment Conditions

The hydrocarbon selectivity appear to relate strongly on the pretreatment procedure. After decomposition of supported cobalt salts *via* calcination in an oxidizing atmosphere, the catalysts are reduced in hydrogen. Because of a high surface area, porosity, stability and weak metal support interaction, silica has been especially convenient for the design of cobalt FT catalysts for fixed-bed reactor .[31-35]It has been reported that catalyst porosity is one of the properties needed for the design of FT catalysts with a desired metal dispersion and it has been found that in the catalysts prepared by impregnation with cobalt nitrate, with a wide range of cobalt surface densities, cobalt dispersion are largely influenced by the porous structure of the support.

#### Experimental Conditions

Conventional FT catalyst screening consists of comparing the catalytic performance at the same experimental conditions (temperature, pressure, amount of catalyst ). The measured output values of catalyst screening are typically overall activity (syngas conversion), selectivities (methane, light and heavy hydrocarbons, carbon dioxide), stability, and catalyst behavior during the start-up activation steps. Reaction conditions have an important effect on product selectivities in FT synthesis [23]. The main experimental conditions are listed below.[23-27]

#### A) $H_2/CO$ feed ratio.

It is well known that the H<sub>2</sub>/CO ratio in the reaction atmosphere plays a very important role in FT synthesis, and influences the product selectivity directly.

### B) Reaction temperature.

Temperature is a basic process factor that has a deep effect on the overall yield of a FT reactor. Temperature is normally used in order to control the distribution of products in the reaction. The reaction temperature also has an efficacious effect on the CO conversion and catalytic performance of the catalysts [37]. All reactions occurring in FT process are acutely exothermic, so that control of temperature is extremely intransitive to ensure the reaction goes to selective products. On the other hand, this parameter also affects the rate constant according to the Arrhenius-type rate equation:

$$k = k_0 \exp(-E_a/RT) \quad (17)$$

The logarithm of the reaction rate constant (k) as a function of the reverse of temperature gives a straight line with negative slope (-E<sub>a</sub>/R). In general, the FT reaction temperature for production of C<sub>2</sub>-C<sub>4</sub> light olefins preferably should not be too low or too high. At high temperature the selectivities of CH<sub>4</sub> and CO<sub>2</sub> (as unwanted products), were enhanced, as well as the formation of large amount of coke (another unwanted product) [39]. Lower temperature is preferential for chain growth and the production of heavy hydrocarbons [39].

### C) Reaction pressure :

In commercial process, the FT synthesis reaction usually operates under high pressure. The total syngas pressure is an important catalyst screening parameter. Variation of pressure is also applied in directing the FT process toward desired products. The results of FT catalyst screening at atmospheric and high pressure could yield different results. Higher pressures and higher carbon monoxide conversions would probably lead to saturation of catalyst pores by liquid reaction products. CO conversion increases significantly with increasing reaction temperature. Methane and CO<sub>2</sub> selectivities increase with temperature, as well. It has been reported that the changes in CO conversion with reaction temperature may hit a maximum along with significant increase in CH<sub>4</sub> and CO<sub>2</sub> production. FT synthesis catalyst activity can be increased at high temperature, but selectivities of unfavorable products such as CH<sub>4</sub> or CO<sub>2</sub> are also enhanced sharply. So, catalysts showing high activity at low temperature are needed [32-37]. Bremaund *et al.* [36] studied the influence of syngas composition on the transient behavior of Co/Al<sub>2</sub>O<sub>3</sub> catalyst for FT synthesis. When using freshly activated catalyst, they found that at carbon monoxide conversion higher than 30% the FT reaction rate is gradually decreased with time, while no deactivation is observed at low carbon monoxide conversion. We studied the effect of different operational parameters on the catalytic performance and structure of different catalysts [35,39]. The results showed that process conditions strongly affected the structure and catalytic performance of the catalysts and changed the CO conversion and selectivities toward different products.

### Cobalt FTS Catalyst Deactivation :

Catalyst deactivation is a major challenge in cobalt based catalyst for FT synthesis. While cobalt-catalyzed FT synthesis is advantageous in carbon utilization as compared to processes using iron, cobalt is more expensive necessitating longer catalyst life [37-39]. Catalyst stability therefore is an important performance variable in cobalt catalyzed FT processes. Cobalt catalysts seem to undergo various intrinsic deactivation processes during FT synthesis. Thus, for example, resistant carbon buildup on the active metal surface was proposed as a deactivation channel in CO hydrogenation.

### Main Objectives of this Review

The goal of the present review is to discuss about the effect of different preparation parameters, process conditions and preparation methods on the catalytic performance of Co catalysts for CO hydrogenation *via* FT reaction. Co catalyst for Fischer-Tropsch synthesis and also affect the rate of FT synthesis; control of these parameters is necessary to achieve the desired products. Catalyst synthesis, evaluation of catalytic performance, stability and deactivation are most important steps in the design of Co based catalysts.[33-37]

### IV. SUMMARY AND CONCLUSION

Transition metal oxides are generally regarded as good CO hydrogenation catalysts. Among them Cobalt and iron are the only two metals of choice for industrial applications. Co tends to have a longer lifetime than Fe catalysts and does not have WGS activity which leads to improve carbon conversion to products. Fe also has a stronger tendency than Co to produce carbon that deposits on the surface and deactivates the catalyst. Catalyst synthesis, evaluation of catalytic performance, stability and deactivation are most important steps in the design of Co based catalysts. Various catalyst preparation methods, different support effects, different promoters and catalyst pretreatments and process conditions (T, P and H<sub>2</sub>/CO ratio) are the main parameters[35-39]which control the structure, properties and catalytic performance of cobalt catalysts. These optimizing conditions depend to the catalyst structure and different additives (promoters and supports), preparation methods and conditions. Operational conditions have great effects on the catalytic performance of Co catalyst for Fischer-Tropsch synthesis and also affect the rate of FT synthesis; control of these parameters is necessary to achieve the desired products.

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