



COBALT SUPPORTED ON ZSM-5 ZEOLITE USING KAOLIN AS SILICON AND ALUMINUM SOURCES FOR FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

The use of clay as an alternative source of raw material provides economic routes for the synthesis of ZSM-5. Therefore, the main purpose of this work was to study ZSM-5 synthesis using kaolin as Si and Al source. The zeolite using kaolin as a source of silica and aluminum has been applied as support for a 20wt% Co catalyst. Zeolite ZSM-5 was obtained with kaolin under hydrothermal synthesis at 373K for 48 hours. The kaolin was submitted to heat treatment at 973K for 2 hours before being used in synthesis. The deposition of cobalt on the support ZSM-5CK was performed by means of wet impregnation, using a 0.1-M aqueous solution of cobalt nitrate. The catalytic support and metal-loaded catalyst have been characterized and evaluated for the Fischer-Tropsch Synthesis (FTS) under controlled conditions (T = 593K, P = 20atm, H₂:CO molar ratio = 2) in a fixed bed reactor for 150 hours. From the Temperature Programmed Reduction profiles, two reduction peaks were observed at 629K and 677K, corresponding to the stepwise reduction of Co₃O₄ particles to CoO and then to metallic Co on the support external surface. It was observed with the FTS results that the 20wt% Co/ZSM-5CK catalyst yielded a 10% conversion rate and high selectivity towards the production of C₅⁺ (98%).

KEYWORDS

ZSM-5; kaolin; cobalt; fixed-bed reactor; Fischer-Tropsch synthesis

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1. INTRODUCTION

Fischer-Tropsch Synthesis (FTS) is a well-established technology to indirectly upgrade the abundant coal, natural gas, and renewable biomass resources into highly value-added fine chemicals and super clean fuels free of sulfur, nitrogen, and aromatics (Dry, 2002; Khodakov et al., 2007).

Cobalt catalysts have been found to be most suitable for the production of higher hydrocarbons (Ghampson et al., 2010). Cobalt and iron are the metals which were proposed by Fischer and Tropsch as the first catalysts for syngas conversion. Both cobalt and iron catalysts have been used in the industry for hydrocarbon synthesis.

ZSM-5 is a synthetic zeolite which presents uniform microporous structure, thermal and hydrothermal stability, and high intrinsic acidity, conferring important application for this material in the petrochemical and oil industry. This fact creates a huge supply demand for ZSM-5, and innovations in the preparation of ZSM-5 zeolites using alternative sources and small amounts of templates with the objective of reducing costs and/or desired reactivity have attracted much attention (Wang et al., 2007).

Kaolin is an important type of clay with several industrial applications (Murray, 2000; Castellano et al., 2010), and contains kaolinite as the principal mineral (Chandrasekhar and Ramaswamy, 2002). Before being used in the synthesis of zeolites, kaolin is subjected to a thermal activation process at temperatures above 550°C, which causes its conversion to metakaolin (Mackenzie, 1970; Sanz et al., 1988).

Brazil is today one of the largest producers of processed kaolin, which has extensive reserves of this clay. Due to the nature and mineralogical composition, kaolins of different origins have been used in the preparation of synthetic zeolites. These factors have raised interest in studying and developing processes for the synthesis of zeolites from calcined kaolin, aiming at its application in environmental technology, adding to the fact that the country has no significant reserves of natural zeolites of commercial value (Zola et al., 2007).

Zeolites, especially ZSM-5, are a preferred support when targeting gasoline production, due to several reasons: their pore structure enables size

and shape selectivities, the acidic surface supports reactions like oligomerization, cracking and aromatization, they are coking resistance, and are stable under FTS conditions (Udaya et al., 1990). Jong and Cheng (1995) used ZSM-5 zeolites as support for cobalt-based catalysts. In a more detailed study the ZSM system was examined by Bessel (1993, 1994 and 1995), with special emphasis on the channel size. Therefore different ZSM zeolites, namely ZSM-5, ZSM-11, ZSM-12 and ZSM-34, were applied. Zola et al. (2007) studied the textural and chemical properties as well as the catalytic behavior of 10wt% cobalt supported on H-USY, H-Beta, H-Mordenite, and H-ZSM-5 zeolites in the FTS.

Rodrigues et al. (2011) described the production of bifunctional catalysts using the incipient humidity method, producing catalysts with 15wt% cobalt supported in an SBA-15 molecular sieve, to be applied in the FTS. X-ray diffraction measurements showed that the calcined cobalt catalyst did not modify the structure of SBA-15, proving that Co was present under the form of Co_3O_4 in the catalyst. The addition of cobalt in the SBA-15 decreased the specific superficial area of the molecular sieve. The 15wt% Co/SBA-15 catalyst had a 40% CO conversion rate and high selectivity towards the production of C_5^+ (53.9% after 8 hours).

Sousa et al. (2011) studied the synthesis, characterization and testing of catalysts for the FTS. The preparation of a mesoporous molecular sieve, Si-MCM-41, was confirmed by X ray diffraction. The deposition of cobalt on the MCM-41 support was carried out by wet impregnation, using an aqueous solution of cobalt nitrate. The images obtained from TEM clearly showed good dispersion of cobalt on the support (MCM-41). The obtained catalysts containing different cobalt concentrations were evaluated for the FTS. Increasing the temperature increases the selectivity to olefins with the 15wt% Co/MCM-41 catalyst, and also increases the selectivity to methane with the 5wt% Co/MCM-41 catalyst.

Rodrigues et al. (2012) evaluated the catalytic properties of a Ru-Co/SBA-15 catalyst for Fischer-Tropsch Synthesis (FTS). This catalyst was prepared by the wet impregnation method. The FTS using the catalyst was carried out to evaluate the catalyst activity and its effect on the FTS product

distribution. The synthesis was carried out in a slurry reactor operating at 513K, 20atm, with a 1:1 CO:H₂ molar ratio. X-ray diffraction showed that the calcined cobalt catalyst did not modify the structure of SBA-15, proving that Co was present under the form of Co₃O₄ in the catalyst. The addition of cobalt in the SBA-15 decreased the specific superficial area of the molecular sieve. The FTS activity and C₅⁺ hydrocarbon selectivity increased with the addition of Ru, which was attributed to the increased number of active sites resulting from higher reducibility and the synergistic effect of Ru and Co. The Ru-Co/SBA-15 catalysts showed moderate conversion rates (around 40%) and high selectivity towards the production of C₅⁺ (80wt%).

Our research group (LABNOV – Development of New Materials Laboratory, UFCG, Brazil) has published a series of papers (Rodrigues et al., 2011, Rodrigues et al., 2012; Sousa et al., 2011) on the preparation, characterization and testing of catalysts for the Fischer-Tropsch Synthesis (FTS).

In view of this, we highlight the importance of studying the synthesis of ZSM-5, mainly focusing on economic routes, such as the use of clay as an alternative source of raw material. Therefore, the main purpose of this work was to investigate the ZSM-5 synthesis using kaolin as Si and Al source. The innovation of this work is its target on the use of a Co/ZSM-5 catalyst for FTS in a fixed-bed reactor.

2. EXPERIMENTAL

2.1 Materials

Kaolin, acquired in the town of Caiçara, Rio Grande do Norte (Brazil), was used in the synthesis of the ZSM-5 zeolite as an alternative source of silica and aluminum. It was previously submitted to thermal treatment. The kaolin samples were sieved according to the Brazilian ABNT standard N^o 200 (0.074mm).

Silica aerosil 200, tetrapropylammonium bromide [TPA-Br(CH₃CH₂CH₂)₄NBr], sodium hydroxide, ethyl alcohol, and sulfuric acid were purchased from Degussa, Aldrich and Vetec.

2.2 Modification of kaolin

The kaolin powder was dispersed in a solution of silica sol, with a kaolin:silica mass ratio of 1:2. After stirring for 2 hours, the mixture was dried at 433K. The thermal treatment of this mixture was performed in a muffle furnace at 973K for 2 hours. The heating rate increased from ambient temperature to the desired temperature at 278K per minute and then stabilized for 2 hours (Gutierrez et al., 2008), after which the temperature gradually decreased upon exposure to air. The product was named as calcined kaolin (CK).

2.3 Procedure of the hydrothermal synthesis of the ZSM-5 zeolite

ZSM-5 was hydrothermally synthesized, with kaolin as Si source and Al source. Concentrated sulfuric acid was used to adjust the gel pH. TPABr was used as a structure-directing agent (organic template). The initial mixtures were formed using the following procedures (Feng et al., 2009; Lam, 1987): TPABr and the seeds of the pre-synthesized ZSM-5 zeolite were first dissolved in deionized water, as separate solutions, under stirring at room temperature. A mixture of the mineralizing agent (NaOH) and calcined kaolin was also dissolved in deionized water under stirring. The solution with seeds of the ZSM-5 zeolite was added to the TPABr solution under constant agitation and then this mixture was added to the NaOH calcined kaolin solution. Ethanol was then added dropwise to the mixture, acting as a co-template. The final pH of the mixture was adjusted with sulfuric acid (final pH = 11). After stirring for 1 hour at room temperature the mixture was placed in a 70mL stainless steel autoclave and allowed to react in an oven at 443K for 48 hours. After crystallization, the solid product was centrifuged and thoroughly washed with deionized water. A product was obtained by drying the solid at 343K for 24 hours followed by calcinations at 823K for 6 hours under an air atmosphere to remove the organic template, producing the ZSM-5CK.

2.4 Preparation of the Co/ZSM-5CK catalyst

The Co/ZSM-5CK catalyst containing 20wt% Co was prepared by wet impregnation of the zeolite sample with a 0.1-M aqueous solution of cobalt nitrate (Co(NO₃)₂·6H₂O), under continuous stirring

at ambient temperature for 30 minutes. Then, the catalyst was dried at 373K for 24 hours, and finally submitted to the thermal process under nitrogen atmosphere at a flow rate of 100mL/(gcat.min), from room temperature to 473K with a heating ramp of 283K/min, and maintained at this temperature for 1 hour. After this period, the nitrogen flux was replaced with synthetic air and the solid material was heated at 275K/min from 473 to 723K, and maintained at this temperature for 2 hours.

2.5 Characterization

The surface composition of the catalysts was determined with a Shimadzu EDX-700 X-ray Energy Dispersion Spectrophotometer (EDX). The X-ray diffraction (XRD) measurements were performed in a Shimadzu XRD-6000 equipment with Cu K α radiation (40kV, 30mA) in the 2 θ range of 2.0°–80.0°. The crystallite phase was characterized based on the Joint Committee on Powder Diffraction Standards (JCPDS) data. Co₃O₄ crystallite size distribution was determined with the Scherrer equation.

Temperature Programmed Reduction (TPR) assays were carried out using a quadrupole mass spectrometer (Omnistar) connected to a computer. In order to examine the reducibility of Co species in calcined catalysts, the TPR measurements were performed with a heating rate of 10K/min, up to 1173K in a stream of 2.0 vol% H₂ diluted with argonium.

N₂ adsorption-desorption experiments were conducted at 77K using a Micrometrics Surface and Pore Size Analyzer, model ASAP 2020. Prior to the experiment the sample was degassed at 573K for 18 hours. The surface area was obtained using the BET model. The pore size distribution was evaluated from the desorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

2.6 Fischer-Tropsch Synthesis (FTS)

The catalytic activity of the compounds prepared for the FTS was assessed on a fixed-bed reactor. The reaction was performed at 20atm and started after the temperature was stabilized by the Co/H₂/He mixture at a flow rate of 30mL/min to ensure constant space velocity for the experiment. The total reaction time was approximately 150

hours. The feed gas was a mixture of 32wt% CO, 64wt% H₂, and 4wt% He, all supplied by White Martins. Helium was used as an internal standard to calculate the total CO conversion. These gases passed through filters at room temperature to remove O₂ and water traces. The reaction products were analyzed on-line by gas chromatography, in a Shimadzu GC-17A gas chromatographer. For gas samples, the phase column used was a Haysep D 80/100 6m-1/8in.

2.7 Conversion and hydrocarbon selectivity

The conversion of carbon monoxide into hydrocarbons (X_{CO}) was determined based on the analysis of the data obtained with a TCD detector, by analyzing the difference in thermal conductivity, and applying Equation (1):

$$X_{CO} (\%) = \frac{n_{CO}^o - n_{CO}}{n_{CO}^o} \times 100 \quad (1)$$

where $X_{CO}(\%)$ is the conversion of carbon monoxide into hydrocarbons; n_{CO}^o and n_{CO} are the initial and final concentration of carbon monoxide in the reactor, respectively. The selectivity of hydrocarbons was calculated with Equation (2):

$$S_{C_{5+}} = 1 - S_{CO_2} - \sum_{n=1}^4 S_{C_n} = 1 - S_{CO_2} - S_{C_1} - S_{C_2} - S_{C_3} - S_{C_4} \quad (2)$$

where S_{C_n} is the selectivity of a hydrocarbon with n carbon atoms.

3. RESULTS AND DISCUSSIONS

Figures 1 and 2 show the XRD pattern of the ZSM-5CK zeolite and 20wt% Co/ZSM5CK catalyst. According to the XRD pattern of the ZSM-5CK zeolite, it is possible to verify that the hydrothermal synthesis and the use of calcined kaolin as an alternative source of Si and Al was effective for the majority phase formation of the ZSM-5 zeolite, with intense peaks and well-defined features of a material with high crystallinity, especially those located at 2 θ = 7-9° and 2 θ = 23-25°, which are typical of MFI zeolitic materials (Kokotailo et al., 1978). It is also possible to observe that the synthesized ZSM-5CK zeolite

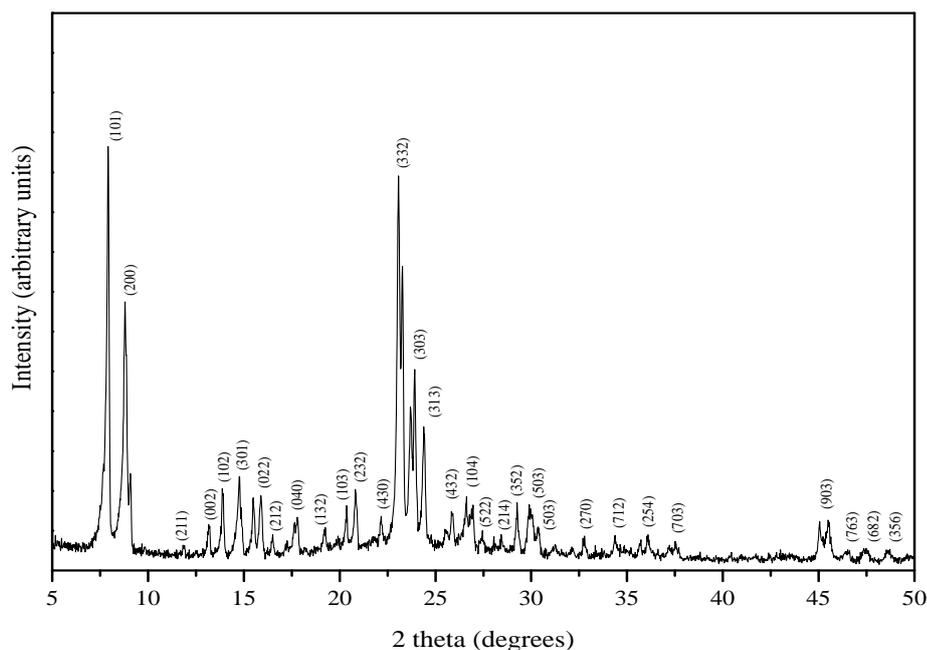


Figure 1. X-ray patterns of the ZSM-5CK zeolite.

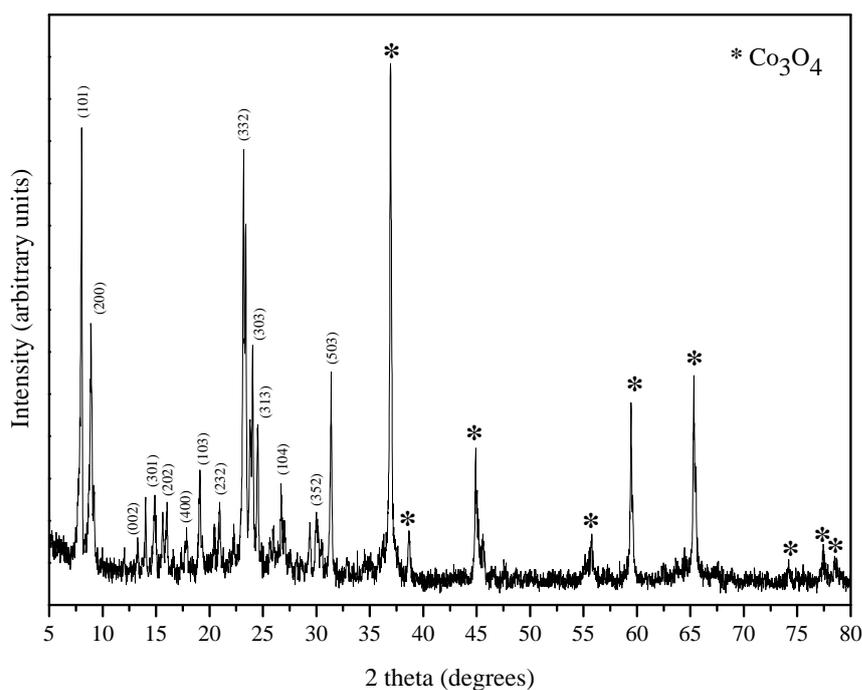


Figure 2. X-ray patterns of the 20wt% Co/ZSM-5CK catalyst.

showed a significant enlargement in the basal diffraction peaks, characterizing the nature of nanometer particles. All these aspects are compatible with the standard sample.

It is also indicated that the characteristic pattern for the ZSM-5CK zeolite structure was maintained after cobalt impregnation. XRD analysis

also shows peaks at $2\theta = 37^\circ$, attributed to the cobalt structure located at external surface of the zeolite. From these XRD data, it was possible to conclude that the ZSM-5CK zeolite induces the formation of typically larger cobalt particles, in average, in agreement with textural analyses (Wang et al., 2000). The average Co_3O_4 crystallite size calculated was 59nm.

Table 1. Chemical compositions of the ZSM-5CK zeolite and the 20wt% Co/ZSM-5CK catalyst samples.

Sample	SiO ₂	Al ₂ O ₃	Co ₃ O ₄	Co	Impurities
ZSM-5CK	84.19	13.86	–	–	1.21
20wt% Co/ZSM-5CK	61.50	10.26	27.00	19.5	1.70

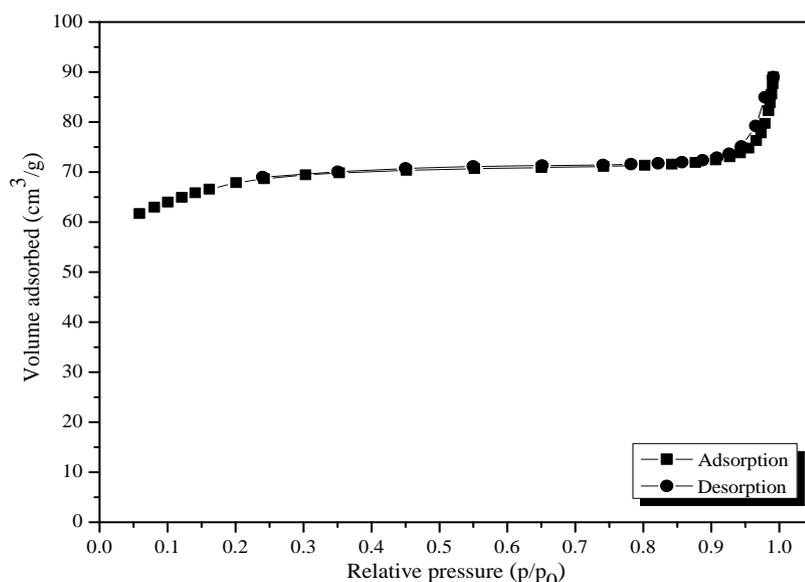
The chemical compositions of the ZSM-5CK zeolite and the 20wt% Co/ZSM-5CK catalyst samples are displayed in Table 1.

According to the data in Table 1, it is possible to verify that the ZSM-5CK zeolite showed high percentage of silicon oxide (SiO₂) and a lower SiO₂/Al₂O₃ ratio when compared with the standard sample. According to the literature, the SiO₂/Al₂O₃ ratio which is suitable for the synthesis of ZSM-5 zeolite must be between 15 and infinity, in order to obtain a product with high crystallinity which is capable of promoting ion exchange (Gianetto, 1990). However, the ZSM-5CK zeolite showed a value below the theoretically predicted. On another approach, some authors reported that this ratio could be less than 15 (Auerbach et al., 2003; Szostak, 1989). The solid SiO₂/Al₂O₃ ratio obtained in our assays (6.07) is less than that in the preparation gel (15.0), because of the aluminum source used in the synthesis of ZSM-5 zeolite and kaolin. This therefore justifies the low SiO₂/Al₂O₃ ratio, which is still in agreement with the literature (Auerbach et al., 2003; Szostak, 1989).

The analyses performed by EDX revealed that a 20wt% Co was effectively incorporated in the ZSM-5CK structure. It was possible to verify the presence of cobalt oxide (Co₃O₄) in the samples.

Figures 3 and 4 show the N₂ adsorption-desorption isotherms at 77 K for the calcined ZSM-5CK zeolite and 20wt% Co/ZSM-5CK catalyst.

By analyzing the adsorption-desorption N₂ isotherm of the ZSM-5CK zeolite (Figure 3), it is possible to observe that it presents a type-I hysteresis profile, typical of microporous materials, with which adsorption occurs at low pressures due to strong interactions between the pore walls and the adsorbate. Moreover, the exposed surface lies inside the micropores, and, once it is filled with the adsorbate molecules, the entire surface is practically entirely covered, impairing further adsorption. These features are in accordance with other reports in the literature that focus on the use of calcined kaolin to obtain zeolites (San Cristóbal et al., 2010; Wang et al., 2007). On the other hand, after impregnation of the cobalt in the ZSM-5CK zeolite, the hysteresis profile was modified to type

**Figure 3.** Adsorption-desorption N₂ isotherms of the ZSM-5CK zeolite.

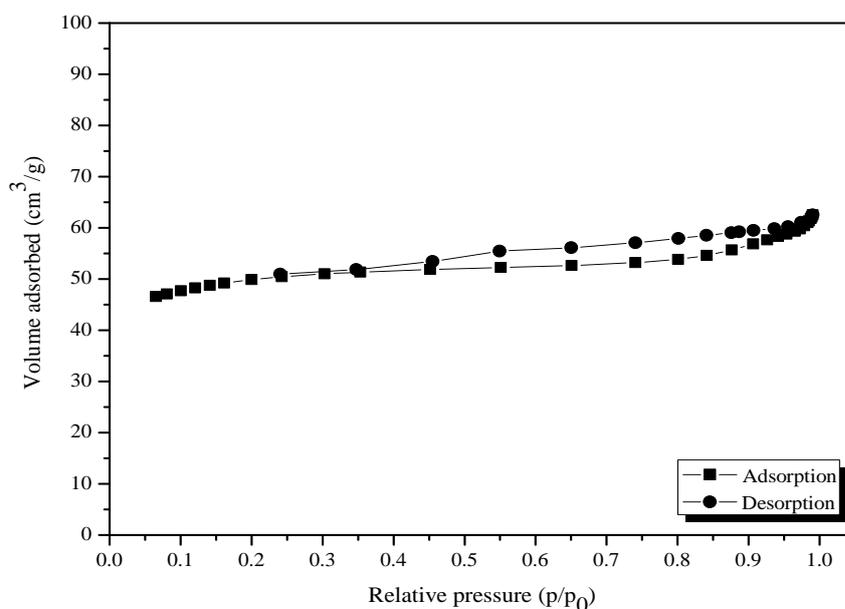


Figure 4. Adsorption-desorption N_2 isotherms of the 20wt% Co/ZSM-5CK catalyst.

III (Figure 4). This type of hysteresis provides the same geometrical characteristics of the particles and pores attributed to materials that exhibit type-IV hysteresis, which is the case of solids formed from clusters of particles with pores of different geometries, for example, plates or cubic particles with uniform size and shape, typical of activated carbons and zeolites. This is indicative of the presence of Co_3O_4 on the structure of the material, since this is a spinel belonging to the cubic face-centered crystal system.

The textural analysis of the ZSM-5CK calcined and 20wt% Co/ZSM-5CK samples are presented in Table 2.

The BET analysis showed that the ZSM-5CK zeolite (Table 2) presented a specific surface area of $232 \text{ m}^2/\text{g}$ and pore volume of $0.22 \text{ cm}^3/\text{g}$. Was observed a decrease in surface area of 27% (232 to $169 \text{ m}^2/\text{g}$) and in the pore volume about 59% (0.22 to $0.09 \text{ cm}^3/\text{g}$), which is mostly due to effects

caused by the presence of the Co_3O_4 phase. The decrease in S_{BET} values may be due to blocking of some zeolite pores with cobalt moieties formed on the surface. These results are in accordance with those obtained by [El-Bahy et al. \(2008\)](#). The values of V_p^{total} and D_p decreased with cobalt impregnation, indicating incorporation of Co ions in the pores of ZSM-5. In general, the surface texture data is in agreement with the XRD data for corresponding particle sizes.

A representative SEM image of ZSM-5CK is given in Figure 5 and shows the formation of agglomerates of particles which present the symmetry of the orthorhombic type typical of ZSM-5 zeolite structures, without cracks on the layers. However, the formation of secondary phases is not observed in a magnitude of 10000x. This is clearly seen on the surface between the crystals and the deposition of material with different aspects of the zeolite crystals, which are assigned to lamellar silica and fragments of kaolinite.

Table 2. Textural analysis of the ZSM-5CK calcined and 20wt% Co/ZSM-5CK samples.

Sample	^a $S_{BET} / (\text{m}^2/\text{g})$	^b $V_p^{total} / (\text{cm}^3/\text{g})$	^c D_p / nm
ZSM-5CK	232	0.22	12.30
20wt% Co/ZSM-5CK	169	0.09	8.42

^a S_{BET} – specific surface area

^b V_p^{total} – total specific pore volume

^c D_p – average pore diameter calculated by the BJH

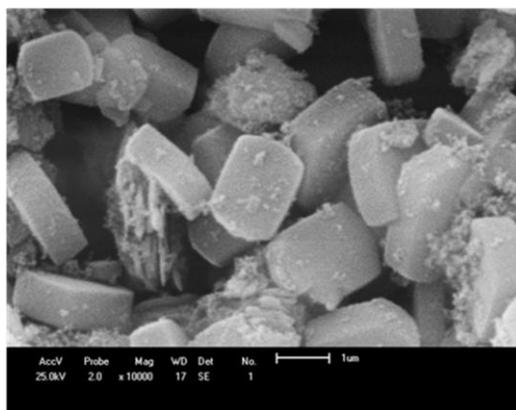


Figure 5. SEM image of the ZSM-5CK zeolite.

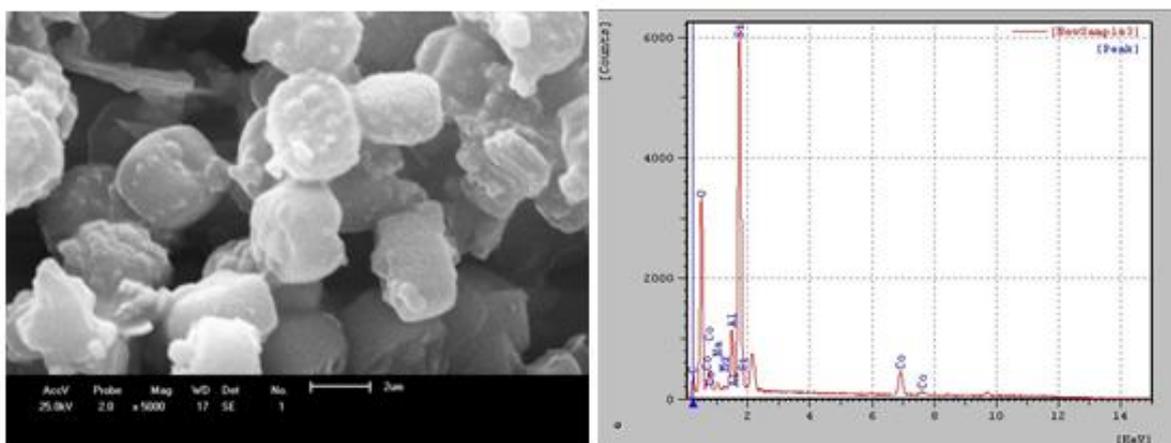


Figure 6. SEM image of the 20wt% Co/ZSM-5CK catalyst and spectra obtained by EDS analysis.

The micrograph (Figure 6) shows the morphology of the 20wt% Co/ZSM-5CK catalyst. In general, this catalyst has a morphology made up of agglomerates of particles which have symmetric structure typical of ZSM-5 zeolite, without cracks on its layers. Therefore, it was concluded that the processes of impregnation and calcination did not affect the structure of this catalyst, as evidenced by XRD analysis (Figure 2). By chemical analysis using EDS coupled to SEM, the obtained spectrum reveals the presence of cobalt in the sample. The EDS data qualitatively agree with the EDX data.

Figure 7 shows the TPR profile of the 20 wt% Co/ZSM-5CK catalyst, after calcinations. H_2 -TPR measurements are used to probe the reducibility, and as a result they give more information on the nature of cobalt species.

Signals for Co-oxide reduction are clearly visible.

For the 20wt% Co/ZSM-5CK catalyst, the TPR profiles showed two reduction peaks at 356 and 434°C respectively. The first is associated with Co-oxide species like Co_3O_4 ($Co^{3+} \rightarrow Co^{2+}$) (Resini et al., 2003). The second is attributed to Co oxidation ($Co^{2+} \rightarrow Co^0$) (Bustamante et al., 2002).

Figure 8 shows the curves of the CO conversion and selectivity of the products formed as a function of the reaction time for the 20wt% Co/ZSM-5CK catalyst.

According to the data obtained for the 20wt% Co/ZSM-5CK catalyst, high stability was observed reaching a conversion of CO of around 10% (Figure 8a) which remains unchanged for a period of approximately 130 hours of reaction. As shown in Figure 8b, the catalyst was highly selective to C_5^+ hydrocarbons, without the generation of lower

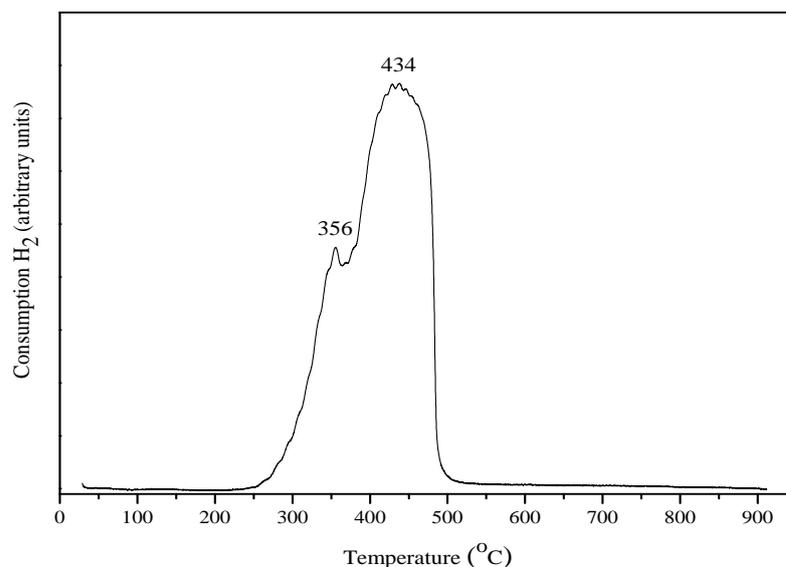


Figure 7. TPR of the 20wt% Co/ZSM-5CK catalyst.

hydrocarbons (C_2 - C_4). The production of CO_2 and CH_4 can be detected, but in very small amounts (less than 5%). Despite this high selectivity, this reaction should be repeated with a higher load of starting materials, in order to compare the selectivities of monometallic catalysts in iso-conversions.

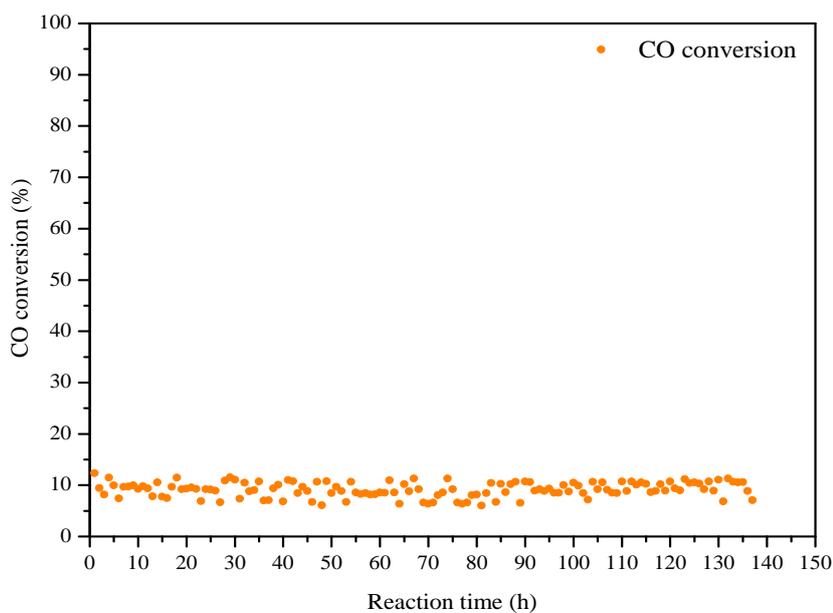
Low CO conversion rates provided by this catalyst are attributed mainly directly to the amount of cobalt in the support. By observing the TPR profile of this catalyst (Figure 7), it is possible to confirm that it presents identical stages of reduction observed for Co_3O_4 , indicating that there is little interaction of cobalt with the surface of this support. Because the TPR experiment shows that predominant cobalt species in the latter are not reducible under the reaction conditions, the low carbon monoxide conversion is attributed to the lower amount of metallic cobalt present in the catalyst. Another possibility may relate to calcined kaolin, which was used as a source of silicon and aluminum to prepare this support. This may have affected the dispersion of the metal, leading to lower activity, but creating sites which further promote chain growth.

The presence of some amount of unreduced cobalt (interacting with the ZSM-5CK support) enhances the selectivity to C_5^+ (gasoline), whereas a higher reduction degree of cobalt favors the production of higher molecular weight hydrocarbons (waxes).

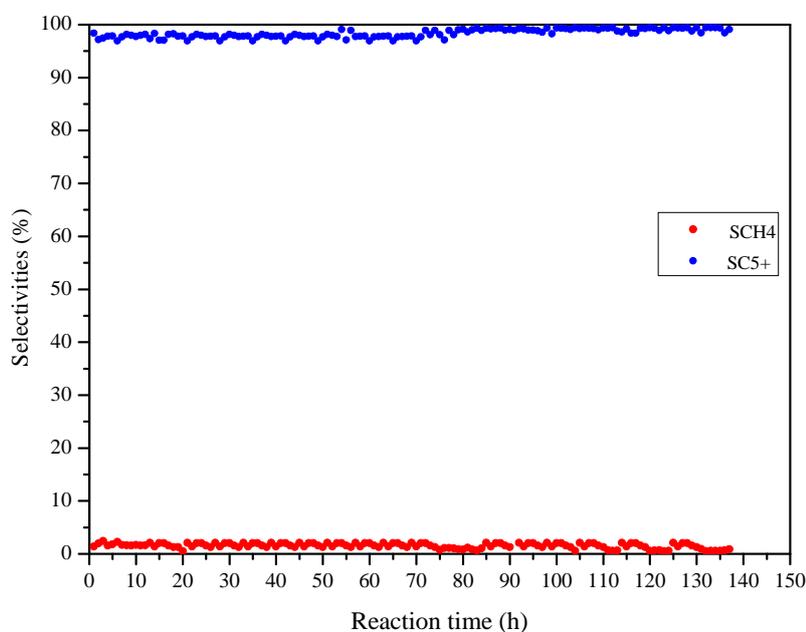
According to the observations of Schulz et al. (2002), the surface segregation of cobalt, by the strong chemisorption of CO, produces a large increase in the number of active sites, which are divided into low and high local coordination. This fact explains the distribution of products obtained by increasing the proportion of C_6^+ hydrocarbons and reduction of light hydrocarbons.

Ernst et al. (1999) studied the activity and selectivity of Co/ SiO_2 catalysts in the FTS. An increase in activity was observed with increasing area, and higher selectivity for hydrocarbons of high molecular weight.

The choice of the best support for catalysts for this reaction involves the observations of various factors, including acidity, dispersion effects, porosity, electronic modifications and strong metal-support interactions. An important aspect in the development of catalysts with high activity in the FTS is the increased number of active sites that are stable under certain reaction conditions, enabling high dispersion of the active phase. The support has a strong influence on the reducibility, activity and selectivity of the reaction; for example, iron catalysts supported on silica have lower reducibility and catalytic activity due to variations in the surface structure and interactions between the iron and silica (Schulz et al., 2002).



(a)



(b)

Figure 8. Conversion of CO as a function of reaction time (a) and selectivity of the products according to the reaction time (b).

4. CONCLUSIONS

The ZSM-5 zeolite was synthesized by the *in-situ* hydrothermal crystallization method with thermally-treated kaolin. This study demonstrated that it is possible to synthesize ZSM-5 with kaolin as an alternative source of Si and Al.

According to the XRD results, EDX chemical analysis and N₂ adsorption assays, cobalt was

incorporated into the support (ZSM-5CK). X-ray diffraction analyses showed that the characteristic pattern of the ZSM-5CK zeolite structure was maintained after addition of metallic cobalt. However, the addition of cobalt in the ZSM-5CK zeolite decreased the specific superficial area of the molecular sieve.

The potential application of the cobalt/ruthenium catalyst supported in

mesoporous SBA-15 was assessed in the Fischer-Tropsch synthesis. The results for the FTS using the 20wt% Co/ZSM-5CK catalyst indicated that a conversion rate of 10% can be obtained, with high selectivity towards the production of C_5^+ (98%).

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