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# **Zeolites as Potential Structures in Obtaining Jet Fuel Through the Fischer-Tropsch Synthesis**

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Additional information is available at the end of the chapter

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## **Abstract**

Due to the constant expansion of the aviation sector, the global air industry has performed the search for alternative fuels to petroleum-derived aviation kerosene, which present low emission of greenhouse gases and other pollutants, in addition to supplying the engines and aircraft already in operation using the existing distribution infrastructure. Thus, one alternative that has been studied is the synthetic kerosene derived from gasification processes followed by Fischer-Tropsch synthesis. Several features seem to be crucial in controlling product selectivity in the aviation fuel range, among them are the zeolitic support, acidity, and promoters. Therefore, the effect of these parameters in the Fischer-Tropsch synthesis is discussed in this chapter and, finally, the zeolitic catalysts that, according to the literature, have significant potential in obtaining synthetic aviation fuel are evidenced.

**Keywords:** zeolites, aviation kerosene, Fischer-Tropsch synthesis, acidity, promoters

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## **1. Introduction**

The air transport sector, due to constant expansion, is being pressured to reduce their CO<sub>2</sub> emissions, since aviation is responsible for 10% of the emissions in transport sector. In addition, because of the prospects for growth in this sector, there is evidence of a further increase in CO<sub>2</sub> emissions in the coming years [1]. For this reason, the airlines associated with

the International Air Transport Association (IATA) pledged to improve fuel efficiency by 1.5% annually to 2020, cap net emissions from 2020 with carbon-neutral growth and cut net emissions in half by 2050 compared to 2005 [2]. Such obligations, in the future, may limit the civil aviation market and stimulate the search for alternatives. However, the demand for fuels tends to expand, since the passenger demand will be more than doubling from 3.3 to 7.3 billion by 2034 [3], even with the possible gains in energy efficiency (estimated between 30 and 50%), from improved aerodynamics, reducing the weight of the aircraft, the advances in technology of thrusters, and the adoption of best practices in air traffic management [4].

In fact, historically, since the first aircraft was manufactured, the airline industry has been trying to decrease the fuel consumption through the improvement of technologies used. Although there is a decrease in emissions over the years, due to new technologies employed, the speed of which can perform this benefit is compromised by the fact that airlines maintain their assets in use for about 40 years, due to the high investment cost. Thus, the new technologies have to wait until the fleet is replaced [5].

In this context, the global air industry has performed the search for alternative fuels to petroleum-derived aviation kerosene, which present low emission of greenhouse gases and other pollutants, in addition to supplying the engines and aircraft already in operation using the existing distribution infrastructure [6]. Therefore, one alternative that has been studied is the synthetic kerosene derived from gasification processes followed by Fischer-Tropsch synthesis (FTS). In this synthesis route, the raw material (coal, natural gas, or biomass) is transformed into syngas, a mixture of carbon monoxide and hydrogen, which is converted by means of a metal catalyst on FTS, forming hydrocarbons of different sizes. The final step is the processing and fractionation of products to produce a fuel with appropriate properties to be used in the airline industry [7].

The literature shows that the structure of the support used in the catalyst can be one of the key features in obtaining products in the aviation fuel range. When the catalytic reaction occurs within the pores of a zeolite, the size and shape of the canals and cavities can be used to select the desired reaction path, making use of "restricted transition state selectivity" or, also, through the "product selectivity." In the first case, the reaction intermediates and/or transition states are sterically limited due to the shape and size of the microporous lattice [8]. In the second case, the product selectivity refers to discrete diffusivities of the reaction products formed with respect to the microporous architecture and crystal size of the catalyst particles. If the molecules formed are very large compared to the pore size, the product diffusion may not occur, be extremely slow, or be completed after the occurrence of secondary reactions, such as cracking and isomerization, among others [8, 9]. In this way, specific structures with unique characteristics can direct the formation of products with particular chain length.

Another feature that seems to be crucial in controlling product selectivity is the acidity. The acid sites of the zeolites can promote cracking, isomerization and aromatization reactions. This property can help in overcoming the limitation of Anderson-Schulz-Flory (ASF) distribution and adjustment of the Fischer-Tropsch products in a specific distribution [10]. This can also reduce the need for subsequent treatments to Fischer-Tropsch synthesis, which could lead to a significant reduction in process costs [11].

Finally, one must take into consideration the use of specific promoters, which can provide desirable characteristics to the catalysts, such as increasing the reaction rate and greater stability and selectivity of the hydrocarbons  $C_{5+}$  [12, 13]. The promoters may direct the formation of products at a particular chain length, especially when combined with a structure and a specific acidity [11, 14].

However, despite the wide literature directing the production of synthetic fuels, there is still much to be studied on the aviation kerosene, since the vast majority of articles have focused on the production of gasoline and/or diesel [15–18], or simply the formation of products in the range of liquid hydrocarbons  $C_{5+}$  [13, 19–23]. For this reason, the main objective of this chapter is to analyze zeolitic structures studied in the literature, besides the influence of acidity and promoters, which have significant potential in obtaining fuel in the range of aviation kerosene (C8–C16) through the Fischer-Tropsch synthesis.

## 2. Conventional aviation fuel

The petroleum refining occurs through a process of fractional distillation, in which crude oil is heated and its different components come boiling at various temperatures, and later being condensed. Therefore, specific components are retrieved in different temperature ranges.

The lowest boiling fraction, taken from the top of the distillation column, is called naphtha, which is mainly processed further to make motor gasoline. The second fraction of about 33% of the crude oil input contains the raw material for jet fuel production. This fraction is further processed in the distillate hydrotreater to obtain the desired products. Basically, kerosene is originated as a straight-run (distilled) petroleum fraction with boiling temperature ranging from 205 to 260°C [24]. Subsequent fractions correspond to components in the range of diesel fuel and residues, and the latter can be distilled under vacuum, yielding high-value distillate components [25].

The petroleum processing through fractional distillation is still the dominant technology in the production of aviation kerosene; besides, this fuel accounts for 6.3% of the total amount of crude oil consumed [24]. However, the large fluctuations in the price of petroleum, the concern about the pollutants emitted, and the increase in passenger demand show a strong incentive for the airline industry to invest in alternative sources of fuel.

## 3. Synthetic aviation fuel

The airline industry bet on fuels that are chemically indistinguishable from conventional fuel and can be mixed in order to provide similar performance and security, without change in the aircraft systems and engines or on distribution and storage infrastructure. One of the most promising alternative processes for obtaining aviation kerosene is the Fischer-Tropsch process.

Currently, Semi-Synthetic Jet Fuel (SSJF) obtained by Fischer-Tropsch process and hydroprocessing, mixed with JET-A1, is already approved by ASTM D7655, limited to 50% proportion.

One of the reasons that the SSJF fuel cannot be used without restriction in civil aviation, especially those derived from natural gas or biomass, is the fact that these products do not present aromatic hydrocarbons, not answering, so, to the specifications imposed by the existing standard (minimum of 8% aromatics) [26].

The lack of aromatic components in the fuel results in higher freezing points and lower densities. The freeze point of a fuel composition is an important factor in determining whether it is suitable for aviation use, for which low-temperature conditions are experienced at high altitudes. Therefore, it is vital that the fuel composition does not freeze or cause flow to be restricted during operation; otherwise, the consequences could be disastrous [27]. In addition, the deficiency of aromatics in aviation kerosene can also cause shrinking of elastomers present in the storage and distribution system, which can lead to fuel leaks [28].

One of the advantages of using semi-synthetic kerosene is cleaner burning, since there is a lower emission of sulfur compounds [28], leading to an increase in the useful life of the combustor and turbine. Moreover, the emission of particulate compounds is lower compared to conventional fuel [24]. Therefore, the synthetic fuel blend with the conventional allows aggregating the advantages of synthetic fuel, while it is appropriate in relation to pre-established standards.

Currently, there is also the Fully Synthetic Jet Fuel (FSJF). The SASOL was the first and only one to produce this type of fuel for unrestricted use in civil aviation, from 2008, proving that the fuel produced behaved as the conventional in all aspects of storage, handling, and flight performance [7].

Coal-derived fuels are rich in naphthene compounds [29]. Due to the historic necessity by SASOL to produce diesel and gasoline fuel from their coal reserves located in South Africa, the catalysts and operating conditions have a different focus than other plants currently online and/or being developed [7]. This fact probably contributed to the success in obtaining the Fully Synthetic Jet Fuel from the Fischer-Tropsch synthesis.

The process consists of a mixture of five main blends, of which fractions of kerosene can be obtained. These blends come from the Fischer-Tropsch process or products generated in coal gasification. Therefore, the blend in greater amount is obtained from the Fischer-Tropsch process. The other four blends are obtained from heavy fractions of naphtha, commonly used in the production of gasoline, or light fractions of distillate, usually used in the production of diesel [7].

## **4. The Fischer-Tropsch synthesis**

### **4.1. The Fischer-Tropsch reaction**

The Fischer-Tropsch process has four main steps. The first stage corresponds to the production of synthesis gas, which is a mixture of hydrogen and carbon monoxide. In the second step, the removal of unwanted compounds and carbon dioxide from syngas occurs. The third step

corresponds to the Fischer-Tropsch reaction, in which the formation of hydrocarbons occurs. After this step, the products undergo treatments of hydrocracking and isomerization in order to acquire the necessary features to be used as fuel.

Among the products obtained in Fischer-Tropsch synthesis are the alkenes (olefins), alkanes (paraffins), and oxygenates (e.g., alcohols, aldehydes, carboxylic acids, and ketones), in addition to water [30]. The nature of oxygenated compounds is determined by the catalyst type and reaction conditions. The paraffins are generally straight chains, forming products in the range of gasoline, diesel oil, aviation kerosene, and waxes [31].

The temperature and reaction pressure are some of the most important parameters in the SFT to obtain products at a specific desired range. Currently, there are some well-defined conditions: the Low-Temperature Fischer-Tropsch (LTFT), the High-Temperature Fischer-Tropsch (HTFT), and pressures in the range of 10–40 bar. In LTFT process, iron or cobalt catalysts are typically used at approximately 230°C, yielding mainly products in the kerosene range, diesel, and waxes. In the HTFT process, iron catalysts are typically used at approximately 340°C, yielding mainly products in the range of gasoline and olefins [32]. These different behaviors occur because at elevated temperatures the reaction rate and quantity of secondary products increases, which leads to a reduction in the average chain length of the molecules, with a corresponding increase in methane formation [33].

On the operating pressure, the literature shows that the increase in the value of this parameter provides an increase in carbon monoxide conversion and C<sub>5+</sub> selectivity [11, 34–36]. The increased conversion of carbon monoxide is explained by the greater amount of C<sub>1</sub> intermediates, which increase the propagation rate [35]. In the same context, the increase in C<sub>5+</sub> selectivity occurs due to the higher concentration of syngas, leading to a higher propagation rate of the carbon monoxide polymerization reaction and, therefore, higher concentrations of long-chain hydrocarbons [37].

The overall reaction of Fischer-Tropsch synthesis is highly exothermic and is subject to limitation diffusional, which can affect the distribution of final products and lead to the deactivation of catalysts [38]. The overall reaction is represented below:



Secondary reactions, according to the literature [39, 40], are represented as

Paraffins

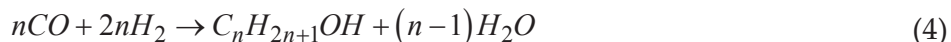


Olefins





## Alcohols



## Methane



## Water-gas shift reaction



## Coke deposition



## Boudouard reaction



The distribution of products in the Fischer-Tropsch synthesis follows the Anderson-Schulz-Flory distribution [41], which is expressed as follows:

$$W_{n/n} = (1 - \alpha)^2 \cdot \alpha^{(n-1)} \quad (9)$$

where  $W_{n/n}$  is the weight fraction of hydrocarbon molecules containing  $n$  carbon atoms, and  $\alpha$  the chain growth probability or the probability of molecule to continue reacting to form a longer chain.

The product selectivity is then determined by an ideal  $\alpha$  value. Smaller  $\alpha$  values are obtained when short-chain hydrocarbons are produced ( $C_1$ – $C_4$ ), while higher values of  $\alpha$  are obtained when heavier hydrocarbons are formed ( $C_{21+}$ ). Therefore, the Anderson-Schulz-Flory model is not selective for the hydrocarbon's intermediate range, which is in the vast majority of the cases the most desired products [42]. For example, according to the Anderson-Schulz-Flory model, the maximum product selectivity in gasoline range ( $C_5$ – $C_{11}$ ) and diesel ( $C_{10}$ – $C_{20}$ ) is approximately 45 and 35%, respectively.

According to Zhang et al. [42], the catalytic factors that exert greater influence in the activity and selectivity of catalytic in the FTS are the type of support, the promoters, and the active

phase and its size, chemical state, and microenvironment in which it inserts. Therefore, the development of selective catalysts, which can direct the formation of hydrocarbons in the desired range, is one of the biggest challenges in the synthesis of catalysts for Fischer-Tropsch synthesis.

#### 4.2. Influence of zeolitic support

The support structure used in the catalyst can be one of the key features in obtaining products in a specific range. When the catalytic reaction occurs within the pores of zeolite, the size and shape of the channels can be used to select the desired reaction path making use of the “shape-selectivity.” This occurs when the spatial configuration around reactants, products, transition state, or a reaction intermediate located in the intra-crystalline volume is such that only certain configurations are possible [8]. Therefore, specific supports may direct the formation of products with a particular chain length.

Molecular shape selective is observed frequently when using zeolite catalysts because of their two- or three-dimensional nature. Zeolites have unique advantages which render them particularly attractive for a variety of conversions and processes of industrial interest [9]:

- zeolites have pore dimensions comparable to molecular size and reactions occur within their intra-crystalline space;
- the active center concentration, exchanger cations or metals with catalytic properties and/or acidic sites, usually depends directly on their aluminum content, which can be varied;
- zeolites are thermally stable, which enables their operation as catalysts in a broad temperature range.

An advantage of the catalysts with shape selectivity is the formation of products not predicted in the equilibrium composition. The thermodynamic equilibrium laws are valid only if the catalytic and non-catalytic reactions are truly the same, and yield identical products. However, these considerations may not be obeyed in chemical processes. The catalytic reactions inside the pore channel of a shape-selective catalyst can be substantially different from those that occur in homogeneous catalytic or non-catalytic reactions involving the same reactants, due to the selectivity mechanisms characteristic of each structure [43].

The selectivity mechanisms of catalysts with shape selectivity are described briefly below:

- Reactant selectivity: it describes the phenomenon in which microporous catalysts act as molecular sieves and exclude molecules larger than the opening of pores in the structure, while allowing the entry of smaller molecules; this type of selectivity depends on intra-pore diffusional characteristics of reacting molecules [43];
- Product selectivity: it refers to the selective formation of certain products, when there are other potential products whose formation is also thermodynamically feasible but is limited because of their limited diffusion out of pore; smaller molecules can diffuse through the micropores, while larger molecules require more time to remain inside the structure [43];



this allows these molecules to undergo secondary reactions of isomerization and cracking, among others;

- Restricted transition state-type selectivity: it occurs when the spatial configuration around a transition state or a reaction intermediate located in the intra-crystalline volume is such that only certain configurations are possible; this means that the formation of reaction intermediates and/or transition states is sterically limited due to the shape and size of the microporous lattice allowing the access of the species formed to interact with the active sites [8].

Despite the vast majority of articles presenting the formation of gasoline or diesel fuel through the Fischer-Tropsch synthesis as an objective, some zeolites can be identified with considerable potential in the production of hydrocarbons in the aviation kerosene range. This stems from the fact that these structures present structural and acidic properties that give significant shape selectivity to products or transition states to the catalysts.

Bessel [44] investigated bifunctional catalysts of cobalt supported in zeolites ZSM-5, ZSM-11, ZSM-12, and ZSM-34 to the Fischer-Tropsch synthesis. The use of bifunctional catalysts composed of active metal and zeolite in acidic form aimed to overcome the typical nonselective Anderson-Schulz-Flory product distribution arising from conventional catalysts. In this type of catalyst, the active metal is responsible for the growth of the primary straight-chained hydrocarbon product, which undergoes further restructuring at the zeolite acid sites to produce a more branched hydrocarbon product of limited chain length. Despite having the lowest conversion of carbon monoxide (45%), among the catalysts studied, Co/ZSM-34 showed the highest selectivity to hydrocarbons in the jet fuel range (over 30%). This result was not expected because the ZSM-34 was the zeolite that showed the highest acidity; however, this also presents the more complex structure, with the largest (6.7 Å) and smallest (3.6 Å) diameters of channels among the zeolites used. In this case, the accessibility to the active sites and pore structure appears to be more important than the acidity in obtaining products in the aviation kerosene range.

Zola et al. [45] synthesized cobalt catalysts with 10% metallic phase supported through wet impregnation in zeolites Beta, USY, mordenite, and ZSM-5. The catalyst supported on zeolite USY presented the highest carbon monoxide conversion values (19%) and activity in Fischer-Tropsch synthesis. Hydrocarbon production in the jet fuel range also appears to be greater for this catalyst. The USY zeolite has a three-dimensional system of channels and large micropores, which favors the accessibility to catalytic sites. Therefore, these characteristics seem to favor the formation of products with a specific chain length in Fischer-Tropsch synthesis.

Ngamcharussrivichai et al. [17] investigated the performance of cobalt-based catalysts supported on silica, alumina, montmorillonite, and three zeolites (ZSM-5, USY, and MCM-22) in Fischer-Tropsch synthesis, 10 bar, and 230°C. The catalysts supported on USY and montmorillonite showed the carbon number distribution to be narrower and lower occurrence of waxes compared to catalysts supported on silica and alumina, because the zeolitic structure limits the growth of hydrocarbon chain. The material acidity also contributed to narrow the carbon number distribution; however, the zeolitic structure was still the most relevant feature.

Among the Co/SiO<sub>2</sub>, Co/USY, Co/ZSM-5, and Co/MCM-22 catalysts, the second and the third ones showed the distribution of carbon number more similar to the aviation kerosene (C<sub>8</sub>–C<sub>16</sub>). In addition, when a support with acidic characteristics was used, the formation of C<sub>12+</sub> significantly decreased, probably due to the higher occurrence of cracking reactions.

Martínez et al. [18] studied the catalytic properties of ZSM-5, MCM-22, IM-5, and ITQ-2 zeolites, all with 10-membered ring pore openings (10-MR) and Si/Al ratio similar. The study aimed to form products in the gasoline range through the Fischer-Tropsch synthesis. Hybrid catalysts (zeolite + silica) were tested for at least 7–8 h of reaction showing conversions around 50%. The presence of zeolites in hybrid catalyst increases the selectivity to products C<sub>2</sub>–C<sub>4</sub> and gasoline (C<sub>5</sub>–C<sub>12</sub>), as well as reduces the selectivity to diesel (C<sub>13</sub>–C<sub>22</sub>) and waxes (C<sub>23+</sub>). The hybrid catalysts with zeolites MCM-22 and IM-5 showed very similar products and the lower yields to iso-C<sub>5–8</sub>. The decreased formation of C<sub>23+</sub> and the greater and lesser C<sub>13–22</sub> formation and C<sub>5–12</sub>, respectively, among the hybrid catalysts, suggest that the MCM-22 and IM-5 zeolites may have a narrower distribution of products, which can provide a higher yield of hydrocarbons in the aviation kerosene range (C<sub>8</sub>–C<sub>16</sub>). These properties are probably related to the unique features of the zeolitic structures used, as, for example, the presence of supercages in the case of MCM-22.

Kibby et al. [46] performed the synthesis of a hybrid catalyst, which was composed of Ru and Co, as active metals, ZSM-12 and ZSM-5 zeolites, as supports, and alumina as base. The intention was to synthesize a catalyst which maximizes the formation of C<sub>5+</sub> products, were free of the solid phase (waxes), and minimize the formation of gaseous products (C<sub>1</sub>–C<sub>4</sub>) in the Fischer-Tropsch synthesis, so the product would not need to undergo further hydrocracking process. The hybrid catalyst using ZSM-5 produced a greater quantity of gaseous products and the average molar mass of hydrocarbons was lower when compared to hybrid catalyst with ZSM-12. In addition, the catalyst using ZSM-12 yielded a larger amount of products in the aviation kerosene range (C<sub>8</sub>–C<sub>16</sub>) than the hybrid catalyst with ZSM-5. Apparently, ZSM-5 is more effective in the isomerization of C<sub>4</sub>–C<sub>9</sub> olefins, while ZSM-12 is more active in isomerization of C<sub>10</sub> olefins, the latter leading to the formation of products with a longer length of chain. The reasons for this behavior are still not very well known, although the straight channels of ZSM-12 can carry heavier olefins faster. The authors concluded that the understanding of metal deposition rules on the support, the morphology and structure of zeolites, optimization of acid functions, activation, and process conditions are essential for obtaining the desired hydrocarbon range during the Fischer-Tropsch synthesis.

### 4.3. Influence of acidity

The microporous structure of zeolites provides a large internal surface area that allows a large concentration of active sites accessible to reactants, together with notable selectivity effects related both to diffusion of reactants and products inside the pore system and to steric constraints on intermediates and transition states. All these features influence the overall catalytic performance of acid zeolites, and make difficult to establish an acidity scale and a clear correlation between acidity and catalytic activity [47].

Two types of acid sites, Brönsted and Lewis, can be formed on the zeolite surface. Thus, Brönsted acid sites are generated when  $\text{Si}^{4+}$  is isomorphically replaced by a trivalent metal cation such as  $\text{Al}^{3+}$ . This substitution creates a negative charge in the lattice that can be compensated by a proton [48]. These protons can be present in the medium depending on the reactants that were used in the material synthesis, exerting the function of compensation cations. To replace these cations and consequently form a Brönsted acid site, ion exchange procedure is conducted with an aqueous solution of ammonium chloride, followed by washing to remove residual chloride, and calcination [49]. At high temperatures, the remaining protons can acquire mobility and be lost as water molecules, followed by the formation of Lewis acid sites, due to the isomorphous substitution of Al by Si [8].

It is evident that the amount of acid sites in the zeolite is related to the Si/Al ratio. The smaller the Si/Al ratio, more aluminum is present in the structure and increases the amount of compensation cations and the number of acid sites when the zeolite is in protonic form. However, the generation of acidic sites is associated with the imbalance of charges generated by isomorphous substitution of different load cations. Therefore, the greater the number of aluminum atoms, more unbalanced will be the zeolitic framework [49]. Due to this fact, the reduction of Si/Al ratio makes the zeolite structure to become less stable and may even damage the crystalline arrangement, besides having influence on the strength of acid sites.

In fact, not all acid sites have the same acid strength, because this feature depends on the number of aluminum atoms near the aluminum atom, which supports the acid site [50]. The more isolated is the trivalent atom, the greater the acid strength.

From the change of the Si/Al ratio of the zeolitic structure, through either synthesis or post-synthesis treatments, it is possible to change not only the total number but also the electronic density on the bridging hydroxyl group, and consequently to change the acid strength of the Brönsted acid site [51]. The control of acid strength as well as the density of acid sites of zeolite catalysts has also led to successful catalysts and processes in the field of oil refining and petrochemistry [48].

For the incorporation and/or suitability of the acidic species of Lewis or Brönsted, there are many synthetic strategies that can be developed, such as impregnation, deposition, precipitation, calcination, and reduction, among others. Structural variations are diverse and numerous chemical species can be incorporated into the support, in composition, oxidation states, and chemical environments in different ways [49].

In order to evaluate the influence of acidity on catalysts, Bessel et al. [52] showed that acid zeolitic structures have a tendency to catalyze secondary reactions in the Fischer-Tropsch synthesis, from olefinic products. Secondary reactions include oligomerization, isomerization, cracking, and hydrogen transfer, thus obtaining more branched products with a shorter chain length compared to the catalysts using supports with less or no acidity.

Ravishankar et al. [53] synthesized cobalt catalysts using MCM-22 as support, through wet impregnation. The Fischer-Tropsch synthesis was performed at  $280^\circ\text{C}$ , 12.5 bar, and  $\text{H}_2/\text{CO} = 2$ . Samples with lower Si/Al ratio showed the most selectivity to methane. These results also confirm the higher cracking of the products and, consequently, a lower selectivity to  $\text{C}_{5+}$  when

using catalysts that are more acidic. It is well known that Fischer-Tropsch synthesis selectivity depends on the conversion level and one would expect an increase of  $C_{5+}$  selectivity with increasing the carbon monoxide conversion. However, the  $C_{5+}$  selectivity values obtained for the cobalt catalyst supported on MCM-22 with high Si/Al ratio (200) and different cobalt loadings seem to be independent of the conversion level. The authors justify the increased  $C_{5+}$  selectivity to the particular properties of the support structure related to shape selectivity, active metal, and Si/Al ratio.

Therefore, it is possible to provide, in most cases, the occurrence of secondary reactions through the presence of acid sites, which may be desirable to obtain hydrocarbons in the aviation kerosene range. The amount and type of sites will depend on intrinsic characteristics of the support, the reaction conditions, and the metallic phase.

#### 4.4. Influence of promoters

In addition to a support with adequate characteristics and good Si/Al ratio, the use of specific promoters may offer desirable features to catalysts, such as, for example, increased reaction rate, greater stability, and  $C_{5+}$  selectivity. According to Iglesia [54], promoters can be classified as chemical and structural, increasing the amount of active sites and the activity per site, respectively. The general effect has been postulated to be due to many factors, including (1) intimate electronic contact changing the local band structure of the metal, (2) ensemble-type geometric effects, (3) reducing deactivation by carbonaceous deposits, and (4) enabling more surface sites to be reduced by hydrogen spillover during the initial activation [55].

According to the literature, one of the promoters who presented good results when incorporated into cobalt catalysts was manganese. Dinse et al. [12] investigated the use of this promoter for cobalt catalysts in the Fischer-Tropsch synthesis. The catalytic performance of the samples was carried out at 220°C,  $H_2/CO = 2$ , and operating pressure between 1 and 10 bar. At low pressures, the addition of promoter in the catalyst led to a decrease in methane selectivity and increased  $C_{5+}$  selectivity, while the formation of  $C_2-C_4$  hydrocarbons suffered no influence. At high pressures, in addition to a decrease in methane selectivity and increased  $C_{5+}$  selectivity, there was also an increase in  $C_2-C_4$  selectivity, as well as a large increase in olefins/paraffins in  $C_2-C_4$  range.

Dinse et al. [12] attributed the selectivities obtained for  $Co/SiO_2$  and  $Mn-Co/SiO_2$  catalysts to the equilibrium constant for CO adsorption, which is greater than the equilibrium constant for  $H_2$  adsorption in the presence of manganese, resulting in a reduction in  $H_2/CO$  ratio and a consequent increase in chain length of products. Selectivity differences in different pressures are also assigned mostly to the  $H_2/CO$  ratio, which decreases with the increase of the total pressure of reaction and, also, to the increase of  $\alpha$ -olefins reincorporation in chain growth process. Therefore, the manganese exerts significant influence in obtaining long-chain hydrocarbons, and again the importance of reaction conditions in obtaining hydrocarbons in a specific range is evident.

Khobragade et al. [13] synthesized  $Co/SiO_2$  catalysts using K and  $CeO_2$  as promoters, from the sol-gel method, in order to evaluate the performance in Fischer-Tropsch synthesis. Among the



samples tested, the catalyst promoted with cerium presented the highest  $C_{5+}$  selectivity, while the catalyst promoted with potassium presented higher methane selectivity. The behavior of the catalyst promoted with potassium was expected by its use to be more suitable when using iron as active metal, due to the higher reaction temperatures required for this catalyst [56]. In addition, potassium can cause poisoning of catalysts using cobalt as active phase [20]. According to Khobragade et al. [13], the behavior of the catalyst promoted with  $CeO_2$  occurs due to a decrease in the hydrogenation rate during the Fischer-Tropsch synthesis, in which the adsorption of  $H_2$  is suppressed in favor of chain growth. This can occur due to partial reduction of  $CeO_2$ , which would change the electronic properties of cobalt atoms through oxidation. It was also verified that most of the products were in the diesel range, probably due to the increase of active carbon species ( $-CH_2-$ ) in the catalyst. Cerium probably decreases the surface of metallic cobalt, resulting in a different chain growth and more favorable to the formation of  $C_{5+}$  hydrocarbons. This effect of the promoter is obtained because of the close interaction with the species of cobalt.

A way of aggregating the advantages of various promoters and brackets in the same catalyst is the use of hybrids and multifunctional catalysts. Teiseh et al. [14] showed that the use of a multifunctional hybrid catalyst ( $Co-SiO_2/Mo-Pd-Pt-HZSM-5$ ) produces more hydrocarbons in kerosene range than that of a conventional catalyst ( $Co/SiO_2$ ). In this case, the presence of molybdenum in the hybrid catalyst leads to a combination of carbonium ions (oligomerization of olefins), which contributes to the formation of paraffin in the kerosene range.

In this same context, Yan et al. [11] studied the performance of multifunctional catalysts in the Fischer-Tropsch synthesis, using alumina as support, cobalt and iron as active metals, and potassium and molybdenum as promoters ( $K-Fe-Co-Mo/\gamma-Al_2O_3$ ). In this case, the potassium can increase the selectivity and stability of the catalysts in the presence of iron. The multifunctional catalyst was used with the intention to reduce the number of steps necessary to obtain a jet fuel by Fischer-Tropsch synthesis. The syngas used was obtained from biomass, which typically has a low  $H_2/CO$  ratio [57]. In this case, the simultaneous use of Fe and Co is advantageous because, due to the iron having activity in the water-gas shift reaction, there is a setting in  $H_2/CO$  ratio for higher values, in which the cobalt is more active.

After obtaining the products, distillation was conducted for the removal of short-chain hydrocarbons and waxes. The samples were collected on boiling-point range between 110 and 310°C. The products obtained after distillation step presented features quite similar to the conventional fuel, in relation to both the distribution of organic functions and the number of carbons. Furthermore, the properties of the distilled fraction have become quite similar to jet fuel.

## 5. Potential zeolitic catalysts in obtaining synthetic aviation kerosene

**Table 1** presents the catalysts with significant potential in the production of jet fuel through the Fischer-Tropsch synthesis. The Si/Al ratio of zeolites, the temperatures and pressure

reaction, and the H<sub>2</sub>/CO ratio of the syngas and the carbon monoxide conversion are presented in the table.

References	Zeolitic catalysts	Si/Al molar ratio	Reaction conditions			CO conversion (%)
			Temperature (°C)	Pressure (bar)	H <sub>2</sub> /CO ratio	
Bessel et al. [44]	Co/ZSM-34	>10	240	20	2	45
Ravishankar et al. [53]	Co/MCM-22	220	280	12.5	2	4.5
Zola et al. [45]	Co/USY	7	240	10	2	19
Ngamcharussrivichai et al. [17]	Co/USY	16	230	10	2	38
Ngamcharussrivichai et al. [17]	Co/ZSM-5	19	230	10	2	19
Martínez et al. [18]	Co-SiO <sub>2</sub> /MCM-22	15	250	20	2	50
Martínez et al. [18]	Co-SiO <sub>2</sub> /IM-5	14	250	20	2	50
Teiseh et al. [14]	Co-SiO <sub>2</sub> /Mo-Pd-Pt-ZSM-5	23	250	10	1.9	88
Kibby et al. [46]	Co-Ru/ZSM-12/Al <sub>2</sub> O <sub>3</sub>	45	220	20	2	60

**Table 1.** Catalysts with significant potential in the production of jet fuel through the Fischer-Tropsch synthesis.

According to a review carried out, the zeolitic supports used in catalysts for Fischer-Tropsch synthesis wield great influence on the product's chain length. This occurs due to the fact that the support structure can inhibit or head the formation of certain products. In this case, the zeolite ZSM-34, USY, ZSM-5, ZSM-12, MCM-22, and IM-5 have significant potential in obtaining products in the aviation kerosene range. In addition, the Si/Al ratio in the catalyst, especially in the range of 7–220, involves the presence of acid sites, which may promote secondary reactions that reduce the formation of waxes and narrow the product's selectivity. Another factor that should be considered is the use of promoters, which in mass concentrations of about 1% may confer upon a major activity to the catalyst and assist in the formation of long-chain hydrocarbons. In addition, the Fischer-Tropsch process at low temperatures and pressures between 10 and 20 bar shows more appropriate in obtaining hydrocarbons C<sub>8</sub>–C<sub>16</sub>. Thus, the use of supports with appropriate structural characteristics, specific Si/Al ratio, specific promoters, and suitable conditions of operation shows promise to obtain products with features similar to the jet fuel through the Fischer-Tropsch synthesis.

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