

Fischer–Tropsch synthesis using iron supported on potassic LTL zeolite and modified with Cs

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Available online 18 August 2005

Abstract

Iron catalysts, to be used in the Fischer–Tropsch reaction were prepared using zeolite LTL and zeolite LTL modified with cesium, as supports. X-ray diffraction, specific surface area, atomic emission and absorption spectroscopies, Mössbauer spectroscopy in controlled atmosphere, between room temperature and 22 K, H₂ chemisorption and volumetric oxidation were used to characterize the solids.

Comparing both catalysts, the Cs presence generates a solid with a lower reducibility degree and a lower quantity of Fe⁰ microcrystals inside the pore structure, leading to a lower activity per gram and a higher olefins/paraffins ratio.

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Keywords: CO hydrogenation; Fischer–Tropsch synthesis; Supported Fe; Zeolite LTL; Mössbauer spectroscopy; FeCs/LTL zeolite

1. Introduction

The Fischer–Tropsch (FT) synthesis is still a process in development as an option for commercial hydrocarbon production. The supported metallic catalysts have been widely used in FT [1]. However, the tailoring of a catalyst with high activity, good selectivity towards some interesting products, such as light olefins and with an important structural and functional stability, is still a subject to be solved. Amorphous solids, such as Al₂O₃, SiO₂, C, etc. [2,3], were used as catalyst supports but they show a broad distribution of pore sizes, sometimes showing a multi-modal pore size distribution, which induce a broad distribution of Fe⁰ particles. Considering that Fe⁰ crystals are the active phase of the reaction and that FT is a “structure sensitive reaction” [4] the presence of a broad range of particle sizes should contribute to a selectivity loss.

In order to look for a solution to this problem, solids with ordered pore structure and high surface area, such as the zeolites, seem to be very useful. These solids are being used as support of various catalysts because they can display shape selectivity effects in some reactions. Since the zeolite channels cannot exceed 1 nm in diameter, the metallic particles cannot grow beyond this size. However, it is known that in Fe-exchanged ZSM-5 and Y-zeolite systems [5], the iron goes into the zeolite pore structure after impregnation, but it migrates out of the pores [5] by mechanisms which are not understood yet [6] when these systems are subjected to reduction treatments. When this happens, the beneficial effect of the zeolite channel structure no longer influences the outcome of the reaction.

In previous works [7,8], we have reported that an important fraction of Fe crystal oxide remains inside the potassic form of the zeolite L structure (LTL) using the “alkaline microinjection” method. This means that due to the low hydrophobicity degree of this zeolite produced by a low Si/Al ratio the impregnating solution may go easily

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into the channels network of the zeolite. Therefore, the K^+ ions released by ion exchange with Fe^{3+} in Fe-LTL produce an increase of the pH of the solution [9] that fills the zeolite channels, thus causing the precipitation and “anchoring” of Fe oxi-hydroxides inside the pores. Afterwards, during the reduction stage some migration of the Fe^0 crystallites occurs out the pores [9]. The special and specific combination of: (a) very narrow channels, (b) small iron metallic “clusters” inside these channels and (c) the K^+ ions presence also inside these channels produced desirable results [10].

Keeping in mind that high support basicity increases the olefins production [8], the aim of the present work is to obtain an iron catalyst supported on LTL zeolite exchanged with Cs with the purpose of increasing the olefins production. The results obtained were compared with those found for Fe/LTL and the activity and selectivity results of both catalysts were analyzed in connection with their structural properties.

2. Experimental

Two iron catalyst precursors were prepared using two different supports: (a) the commercial form of the zeolite LTL (Tosoh Corp.), with the ideal unit cell composition of dehydrated form of $K_9Al_9Si_{27}O_{72}$ and (b) the same zeolite exchanged with $CsNO_3$ aqueous solution (0.3 M) at room temperature (RT), during 6 days, washed, centrifuged, dried, at 393 K during 48 h and calcined at 863 K during 16 h (Cs-LTL). The supports were impregnated with $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution (pH 0.5) of an iron salt concentration enough to yield solids with about 5% (w/w) of iron, following the procedure showed in Fig. 1. The outgassing of the supports was carried out with the purpose to eliminate the present water inside the zeolite channels. Before impregnation, the system was filled with ultra high purity He, at 500 Torr. The thermal program used in the calcination step was described in Ref. [11]. The obtained precursors were named p-Fe/LTL and p-FeCs/LTL and were reduced as it is described in Fig. 1. The resulting solids were called c-Fe/LTL and c-FeCs/LTL.

The samples were characterized by X-ray diffraction (XRD), nitrogen adsorption (BET), atomic absorption (AA), atomic emission (AE), Mössbauer spectroscopy (MS) at 298 and 22 K, H_2 chemisorption and volumetric oxidation.

The Mössbauer spectra were obtained in transmission geometry with a 512-channels constant acceleration spectrometer. A source of ^{57}Co in Rh matrix of nominally 50 mCi was used. Velocity calibration was performed against a 12 μm thick α -Fe foil. All isomer shifts (δ) mentioned in this paper are referred to this standard. The temperature between 22 and 298 K was varied using a Displex DE-202 Closed Cycle Cryogenic System. The Mössbauer spectra were evaluated using a least-squares non-linear computer-fitting program with constraints. Although some spectra display

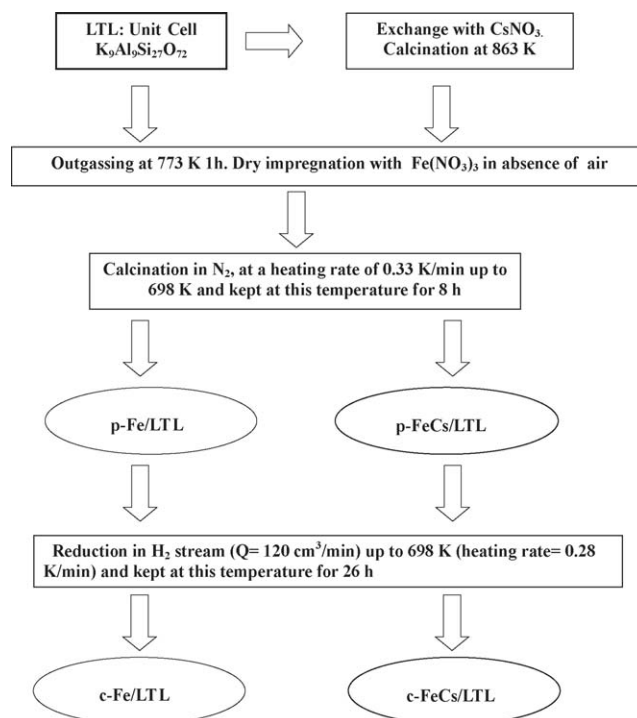


Fig. 1. Schematic representation of the catalyst synthesis.

magnetic relaxation, for simplicity, Lorentzian lines were considered with equal widths for each spectrum component. The spectra were folded to minimize geometric effects. The spectra of the reduced samples were obtained in hydrogen atmosphere using a cell specially built for this purpose to be used inside the cryogenic system [12].

The H_2 chemisorption and volumetric oxidation experiments were carried out in a conventional volumetric static equipment [13].

Measurements of activity and selectivity were carried out in a stainless steel fixed bed reactor at 543 K, 1 bar of total pressure, with $H_2:CO$ ratio of 2:1, 20 cm^3/min of total flow and 1.5 h^{-1} of WHSV. The reaction products were analyzed by gas chromatography using FID and TCD detectors. Two columns were necessary to evaluate all reaction products: a capillary GS-alumina and a Chromosorb 102 packed column.

3. Results and discussion

Fig. 2 shows a representative scheme of a LTL zeolite structure. It can be seen the location of the different types of sites. The K^+ ions located in the D sites are the only accessible at RT [14,15]. Therefore, they are able to be exchanged by the Fe^{3+} ions arising from the impregnating salt.

When the LTL zeolite is treated with an aqueous solution of $CsNO_3$ at RT, the K^+ ions in D sites are exchanged by Cs^+ ions. During the calcination step,

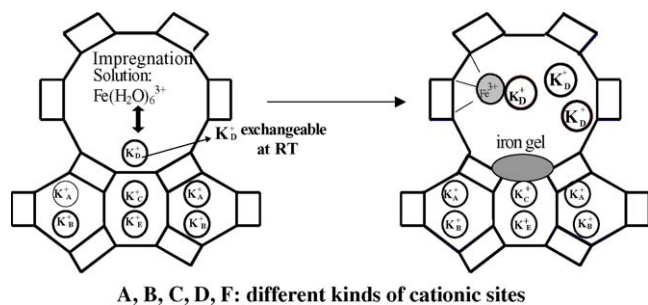


Fig. 2. Representative scheme of a LTL zeolite structure.

previous to the impregnation with the iron salt, the Cs⁺ are exchanged with the K⁺ ions located in the A sites of the zeolite [15] maintaining the characteristics of zeolite principal channel without changes (Fig. 3). Taking into account the definitive location of Cs⁺ ions, its electrostatic effect must be considered as a long range one since these ions are not in contact with metallic iron.

The maintenance of the Cs-LTL crystalline structures after the processes of exchange and calcination was corroborated by XRD (Fig. 4). The same diffraction peaks than LTL are observed, although with a decrease in their relative intensities. This intensity decrease can be due to a decrease in crystalline degree after the exchange and calcination steps. In order to simulate the iron impregnation effect on the LTL structure, the solid was impregnated with a HNO₃ solution (pH 0.5). After calcinations, the structure maintenance with a crystalline degree loss was also observed (Fig. 4).

Table 1 displays the iron and potassium contents, determined by AA, the cesium loading determined by AE and the surface areas of the solids. The decrease of the specific surface area between LTL and CsLTL can be

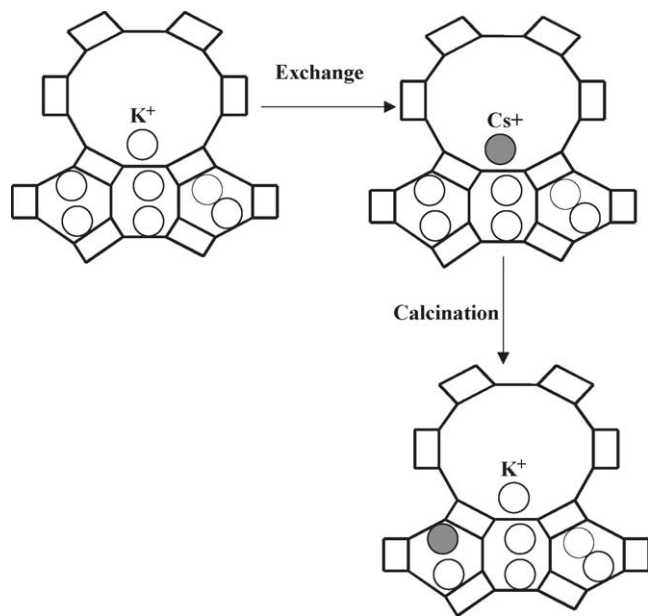


Fig. 3. Scheme of the exchange-calcination processes of zeolite LTL with CsNO₃.

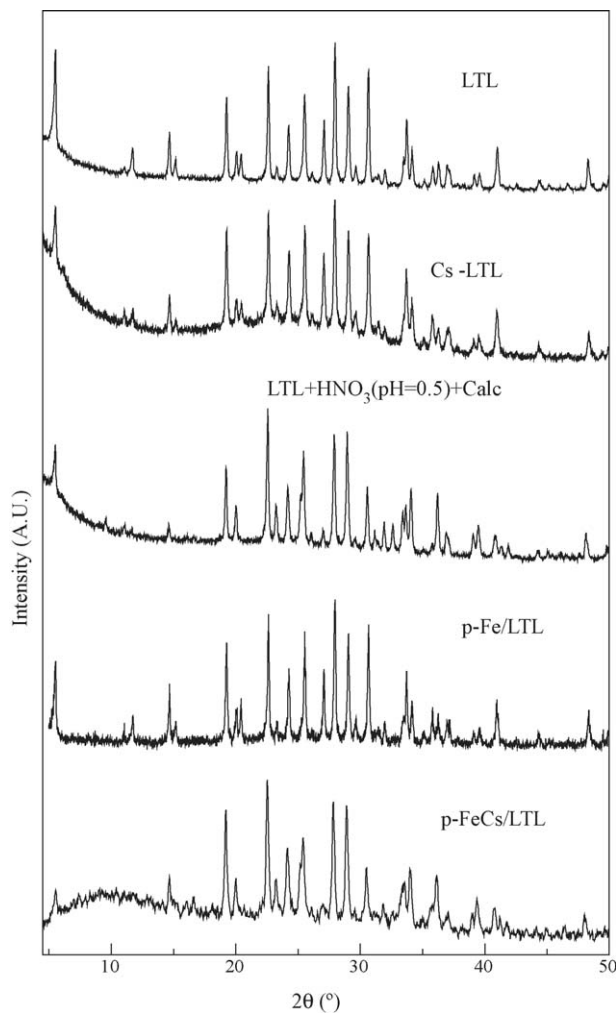


Fig. 4. XRD patterns of the samples.

attributed to the crystallinity loss. Instead, the important *S_g* diminution of the precursors, compared with their own supports, could be assigned to two effects:

- Crystallinity loss due to the acidic impregnation medium.
- Iron oxide presence inside the channels and/or in the mouth of the zeolite channels blocking the total pore access. Considering that the pores are not interconnected in LTL zeolite, a great surface area decrease can be explained in spite of the low iron content.

The Mössbauer spectra of p-Fe/LTL and p-FeCs/LTL at 298 and 22 K are shown in Fig. 5. A paramagnetic doublet

Table 1
BET and atomic absorption results of the samples

Sample	<i>S_g</i> (m ² /g)	K (%) (w/w)	Cs (%) (w/w)	Fe (%) (w/w)
LTL	290	13.1	–	–
Cs LTL	127	7.4	16.6	–
p-Fe/LTL	45	13.1	–	5.4
p-FeCs/LTL	27	7.4	16.6	5.4

S_g, specific surface area.

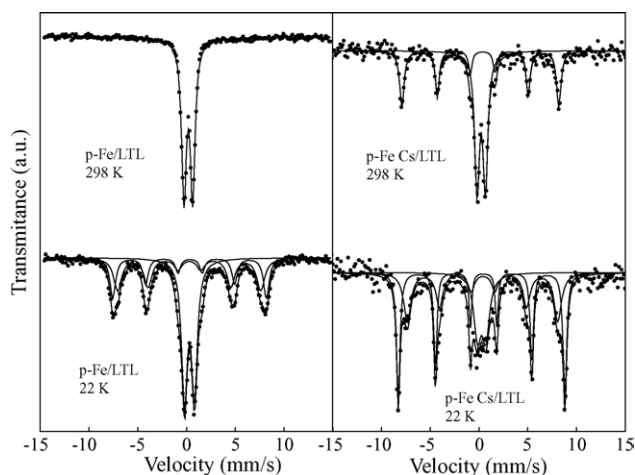


Fig. 5. Mössbauer spectra of the precursors at 298 and 22 K.

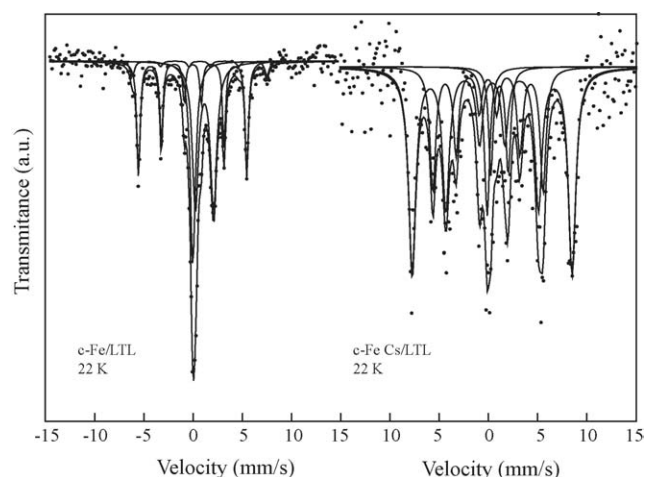


Fig. 6. Mössbauer spectra of the catalysts at 22 K.

can be observed in both precursors at RT. An additional sextet is present in p-FeCs/LTL. When the temperature diminishes to 22 K, a second magnetic sextet is observed in p-FeCs/LTL, while, two sextets and a doublet appear in p-Fe/LTL. The Mössbauer hyperfine parameters (Table 2) correspond to two different Fe^{3+} species: $\alpha\text{-Fe}_2\text{O}_3$ and/or Fe^{3+} exchanged with the support. The magnetic parameters obtained for the two sextets in p-Fe/LTL spectrum at 22 K, are in agreement with those found for the “core” and “shell” of $\alpha\text{-Fe}_2\text{O}_3$ clusters [16]. Assuming that the particles are spherical and homogeneous, an average cluster diameter of 0.9 nm can be estimated considering the areas ratio of both sextets. This size indicates that the particles could be located inside the zeolite channels. This result and the decrease of the surface area (as it was mentioned previously) would corroborate the existence of microcrystals situated mainly inside the zeolite channels. The remainder doublet was assigned to Fe^{3+} exchanged with the support and/or $\alpha\text{-Fe}_2\text{O}_3$ crystallites with sizes lower than

0.9 nm. On the other hand, the existence of a sextet at 298 K in p-FeCs/LTL indicates the presence of $\alpha\text{-Fe}_2\text{O}_3$ fraction with bigger crystal size than that observed in p-Fe/LTL. This fraction does not change its percentage when the temperature decrease and they should be located outside the zeolite channels. These $\alpha\text{-Fe}_2\text{O}_3$ crystals do not show the Morin transition therefore their sizes could be lower than 20 nm [17]. Besides, the second sextet becomes from the magnetic ordering of some particles that are superparamagnetic at RT. The Mössbauer parameters of this second sextet are assignable to the “core” of very small $\alpha\text{-Fe}_2\text{O}_3$ particles (with lower hyperfine field). The signal corresponding to the “shell” fraction is not detected at this temperature indicating that the particle size must be slightly higher than 0.9 nm. Therefore, in p-FeCs/LTL the $\alpha\text{-Fe}_2\text{O}_3$ crystals are mainly located at the external surface of the zeolite.

Fig. 6 shows the Mössbauer spectra of both catalysts at 22 K in hydrogen atmosphere. Both spectra display the presence of two magnetic sextets, one paramagnetic doublet

Table 2
Mössbauer hyperfine parameters of p-Fe/LTL and p-FeCs/LTL

Species	Parameters	p-Fe/LTL		p-FeCs/LTL	
		298 K	22 K	298 K	22 K
$\alpha\text{-Fe}_2\text{O}_3$	H (T)	–	49.3 ± 0.1	–	47.9 ± 0.2
Magnetic	$\delta(\text{Fe})$ (mm/s)	–	0.50 ± 0.01	–	0.50 ± 0.02
Core	2ϵ (mm/s)	–	-0.06 ± 0.02	–	-0.05 ± 0.04
$\alpha\text{-Fe}_2\text{O}_3$	H (T)	–	46.3 ± 0.1	–	–
Magnetic	$\delta(\text{Fe})$ (mm/s)	–	0.46 ± 0.01	–	–
Shell	2ϵ (mm/s)	–	-0.03 ± 0.02	–	–
Fe^{3+}	Δ (mm/s)	–	1.03 ± 0.01	–	–
Exchanged	$\delta(\text{Fe})$ (mm/s)	–	0.46 ± 0.01	–	–
Fe^{3+} oxide and/or	Δ (mm/s)	0.90 ± 0.01	–	0.85 ± 0.01	0.85 ± 0.04
Fe^{3+} (exchanged)	$\delta(\text{Fe})$ (mm/s)	0.34 ± 0.01	–	0.34 ± 0.01	0.38 ± 0.03
$\alpha\text{-Fe}_2\text{O}_3$	H (T)	–	–	50.0 ± 0.1	53.0 ± 0.1
	$\delta(\text{Fe})$ (mm/s)	–	–	0.37 ± 0.01	0.48 ± 0.01
	2ϵ (mm/s)	–	–	-0.24 ± 0.02	-0.21 ± 0.01

H : hyperfine magnetic field, δ : isomer shift (referred to $\alpha\text{-Fe}$ at 298 K), 2ϵ : quadrupole shift and Δ : quadrupole splitting.

Table 3
Mössbauer hyperfine parameters of c-Fe/LTL and c-FeCs/LTL

Species	Parameter	c-Fe/LTL 22 K	c-FeCs/LTL 22 K
Fe ⁰ (magnetic)	<i>H</i> (T)	34.1 ± 0.1	34.8 ± 0.2
	δ(Fe) (mm/s)	0.12 ± 0.01	0.07 ± 0.03
	2ε (mm/s)	−0.02 ± 0.01	0.00 ^a
Fe ₃ O ₄ (magnetic)	<i>H</i> (T)	42.8 ± 0.6	50.4 ± 0.1
	δ(Fe) (mm/s)	0.70 ± 0.09	0.49 ± 0.02
	2ε (mm/s)	0.00 ^a	0.00 ^a
Fe ²⁺ (exchanged)	Δ (mm/s)	1.84 ± 0.03	1.76 ± 0.09
	δ(Fe) (mm/s)	1.31 ± 0.01	1.24 ± 0.05
Fe _{sp} ⁰	δ(Fe) (mm/s)	0.14 ± 0.01	−0.02 ± 0.05

H: hyperfine magnetic field, δ: isomer shift (referred to α-Fe at 298 K), 2ε: quadrupole shift and Δ: quadrupole splitting.

^a Parameter held fixed in fitting.

and one superparamagnetic singlet. The hyperfine parameters showed in Table 3 are characteristics of magnetic Fe⁰ (Fe⁰ (m)), Fe₃O₄, Fe²⁺ exchanged with support and superparamagnetic Fe⁰ (Fe⁰ (sp)) [13].

Table 4 shows the percentage of each Fe species at 22 K. The Fe⁰ (sp) fraction indicates the existence of very small particles in both catalysts, suggesting that the microcrystals must be located inside the zeolite channels, avoiding the sintering process during the reduction treatment.

Comparing both catalysts (Table 4), the presence of Cs leads to a smaller iron reducibility degree and a higher fraction of iron crystallites located outside the channels.

The experimental O₂ uptake necessary for the complete re-oxidation of the reduced samples was measured (Table 5). There is a good agreement between this value and the theoretical O₂ consumptions calculated from the percentages of each species obtained from MS at 22 K assuming equal free recoilless factors for all iron species. The crosschecking of volumetric oxidation results with the MS of the catalysts is very sensitive and the only reliable method to check the validity of the Mössbauer species assignments in very complex spectra.

In order to determine the number of Fe⁰ surface atoms, the H₂ chemisorption technique at 673 K and a pressure

range 10–80 Torr was used, since we have demonstrated that the CO chemisorption is an inappropriate method for this system [18]. The high H₂ uptake and contact time, necessary to reach the equilibrium pressure, allowed us to verify the existence of very small Fe crystals. Three hours were necessary to reach the equilibrium at the first point of the isotherm and 1 h for each other point. This indicates the presence of diffusional hindrance, which is consistent with the existence of very small Fe crystals inside the zeolite channels. Assuming that hydrogen atoms are only chemisorbed by the Fe⁰ surface atoms and considering that there are two fractions of Fe⁰ crystals [18], it is possible to evaluate their average diameters.

Assuming a semi-spherical shape, the fraction of microcrystals located inside the zeolite structure cannot exceed the 2.6 nm diameter, considering the dimensions of the channel. This fraction is superparamagnetic (Fe⁰ (sp)) in the Mössbauer spectra of both samples, like that found by Bødker et al. [19] and their percentages were obtained from these spectra. The theoretical H₂ amount chemisorbed by this fraction, with a stoichiometry Fe:H = 1:1, was calculated using the sizes and the percentages above mentioned. Then, subtracting this quantity from the experimental H₂ uptake, we obtained the chemisorbed H₂ by the magnetic Fe⁰ crystals located out of the zeolite structure (Fe⁰ (m)). The average diameters calculated for this fraction in both catalysts are shown in Table 5.

The more important differences between both catalysts are:

- A higher fraction of very small Fe⁰ crystals located inside the zeolite structure in c-Fe/LTL. In this catalyst, the inner crystals represent the 80% of the total active sites while in c-FeCs/LTL this fraction is 33%.
- A smaller reducibility degree in c-FeCs/LTL.

The activity and selectivity results are shown in Table 6 and Fig. 7. In pseudo-steady state, the activity per gram of c-Fe/LTL is five times higher than in c-FeCs/LTL. This result is in agreement with the lower reducibility degree of c-FeCs/LTL leading to a lower hydrocarbon per gram production.

Table 4
Percentages of iron species obtained from Mössbauer spectroscopy at 22 K

	Species (%)			
	Fe ⁰ (m) (magnetic)	Fe ₃ O ₄ (magnetic)	Fe ²⁺ (exchanged)	Fe ⁰ (sp) (superparamagnetic)
c-Fe/LTL	31 ± 3	6 ± 3	39 ± 3	24 ± 2
c-FeCs/LTL	27 ± 5	56 ± 7	9 ± 3	8 ± 2

Table 5
O₂ uptake values, H₂ chemisorption and Fe_m⁰ average volumetric-superficial diameters (*d*_{va}) of the catalysts

	Experimental O ₂ uptake (μmol O ₂ /g)	Theoretical O ₂ uptake (μmol O ₂ /g)	H ₂ uptake (μmol H ₂ /g)	<i>d</i> _{va} Fe _m ⁰ (nm)
c-Fe/LTL	484 ± 24	522 ± 30	44	≥23.2
c-FeCs/LTL	378 ± 19	320 ± 41	32	≥5.8

Table 6
Activity and selectivity results of the catalysts at pseudo-steady state

	c-Fe/LTL	c-FeCs/LTL
Total hydrocarbon production (molecules/(g s × 10 ⁻¹⁶))	11	2
C ₁ (wt%)	45	27
Olefins/paraffins ratio	0.53	4.20
CO conversion (%)	4.5	1.0

Besides, considering that the Fe⁰ (sp) crystals are located inside the zeolite channels, the CO dissociation is facilitated by the strong electrostatic fields generated inside the zeolite structure [20]. This leads to an increase of the activity when the Fe⁰ (sp) fraction is higher.

In both catalysts the methane yield is quite high. This behavior is characteristic of supported catalysts with very small and isolated metallic particles. In these solids, the chain propagation finishes at low molecular weight hydrocarbons (up to C₄). Since there are not enough CH_x neighbor groups, growth would not occur on them [21].

The selectivity data were collected at the same operative conditions, and consequently at different conversion levels. It is known that for Fischer–Tropsch reaction the selectivity depends upon the conversion level. However, Vannice et al. [22] claimed that within the conversion range from 1 to 5%, the selectivities were not markedly altered in iron supported on carbon with 5% of iron loading. Besides, other authors [23,24] have found, for iron supported on manganese oxide, that the olefins/paraffins ratio is independent of the CO conversion in different conversion range (between ≈0.5–4 and ≈45–60%). According with these results we compared the selectivities of both catalysts analyzing the olefins/paraffins ratio. A higher total olefins/paraffins ratio (Table 6) was obtained in c-FeCs/LTL. The same tendency was observed comparing the olefin/paraffin ratio for each hydrocarbon between C₂ and C₅ (Fig. 7). These results could be related with the higher basicity of the support promoted with Cs and with the activation energy increase for

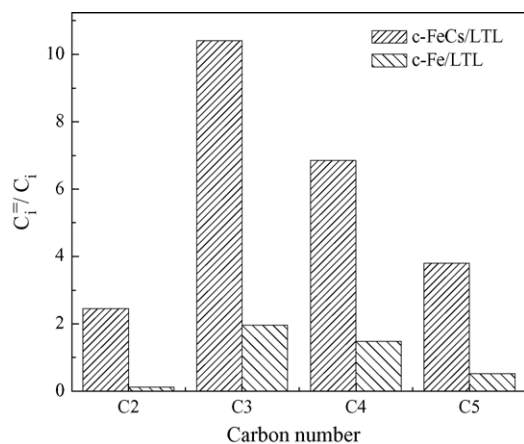


Fig. 7. Selectivity ratios of the catalysts in the Fischer–Tropsch reaction at the steady state.

the H₂ chemisorption in c-Fe/LTL due to the presence of a higher fraction of small Fe⁰ crystals [25]. Therefore, in c-Fe/LTL, the quantity of weakly chemisorbed H₂ would be higher than in c-FeCs/LTL and a higher amount of active H₂ would be available for the olefins hydrogenation considering that the reaction temperature is lower than that necessary to reach the maximum H₂ adsorption (543 K versus 673 K) [26].

Due to the low CO conversion levels we did not detect the CO₂ in reaction products with TDC detector, therefore we conclude that this value must be below of the detection limit (lower than 10 ppm at the highest sensibility).

4. Conclusions

The use of potassic LTL zeolite as support of iron allowed us to locate a Fe⁰ fraction inside the zeolite channels, which contributes with the 80% of the total active sites.

After locating Cs⁺ ions into the hexagonal prisms of the zeolite by exchange with K⁺, a lower iron reducibility degree and a lower Fe⁰ microcrystals fraction located inside the channels were obtained. Taking into account that the Cs⁺ ions are “isolated” into the hexagonal prisms, their electrostatic effect can be considered as a “long-range” one.

These structural differences lead to a catalyst five times more active in the Fischer–Tropsch reaction (c-Fe/LTL). On the other hand, the Cs⁺ presence increases the olefins/paraffins ratio eight times diminishing the methane production.

Acknowledgements

The authors acknowledge support of this work by Consejo Nacional de Investigaciones Científicas y Técnicas (PIP 02133), ANPCyT (PICT 14-11267), Comisión de Investigaciones Científicas de la Provincia de Buenos Aires and Universidad Nacional de La Plata, Argentina.

They also thank Prof. K. Segawa (Sophia University, Tokyo, Japan) for providing the zeolite L from Tosoh Co., Japan.

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