

A Review of Fischer-Tropsch Synthesis on the Cobalt Based Catalysts

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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 H₂/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. 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 micro- fixed-bed reactor.

Keywords: Light olefins, Fischer-Tropsch synthesis, Co-based catalyst, Catalyst deactivation

INTRODUCTION

History of Fischer-Tropsch Synthesis

The synthesis of hydrocarbons from CO hydrogenation over transition metal catalysts was discovered in 1902 when Sabatier and Sendderens produced CH₄ from H₂ and CO mixture passed over Ni, Fe and Co catalysts. In 1922, Hans Fischer and Franz Tropsch proposed the synthol process, which gave under higher pressure (>100 bar) a mixture of aliphatic oxygenated compound via reaction of carbon monoxide with hydrogen over alkaliized iron chips at 673 K. This product was transformed after heating under pressure into "synthine", a mixture of hydrocarbons. The German industry wanted synthetic gasoline and motor fuel, and the research was turned towards catalysts and process that mainly gave olefinic and paraffinic hydrocarbons.

Succeeding these initial discoveries, considerable effort went into developing catalysts for this process. The first catalyst that produced higher hydrocarbons at atmospheric 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 somewhat more active. Nickel was also found to be an interesting and active component for this purpose. The researchers experienced that the use of a catalyst support, mainly Kieselguhr, thorium and alkali promotion increased the stability and activity of the catalyst. 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, ThO₂, MgO and Kieselguhr. These fuel plants were of great importance to Germany during the Second World War, however many of them were destroyed after the war. The price of the crude oil decreased, and the Fischer-Tropsch

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(FT) process became uneconomical. As a consequence of the price drop, plants for new plants in many countries were not realized. Only in South Africa there has been a continuous production of synthetic fuel from coal since 1950's. After World War II, ARGE (Arbeitsgemeinschaft Ruhrchemie und Lurgi) using a fixed bed FT reactor developed a large-scale process. At the same period, Kellogg based on circulating catalyst bed proposed a new technology. Sasol in South Africa realized both the ARGE and Kellogg processes. In 1955, the Sasol One plant was built in Sasolburg; the Natref crude oil refinery was commissioned in 1966. The oil crisis in 1973 led to a jump in the crude oil price, and this in turn led to renewed interest for FT process as a way to convert natural gas and coal to liquid fuel. Sasol Two and Three began production in Secunda, in 1980 and 1982, respectively [1]. Main Sasol accomplishments regarding the catalysts and reactors design and also FT synthesis processes have been summarized in a recently published monograph [2]. 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 more valuable middle distillates and lubricants. Today, the research is systematically directed towards three main aspects: Catalysts, reactor design and process development. A comprehensive bibliography of FT synthesis in literature, including journal and conference articles, book, government reports and patents can be found in the FT Archive at 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 a bibliography of the large body of 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. Many excellent

reviews of FT synthesis have been drawn upon for this report an attempt to summarize, the chemistry, catalyst development, commercial process, reactor development and economics of FTS [3-9].

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, and both of them can be converted into syngas (a mixture of CO and H₂) by either partial oxidation or steam reforming processes. Possible reactions of synthesis gas are shown in Fig. 1. Reforming of natural gas with either steam or carbon dioxide, or by partial oxidation produces synthesis gas. The most important reactions are:



Usually, synthesis gas with a stoichiometric ratio of hydrogen and carbon monoxide is obtained using the combination of synthesis gas production processes. If synthesis gas with a H₂/CO ratio lower than 2 is used, the composition is not stoichiometric for the FT reactions; at this state the water gas shift reaction is useful to alter the H₂/CO ratio to 2. Figure 2 shows the application ranges for iron (high WGS-activity) and cobalt catalysts (no WGS activity). Inexpensive iron catalysts in comparison to cobalt can directly convert low H₂/CO ratio synthesis gas without an external shift reaction [10-12]. The reaction of FT synthesis on iron catalysts can be simplified as a combination of the reaction and the water gas shift (WGS) reaction:

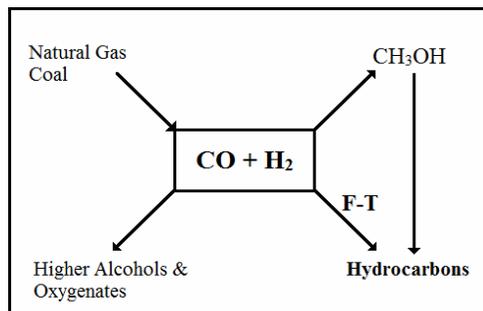


Fig. 1. Possible reactions from synthesis gas.

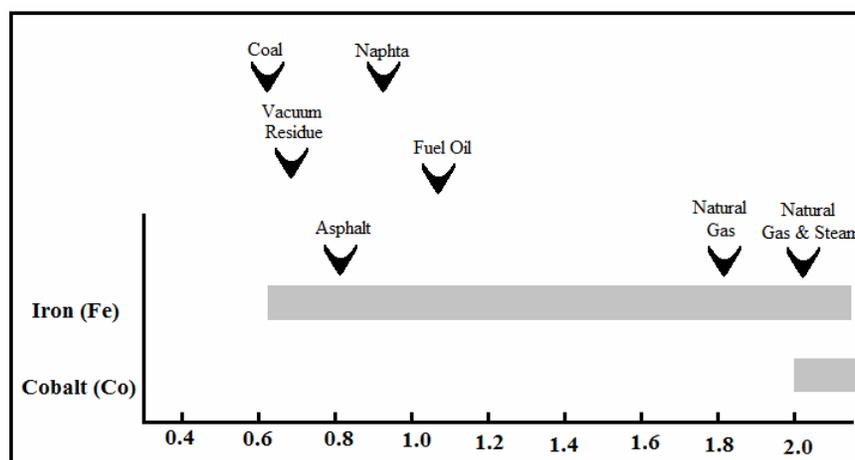
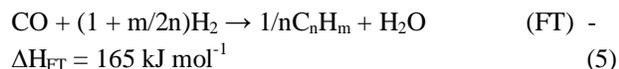


Fig. 2. Feedstocks and catalysts.



Where n is the average carbon number and m is the average number of hydrogen atoms of the hydrocarbon products. Water is a primary product of the FT reaction, and CO_2 can be produced by the WGS reaction. Figure 3 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.

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_2 groups while the growing alkyl chain remains chemisorbed to the metal surface at the terminal methylene group. Chain termination

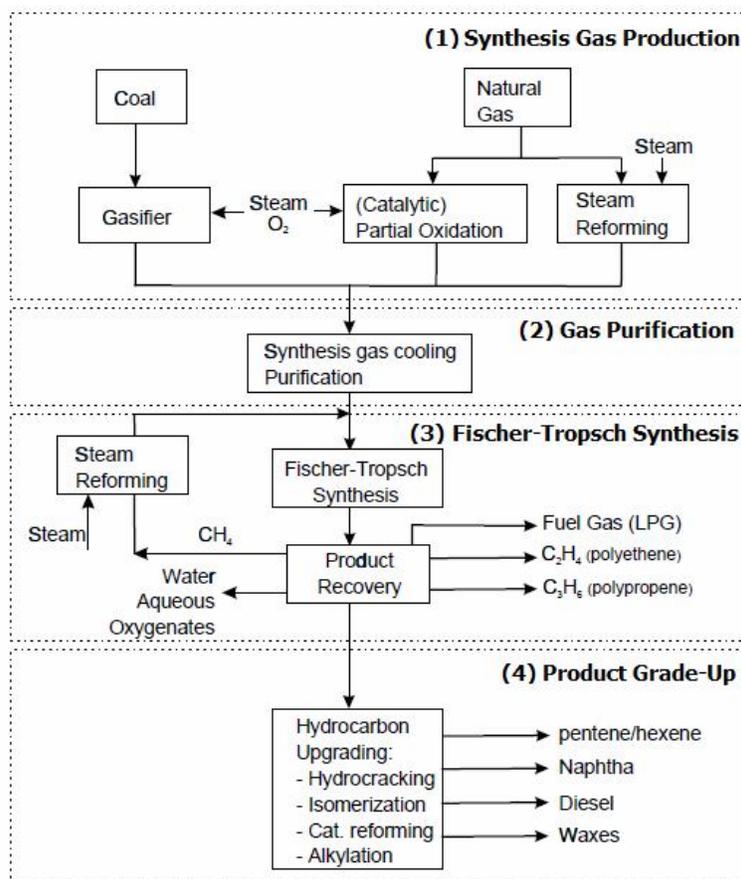
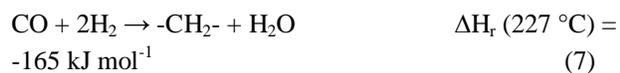


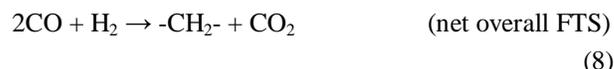
Fig. 3. Overall process scheme Fischer-Tropsch.

is carried out at any time during the chain growth step to yield either α -olefin or n-paraffin once the product desorbs.

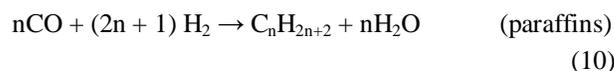
The hydrogenation of CO in FT synthesis consists of many complex serial parallel reactions. The main products of FT synthesis, with cobalt or iron based catalyst, are hydrocarbons ranging from methane to high boiling point paraffins. The following is the FT synthesis reaction:

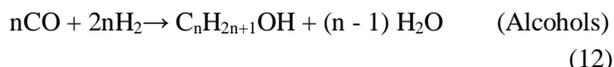
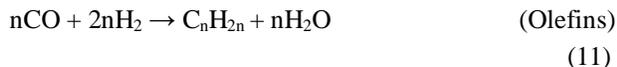


The water gas shift (WGS) reaction is a secondary reaction that readily occurs when Fe catalysts are used. Combining reaction one (above) with reaction six (in previous section) gives the net reaction for Fe catalyzed FT synthesis (reaction 8).



The required H_2 to CO ratio for the cobalt catalyst is 2.15, but since the iron catalyst performs WGS in addition to the FT reaction, the H_2 to CO ratio can be slightly decreased for the iron catalyst [3]. Specific FT synthesis products are synthesized according to the following reactions:





Another competing reaction that becomes important in FT synthesis is the Boudouard reaction:



Carbon deposition on the catalyst surface causes catalyst deactivation.

Fischer-Tropsch Products Distribution

FT synthesis is kinetically controlled and the intrinsic kinetics is a stepwise chain growth, in effect the polymerization of CH₂ 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. 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_n: weight fraction of the product of carbon number;

n: number of carbon atoms;

α: probability of chain growth;

(1 - α): probability of chain termination.

This equation is graphically represented in Fig. 4. It clearly displays the predicted distributions for several products and product ranges of particular interest. Irrespective of operating conditions, the FT reaction always produces a

range of olefins, paraffins, and oxygenated compounds (alcohols, aldehydes, acids, and ketones). There are several unique aspects of FT products. Regardless of the product type, they are predominantly linear with high olefinicity. In fact, the paraffin-to-olefin ratio is lower than thermodynamically predicted. The olefins that do form are predominantly terminal (alpha). A considerable amount of monomethyl chain branches form and the degree of branching decreases as the chain length increases. Theoretically, only methane can be produced with 100% selectivity. The only other product that can be produced with high selectivity is heavy paraffin wax. The gasoline product fraction has a maximum selectivity of 48%. The maximum diesel product fraction selectivity is closer to 40% and varies depending on the range of carbon numbers in the product fraction. The plot of ASF distribution function (Fig. 4), also showed that it is difficult to produce C_{2-3} and C_{5-7} with good selectivity, while the selectivity of C₁ may reach to a maximum of 100%. Therefore, for the sake of selectivity, the challenge is to break through the ASF distribution function [13]. The main parameters that influence the distribution of products are: pressure, reactor temperature, catalyst type, feed gas composition, and promoters.

Active Metals for Fischer-Tropsch Reaction

Few metals show activity on FT reaction: the main required characteristics are dissociative CO adsorption, good H₂ adsorption and at the same time, easy reducibility 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 first supposition, reported in Fig. 5, 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. The insertion of the adsorbed dissociated hydrogen on this carbide produces the active -CH₂- intermediate that gives rise to the propagation step. The growing alkyl chain desorbs from the metal by hydrogenation, forming paraffins, or by β-scission, forming olefins. After this first supposition, several different mechanistic pathways have been elaborated, but all of them contemplate an initiation, propagation and termination

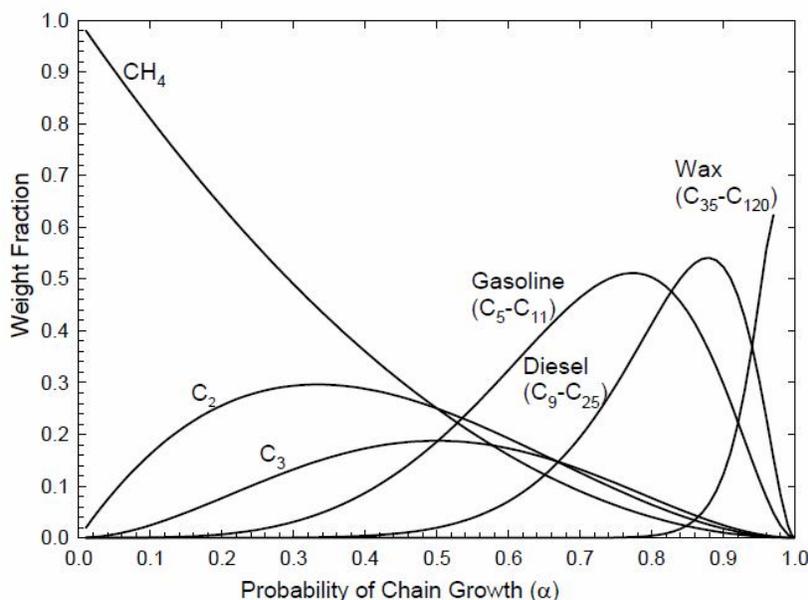


Fig. 4. Anderson-Schulz-Flory distribution.

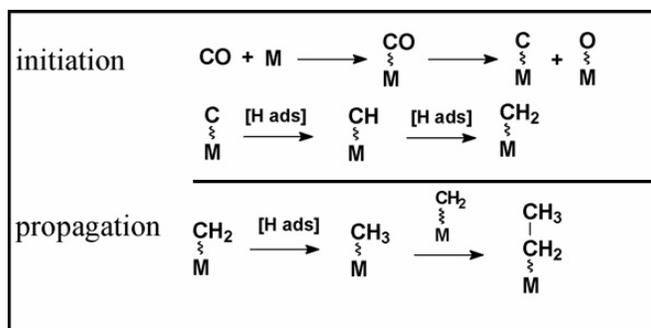


Fig. 5. Classic mechanistic pathway of CO hydrogenation.

step. 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. 6. Group

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. 7 [13]. 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

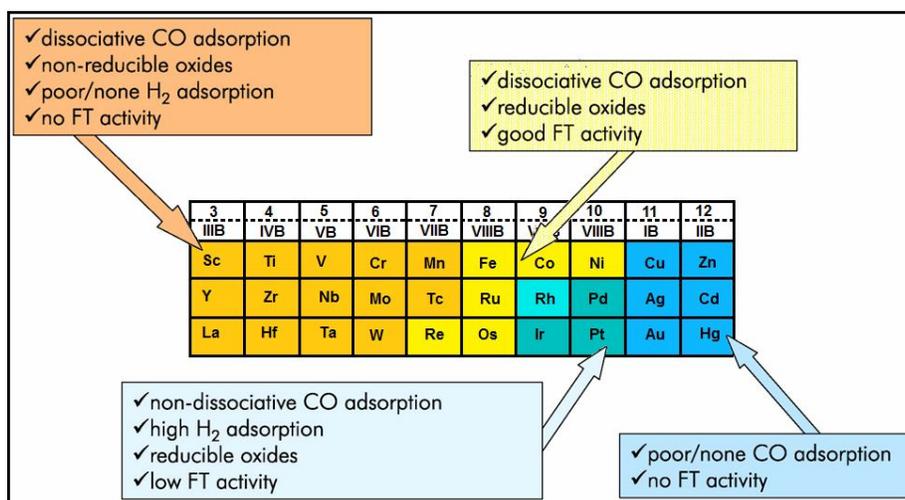


Fig. 6. Transition metals behavior for FT reaction.

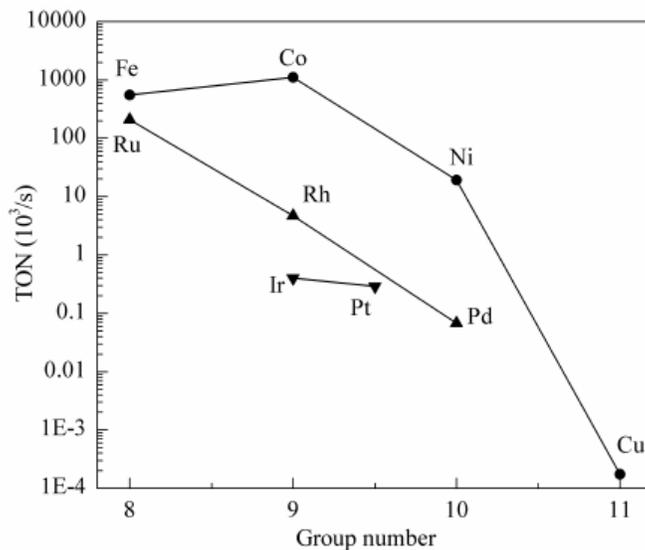


Fig. 7. The activity order of various transition metals for CO hydrogenation.

purposes. Cobalt and iron are the only two metals of choice for industrial applications [15-17]. Fe is very active and has WGS activity; Fe readily forms carbides, nitrides, and carbonitrides with metallic character that also have FT synthesis activity. Fe also has a stronger propensity than Ni or Co to generate carbon that deposits on the surface and

deactivates the catalyst. Co tends to have a longer lifetime than Fe catalysts and does not have WGS activity, which leads to improved carbon conversion to products because CO₂ is not formed. 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 feedstocks, as those obtained from coal or biomasses. 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.

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. This review also deals with deactivation process and its main effective parameters.

CATALYST PREPARATION PROCEDURES

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. In the active phase deposition step, cobalt spread on the porous support and provide the cobalt precursor. The characteristics of the supported cobalt catalyst can be influenced by different promoters such as noble metals and oxides. 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.

Co-Precipitation Procedure

The preparation of catalysts by co-precipitation is technically very important. However, precipitation is usually more demanding than several other preparation techniques, due to the necessity of product separation after precipitation and large volumes of salt-containing solutions generated in precipitation process. Co-precipitation is appropriate for the production of a homogeneous catalyst components distribution. A good dispersion of Catalyst

components is difficult to achieve by other means of preparation, and thus co-precipitation will remain the main technique in the manufacture of heterogeneous catalysts, in spite of the detriments associated with such processes. These detriments are higher technological requirements, the difficulties in following the precipitated product quality during the precipitation process, and the obstacles in maintaining a constant product quality all over the whole precipitation process, if the precipitation is performed discontinuously. General flow scheme for the preparation of a precipitated catalyst is displayed in Fig. 8. In order for solid to precipitate from solution, first a nucleus has to form. The particle formation is controlled by free energy of agglomerates of the solution constituents. The total free energy change due to agglomeration, ΔG , is determined by

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

ΔG_{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

ΔG_{others} : summarizes all other contributions.

It is generally favorable to precipitate the favorite material, in such a form that the counter ions of the precursor salts and the precipitation agent, which can be occluded in the precipitate during the precipitation, can easily be removed by a calcination step. The co-precipitation 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]. Khassin *et al.* prepared cobalt-alumina catalysts using co-precipitation of Co^{2+} and Al^{3+} ions or Co^{2+} ion precipitation onto freshly prepared Mg-Al or Zn-Al hydrotalcite [20]. It has been reported that hydrotalcite decomposition yields cobalt oxide phase supported by a highly inverted spinel-like structure. Co-Ce catalysts were also prepared using co-precipitation procedure [22,23]. Xue *et al.* prepared cobalt-cerium oxide catalyst using co-precipitation of Co^{2+} and Ce^{3+} by adding of K_2CO_3 solution to the mixed of $\text{Co}_2(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3$ solutions at room temperature. The prepared catalysts are referred to as CoCe_x (x indicates the molar ratio of Co/Ce) and pure oxides are

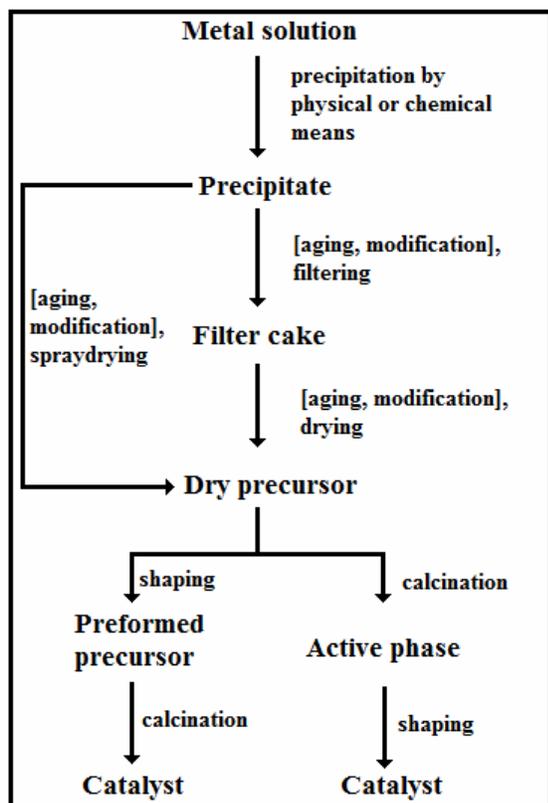


Fig. 8. Preparation scheme for precipitated catalysts.

referred to as Co_3O_4 and CeO_2 according to the XRD results [23]. They reported that a proper amount of CeO_2 could improve the reduction ability of Co^{3+} to Co^{2+} , especially when $x = 0.05$. Their obtained results also showed that the addition of CeO_2 to the cobalt spinel leads to an enhanced catalytic performance activity. Keyser *et al.* used co-precipitation method for synthesis of cobalt/manganese catalyst; according to their obtained results, the synthesis performance of co-precipitated Co/Mn catalyst in form of extrudates was successfully evaluated in fixed tubular reactor comparable with the industrial scale reactors [26]. Zirconia-supported cobalt catalysts were prepared by Chen *et al.* [29] using co-precipitation of mixed cobalt nitrate and zirconyl chloride with Na_2CO_3 solution. In the catalysts, the bulk Co/Zr ratio varied from 20 to 80%. We also used co-precipitation procedure for synthesis of different catalysts containing cobalt [30-41]. In all of our previous research

works, for synthesis of catalysts using co-precipitation method, different metallic solutions were prepared and then using the precipitate agent (Na_2CO_3) the precipitate was obtained. Then after suitable ageing time the obtained precipitate was filtered and washed several times with warm distilled water until no further Na^+ was observed in the filtrate [42]. The obtained precipitate was dried and calcined to obtain final catalyst. The schematic representation of catalyst preparation *via* co-precipitation procedure used in our research works is displayed in Fig. 9.

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. The further sol particles condensation into a three-dimensional network generates a gel. Alternatively, a gel can be generated by destabilizing a preformed sol solution. In either case the materials are referred to alcogel (or almagel) when alcohol is used as a solvent, and aquagel (or aquagel) when water is used. By either evaporative drying or drying with supercritical extraction the encapsulated liquid can be removed from a gel, the solid products are known as a xerogel or an aerogel, respectively. 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 10 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.

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:

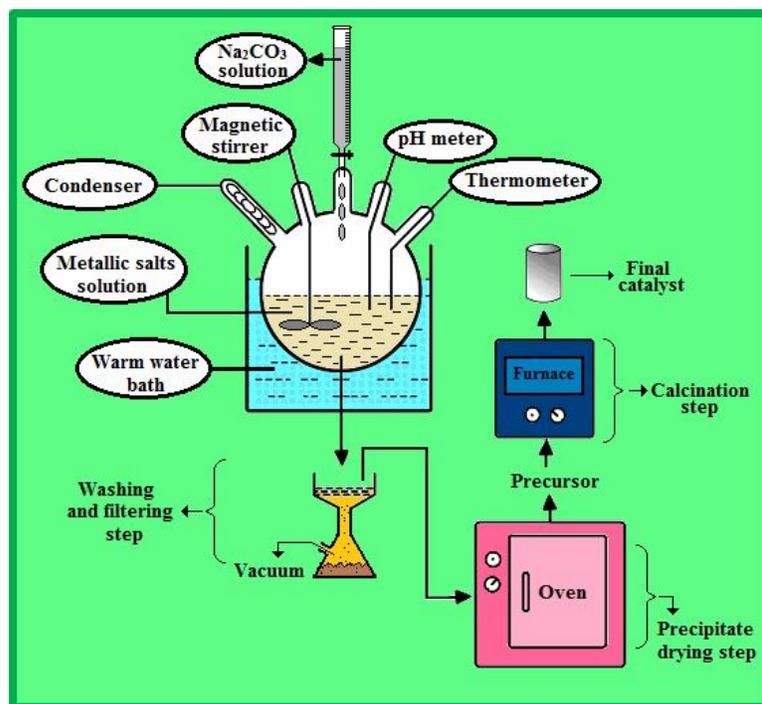


Fig. 9. Schematic representation of co-precipitation procedure.

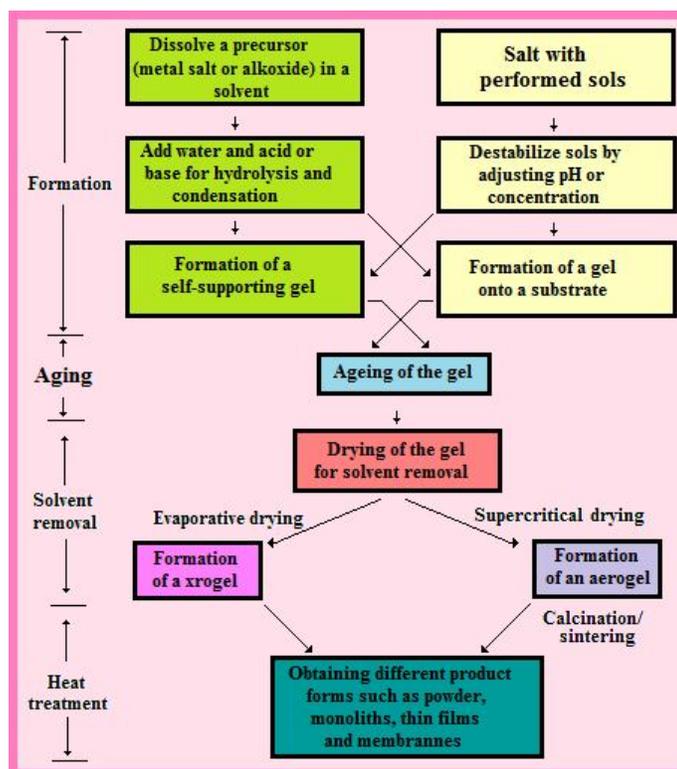
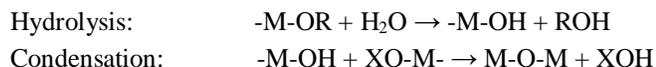


Fig. 10. Schematic diagram of various steps of sol-gel process.



where X can either be H or R (an alkyl group). Such a description oversimplifies the overall process because it does not correctly represent the molecular formulas of the intermediates and end products, nor does it depict the simultaneous occurrence of two reactions.

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. Most supercritical drying experiments have been done with alcohol because of its use as a solvent in the sol-gel step.

Calcination. After the removal of pure liquid, further heat treatment is necessary to convert a xerogel or aerogel into a catalytically useful form. 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. The process can also cause the material to crystallize into different structural forms. Thus, the physical characteristics of a product depend on parameters such as temperature, heating rate, time and gaseous environment. Guzzi *et al.* used sol-gel procedure in their research work for synthesis of Co-Re catalyst for CO hydrogenation [53]. In their research work, the required amount of $Co(NO_3)_3 \cdot 6H_2O$ and NH_4ReO_4 were dissolved in ethyleneglycol and ethanol

mixture at 80 °C; after stirring for 10 min, tetraethylorthosilicate was added to the solution and mixed at 80 °C for 3 h to give homogeneous transparent solution. Then $H_2O/EtOH$ mixture was added to the transparent solution and stirred at 110 °C for overnight to give transparent monolygthic gel. The gel dried at 140 °C in vacuum, produced and treated. The obtained results showed that reduction of the Co^{2+} ions in the sol/gel samples prepared by means of ethyleneglycol and hexyleneglycol, as gelatin agents, could be facilitate indicated by TPR, XRD and TEM [53]. They also reported that in the CO hydrogenation over the sample the C_2-C_4 fraction are formed predominantly.

Madikizela *et al.* [54] used two approaches to the sol-gel method of preparing catalysts: (1) co-gelling all the catalyst components together and (2) a modified sol-gel method that involves preparation of the support using a traditional sol-gel method followed by impregnation of the sol-gel titania with metal oxide precursors. It has been reported that cobalt oxide species that were easy to reduce as well as cobalt-titanate species that were not easy to reduce are formed when the sol-gel method was combined with the incipient wetness method to make Co/TiO₂ catalysts. Reducibility studies showed that titania-supported cobalt catalyst promoted with 5 wt% zinc, calcined at 300 °C, reduced at lower temperature when zinc was impregnated before cobalt compared to that catalyst in which zinc impregnated after cobalt [54]. They also reported that the modified sol-gel prepared catalysts showed a very low activity and CO conversion (on a Co mass basis) in the FT synthesis compared to catalysts prepared by the incipient wetness method using Degussa titania as the support [54-56]. The sol-gel preparation method could be coupled with drying at supercritical conditions. Erying *et al.* [57] reported preparation of three cobalt catalysts supported by aerogel with cobalt loading varying from 2% to 10%. Transmission electron microscopy showed the presence of discrete cobalt metal particles of 50-70 nm for 2% and 6% loadings. The 10% Co catalyst exhibited long needles of cobalt. We also used sol-gel procedure for synthesis of different catalysts containing cobalt [40,58,59].

Impregnation Procedure

Impregnation is another preparation method that is most

often used for preparation of cobalt catalysts for FT synthesis [60-71]. The main characteristic of this preparation method is that the active phase and support (binder) are prepared separately. Incipient wetness impregnation is the most common method to prepare cobalt-supported catalysts. In this method a solution of cobalt salt, typically cobalt nitrate, is contacted with a dry porous support. After being contacted, the solution is aspirated by the capillary forces inside the pores of the support. The incipient wetness occurs when all pores of the support are filled with the liquid and there is no excess moisture over and above the liquid required to fill the pores. Reproducible synthesis of cobalt catalyst requires careful control of all impregnation parameters: temperature and time of support drying, rate of addition of impregnating solution, temperature and time of drying, *etc.* [72]. Girardon *et al.* [65] prepared cobalt catalyst via incipient wetness impregnation with aqueous solutions of cobalt nitrate or cobalt acetate. Cab-osil M-5 fumed silica was used as a catalytic support. Before impregnation Cab-osil M-5 was agglomerated by wetting and dried at 373 K. The concentrations of the impregnating solutions were calculated to obtain 10% cobalt in the final catalysts. After impregnation the catalysts were dried overnight in an oven at 363 K. After oxidative pretreatment the catalysts were reduced in a flow of hydrogen at 673 K for 5 h. They reported that the concentration of amorphous cobalt silicate can be minimized by the efficient control of the heat flow at the stage of cobalt acetate decomposition. Endothermic decomposition of cobalt nitrate at relatively lower temperatures leads to higher cobalt dispersion but decreases cobalt reducibility. The FT reaction rates were found to be a function of the number of cobalt metal sites; a higher concentration of cobalt metal sites in the catalysts prepared *via* soft decomposition of cobalt nitrate results in the most catalytic activity. It was shown that low-temperature decomposition of cobalt acetate, which increased the concentration of cobalt metal surface sites, could significantly enhance the FT catalytic performance [65]. Spadaro *et al.* also used impregnation procedure for preparation of Co-Ce catalyst [68]. In this research work, incipient wetness catalysts were prepared by the stepwise addition of a $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution to a powder CeO_2 sample obtained by the combustion method. They

investigated the physicochemical properties of low-loaded Co/ CeO_2 catalysts and the effect of preparation method and Co loading on the structure, dispersion and catalytic behavior in the FT synthesis reaction assessed. They have found that the preparation method markedly affects the structure, reducibility and dispersion of Co/ CeO_2 catalyst and the performance of Co/ CeO_2 catalysts in the FT synthesis depend on the dispersion of the active phase and Co- CeO_2 metal-support interactions. They have also reported that a synergistic role of Co and CeO_2 matrix in the chemisorptions of reactant molecules controls the reactivity of the title system in the FT synthesis reaction [68]. Zhang *et al.* [73] found that pretreatment of silica with acetic acid, 1-propanol prior to impregnation resulted in higher cobalt dispersion and better activity in FT reaction. It was found that pretreatment by organic solvent has modified the surface properties of silica, enhancing simultaneously cobalt dispersion and reducibility. Pretreatment of alumina with ammonia, ammonium nitrate, acetic acid and ethanol prior to impregnation also affects the texture, acidity of the support and catalytic performance of the final catalysts [74]. The number of acid sites decreased in the ammonia and ammonium-nitrate-treated alumina, while in the acetic acid-treated-alumina, the concentration of acid sites increased. Higher carbon monoxide conversion and C_5^+ selectivity were observed on less acid ammonia and ammonium-nitrate-treated catalysts. Initial pretreatment of alumina and titania by TEOS was reported to reduce formation of inactive mixed oxide species [75]. We also used impregnation procedure for preparation of Co-Fe-Mn supported catalyst [40].

The MgO support was first calcined at 600 °C in flowing air for 6h before impregnation. For Fe-Co-Mn/90 wt% MgO catalyst, calculated amounts of iron nitrate, cobalt nitrate and manganese nitrate were dissolved in distillate water and directly impregnated into the MgO support using incipient wetness. The obtained suspension was then rotated and aged for 3 h in a rota-evaporator at 60 °C. The aged suspension was then filtered, followed by drying at 120 °C for 16 h to give a catalyst precursor. In order to obtain the final calcined catalyst, the precursor was then calcined at 600 °C for 6 h in static air to obtain the final catalyst.

We used these different preparation methods for

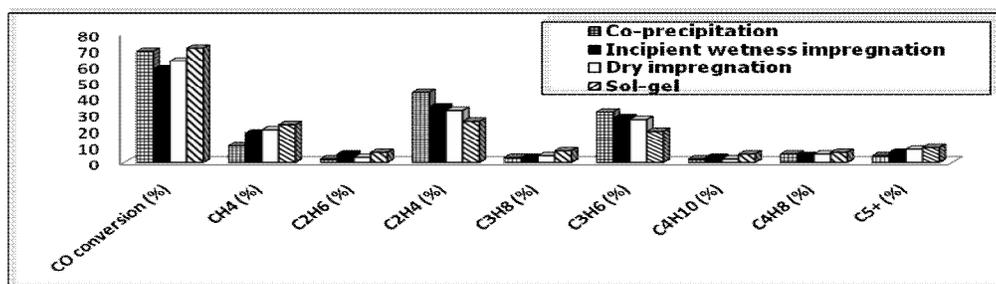


Fig. 11. Effect of preparation method on the catalytic performance.

synthesis of Fe-Co-Mn catalyst in our previous research work [40]. Then all of these catalysts were tested under the same operational conditions for CO hydrogenation *via* FT synthesis. The obtained results are presented in Fig. 11. As can be seen, preparation method affects the catalytic performance and these samples have different CO conversion and product selectivities and the co-precipitated catalyst has shown the best catalytic performance for production of C₂-C₄ light olefins.

MAIN PART OF THE CATALYSTS

Although some catalytic materials are composed of single substances, most catalysts have three types of easily distinguishable components: (1) active component, (2) a support or carrier and (3) promoters. Active components are responsible for the principal chemical reaction. The active metals for FT synthesis were discussed in details in section 1.5.

Support Effect

Support, or carrier, perform many functions, but most important is maintenance of high surface area for the active component. Supports function as stable surfaces over which, the active component is dispersed in such a way that sintering is reduced. The support itself must be secure from thermal growth, which means high melting point at least higher than that of the active component. Porosity is necessary for high surface area within the pellet, but pore shape and size distribution are critical secondary factors when diffusion resistance is present [76]. The best supports are those that are easily manipulated to produce optimum

texture properties. The most direct influence of the support is on dispersion and morphology [72,77]. Both the structure and performance of cobalt catalysts depend on the support. The principal function of the catalyst support is to disperse cobalt and produce stable cobalt metal particles in the catalysts after reduction. The porous structure of the support could control the size of the supported cobalt particles. On the other hand, FT synthesis is an exothermic reaction and supports also dissipate the heat released by FT reaction and thus reduce a temperature gradient in fixed bed reactors. Support could also affect the structure and electronic properties of small cobalt metal particles.

The choice of the support for making light olefins *via* CO hydrogenation is dictated by several factors including basicity, dispersion effect, electronic modification and strong-metal support interaction (SMSI) [13]. Al₂O₃, SiO₂, TiO₂, MgO, zirconia and carbon are widely used as supports in FT synthesis. Banchi *et al.* [78] studied the FT synthesis over the Co/SiO₂ catalyst prepared by the sol-gel procedure. They were observed an excellent correlation between characterization data and catalytic performance of the Co/SiO₂ catalyst and good conversion were obtained for 10 and 30wt% Co. Saib *et al.* [79] showed that the catalyst supported by silica with an average pore diameter of 10 nm was most active and selective for hydrocarbons. Jacobs *et al.* [80] were investigated the effect of different supports on the reducibility and catalytic performance of cobalt catalyst for FT synthesis. It was found that from an initial catalytic activity standpoint, the number of available sites on the Co surface is directly proportional to the amount of H₂ desorbed per gram of catalyst. Therefore, Although Al₂O₃ catalysts are more difficult to reduce, the net results is that

the availability of surface sites after reduction at 623K is still much higher than that for the SiO₂ and TiO₂ supported catalysts. Xiong *et al.* [81] reported a significant effect of alumina porosity on the structure of supported cobalt catalysts and their performance in FT synthesis. The alumina carrier was calcined at different temperatures to obtain a support with different pore sizes. It has been reported that cobalt oxide strongly interacts with the alumina support, forming relatively small cobalt crystallites [72]. Zhang *et al.* [82] investigated the effect of magnesia on the catalytic performance of alumina supported cobalt catalyst for FT synthesis. It was found that the formation of a cobalt surface phase, which strongly interacts with the alumina support, can be effectively suppressed by modification of a small amount of magnesia. Large amounts of magnesia restrained the reduction of the catalysts due to the formation of MgO-CoO solid solution. Xiong *et al.* [83] studied the effect of zirconia loading on the catalytic performance of Co/Al₂O₃ catalyst for FT synthesis. It was found that increasing zirconium loading effectively inhibited the formation of CoAl₂O₄ phase on the catalyst. It gave rise to the increase of Co metal active sites and reducibility, leading to the increase of CO hydrogenation activity and C₅⁺ selectivity for FT synthesis.

Promoter Effect

A promoter is the third agent which when added, often in small amounts, results in desirable activity, selectivity or stability effects [84]. It is commonly accepted that promoters may persuade these useful effects in several ways. All this has led researchers to come up with an assortment design for promoter effects and the following names have been given to the various promoters in the Co FT research works: electronic promoters, textural promoters, structural or structural promoters, stabilizers and catalyst-poison-resistant promoters. It is sometimes difficult to precisely define the observed function of a promoter since many of the above-mentioned effects tend to overlap in practice. Furthermore, the degree to which additives improve a catalyst's performance in the positive or negative way is also dependent on the amount of the additive, the support oxide under consideration and the accurate preparation procedure, causing them to act either as a promoter or a poison. In line with this reasoning, the term

modifier should be more appropriate according to Paal and Somorjai [85]. Numerous studies have shown that introduction of noble metal (Ru, Rh, Pt and Pd) has a strong impact on the structure and dispersion of cobalt species, FT reaction rates, and selectivities. Introduction of noble metals could result in the following phenomena: much easier reduction of cobalt oxide particles, formation of bimetallic particles and alloy, a lower fraction of barely reducible mixed oxides, enhancement in cobalt dispersion, inhibition of catalyst deactivation, appearance of additional sites of hydrogen activation and an increase in the intrinsic reactivity of surface sites.

Zhang *et al.* [86] investigated the effects of Pt and Ru on the carbon nanotube supported cobalt catalysts for FTS. Their obtained results showed that promotion with 0.2wt% of Pt and Ru resulted in a significantly enhanced cobalt reduction. They also found that for Pt and Ru promoted carbon nanotube-supported cobalt catalyst, the reduction temperature of cobalt oxide species shift to lower temperatures and the reducibility of the catalyst improved significantly. It was found that addition of small amount of Pt and Ru resulted in an increase in C₅⁺ hydrocarbon selectivity. Jalama *et al.* [87] studied the effect of the addition of Au on the Co/TiO₂ catalyst for FT synthesis, they were found that the increase of Au content in the catalyst improved the Co dispersion and consequently the catalytic activity in the FT reaction. They also reported that further increase of Au loading above 1wt% for the Co/TiO₂ catalyst leads to an increase in methane selectivity, believed to be due to a WGS reaction catalyzed by Au particles in the catalysts. Xiaoping *et al.* [88] were studied the role of CeO₂ promoter in Co/SiO₂ catalyst for FT synthesis, their obtained results showed that the addition of a small amount of CeO₂ inhibited the reduction of Co₃O₄ and decreased the particle size and the electron density of the cobalt atom. The results indicated that CeO₂ also improved the dispersion of cobalt, the adsorption and dissociation of H₂ and the amount of active sites on the catalyst surface; this is because of the partial reduction of CeO₂ to CeO_{2-x} during FT synthesis. Ma *et al.* [89] investigated the effect of promoters on the catalytic performance of Fe-Co/SiO₂ catalyst for FT synthesis; they were found that Zr promoter caused weaker metal-metal and metal-support interactions, which made the catalyst easily be reduced and improved the catalytic

properties. Their obtained results showed that low K loadings enhanced the activity of the Fe-Co/SiO₂ catalysts and high potassium loading led to stronger metal-metal interactions, which made the reduction of the catalysts harder and increased the secondary hydrogenations. Tsubaki *et al.* [90,91] found that addition of small amount of Ru to cobalt catalysts remarkably increased the extent of cobalt reduction, whereas modification with Pt and Pd did not have any effect on cobalt reducibility. Pt and Pd were found to promote mostly cobalt dispersion. The cobalt catalysts promoted with noble metals displayed the following order of FT catalytic activity: CoRu > CoPd > CoPt > Co [72]. Pd and Pt-containing samples also showed higher methane selectivity than Co and CoRu samples.

We investigated the effect of different supports and promoters on the catalytic performance and structure of different catalysts for FT synthesis in our previous research works [34-36,41]. The obtained results showed that different supports and promoters affect the structural properties of the catalysts and consequently affect the catalytic performance (CO conversion and products selectivities).

OPERATIONAL PARAMETERS

One of the main factors with a marked 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 [92]. A weak cobalt support interaction in silica-supported catalysts promotes high cobalt reducibility. Minimization of the concentration of barely reducible cobalt silicate and maximization of cobalt-metal dispersion would therefore result in a better catalytic performance. Previous reports

[93-95] have shown that cobalt metal dispersion in the final catalysts is usually affected by Co₃O₄ dispersion in the oxidized catalyst precursors. It has been reported that catalyst porosity is one of the properties needed for the design of FT catalysts with a desired metal dispersion [96-99] 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. Larger and easier reducible cobalt particles are detected in wider pore support. Girardon *et al.* [100] studied the effect of cobalt precursor and pretreatment conditions on the structure and catalytic performance of Co/SiO₂ catalyst for FT synthesis. Their obtained results showed that the cobalt precursor and its pretreatment conditions strongly influenced both the structure of supported cobalt species and their catalytic behavior in FT synthesis. Depending on the pretreatment conditions and the exothermicity of cobalt precursor decomposition, supported cobalt ions either agglomerate into Co₃O₄ crystallites or react with silica, yielding amorphous cobalt silicate. The endothermicity of cobalt nitrate decomposition favors Co₃O₄ crystallites, whereas the exothermicity of cobalt acetate decomposition leads to barely reducible cobalt silicate. Endothermic decomposition of cobalt nitrate at relatively lower temperatures leads to higher cobalt dispersion but decrease cobalt reducibility [100]. Jongsomjit *et al.* [101] found that the addition of CO during standard H₂ reduction of Co/Al₂O₃ catalyst produced specific activities about four times greater than when the catalyst reduced without CO addition. Apparently, most of this increase due to the increase in Co reducibility and dispersion. Duvenhage *et al.* [102] reported that the reduction temperature of Fe:Co/TiO₂ catalyst influenced the FT activity and selectivity and a low reduction temperature (250 °C) resulted in a highly dispersed and difficult to reduce catalyst. A high reduction temperature (400 °C) generated a catalyst with low dispersion and high reducibility, but poor activity. The higher reduction temperature generated catalysts with lower BET surface area and increased surface Fe content.

Experimental Conditions

Conventional FT catalyst screening consists of comparing the catalytic performance at the same

experimental conditions (temperature, pressure, space velocity and amount of catalyst or active phase). 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 [103]. The choice of the operating conditions and reactor represents the major challenge of FT catalyst screening. The catalyst specifications and operating conditions govern the composition of the products; a number of review papers are available on various aspects of FT synthesis in the literature [3,104-108]. The main experimental conditions are listed below.

A) H₂/CO feed ratio. It is well known that the H₂/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, where one product may preponderate at lower temperature (kinetically controlled) and another prevails at higher temperature (thermodynamically controlled). The reaction temperature also has an efficacious effect on the CO conversion and catalytic performance of the catalysts. 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_a/R). The effect of temperature on the rate constant is studied by the authors [39] and the obtained results are presented in Table 1 and Fig. 12. The logarithm of the reaction rate constant (k) as a function of the reverse of temperature gives a straight line with negative slope (-E_a/R).

In general, the FT reaction temperature for production of C₂-C₄ light olefins preferably should not be too low or too high. At high temperature the selectivities of CH₄ and CO₂ (as unwanted products), were enhanced, as well as the formation of large amount of coke (another unwanted product) [39]. On the other hand, lower temperature is preferential for chain growth and the production of heavy hydrocarbons [39].

C) Reaction 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. These differences could be interpreted in terms of different concentrations of reagents in gaseous and liquid phases, catalyst restructuring and deactivation. In commercial process, the FT synthesis reaction usually operates under high 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 [97]. A different composition of the liquid phase in catalyst pores at high synthesis gas pressures could affect the rate of elementary steps and carbon monoxide and hydrocarbon concentrations. Malek abbaslou *et al.* [109], reported that the CO conversion increases significantly with increasing reaction temperature. Methane and CO₂ 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 CH₄ and CO₂ production. Temperature also affects product distributions shifting toward lower molecular weight hydrocarbons [110,111]. The average 1-olefin content of the products may double with 10 °C decrease in the reaction temperature. It seems that hydrogenation is intensified with temperature. Besides, a higher temperature results in higher rates of the secondary reactions such as isomerization, hydrogenation and re-adsorption of the 1-olefins [112]. Sun *et al.* [113] indicated that the FT synthesis catalyst activity can be increased at high temperature, but selectivities of unfavorable products such as CH₄ or CO₂ are also enhanced sharply. So, catalysts showing high activity at low temperature are needed.

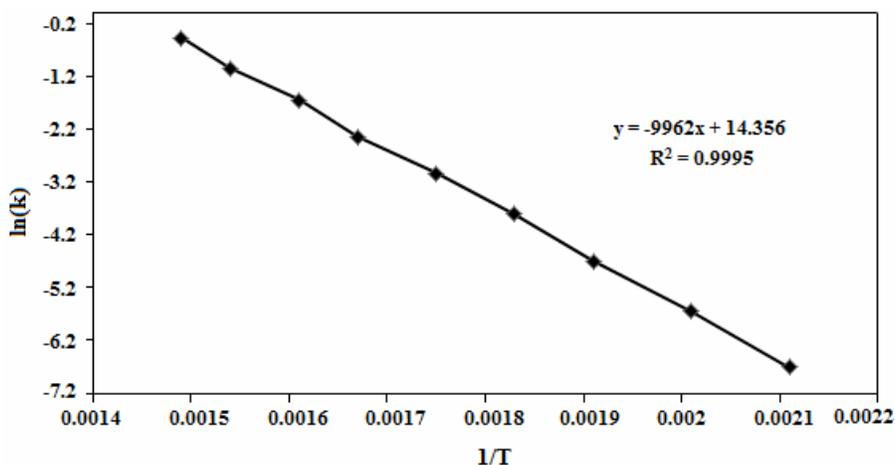


Fig. 12. Arrhenius plot of rate constant (k) using, reaction conditions $T = 473$ - 673 K, $P = 1$ bar, $H_2/CO = 2/1$ and $GHSV = 4500$ h^{-1} .

Table 1. The Values of Rate Constant at Different Temperatures

Parameter	Value ($mmol\ min^{-1}\ g^{-1}$)
$K_{(473)}$	0.00123
$K_{(498)}$	0.00352
$K_{(523)}$	0.00912
$K_{(548)}$	0.02240
$K_{(573)}$	0.04810
$K_{(598)}$	0.09601
$K_{(623)}$	0.19210
$K_{(648)}$	0.035211
$K_{(673)}$	0.062423

Malek abbaslou *et al.* [109] also reported that when the pressure is increased beyond a certain point, the syngas conversion begins to decrease with further increase in the pressure. This is due to significant decrease in bulk diffusivity at high pressures. Beyond an optimal pressure, the negative influence of decreasing bulk diffusivity outweighs the positive enhancement in heavy products extractability and longer syngas contact time at high pressures [114]. The olefin selectivity at a given carbon number increases with pressure up to a certain pressure. For

example, Bochniak and Subramaniam [115] have reported that in the case of hexane, density becomes less sensitive to the pressure beyond 5.5 MPa. It seems that higher desorption of α -olefins at higher pressure inhibits reactions such as hydrogenation and/or polymerization resulting in higher olefin selectivities. Elbashir and Roberts [114] have addressed the effect of reaction pressure on chain growth probability (α -value). No significant effect of pressure on α -value is observed within the studied pressure range, except a slight decrease at 8.0 MPa. It has been reported that the

effect of pressure on the product distribution is more pronounced at high reaction temperature than that at low reaction temperature [111]. They suggested that the influence of temperature or pressure on the reaction behavior should not only be taken into consideration independently but also through their impact on the phase behavior of the reaction medium.

Bremaund *et al.* [116] studied the influence of syngas composition on the transient behavior of Co/Al₂O₃ 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. The deactivation is probably due to reoxidation of cobalt particles by water.

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. According to the obtained results of our research work [41] on the Fe-Co-Mn/MgO catalyst, the best operational conditions for production of C₂-C₄ light olefins were found to be T=300°C, P = 1 bar, H₂/CO = 2/1 and GHSV = 4500 h⁻¹. In the same investigation on the Co-Ce/SiO₂ catalyst [35], it was found that the optimize reaction conditions were found to be T = 450 °C, P = 1 bar and H₂/CO = 2/1 for production of light olefins.

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 [117]. 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. Bartholomew reviewed the mechanisms of catalysts deactivation, which were classified into six types:

Poisoning, fouling, sintering, vapor compound formation accompanied by transport, attrition/crushing and vapor-solid or solid-solid reaction [118]. The FT catalysts are usually very sensitive to poisoning, and purification of the synthesis gas is therefore an important part of the process, particularly for processes using coal and biomass as feedstocks [119]. The loss of activity is also related to process conditions such as temperature, pressure, conversion, partial pressures of synthesis gas and steam and the type of reactor (fixed-bed or slurry). Hence, reproduction of a realistic FT environment in deactivation studies is fundamental. The deactivation behaviors of Co catalysts were mainly due to the following reasons: oxidation of metal cobalt, metal migration into the support lattice resulting in the formation of the inactive FT compound (*e.g.* silicate, aluminate and titanate) the aggregation and growth of metal cobalt on the surface of catalyst and the loss of metal cobalt because of attrition (especially for the three-phase slurry bed reactor) [120]. On the other hand, FT synthesis is exothermic reaction and because of hotspot formation on the catalyst surface [121], carbon will be formed, which may damage the structural integrity of the catalyst, and the desirable selectivity can be decreased during the reaction. This is a common issue in the FT synthesis and in this purpose a slurry phase reactor can be effective at low reaction temperature for the inhibition of hot spot formation due to the good mixing and thermal removal [122,123]. Nurunnabi *et al.* [124] studied the effect of Mn addition on activity and resistance to catalyst deactivation for FT synthesis. Their obtained results showed that: (1) In the slurry phase FT reaction under pressurized conditions, low reaction temperature such as 493 K over Ru/c-Al₂O₃ showed high CO conversion, C₅⁺ selectivity and low CH₄ selectivity and compared to 513 and 533 K.

(2) Ru/Mn/γ-Al₂O₃ catalyst exhibited excellent catalytic activity and resistance to catalyst deactivation, while Ru/γ-Al₂O₃ was deactivated with time on stream. This can be related to the effect of Mn addition to the support due to the increase of the density of Ru active atoms on the surface. The variation in the catalytic activity during CO and CO₂ hydrogenations for synthesizing the heavy hydrocarbons has been studied as well [125,126]. Liu *et al.* [127] reported the co-feeding effects of carbon dioxide with CO on FT synthesis on iron-manganese based catalyst. They reported

Table 2. Catalytic Performance of Co/ γ -Al₂O₃ Catalyst (Reaction Conditions: P = 20 bar, T = 220 °C, SV = 2000 L/kg_{cat}/h and H₂/CO = 2) [129]

CO ₂ Conc.(%)	Time on stream (h)	CO conversion (C-mol %)	Selectivity (mol %)		
			C ₁	C ₂ -C ₄	C ₅ ⁺
0	15	61.1	10.8	11.8	77.4
	30	54.8	12.2	12.1	75.7
	45	46.4	17.6	13.7	68.7
	60	41.3	19.6	15.6	64.8
20	15	60.9	10.0	10.9	79.1
	30	55.4	13.0	11.8	75.2
	45	39.1	21.9	13.6	64.5
	60	34.6	22.6	13.6	63.8

that co-feeding of CO₂ during FT synthesis showed a little effect on catalytic activity. Studying FT synthesis on cobalt-based catalysts, Schaub *et al.* [128] reported that CO₂ contained in syngas is preferentially removed to reduce the reactor size especially for the operation of SBCR (slurry bubble column reactor). They also reported that CO₂ acts as an inert gas on cobalt-based catalysts, and it has a negative effect on reaction rate leading to deactivation of Co-La-Ru-SiO₂ catalyst. Kim *et al.* [129] studied the effect of CO₂ in the feed stream on the deactivation of Co/ γ -Al₂O₃ for FTS. Their obtained results showed that the presence of CO₂ in the feed gas affects the rate catalytic hydrogenation of CO as well as products distribution. CO₂ behaves as a mild oxidizing agent on reduced Co/ γ -Al₂O₃ under the reaction temperature at 220 °C and 20 bar. The decrease of CO conversion and C₅⁺ selectivity with CO₂ addition is found during FT synthesis reaction. The decreased catalytic activity and C₅⁺ selectivity are attributed to the partial surface oxidation of cobalt metal by CO₂ exposure. The product distributions on Co/ γ -Al₂O₃ catalyst at selected time intervals are presented in Table 2. As it is seen, the selectivity of CH₄ increased with increasing time on stream under both reaction conditions, with and without CO₂ addition, with decreased selectivity to C₅⁺ until 30 h on stream. The selectivities of C₅⁺ are similar for both reaction conditions. However, from 45 h on stream, the selectivity of C₅⁺ has abruptly decreased with the concomitant decrease in

CO conversion [129].

Iglesia has stated that small crystallites appear to be less active for CO hydrogenation than larger crystals [130]. This was attributed to stronger support interactions, reflected in the incomplete reduction of CoO and even the re-oxidation of Co metal by water formed in the FT synthesis. It has also been suggested that crystallites of 5-6 nm may re-oxidize and deactivate rapidly in the presence of water at typical FT synthesis conditions. The formation of mixed metal-support compounds is known to occur already during the preparation of the catalyst. Calcination and reduction are the steps with high potential for mixed oxide formation [131]. The metal loading is also a critical parameter in metal-support compound formation. Higher diffusion of cobalt ions into the support lattice has been observed for lower loadings. Other parameters such as the pH of the impregnating solution during catalyst preparation may be significant [132]. It has been suggested that promoters, *e.g.* Re, may play an important role in obstructing the diffusion of cobalt into the support by occupying the defect sites of the alumina where the diffusion takes place [133]. A magnesium promoter was incorporated to inhibit the effect [134,135]. Sintering has already been proposed as a reason for FT catalyst deactivation by Fischer and Tropsch. Since the early works by Fischer and Tropsch, many reports have linked deactivation with sintering as described below. Sintering of cobalt crystallites may be accelerated in the

presence of water [136]. A number of studies related to the effect of water in the catalyst deactivation of FT synthesis, suggest sintering of cobalt crystallites as one of the main deactivation mechanisms. Bertole *et al.* investigated the effect of water using a rhenium promoted unsupported cobalt catalyst [137]. They showed that the periodic addition of water at 210 °C and high partial pressures (4 and 8 bar) resulted in a permanent loss of activity (starting conditions 10 bar H₂, 5 bar CO, 8 bar inert and ~11% CO conversion). A subsequent hydrogen treatment recovered only 80% of the activity. The CO adsorption capability of the catalyst was reduced which supports the hypothesis of loss of active surface area due to sintering of cobalt crystals.

High temperature is the main other factor leading to sintering phenomenon. FT synthesis is a highly exothermic reaction and the potential for sintering is therefore relatively high. Special attention should therefore be given to the choice of reactor, since isothermal conditions are important. Fixed-bed reactors have poor heat transfer rates and hot spots may arise during operation [138]. However, with proper design and the use of multi-tubular fixed-bed reactors these limitations can be overcome [139]. Slurry reactors have the advantage of isothermal conditions due to a higher heat transfer coefficient [140].

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 H₂/CO ratio) are the main parameters which control the structure, properties and catalytic performance of cobalt catalysts. Along with optimizing this parameters the CO conversion and selectivity toward desired products are improved. These optimizing conditions

depend to the catalyst structure and different additives (promoters and supports), preparation methods and conditions. First objective of any catalyst preparation is to generate the optimal number of active sites and the goal of FT catalyst preparation is to generate a significant concentration of stable cobalt metal sites depends on the size of cobalt particles and their reducibility. 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 fraction.

The present review discusses about the main FT catalyst preparation procedure, different supports and promoters effects, operational conditions and Co catalysts deactivation.

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