SBA-15 modified by incorporation of alkali metals. Effect of its structural changes on the catalytic properties of Fe/SBA-15 system in the Fischer-Tropsch synthesis.

Leonardo A. Cano[a], Maria V. Cagnoli[b], José F. Bengoa*[b], and Sergio G. Marchetti[b]

Abstract: A mesoporous SBA-15 solid was doped with Li, K or Cs. These systems were used as supports of iron nanoparticles and each composite was utilized as catalyst in the Fischer-Tropsch synthesis. After the activation treatment the same Fe species were detected in all solids: FeO, α-Fe and Fe²⁺ inside SBA-15 walls. However, the species percentages and their distribution were different according to the dopant present. In all “working” catalysts a mixture of carbides Fe₂C and α-Fe₂₃C₆, FeO and ions Fe²⁺ inside the SBA-15 walls were found. Alkali cations produce different amount and strength of basic sites. At 1 atm and T=703 K, the catalytic activity order was: Li > K > no doped > Cs and the alkali metals favored the production of olefins. At 20 atm, the activity was considerably higher, even at a temperature as low as 543 K, which was attributed to structural properties of the support and to diffusional effects. All catalysts showed a promising hydrocarbon production in the gasoline range. The influence of alkali metals was discussed in terms of electrostatic effects and the limited hydrocarbon chain growth was attributed to the control over size of active iron species.

Introduction

The depletion of crude oil has stimulated the utilization of nonpetroleum feedstocks including coal, natural gas, shale gas, coal-bed methane biogas, and biomass to produce liquid fuels and chemicals. One of the most practical ways for the transformation of nonpetroleum carbon resources is the production of synthesis gas (syngas, CO+H₂) by gasification in a first step, and then, the conversion of syngas into liquid fuels using the Fischer-Tropsch Synthesis (FTS). This process is a stepwise polymerization reaction and the products follow, in general, the Anderson-Schulz-Flory distribution. Although the FTS has been extensively studied for more than fifty years, recently, the research in this field has been increased, showing a renewed interest [1]. The problems associated with current oil extraction and processing technologies, the more stringent environmental regulations and the need for new investments in the refinery sector, makes the process of converting syngas to liquid hydrocarbons more interesting and viable for the industrial production. Therefore, efforts to increase basic and applied knowledge in FTS appear to be attractive. Different metals are active in this synthesis; however, due to its costs and availability, catalysts based on Fe and Co are the usually commercial used for this process [2]. When iron is employed, the FTS occurs simultaneously with the water–gas shift (WGS) reaction. It consumes CO and water (by-product of FTS) and produces additional H₂ and CO₂. For this reason, iron catalysts are the best choice when a syngas poor in hydrogen is used. This situation occurs if the syngas is produced by gasification of coal or biomass. Besides, iron catalysts are preferred to cobalt ones, since they have lower cost, selectivity to methane and sensitivity to poisons, and higher flexibility to lead the selectivity to alkenes, oxygenates, or branched hydrocarbons, depending on the promoters or the operative variables used [3]. A large literature about Fe catalysts is available; however, the chemical states of the active sites and the relevant nano effects, in supported systems, are not fully understood. A deep knowledge of these behaviors could help to the understanding of the reaction mechanism and consequently to the development of a new generation of catalysts [4].

Alkali metals, like potassium, are commonly added, as chemical promoters, to different iron catalysts: precipitated, fused and supported. It has been reported that alkali metals increase FTS and WGS activities, and selectivity to olefins and long chain hydrocarbons [5, 6]. Ngantsoue-Hoc et al. [7] studied the impact of different alkali promoters on FTS performances using precipitated Fe-Si catalysts. They found that K was the best promoter, increasing the CO conversion rate at all conversion levels in comparison with the unpromoted catalyst. Instead, Li and Na improved CO conversion at low to moderate conversion values; however, at high conversion levels, they were not effective or even inhibited the CO conversion. These discrepancies can be partially explained by interactions between alkali promoters and the iron species present in the catalyst, whose nature is not well known up to the moment. The increases in activity and selectivity are often explained in terms of the electronegativity, which would produce a charge transfer from alkali promoter to transition metal surface, inhibiting H₂ adsorption but enhancing CO adsorption and dissociation [8]. The role of potassium to increase the selectivity to heavy hydrocarbons was recently investigated by Pendyala [9] using TPR-EXAFS/XANES-TPR experiments. A possible electronic effect, reflected by a systematic increase in the carburization speed when the promoter basicity increases in precipitated (Fe: Si: alkali) catalyst, is showed. Accordingly, Li [10] concluded that potassium promotes new active sites production during carburization and reduction steps of precipitated iron oxides.
assisting a rapid nucleation to generate small iron carbides crystallites. In similar way, Ribeiro et al. [11] investigated the promoter effect of Li, Na, K, Rb, and Cs on the carburization rate in precipitated Fe-Si catalysts using X-ray absorption spectroscopy. They found that the carburization rate was increased in the following order: unpromoted < Li < Na < K = Rb = Cs. On the other hand, Xiong, et al. [12] studied the effect of group I alkali metals on Fe/carbon nanotubes catalysts in Fischer-Tropsch synthesis. They found that Li enhanced in a small extent the reducibility of the catalyst whereas Na and K slightly inhibited its reduction.

In summary, there is not a general agreement about the influence of alkali promoters on the performance of iron catalysts in FTS. An additional difficulty appears as consequence of the diverse structural properties of the different class of iron catalysts used: low specific surface in fused systems, presence of textural promoters in precipitated solids or system of nanoparticles on different types of supports. Currently, there is a special attention on iron supported catalysts. They have greater resistance to attrition than bulk catalysts. This advantage allows their use in low cost reactors, such as slurry type. Therefore, is attractive to develop Fe supported catalysts with good activity and selectivity. However, this type of solids introduces new challenges in order to interpret the results because there is some earlier evidence that FTS is a "structure sensitive" reaction [13, 14]. That means that the activity and selectivity of the catalyst is a function of the crystal size of the active phase (generally in the range of 1-10 nm). Recently, this property was confirmed for Co and Fe supported catalysts [15-18]. In this way, it would be possible to increase the selectivity of FTS by two effects: obtaining supported iron oxide nanoparticles with a determined average diameter and a narrow size distribution and using metal alkali as promoters. In order to "tailor" the size and the width of size distribution, an "inert" support with a narrow pore size distribution and thermal stability must be selected. In addition, the pore diameters must be large enough to locate the iron oxide crystals inside them, avoiding their migration to the external surface during the activation and the use steps. These conditions seem to be fulfilled by the mesoporous solid named SBA-15 network. This carbosilicate is a class of iron mixed oxides or carbides doped with alkali and alkaline earth metals. These are used as supports for iron nanoparticles in order to "tailor" the size and the width of size distribution, an "inert" support with a narrow pore size distribution and thermal stability must be selected. In addition, the pore diameters must be large enough to locate the iron oxide crystals inside them, avoiding their migration to the external surface during the activation and the use steps. These conditions seem to be fulfilled by the mesoporous solid named SBA-15 network. This carbosilicate is a class of iron mixed oxides or carbides doped with alkali and alkaline earth metals. These are used as supports for iron nanoparticles to produce doped Fe/SBA-15 catalysts in order to increase their activity and selectivity towards hydrocarbons in gasoline range when they are used in the FTS. Bearing in mind the consequence of the active crystal size on the catalytic results of this process, efforts were performed to control the average size and width of Fe active phase distribution.

Results and Discussion

The preservation of the structural properties of the mesoporous SBA-15, after incorporation of alkali metals, was verified by XRD and textural measurements and these results were reported in a previous publication [26]. The Fe impregnation treatment and the subsequent calcination in NO (1% v/v)/He flow, carried out to obtain the precursors: Fe/SBA-15, Fe/Li-SBA-15, Fe/K-SBA-15 and Fe/Cs-SBA-15 did not modify the structural properties of the mesoporous supports, as it was verified by XRD (Figure 1). The NO/He flow was selected because it has been demonstrated that calcination in NO flow produces, in the Co/SiO2 system, Co nanoparticles with sizes significantly smaller if cobalt nitrate salt is used in the impregnation step [27, 28]. Besides, these authors obtained an important narrowing in particle size distribution when this gas was used instead of air. These results could be explained since NO is one of the nitrogen oxides produced during metal nitrates decomposition; therefore, if it is fed during the calcination process, the salt decomposition would occur in a controlled way and the clustering and growth of the nanoparticles would be avoided.

In Figure 2 are reported TEM micrographs in order to show the iron species location. Figure 2a corresponds to Fe/SBA-15 in dark-field mode. This Figure shows the presence of iron oxide nano-cylinders along SBA-15 channels. It can be seen that bright areas, corresponding to iron species, are aligned following the channels path. This is an evidence of the position of this species inside the SBA-15 pores. The length of 73 nanocylinders was measured and a distribution of this dimension was obtained. The histogram of these sizes was fitted assuming a log-normal distribution and the average value obtained was of 7.6 ± 0.3 nm (Figure 3). Figures 2b and 2c belong to Fe/K-SBA-15 and Fe/Cs-SBA-15, respectively. These pictures were
obtained parallels to the axis of the support channels. There it can be observed the mouths of empty pores of SBA-15 (lightest zones) with a hexagonal arrangement and some pores filled with iron oxide (darkness regions). It can be noticed that filled channels are surrounding by several vacant pores.

Table 1 displays BET results and the metal content (Fe and alkali metals) of each precursor determined by AE and AA spectroscopy. The decline of Sg values could be attributed to two effects in the doped catalysts. The modification of SBA-15 with alkali metals, without iron, produced a decreasing of specific surface areas between 30 and 60% with respect to pure SBA-15 [26]. When the doped supports were loaded with iron species, this fall was increased reaching values of about 70% with respect to pure SBA-15. That is, in doped precursors the Sg decreasing is produced by the simultaneous presence of iron species and alkali metals. On the other hand, as it was detected by TEM micrographs, only some channels of SBA-15 were filled with iron oxides nano-cylinders. Instead, a great number of them remain empty. Therefore, in the evaluation of Dp from N2 adsorption measurement, using the BJH model, only these empty pores are taken into account and the average pore diameter remains unaltered.

**Table I** - Textural properties, iron and alkali metal loadings for the precursors.

| Sample      | Sg (m²/g) | Dp (nm) | Ve (cm³/g) | e (nm) | Fe content (% w/w) | Alkali content (% w/w) |
|-------------|-----------|---------|------------|-------|-------------------|-----------------------|
| SBA-15      | 893       | 8.2     | 1.09       | 6.8   | —                 | —                     |
| Fe/SBA-15   | 519       | 7.0     | 0.6        | 6.2   | 15.6              | —                     |
| Fe/Li-SBA-15| 287       | 8.2     | 0.6        | 4.2   | 9.7               | 0.11                  |
| Fe/K-SBA-15 | 309       | 7.0     | 0.4        | 5.6   | 12.5              | 0.40                  |
| Fe/Cs-SBA-15| 371       | 7.2     | 0.5        | 6.0   | 12.2              | 2.17                  |

Sg: Specific surface area  
Dp: average pore diameter  
Ve: specific pore volume  
e: wall thickness

Table II shows the CO₂ adsorption results for each precursor expressed in μmol CO₂/m² exposed of precursor. It should be noted that SBA-15 support did not present CO₂ desorption. This fact denotes the absence of basic Lewis sites in the undoped support, in concordance with previous results [29].

It is observed that all precursors have three CO₂ desorption maxima in well-differentiated temperature ranges (Figure 4). These maxima correspond to CO₂ adsorbed on basic sites with different adsorption strength: weak, intermediate and strong. Bearing in mind that SBA-15 without dopants did not adsorb CO₂, the existence of these peaks in non-doped Fe/SBA-15 must be associated to the presence of iron oxide nanoparticles produced during the preparation of the precursors. Xu et al. have found that iron catalysts supported on silicalite showed two peaks at similar temperatures to the two first ones present in our precursors [30]. Besides, our peak at the highest temperature could be attributed to a fraction of smaller iron oxides nanoparticles with surface O²⁻ more coordinatively unsaturated.

**Figure 1**: XRD patterns of precursors.
This article is protected by copyright. All rights reserved
of these compounds are: \( \text{Li}_2\text{O} \): 1711 K, KOH: 633 K and CsNO\(_2\): 687 K and that the precursors were calcinates at 723 K, could be speculated that KOH melted during this step of preparation producing a spreading on SBA-15, increasing its dispersion.

Table II. CO\(_2\)-TPD results of the precursors.

| Precursor | 1\(^{st}\) Peak | 2\(^{nd}\) Peak | 3\(^{rd}\) Peak | CO\(_2\) uptake of (1+2) peaks | Alkaline metal dispersion (%) |
|-----------|--------------|--------------|--------------|----------------|-----------------------------|
|           | \( T \) (K)  | Evolved CO\(_2\) (\( \mu \text{mol/m}^2 \times 10^4 \)) | \( T \) (K)  | Evolved CO\(_2\) (\( \mu \text{mol/m}^2 \times 10^4 \)) | \( T \) (K)  | Evolved CO\(_2\) (\( \mu \text{mol/m}^2 \times 10^4 \)) |
| Fe/SBA-15 | 369         | 1.0          | 614         | 2.1          | 835         | 3.7          | 3.1 |
| Fe/Li-SBA-15 | 358     | 23.0         | 441         | 28.0         | 608         | 7.0          | 51.0 | 0.7 |
| Fe/K-SBA-15 | 319     | 20.0         | 363         | 30.0         | 547         | 21.0         | 50.0 | 1.5 |
| Fe/Cs-SBA-15 | 320    | 3.8          | 356         | 4.3          | 596         | 4.0          | 8.1  | 0.2 |

Using the maxima temperatures of CO\(_2\) desorption peaks a qualitative order of the strength of the basic surface sites was estimated. If this value is high, the CO\(_2\) desorption heat is greater and the basic strength of the site where the molecule was adsorbed is greater too [36]. According to the literature, an increase in the basic strength would be expected when the atomic weight of the alkali metal increases, but our results shows the following site strength order: Fe/Li-SBA-15 \( \approx \) Fe/K-SBA-15 \( \approx \) Fe/Cs-SBA-15. Comparing the three supports obtained in this work the Li-SBA-15 support is the one that exhibits the greatest basic strength for both weak and intermediate sites. In previous works, it has been reported that the Li generates more basic and stronger sites than expected [31,37].

To get more information about the structural properties of these precursors, the diffractionograms of all of them at high angles (\( 2\theta = 5-90^\circ \)) are reported in Supplementary Information. The poor quality of these patterns was determined by the characteristics of the samples. As it can be seen in Figure 1S1, a broad diffraction peak at about \( 2\theta = 24^\circ \), typical for a highly disordered SiO\(_2\) phase of SBA-15 [38], prevail in all solids. Besides, other two diffused peaks, in position compatible with iron oxides can be detected (\( 2\theta = 33^\circ \) and \( 2\theta = 62^\circ \)). The pronounced broadening and the scarce definition of these signals prevent to estimate crystallite size from the results of this technique. Notwithstanding, it can be concluded, at least in a qualitative way, that the iron species are present as very small nanoparticles. This conclusion is coherent with TEM results as it was previously explained.

Signals, attributable to Li\(_2\)O and KOH, were not detected and only one peak, that could belongs to CsNO\(_2\), was visible at \( 2\theta = 44.5^\circ \). It must be remember that, in order to maintain the Fe/M (M: alkali metal) atomic ratio constant, the weight percentage of cesium is about 20 times higher than that the lithium and 5 times than potassium. This fact would justify the detection of this peak.

Mössbauer spectroscopy of fresh catalysts

Figure 5 displays the Mössbauer spectra of the activated and fresh catalysts (at zero reaction time) at 298 and 30 K. All of them were registered in hydrogen atmosphere using the cell mentioned in Experimental Section with the aim to avoid the air contact and possible re-oxidations. The Mössbauer spectrum of activated Fe/SBA-15 at 298 K displays an asymmetric doublet with a shoulder at the positive velocities side, and broad lines that could be attributed to paramagnetic and/or superparamagnetic species (sp). In order to obtain a more precise species assignments the spectrum at 30 K was acquired.

It must be remarked that due to the high complexity of the spectrum at 30 K a conventional fitting process was not carried out. In a first step a set of hyperfine parameters, typical of the species that could be present, was fixed and the areas were fitted freely. Once these areas converge to a minimum, they were fixed and the isomer shift (\( \delta \) and quadrupole splitting (\( \Delta \)) of the doublets and the hyperfine magnetic field (H) of the sextuplets were fitted freely. A decreasing in the hyperfine magnetic fields due to crystal size effects was considered. Instead, the isomer (\( \delta \) and quadrupole (\( \Delta \)) shifts were fixed taking into account that they cannot be affected by the crystal size. Maybe the fittings obtained with this methodology lead to several minima, but they will have very small differences between them. In order to select the best set of values, the sample story and chemical and physical concepts were considered too.

Mössbauer parameters are displayed in Table A of supplementary information. In Table III are shown the percentages of each iron species present in the fresh activated catalysts. The spectrum at 30 K was fitted with six sextuplets and two doublets. Five of these sextuplets can be assigned to the five crystallographic Fe\(_3\)O\(_4\) sites [39]. The additional sextuplet has hyperfine parameters characteristics of \( \alpha \)-Fe [40]. Finally, the two doublets can be attributed to Fe\(^{2+}\) ions located in tetrahedral and octahedral sites inside SiO\(_2\) walls of SBA-15 [40].

The same species are present as paramagnetic or in a superparamagnetic (sp) regime in the spectrum at 298 K. In this way, it can be detected two singlets corresponding to superparamagnetic \( \alpha \)-Fe [40] and Fe\(_3\)O\(_4\) [41] and two doublets assigned to paramagnetic Fe\(^{2+}\) ions diffused inside the silica walls and/or Fe\(_2\)O\(_3\) (sp).

It can be concluded that only about 10% of the total iron loading could be reduced beyond Fe\(_2\)O\(_3\) or Fe\(^{2+}\). Besides, an important diffusion of iron ions inside SBA-15 walls occurs during the activation step. Bearing in mind that before activation only 4% of the total iron loading has diffused inside the walls [42] it could be inferred that two competitive routes would exist during sample reduction: one of them lead, as a final product, to \( \alpha \)-Fe and the other produces Fe\(^{2+}\) ions, which diffuse very quickly inside the SBA-15 walls, and are stabilized there. Considering the final
are superparamagnetic at 298 K, a migration of the nanoparticles outside the SBA-15 channels with sintering could be discarded.

Table III - Percentages of the species present in the activated catalysts at 30 K.

| Species (%)        | Fe/SBA-15 | Fe/Cs-SBA-15 |
|--------------------|-----------|--------------|
| α-Fe               | 11 ± 2    | 8 ± 1        |
| FeO₂               | 42 ± 13   | 65 ± 6       |
| Fe²⁺               | 47 ± 4    | —            |
| Fe₂SiO₄            | —         | 22 ± 4       |

The spectra of the activated samples doped with alkali metals at 30 K are extremely complex due to the large number of peaks and to the presence of superparamagnetic relaxation as it can be inferred by the curved background even at this low temperature (Figure 5). Following the same methodology used for Fe/SBA-15 the spectra were fitted with five sextuplets of magnetically blocked FeO₂ [39], one sextet of α-Fe and two doublets of Fe²⁺ ions located in tetrahedral and octahedral sites of the silica walls. However, this procedure did not produce a satisfactory fit. Therefore, it was considered that new species could be present in comparison with Fe/SBA-15 system. Taking into account the chemical elements present in the sample and the treatments carried out, it was proposed that this new species could be fayalite (Fe₂SiO₄). This compound crystallizes in an orthorhombic system with a distorted compact hexagonal packing of oxygen ions. Fe²⁺ ions occupy half of octahedral sites while Si⁴⁺ ions occupy 12.5% of the tetrahedral sites. Fe²⁺ ions are in two different crystallographic sites M₁ and M₂. At room temperature the Mössbauer spectrum shows an asymmetric doublet with different intensities and line widths indicating the presence of two doublets one per each site [43]. However, they are highly overlapped and cannot be distinguished during the spectrum analysis. When the temperature is lower than 65 K a magnetic ordering is produced, and a sextuplet and an octet appear. M₂ site produces eight lines because the electric quadrupole gradient is so intense (due to site distortion) that it cannot be considered as a hyperfine magnetic field perturbation. As consequence, magnetic quantum numbers are not “good numbers”, the transition selection rules (∆m= 0, ±1) are not valid and forbidden transitions may occur (∆m= ±2). Bearing in mind these considerations, the fitting at 30 K was carried out with the same interactions than Fe/SBA-15 but a sextuplet and an octet were included instead of the two doublets of Fe²⁺ ions. To simulate the octet, eight Lorentzian lines were used which were combined in order to generate the corresponding hyperfine parameters using the methodology proposed by Kündig [44] who obtained graphics that allow evaluate H and 2c for any combination of hyperfine magnetic fields and electric quadrupole gradients. There are a satisfactory agreement between the hyperfine parameters obtained from the fitting for both magnetic signals (sextuplet and octet) and that reported in bibliography for Fe₂SiO₄ [45]. From these results can be concluded that a superficial compound like fayalite has appeared in the SBA-15 pore walls due to an important Fe²⁺ diffusion inside them during the reduction step. Considering that in precursor the amount of

Figure 4: CO₂-TPD results of the precursors species percentages, it can be concluded that the diffusion process is faster than the total reduction. Besides, as all species

This article is protected by copyright. All rights reserved
Fe\(^{3+}\) diffused inside silica walls is about 4 % [42] this migration is produced during the reduction step and competes with \(\alpha\)-Fe formation.

It must be remarked that the total amount of \(\text{Fe}^{2+}\) diffused in the support walls in Fe/K-SAB-15 is similar to that detected in Fe-SBA-15 while in Fe/Li-SAB-15 and Fe/Cs-SAB-15 these quantities are lower than in non-doped catalyst. However, in absence of alkali metal, \(\text{Fe}^{2+}\) ions are not magnetically coupled at low temperature. This result would indicate that in Fe-SBA-15 the interatomic distance between iron ions is higher than in alkali metal promoted catalysts. It could be interpreted considering that Fe-SBA-15 has a homogeneous \(\text{Fe}^{2+}\) ions distribution inside SiO\(_2\) walls. Instead, in promoted catalysts there would be regions where \(\text{Fe}^{2+}\) ions are more concentrated allowing the magnetically coupling at low temperature. It could be speculated that this \(\text{Fe}^{2+}\) heterogeneous distribution may be due to the presence of alkali metal ions inside the silica walls as it was demonstrated by XPS measurements [26], the dispersion values obtained from CO\(_2\)-TPD and by the methodology used in the doped support preparation. Therefore, inside the SBA-15 walls there would be regions where are located the alkali ions, leading to a strong electrostatic repulsion of \(\text{Fe}^{2+}\) ions. As consequence these ions would be concentrated in other zones favoring the magnetic coupling leading to fayalite formation.

The remaining signals were fitted in the same way that Fe-SBA-15; five sextuplets corresponding to magnetically blocked \(\text{Fe}_3\text{O}_4\) and one sextet to \(\alpha\)-Fe. Some differences with non-doped catalyst are an over-reduction of the \(\text{Fe}_3\text{O}_4\) and a slight diminution of \(\alpha\)-Fe production (this is more notorious in the catalyst doped with cesium).

The Mössbauer spectra at 298 K of doped catalysts indicate that all iron species present at 30K are detected at room temperature in a superparamagnetic regime. The three spectra were fitted with two singlets and one asymmetric doublet (Figure 5, Table A of supplementary information). The singlet with higher \(\delta\) was assigned to superparamagnetic \(\text{Fe}_3\text{O}_4\) [41] and the other one could be assigned to superparamagnetic \(\alpha\)-Fe [40]. The asymmetric doublet is the convolution of the signals corresponding to \(\text{Fe}^{2+}\) ions in two different crystallographic sites, \(M_1\) and \(M_2\), of fayalite. They are highly overlapped and it is not possible to distinguish them from each other in the spectrum analysis.

Finally, in Fe/Li-SAB-15 and Fe/K-SBA-15 a small sextuplet with hyperfine parameters typical of \(\alpha\)-Fe was detected. The presence of this signal would indicate certain sintering degree but their percentage is extremely small and this effect could be neglected.

It was concluded that in all fresh catalysts \(\alpha\)-Fe, \(\text{Fe}_3\text{O}_4\) and \(\text{Fe}^{2+}\) diffused inside the silica walls were detected. However, some differences must be remarked:

- the alkali metals presence hinder the iron reducibility, decreasing the \(\alpha\)-Fe percentage and increasing the presence of over-reduced \(\text{Fe}_3\text{O}_4\) one, which is an intermediate during reduction step. This result is more evident in Fe/Cs-SBA-15.
Other authors have found similar results [46]. This behavior allows us to infer that there is an interaction between Fe species and surface alkali metals; -in presence of alkali metals, Fe$^{2+}$ ions diffused inside SBA-15 walls are close enough to be magnetically coupled and produce a silicate (Fe$_2$SiO$_4$) instead of isolated paramagnetic Fe$^{2+}$ ions as it was discussed above; - at 298 K in Fe/SBA-15 and Fe/Cs-SBA-15 all iron species present have a superparamagnetic behavior while in Fe/Li-SBA-15 and Fe/K-SBA-15 a negligible fraction of α-Fe is magnetically blocked. Therefore, considering that the channel diameters of the supports have about 8nm it is possible to conclude that the active phase crystals have a controlled size below this value in all catalysts.

**Mössbauer spectroscopy of used catalysts**

In order to determine the iron species present in “working” catalysts, possible crystal size changes during reaction and the influence of the different alkali metals present in support, Mössbauer spectra of catalysts used in FTS during 24 h were collected at 298 and 30 K. Previously, it was verified that this time is enough to reach the pseudo-stationary state for all catalysts. All spectra were registered in the same atmosphere of the catalytic reaction using the cell described in Experimental Section with the aim to avoid the air contact and possible re-oxidations.

All spectra of the used catalysts, obtained at 298 K, looks similar to that of the fresh catalysts displaying an asymmetric doublet with broad lines and a shoulder on the positive velocities side, which could be attributed to paramagnetic and/or superparamagnetic species (sp). Only Fe/K-SBA-15 displays some different aspects, as it will be described below.

However, the spectra at 30 K showed appreciable differences in comparison with that obtained for fresh catalysts at the same temperature (Figure 6). Table B of Supplementary Information displays hyperfine parameters obtained using the same fitting methodology that in fresh catalysts and Table IV shows the Fe species percentages of the catalysts at the pseudo-stationary state obtained from the Mössbauer spectra at 30K. In order to get a satisfactory fitting six sextuplets and two doublets were used. The two sextuplets with higher magnetic hyperfine fields can be assigned to Fe$_3$O$_4$ magnetically blocked. The percentage of this species decreased in all catalysts to a range of about 20 to 30 %. We considered advisable to use several interactions to distinguish the different crystallographic sites of Fe$_3$O$_4$ with these signals poor defined. Instead, only two sextuplets were used, each one represents the average “weighted” population of different sites of Fe$^{3+}$ and Fe$^{2+}$ respectively. It must be remarked that, in comparison with fresh catalysts, magnetite has been oxidized in all used catalysts increasing its Fe$^{3+}$ percentages. The FTS atmosphere can be oxidant or reducing depending on CO, H$_2$, CO$_2$ and H$_2$O mole ratio. The amounts of these species are related to syngas conversion level and to the secondary reactions of “water-gas shift” and Boudouard. Our results indicate that with these catalysts and the operative conditions used the reaction atmosphere was oxidant.

**Table IV - Fe species percentages of the catalysts at the pseudo-stationary state obtained from the Mössbauer spectra at 30K.**

| Species | Fe/SBA-15 F α-Fe/SBA-15 F α-Fe/SBA-15 Fe/Cs-SBA-15 |
|---------|-----------------------------------------------|
| Fe$^{3+}$ | 34 ± 2 | 49 ± 2 | 47 ± 1 | 80 ± 3 |
| Fe$_3$O$_4$ | 27 ± 2 | 24 ± 3 | 29 ± 1 | 16 ± 3 |
| $\gamma$Fe$_3$O$_4$ + ε Fe$_2$C | 39 ± 5 | 27 ± 5 | 24 ± 1 | 4 ± 2 |

The remaining four sextuplets, with small hyperfine magnetic fields, can be assigned to three sites of γ-Fe$_2$C carbide [47] and two sites of ε-Fe$_2$C carbide [48]. The signals corresponding to sites II of γ carbide and I of ε carbide are completely overlapped at low temperature. For this reason the carbide signals were fitted with four sextuplets instead of five. For Fe/Cs-SBA-15 very small amounts of carbide were detected, and the signals belonging to site III of γ carbide and site II of ε-Fe$_2$C are below the error limits. Therefore these signals were not included in fitting.

Analyzing the results it can be observed that for Fe/Li-SBA-15 and Fe/K-SBA-15 the carbide total amount (27 ± 5 % and 24 ± 1 % respectively) exceeds the α-Fe percentages detected in fresh catalysts (7 ± 1 % for Li and 8 ± 1 % for K, respectively). In this way, it could be concluded that the carbide not only is produced from α-Fe but also from Fe$_3$O$_4$ whose percentage decreases. Similar result was obtained in Fe/SBA-15. However, as in Fe/Cs-SBA-15 the total carbide amount detected (4 ± 2 %) is equal to the α-Fe percentage obtained in the fresh solid it can be concluded that in this catalyst, the carbide is exclusively produced from α-Fe. Several authors have found that “working” catalysts have a mixture of iron carbides and oxides [49-54].

Finally, the two doublets can be assigned to Fe$^{2+}$ ions in tetrahedral and octahedral sites inside SiO$_2$ walls [40] (Figure 6, Table IV). It is important to remark that in all doped fresh catalysts the Fe$^{2+}$ ions had produced superficial fayalite. However, in the used catalysts they are present as isolated paramagnetic ions. This result would indicate that these ions have mobility and under the FTS a more homogeneous redistribution of them could occur. In this way, interatomic distances increased, and the magnetic coupling could not take place leading to isolated paramagnetic ions instead of fayalite.

Other interesting result is that, for Fe/K-SBA-15, the Fe$^{2+}$ percentages is the same to that found in the fresh catalyst. However, for Li and Cs these values were considerably increased in the used catalysts, changing from 22 ± 4 % to 49 ± 2 % in Fe/Li-SBA-15 and from 23 ± 5 % to 80 ± 3 % Fe/Cs-SBA-15. These ions are inactives in the FTS, therefore this change produced by the presence of Li and Cs is undesirable.
On the other hand, the great increase in quadrupole splitting of Fe$^{2+}$ located in octahedral sites for Fe/K-SBA-15 and Fe/Cs-SBA-15, compared with the value obtained in Fe/SBA-15, is indicative that these sites are highly distorted. Thus, the presence of alkali ions inside SiO$_2$ network would have affected its structure strongly, verifying the location of the alkali metal inside by SBA-15 wall. This was not observed in Fe/Li-SBA-15 indicating that a much smaller amount of lithium is in the support walls. These results are in the same direction to that obtained by CO$_2$-TPD and by XPS [26]. After the species assignment from the results at 30 K, the spectra at 298 K were fitted with three doublets and one singlet. Doublets with higher isomer shift were assigned to paramagnetic Fe$^{2+}$ in tetrahedral and octahedral sites of the silica walls. The other doublet, with lower isomer shift, was assigned to superparamagnetic carbide and the additional singlet to superparamagnetic magnetite [41]. Fe/K-SBA-15 spectrum at 298 K displays small differences with the other catalysts. In this way, small and poor defined magnetic interactions can be seen at both sides of the central signals. Therefore, three additional sextuplets were added in fitting. They were assigned to I, II and III sites of $\chi$-Fe$_2$C$_5$ carbide [47] and to site II of $\epsilon$-Fe$_2$C which overlaps with site I of $\chi$-Fe$_2$C$_5$ [48]. This fraction would be originated by carburization of the small percentage of $\alpha$-Fe that would have migrated outside SBA-15 channels. Therefore, all species detected at 30 K are present as paramagnetics or in a superparamagnetic regime in the spectra at 298 K. Besides, Fe-K-SBA-15 displays a small magnetically blocked fraction at room temperature.

Comparing the doped catalysts with Fe-SBA-15, after 24 hours of FTS, it can be concluded that in all cases the species detected were $\epsilon$-Fe$_2$C, $\chi$-Fe$_2$C$_5$, Fe$_3$O$_4$ and Fe$^{2+}$ ions diffused inside SBA-15 walls. However, it is interesting to remark the following differences:

- Cs presence has an important negative effect on the structural properties, since Fe mostly migrates inside the support walls being inactive to FTS;
- Fe$^{2+}$ ions diffused into SBA-15 walls have mobility and were redistributed, and as consequence fayalite (Fe$_2$SiO$_4$) disappeared leading to isolated paramagnetic Fe$^{2+}$ ions in the same way that in non-doped catalysts;
- in catalysts doped with K and Cs the SiO$_2$ octahedral site environments have a large distortion in comparison with Fe-SBA-15. This result is coherent with the presence of alkali ions inside the support walls. This effect was not detected in Fe/Li-SBA-15.

Figure 6: Mössbauer spectra of used catalysts.
Catalytic tests

Catalytic tests were carried out at 1 and 20 atm. It must be remarked that to get acceptable conversion levels at 1 atm were assayed several reaction temperatures and 703 K was chosen. This is a severe requirement in comparison with the temperature used in industrial conditions. Notwithstanding, the tests were performed in order to study and characterize the behavior of the different catalytic solids. Alkanes and alkenes up to C\textsubscript{22} were detected as products and oxygenated compounds were not found. Figure 7 shows the CO conversion values measured at different reaction times at 1 atm for the four catalysts.

![Figure 7: CO Conversion throughout the reaction time at 1 atm.](image)

Fe/SBA-15 and Fe/Cs-SBA-15 reach a pseudo-stationary state after approximately 24 h of reaction. In contrast, catalysts doped with Li and K shows a continuous conversion increase. Considering that pressure measurement instrument registered an increase of this variable, this result could be attributed to this effect. It is estimated that the presence of alkali metals on the catalyst surface favors the CO dissociation increasing its conversion (as it is explained below) but at the same time leads to an increase of secondary reactions such as the Boudouard reaction, which is also favored by the high reaction temperature. This reaction produces carbon, which obstructs the catalytic bed, increasing the system pressure. Confirming this reasoning, at the end of the tests a mass of compact coal was found in the catalytic bed when Fe/Li-SBA-15 and Fe/K-SBA-15 were used. In addition, during reaction the chromatographic analysis revealed the presence of a greater amount of CO\textsubscript{2} (the other product of the Boudouard reaction) when the catalysts used were those promoted with Li and K. For this reason, the comparisons between all the catalysts are accurate only at short reaction times (at about 8 h). Taking into account these considerations the following CO conversion order was found Fe/Li-SBA-15> Fe/K-SBA-15> Fe/SBA-15> Fe/Cs-SBA-15. Considering that the total number of basic surface sites created by doping with alkali metals follows the order: Li ≈ K >> Cs and that the strength order was: Li> K ≈ Cs, it is possible to infer that there would be a correlation between these results and the corresponding catalytic activities. Dissociation of CO, assisted by hydrogen or not, is generally seen as the first step in the reaction mechanism in the FTS [56]. Therefore, our catalytic results could be explained by electrostatic effects, of short- and long-range, generated by the alkali metals on Fe. These effects decrease the work function of iron and the bonding and antibonding molecular orbitals of CO fall below the Fermi level of the metal. As consequence, the antibonding level of CO becomes partially filled, and consequently the intramolecular bond is weakened, and its dissociation can be produced more easily [57, 58].

![Table V-Olefin/Paraffin ratio at isoconversion](image)

| Catalyst | CO conversion (%) | Olefin/Paraffin up to C\textsubscript{3} (without C\textsubscript{1}) | Olefin/Paraffin up to C\textsubscript{13} (without C\textsubscript{1}) |
|----------|------------------|-------------------------------------------------|-------------------------------------------------|
| Fe/SBA-15| 9                | 1,6                                            | 1,6                                            |
| Fe/K-SBA-15| 10            | 2,2                                            | 2,2                                            |
| Fe/Li-\textsubscript{15} | 10          | 3,0                                            | 2,0                                            |
| Fe/Cs-SBA-15| 8            | 2,7                                            | 2,8                                            |

These results do not show a direct correlation with the number and strength of basic sites detected. Despite this complexity, it is possible to conclude that the presence of alkali dopants generates a beneficial effect on the olefins production in comparison with non-promoted catalyst. This result could be attributed to the negative charge densities generated on the basic sites (O\textsuperscript{2−}) produced by the presence of alkali dopants. In this way, olefins, which has high electron density in the double bonds, could be strongly repulse due to electrostatic effect and they would be quickly desorbed decreasing the hydrogenation probability to produce paraffins.

Selectivities for different hydrocarbon ranges at these iso-conversion values were also obtained (Figure 8). Light hydrocarbons in the range of C\textsubscript{2}-C\textsubscript{4} were preferentially produced.
The activity order obtained was Fe/K-SBA-15 > Fe/Li-SBA-15 ≥ Fe-SBA-15 > Fe/Cs-SBA-15. This sequence is different to that obtained at 1 atm. Studies of infrared of CO adsorbed on transition metals promoted with alkali metals indicate that there is a remarkable weakening of C-O bond in the first layer of adsorbed molecules [58]. At higher coverages, other CO adsorption states are developed, and the softening of the C-O bond is considerably lower. We conclude that, at higher pressure, surface coverage is increased, and the promoter effect is attenuated.

The products obtained in catalytic tests at 20 atm and 543 K were alkenes and alkanes from methane up to C_{33}, oxygenated products were not found. The CO conversions, at different reaction time, are shown in Figure 9 for all catalysts. Bearing in mind the important diminution in the mole number, characteristic of the FTS, all of them showed a marked conversion increase with respect to the test at 1 atm. It must be highlight that at 1 atm a temperature of 703 K was necessary to get a CO conversion of about 10 %, instead at 20 atm, values in a range between 15 to 25% were obtained at only 543 K. In these conditions was no C formation or blockage of the catalytic bed in any case and an activity level approximately constant, during 48 h, was obtained. We consider that the pronounced difference between the necessary reaction temperatures at 1 and 20 atm is not only consequence of the change in the number moles during the FTS. Instead, we interpreted these results because of the presence of nanoparticles of the active species inside the channels of the SBA-15, which cause their occlusion. Considering that textural measurements indicate that only a fraction of the total channels are blocked, reactive and products could be going into and exit, respectively, thorough the micropores that connect empty mesopores with blocked mesopores. Considering the reduced diameter of the micropores this process could be controlled by diffusion and high temperatures are required at 1 atm. The increase of pressure allows to get a similar result but at a temperature considerably lower. A recent theoretical calculus indicates that, in a system of mesopores connected by micropores, effective diffusivities are increased 50 % when pressure is increased from 1 to 10 atm [59].

Figure 8: Selectivity to different hydrocarbons at iso-conversion.

Figure 9: CO conversion at different reaction times in FTS at high pressure
A mesoporous solid SBA-15 was promoted with Li, K or Cs and then it was used as a support of iron. These composites were utilized as catalysts in the Fischer-Tropsch synthesis. We have proved the creation of basic surface sites, with different quantities and strengths depending on the alkali metal, by CO-

C5 - C12
t.

ons and an oxidation of the Fe

C19+

t without promoter have

of H

C13 - C18
3

diminished in the

considerable diminution in the

doped catalysts should not lead to the alkali metals. Only Fe/K

47x207

indicates that activation step and the synthesis conditions did

n a superparamagnetic regime at room temperature is

both findings show that iron species are changing during the FTS. Besides, the increase of Fe

32+ percentage in

O

C

5

5

intermediate in the reductio

demonstrate that the reaction atmospheric is oxidant.

The SBA-15 walls were found. In comparison with fresh catalysts a re-distribution of Fe

2 ions and an oxidation of the Fe

O4 were detected. Both findings show iron species are changing during the FTS. Besides, the increase of Fe

23+ percentage in

O

Fe3O4 indicates that the reaction atmosphere is oxidant.

The existence of all iron species, in fresh and in “working” catalysts, in a superparamagnetic regime at room temperature is indicative that activation step and the reduction conditions did not produce sintering of them. Only FeK-SBA-15 showed a negligible fraction of iron carbides with magnetic blocking. Therefore, we can conclude that particle size effects are not present and the differences between catalysts could be attributed, exclusively, at the different alkali ions.

In the FTS at 1 atm the activity order obtained was: Fe/Li-SBA-15> Fe/K-SBA-15> Fe/SBA-15 > Fe/Cs-SBA-15. These results can be explained by an electrostatic effect generated by the alkali metals which decrease the work function of iron. We consider important to remark that the preparation sequences of doped catalysts should not lead to deposit the alkali metals on the surface of iron species. Notwithstanding, the electrostatic effects are reflected in the catalytic results. Therefore, it could be deduced that would not be necessary a physical contact between alkali metals and iron species to get promoter effects. Besides, it is possible to conclude that alkali dopants of Group 1 favored the olefins production.

An important conversion increase was observed when the catalytic tests were carried out at 20 atm. This is an expected result taking into account the considerable diminution in the mole number when the FTS occurs. However, we consider that other effect must be present because at 1 atm was necessary to use a temperature as high as 703 K to get an acceptable CO conversion. Instead, at 20 atm, a temperature of 543 K is enough to reach higher activity. We attributed this result to the fact that the iron nanoparticles located inside the SBA-15 channels would block the free movement of reactive and products. Considering that the mesopores of SBA-15 are connected between them by micropores and that only a portion of the mesopores are blocked, reactive could reach the active site across the empty mesopores and the micropores of the walls. At 1 atm, this sequence would be slow and high temperatures would be necessary to speed up the process. Instead, at 20 atm, effective diffusivity can be significantly increased, and the reaction would proceed satisfactorily at low temperature. Other interesting aspect is that the difference between distinct dopants and the catalyst without promoter have decreased. Besides, all catalysts show low methane production, high selectivity towards light gases and an interesting production in the gasoline range between 30 and 40%. It should keep in mind that pressure and temperature used in these tests are like that used in industrial conditions. Therefore, these solids, especially Fe/K-SBA-15, would be promising to produce, with an acceptable level, hydrocarbons in the gasoline range. This selectivity, achieved on chain growth, can be attributed to the crystal size control of the active species. Although the existence of shape selectivity, due to the support pores sizes, cannot be completely discarded.

Experimental Section

Catalyst preparation

The SBA-15 support was synthesized according to the methodology proposed by Zhao et al. [19, 20] using Pluronic triblock copolymer P123 (EO109-PO78-EO109) as organic structure-directing agent and tetraethyl orthosilicate (TEOS) as silica source. Thus, 12 g of Pluronic P123 were dissolved in a solution consisting on 60 ml of HCl solution (37% w/w) in 360 ml of water under stirring at 313 K during 3 h. Then, 27 ml of TEOS were added, and the resulting solution was kept under stirring at 313 K for 24 h. The mixture was statically aged at 363 K during overnight. The solid was recovered by filtration, washed, and dried in air at room temperature (RT). The sample was calcined in air flow (150 cm3/min) heating from RT to 773 K at 1 K/min and kept at 773 K for 6 h. To obtain the promoted supports, Li-SBA-15, K-SBA-15 and Cs-SBA-15, this synthesis was slightly modified following a methodology developed in our laboratory. Together with P123, the corresponding alkali metal nitrate was added. Once the solid was obtained, the remaining water in the synthesis gel, was slowly evaporated in vacuum at 333 K in a rotary evaporator avoiding the filtration step. The alkali metal loadings on SBA-15 were established maintaining the Fe/M (M: alkali metal) atomic ratio constant and equal to that of the commercial catalysts in all samples [60]. All supports were impregnated by the incipient wetness impregnation method with Fe(NO3)3·9H2O ethanolic solution to produce a nominal Fe loading of 15% w/w in a single step. The solids were dried using a rotary evaporator at 313 K for 24 h and finally calcined in NO/He (1% v/v) flow.
(100 cm³/min) from RT to 723 K at a heating rate of 1 K/min and kept at this temperature for 4 h. The samples thus obtained were called Fe-SBA-15, FeLi-SBA-15, FeK-SBA-15 and Fe/Cs-SBA-15.

Catalyst characterization

The samples were characterized by atomic absorption-emission spectroscopy (AA/AE), UV-Vis spectroscopy (UV-Vis), X-ray diffraction at low angles (XRD), transmission electron microscopy (TEM), N₂ adsorption (BET), Mössbauer spectroscopy (MS) and CO₂ desorption at programmed temperature (CO₂-TPD).

The alkali metal content of the solids was determined in a AA/AE Atomic Absorption Instrument Spectrophotometer 457 of Instrumentation Laboratory Inc., while the Fe content was determined in a UV-Vis spectrophotometer Perkin Elmer Lambda 35. The X-ray diffraction patterns at low angles were recorded in Shimadzu equipment, XD3A model, using Cu Kα radiation generated at 40 kV and 40 mA in the range 2θ = 0.5–6° with steps of 0.02° and counting time of 2 s/step.

For TEM measurements a JEOL model JEM-1200 EX II microscope was used. Samples for analysis were prepared by drying a dispersion of the solids on amorphous carbon coated copper grids.

N₂ adsorption-desorption isotherms at 77 K were measured in a Micrometrics ASAP 2020 VTI02 equipment. The samples were previously outgassed at 523 K for 12 h. Textural properties, such as specific surface area (Sₛₐ), specific pore volume (Vₚ), and average pore diameter (Dₚ) were calculated from the experimental data. Combining XRD and BET techniques, the wall thickness (e) was obtained.

The Mössbauer spectra were acquired in transmission geometry with a 512 channels constant acceleration spectrometer. A ⁵⁷Co source in Rh matrix of nominally 50 mg was used. Velocity calibration was performed using a 12 µm thick α-Fe foil. All isomer shifts (δ) mentioned in this work were referred to this standard. A closed cycle cryogenic system (DISPLEX DE-202) was used to modify the temperature between 30 and 298 K. The Mössbauer spectra were evaluated with a commercial fitting program named Recoll [61], using Lorentzian lines and all spectra were folded to minimize geometric effects. The spectra of fresh and used catalysts, in a controlled atmosphere of H₂ or in the reaction gases, respectively, were obtained using a special cell designed and built in our laboratory [62]. In this way the contact of the solids with air was avoided and possible oxidations, during the sample handling and the spectra measurement, can be discarded.

For the CO₂-TPD analysis the samples were activated “in situ” in Ar flow (20 cm³/min) at 973 K for 2 h, cooled to RT and then exposed to a stream of CO₂/Ar (8:100) to adsorb CO₂ until surface saturation. After that the sample was treated in pure Ar flow (90 cm³/min) to remove the physisorbed CO₂. Then, it was heated in Ar flow (20 cm³/min) at 10K/min up to 973 K. The desorbed CO₂ was converted in CH₄ using H₂ flow (20 cm³/min) and a Ni/SiO₂ catalyst at 673 K, then the CH₄ was quantified in a FID detector.

Activity and selectivity measurements

Activity and selectivity measurements at atmospheric pressure and 703 K were carried out in a stainless steel fixed-bed reactor, using H₂-CO flow with 2:1 molar ratio and a space velocity of 1176 h⁻¹ (=450 mg of catalyst and a total flow rate of 20 cm³/min). The catalysts were reduced “in situ” before reaction using hydrogen flow (99.999% purity), at atmospheric pressure and 703 K for 6 h. After the reduction treatment, H₂ flow was replaced by H₂-CO mixture and the catalytic test started. The products were analyzed “online” by gas chromatography using FID and TCD as detectors and two columns: capillary GS-Gas Pro and filled HAYESEP DB 100/120, respectively.

The FTS at high pressure was carried out in a unit of Iconel (Ni-Cr-Fe based alloy mainly) on a small scale. The gases used were: H₂ for sample reduction, N₂ for reactor purge and a mixture of 31.7% CO/64.3% H₂/4% He for the reaction. He was used as an internal standard to calculate the total CO conversion. The reactor was operated at a total pressure of 20 atm, a space velocity of 1176 h⁻¹ (=450 mg of catalyst and a total flow rate of 20 cm³/min) and a reaction temperature of 543 K. The products were analyzed “online” by gas chromatography using FID and TCD as detectors and columns megabore CP-Sil 5 CB and filled CP-PoraBONDQ, respectively.

The different reaction temperatures used at high and low pressure are because at atmospheric pressure, catalysts need a high temperature to reach good conversion levels [16]. Instead, at 20 atm good activity levels are achieved at low temperatures.

Acknowledgements

The authors acknowledge the financial support of FONCyT-ANPCyT (PICT 2017-2808), CONICET and National University of La Plata which allowed the development of this work.

K e y w o r d s: Fischer-Tropsch Synthesis • Mesoporous materials • Alkal cations • Basicity • Mössbauer spectroscopy

[1] Snehesh Shivannah Ail, S. Dasappa, Renewable and Sustainable Energy Reviews, 2016, 58 C, 267-286.
[2] J. Yang, W. Ma, D. Chen, A. Holmen, B.H. Davis, Appl. Catal. A: Gen., 2014, 470, 250-260.
[3] I. Khodakov, W. Chu, P. Fongland, Chem. Rev., 2007, 107, 1692-1744.
[4] W. Chen, T. Lin, Y. Dai, Y. An, F. Yu, L. Zhong, S. Li, Y. Sun, Catal. Today, 2018, 311, 8-22.
[5] J. Li, X. Cheng, C. Zhang, Q. Chang, J. Wang, X. Wang, Z. Lv, W. Dong, Y. Yang, Y. Li, Appl. Catal. A: Gen., 2016, 528, 131-141.
[6] Y. Yang, H.W. Xiang, Y.Y. Xu, L. Bai, Y.W. Li, Appl. Catal. A: Gen., 2004, 266, 161-194.
[7] W. Nigantsoue-Hoc, Y.Q. Zhang, R.J. O’Brien, M.S. Luo, B.H. Davis, Appl. Catal.A: Gen., 2002, 236, 77-89.
[8] G. Zhao, C. Zhang, S. Qin, H. Xiang, Y. Li, J. Mol. Catal. A: Chem., 2008, 286, 137-142.
[9] V.R.R. Pendyala, G. Jacobs, J.C. Mohandas, M. Luo, H.H. Hamdhe, Y. Ji, M.C.Ribeiro, B.H. Davis, Catal. Lett., 2010, 140, 98-105.
[10] S. Li, W. Ding, G.D. Meitzner, E. Iglesia, J. Phys. Chem. B, 2006, 106, 85-91.
[11] M.C. Ribeiro, G. Jacobs, B.H. Davis, D.C. Cronauer, A.J. Kropf, C.L. Marshall, J. Phys. Chem. C, 2010, 114, 7956-7963.
[12] H. Xiong, M.A. Motchelaha, M. Moyo, L.L. Jewell, N.J. Coville, Fuel, 2015, 150, 687-696.
[13] M. Boudart, A. Delbouille, J.A. Dumesic, S. Khammouma, H. Topsoe, J. Catal., 1975, 37, 486-502.
[14] M.A. McDonald, D.A. Storm, M. Boudart, J. Catal., 1986, 102, 386-400.
[15] E.I. Mabaso, E. van Steen, M. Claey, DGMK Tagungsbericht, 2006, 4, 93-100.
[16] L. Caño, M.V. Cagnoli, N.A. Fellenz, J.F. Bengoa, N.G. Gallegos, A.M. Alvarez,S.G. Marchetti, Appl. Catal. A: Gen., 2010, 379, 105-110.
[17] P.B. Radstake, J.P. den Breejen, G.L. Bezemee, J.H. Bitter, K.P. de Jong, V.Freseth, A. Holmen, Stud. Surf. Sci. Catal., 2007, 167, 85-90.
[18] G.L. Bezemee, J.H. Bitter, H. P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kaptein, A.J. van Dillen, K.P. de Jong, J. Am. Chem. Soc., 2006, 128, 3956-3964.
[19] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D.Stucky, Science, 1998, 279, 545-552.
[20] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc., 1998, 120, 24 6024-6036.
[21] F. Martinez, Y.J. Han, G. Stucky, J.L. Sotelo, G. Ovejero, J.A. Meiero, Stud. Surf. Sci. Catal., 2002, 142, 1109-1116.
SBA-15 can be doped with alkali metals and used as support of iron species to obtain promising catalysts for Fischer-Tropsch synthesis. Consequences of promotion can be explained by the presence of surface basic sites and long-range electrostatic effects. Mesoporous channels are partially blocked by nanoparticles of iron species but reactive can achieve the active sites and products can be exit through micropores of SBA-15 walls.