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Study of the Fe/zeolite-L system Part I: Characterization of iron species and their structural properties

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Abstract

Zeolite-L in potassic (ZLK) and acidic (ZLH) forms were used as a support for iron species to obtain two solids, called Fe/ZLK and Fe/ZLH, respectively. ‘‘In situ’’ Mössbauer spectroscopy (MS) between room temperature (RT) and 15 K, volumetric oxidation (VO) and thermogravimetric analyses were used to determine the iron species existent after reduction (Fe^0, Fe^{2+} and Fe_3O_4) and to study their structural properties. In both solids, a similar fraction of very small Fe^0 crystals was found inside the zeolite channels. Intermediate species, like exchanged Fe^{2+}, were also detected in both samples. It was possible to determine that Fe^{2+} ions are located at sites D in Fe/ZLK and sites A in Fe/ZLH. Soft reduction conditions, like slow temperature raise (2 K/min), allowed to maintain metallic Fe crystals inside the zeolite-L structure in contrast with other Fe/zeolite systems.

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Keywords: Zeolite-L; Iron supported on zeolites; Mössbauer spectroscopy; Volumetric oxidation

1. Introduction

Zeolites are interesting materials because of the wide range over which their physical and chemical properties can be varied according to the desired use. Zeolite-L has a structure consisting of symmetric columns of alternating cancrinite cages and hexagonal prisms. These columns are cross-linked with three others by single oxygen bridges between the remaining six vertices of the cancrinite cages. This structure gives rise to the planar 12-membered oxygen rings, which define the minimum free aperture (7.2 and 7.8 Å) of the main channel which runs parallel to the *c*-axis and is bound by six columns of cancrinite cages and hexagonal prisms. The largest free diameter of a section (which is midway between the 12-membered rings) is about 13 Å. The main channels are interconnected by means of non-planar eight-membered oxygen rings of very small free diameter [1,2].

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Zeolite-L has different locations of exchangeable cations; Barrer and Villiger [1] designated five of them as A, B, C, D and E. The cations sited at D are the only ones likely to be ion-exchanged at room temperature (RT) [2,3]. All the exchangeable sites of some commercial forms of zeolite-L are occupied by K^+ ions. In some works, these K^+ ions were exchanged with Fe^{2+} [2,4] and studied by Mössbauer spectroscopy (MS) under various degrees of hydration. The exchange of these cations allows to change the properties of the zeolitic material.

In the present paper, we study the Fe/zeolite-L system prepared by dry impregnation of the zeolite with an Fe salt. This method allowed us to obtain small metallic iron crystals inside the zeolite channels and Fe^{2+} exchanged after a reduction treatment, in contrast to other zeolitic systems, like Fe/ZSM-5 and Fe/zeolite-Y. In Fe/ZSM-5 ion-exchange or dry-impregnation preparation methods do not lead to iron particles inside the zeolitic structure after a thermal reduction [5]. Instead, in Fe/zeolite-Y, only Fe^{2+} inside the zeolite cages can be obtained by ion-exchange after reduction. It is possible to get large metallic iron crystals by dry impregnation but lying on the external surface of the zeolite framework [5]. The Fe/zeolite-L system thus obtained is a potential material to be used as catalyst, since the zeolite channel structure can produce a beneficial effect on the outcome of the chemical reaction.

''In situ'' MS between RT and 15 K, volumetric oxidation (VO) and thermogravimetric analysis (TGA), have been jointly used to adequately characterize a complex supported iron system as Fe/zeolite-L is. Techniques of gas chemisorption, necessary to complete the solids characterization, cannot be used in the same way as in the other iron-supported systems. Therefore, a special study must be performed in our system, as it will be described in Part II of this work.

2. Experimental

2.1. Sample preparation

Potassic (ZLK) and acidic (ZLH) zeolite-L were used as support of iron species. The former, with the ideal unit cell composition of dehydrated form of $K_9Al_9Si_{27}O_{72}$ and 290 m^2/g of specific area, is the commercial form (Tosoh) of zeolite-L. This ideal composition was derived from atomic absorption analysis provided by the supplier. ZLH was obtained from ZLK by exchanging three times with a NH_4NO_3 (3 M) solution for 5 h at 368 K and calcined in air, at 873 K for 22 h. The potassium content (determined by atomic absorption in our laboratory) reduced from $13.1 \pm 0.6\%$ to $3.2 \pm 0.2\%$. The specific area was 345 m^2/g with an ideal unit cell composition of $H_7K_2Al_9Si_{27}O_{72}$. Both BET areas were measured by N_2 adsorption.

An impregnating solution of $Fe(NO_3)_3 \cdot 9H_2O$ ($pH = 0.5$), with a high enough concentration to yield solids of ca. 5% w/w of Fe was used. The samples were dried in air at RT and subsequently calcined in dry N_2 stream from RT up to 698 K at a heating rate of 0.33 K/min, and kept at 698 K for 8 h. Afterwards, they were reduced in flowing H_2 at 60 cm^3/min, after purification through a Pd black bed and a 5 Å molecular sieve. The same procedure as in Ref. [6] was used for the thermal reduction of the samples: 0.5 h at 445 K, 0.5 h at 509 K, 0.5 h at 559 K, 0.5 h at 600 K, 0.5 h at 644 K and 26 h at 698 K. These solids, called Fe/ZLK and Fe/ZLH were characterized by atomic absorption to determine the total iron content (5.84% w/w for Fe/ZLK and 4.95% w/w for Fe/ZLH). After the different thermal treatments, the preservation of the crystalline structure was verified by X-ray diffraction (XRD). A very slight loss of the crystalline character was observed.

2.2. Characterization techniques

2.2.1. MS

The Mössbauer spectra were obtained in transmission geometry, with a 512-channel constant-acceleration spectrometer. A source of ^{57}Co in Rh matrix of nominally 50 mCi was used. All isomer shifts (δ) mentioned in this paper are referred to α-Fe. The temperature between 15 and 298 K was varied using a Displex DE-202 helium-closed-cycle cryogenic system. The spectra were obtained ''in situ'', i.e., keeping the same atmosphere as in the previous treatment of the sample by means of a cell especially designed and built to be used inside the cryogenic system [7].

All spectra were fitted with a program including hyperfine-parameters distributions [8] to account for the different particle sizes and/or crystallographic sites of the iron phases. The species with lorentzian line-shape were fitted with the same program but not including hyperfine-parameters distributions.

2.2.2. VO

Volumetric oxidation experiments — based on the conversion of all iron species in the sample to Fe_2O_3 when heated in an O_2 atmosphere at temperatures higher than 620 K [9] — were performed in a conventional static volumetric equipment with grease-free vacuum valves [6]. Once reduced, the samples were evacuated and oxidized with an appropriate amount of O_2 at 620 K. The experiment was completed when the oxygen pressure no longer varied. The uptake of O_2 was thus determined.

2.2.3. TGA

TGA assays on ZLK, ZLH and Fe/ZLH were carried out using a Shimadzu TGA-50 to study the elimination and uptake of water. Three cycles of heating and cooling, at a rate of 10 K/min from RT to 923 K in 20 cm^3/min of He stream (ca. 10 ppm of H_2O) without previous treatment, were realized. Afterwards, the zeolites were kept for 24 h in air at RT and the weight increase was registered.

3. Results and discussion

3.1. Characterization of the reduced solids by MS

Fig. 1 shows the Fe/ZLK and Fe/ZLH ''in situ'' spectra at 298 and 15 K in H_2 atmosphere. At RT, both display a magnetic sextet and several intense

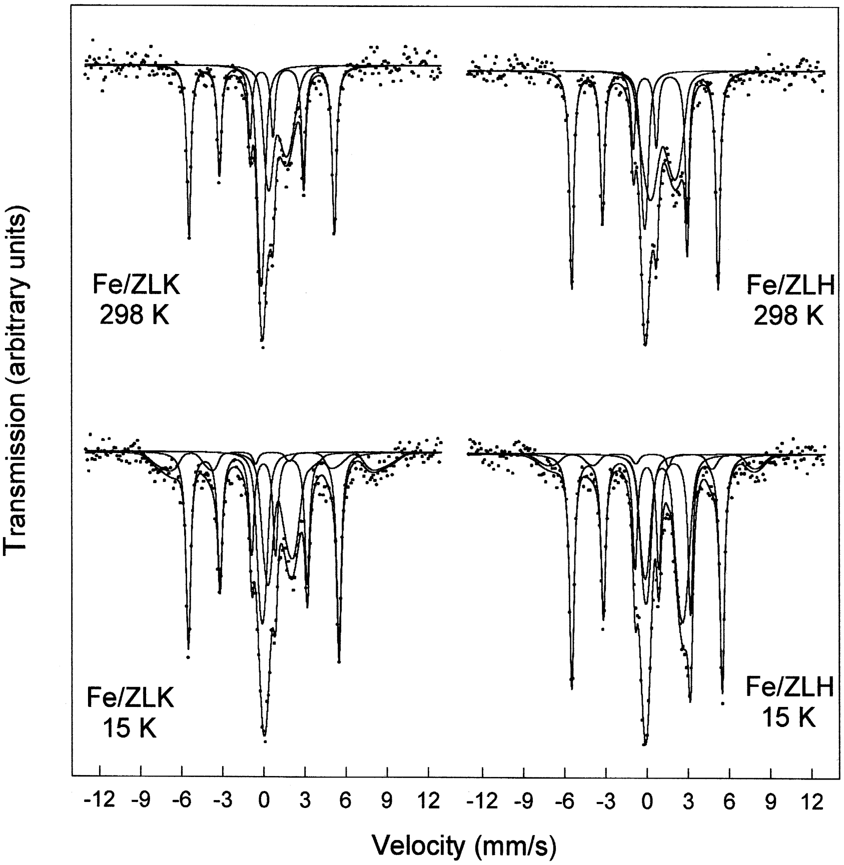

Fig. 1. Mössbauer spectra of reduced samples at 298 and 15 K.

and highly overlapped central signals. The spectra were interpreted in terms of a superposition of one magnetic sextet, one paramagnetic doublet and one singlet. In addition to the above-mentioned signals, a very weak and broad sextet appears at 15 K in both spectra.

The values of the hyperfine parameters at RT and 15 K are characteristic of magnetic Fe^0 (Fe^0(m)), superparamagnetic Fe^0 (Fe^0(sp)), Fe^{2+} and Fe_3O_4 (only at 15 K) in both solids (Table 1). The Fe^0(m) signal that yielded a linewidth lower than 0.35 mm/s, was fitted to single-valued hyperfine parameters. The other subspectra yielded poor results using lorentzian line-shapes and required a fitting to parameters that varied over a range of values. In supported solids, the crystallite size distribution may produce a considerable variation in the local surroundings of the Mössbauer atoms and the hyperfine magnetic field (H) and quadrupole splitting (Δ) may, therefore, vary significantly for probes located at different sites across the crystallites [10]. Besides, the location of the iron ions exchanged in different sites of the support may also cause such behavior. In zeolite-L, the Si/Al ratio is different from the unity, therefore, this may lead to sites with different distributions of Si and Al atoms and, thus, to different environments for the ions [2]. These variations often lead to unequal line broadening and different intensities in the spectra. As a first order approximation, a linear correlation between δ and H for magnetic signals and between δ and Δ for paramagnetic ones can be assumed in fitting [8,10]. Table 1 shows the hyperfine parameters (for the results of fittings with parameter distribution, the average values are displayed).

The signal assigned to α-Fe is magnetically split at RT and 15 K in both solids. According to Bødker et al. [11], these spectra due to particles having an average diameter larger than ≈ 29 Å and, consequently, must be located outside the zeolite channels. These crystals would originate from the reduction of the larger α-Fe_2O_3 crystallites located at the external zeolite surface [12] and/or of the smaller ones, situated inside the channels, but that migrated out of the pores during the reduction.

The central signal, with $\delta \cong 0$ mm/s at both temperatures is still observed at 15 K in both samples, but a decrease of its percentage is accompanied by a simultaneous increase of the linewidth and the percentage of the Fe^0(m) when the temperature decreases (area[Fe^0(m)]/area[Fe^0(sp)] changes from 2.0 to 3.0 for Fe/ZLK and from 2.4 to 3.8 for Fe/ZLH when the temperature decreases from 298 to 15 K). In this evaluation, the areas were normalized taking into account that at 15 K, the signal attributed to Fe_3O_4, which was not detected at RT, appears. The

Table 1
Mössbauer hyperfine parameters and relative spectral areas (at 15 and 298 K) of the iron species in the samples

Temperature (K)	Species	Parameters	Fe/ZLK	Fe/ZLK (relative %)	Fe/ZLH	Fe/ZLH (relative %)
298	Fe^0_M	H (T)	33.0 ± 0.1	46 ± 2	33.1 ± 0.1	51 ± 2
		δ (mm/s)	0.01 ± 0.01		0.00 ± 0.01	
		2ε (mm/s)	$0.00 \pm 0.00^{*}$		$0.00 \pm 0.00^{*}$	
	Fe^0_{sp}	δ (mm/s)	-0.03 ± 0.02	23 ± 4	0.05 ± 0.01	21 ± 1
	Fe^{2+}	δ (mm/s)	1.23 ± 0.04	31 ± 5	1.21 ± 0.02	28 ± 3
		Δ (mm/s)	1.36 ± 0.07		1.80 ± 0.04	
15	Fe^0_M	H (T)	34.1 ± 0.1	45 ± 3	34.0 ± 0.1	50 ± 2
		δ (mm/s)	0.11 ± 0.01		0.11 ± 0.01	
		2ε (mm/s)	$0.00 \pm 0.00^{*}$		$0.00 \pm 0.00^{*}$	
	Fe^0_{sp}	δ (mm/s)	0.02 ± 0.05	15 ± 4	$0.01 \pm 0.00^{*}$	13 ± 1
	Fe^{2+}	δ (mm/s)	1.39 ± 0.04	27 ± 6	1.34 ± 0.01	29 ± 3
		Δ (mm/s)	1.82 ± 0.08		2.72 ± 0.02	
	Fe_3O_4	H (T)	48.6 ± 0.7	13 ± 5	46.9 ± 0.9	8 ± 5
		δ (mm/s)	0.77 ± 0.09		0.50 ± 0.13	
		2ε (mm/s)	$0.00 \pm 0.00^{*}$		$0.00 \pm 0.00^{*}$	

*Parameter held fixed while fitting.

fitting of the spectra was not possible without considering the presence of a singlet at $\delta \cong 0$ mm/s. Besides, as it will be seen later, the concordance with the VO results would not be obtained if this signal is not assigned to Fe^0 species. This behavior indicates that this signal corresponds to very small particles of Fe^0(sp) (at least smaller than ≈ 29 Å [11]). The Fe^0(sp) fraction is very similar in both solids (Table 1), and it arises from the reduction of small Fe_2O_3 crystallites located inside the zeolite channels [12]. However, this Fe_2O_3 fraction is higher in Fe/ZLK than in Fe/ZLH as was demonstrated in Ref. [12] and may have its explanation in the following. Although the impregnating solution goes easily into the channels of the zeolite due to the low hydrophobicity degree produced by the low Si/Al ratio in both samples (Si/Al = 3), in Fe/ZLK, the K^+ ions exchanged by Fe^{3+} produce an increase of pH of the solution [13] that fills the channels of the zeolite causing the precipitation and ‘‘anchoring’’ of ferrhydrite and/or goethite. After calcination, these species would generate the smallest α-Fe_2O_3 microcrystals. The absence of K^+ in the exchangeable sites in Fe/ZLH produces a lower oxide-crystallites quantity inside the channels than in Fe/ZLK [12]. Therefore, in Fe/ZLK system, an important Fe^0 crystallite migration out of the pores occurs during reduction since the crystal sintering is inhibited inside the pores and their diameter cannot exceed 13 Å.

In contrast with zeolite-Y [5], zeolite-L was able to retain very small Fe^0 crystals inside the channels. This different behavior could be assigned to the less severe thermal treatments (e.g., slow temperature raise, 0.33 K/min for calcination and 2 K/min for reduction), instead of structural differences between zeolites, since both are similar. The same conclusion was found [12] for the oxide crystals located inside the zeolite-L channels; a slow water removal prevents the exit of the crystals.

The weak magnetic signal, assignable to Fe_3O_4, that can be seen in the MS at 15 K, can be attributed to the incomplete reduction of the oxides. Its quantity is too small to sort out one more interaction in the spectrum fitted at RT from the statistical noise. Considering that the influence of particle-size reduction on the Mössbauer spectra of magnetite is similar to that of other poorly crystallized, magnetically-ordered materials (as particle size are reduced, the hyperfine fields are reduced below those of the bulk material and the resonant lines become broadened), the particle size of this phase in our samples must be very small. Although in the bulk state, the MS of magnetite at 15 K is very complex, with several subspectra having widely scattered hyperfine parameters [14], the ill-defined signal in our spectra do not justify the fitting with more than one single broad distribution of hyperfine fields.

The Mössbauer parameters of Fe^{2+} in both solids are similar to those found by Fitch and Rees [2] for Fe^{2+} in sites D and/or A of the zeolite-L structure. The ions in sites D [1] are located in a distorted eight-ring formed by the linkage of adjacent columns of hexagonal prisms and cancrinite cages. The metal ions in this site are coordinated to two framework oxygen atoms and two water molecules that belong to the same plane, and to four framework oxygen atoms belonging to the perpendicular one. The two water ligands lie inside the main channel. The sites A are at the center of the hexagonal prisms, two per unit cell, and have closest coordination to six oxygen atoms, which form the inner triads of the six-rings, forming the hexagonal prism [1]. Since the Fe^{2+} ions originate from the reduction of Fe^{3+} exchanged during the impregnation [12,13], we will describe the likely sequence followed by these ions during the different preparation steps. The K^+ or H^+ ions situated in sites D (the only ones accessible at RT [2,3]) are exchanged by the Fe^{3+} ions arising from the impregnating salt. This effect is possible due to the ability of this zeolite to exchange trivalent ions [15]. As it has been shown for zeolite-Y, polyvalent cations have strong preference for sites I, because in those sites, they are bonded to six oxygen atoms that can balance their cationic charge [16]. The sites A in zeolite-L have a structure very similar to sites I in zeolite-Y. Two effects are involved in the cations preference for the sites A in the zeolite-L [3,16]:

- the charge of the cations, and
- the size of the cations.

Therefore, we consider that, during calcination in N_2 stream, in Fe/ZLH, the charge and the size effects produce a displacement of H^+ by Fe^{3+} from the site A. Instead, in Fe/ZLK, the size is the prevailing effect and the Fe^{3+} ions cannot replace the K^{+} ions from the sites A.

The electric field gradient at the nucleus of a resonant atom and its temperature dependence reflect the symmetry of that atom through effects due to crystal field splitting, charge transfer between the central atom and its neighbors, and the distribution of electric charge over the lattice sites. The observed quadrupole splitting may serve to identify that site in the structure in which the Mössbauer atom is located, while at the same time serving as a probe of that site. Yet, because the effects that give rise to the electric field gradient may be quite long-range, the Δ of the Mössbauer atom may also be sensitive to the neighboring sites in the structure, thereby providing information about the whole structure [17].

In our systems, the quadrupole splitting of Fe^{2+} of both samples is different and Δ increases more for Fe/ZLH than for Fe/ZLK when the temperature decreases. Thus, Δ goes from 1.36 to 1.82 mm/s (a change of 0.46 mm/s) for Fe/ZLK and from 1.80 to 2.72 mm/s (a change of 0.92 mm/s) for Fe/ZLH when the temperature decreases from 298 to 15 K (Table 1). According to Fitch and Rees [2], the Fe^{2+} ions in sites A show the largest change of Δ with temperature. Consequently, the Fe^{2+} ions of the present samples are preferentially located in sites A in Fe/ZLH and in sites D in Fe/ZLK. The Fe^{2+} location in the reduced samples will be confirmed by the CO chemisorption experiments (Part II).

Finally, if the Debye model is assumed to describe the lattice vibrations, although the actual Debye temperature (θ_D) for each iron species is not known, a large possible variation of θ_D between species, would produce only a small variation in the f-factor at 15 K. For example, if the θ_D of the two species have a difference as high as 300 K (from 200 to 500 K), their f-factors would have a change of only about 6% [18]. It is therefore reasonable to use equal recoilless fractions to determine the relative contents of the various phases present in both solids from the Mössbauer spectra at 15 K. The percentage of each iron species obtained in this way is nearly equal in both solids (see Table 1).

3.2. Characterization of the reduced solids by VO

The results of experimental oxygen uptake necessary for the complete reoxidation of the reduced samples were: 521 ± 56 μmol O_2/g for Fe/ZLK and 382 ± 21 μmol O_2/g for Fe/ZLH. These values have been corrected, as it will be discussed below. The consumptions of oxygen, calculated from the percentage of each species obtained from the Mössbauer spectra at 15 K were: 553 ± 42 μmol O_2/g for Fe/ZLK and 492 ± 25 μmol O_2/g for Fe/ZLH.

Fig. 2 displays schematic diagrams of the ions at the surfaces of Fe/ZLK and Fe/ZLH systems deduced from our observations. After impregnation with the Fe^{3+} salt, some of the K^{+} or H^{+} ions (located in sites D) are exchanged by Fe^{3+}. These cations generate Fe^{2+} during reduction producing one H^{+} for each reduced cation to maintain the electroneutrality on the surface. This proton is eliminated from the surface as water vapor when the sample is reoxidized at 623 K. This process produces an increase of gas phase pressure. Therefore, the measured O_2 uptake will be lower than the real one and it will be necessary to correct it.

Using the Fe^{2+} percentage determined by MS, and considering that when two Fe^{2+} ions oxidize to Fe^{3+}, one water molecule appears in the gas phase

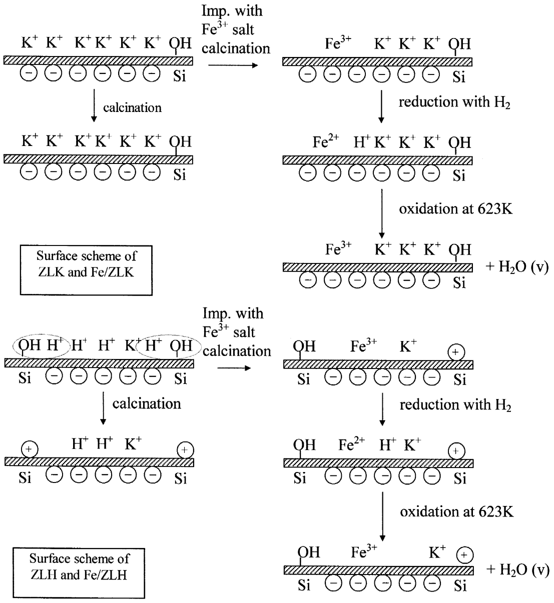

Fig. 2. Surface schemes of the zeolites ZLK and ZLH and their behavior during impregnation with iron salt, calcination, reduction and oxidation steps.

and half O_2 molecule is consumed, it is possible to correct the experimental oxygen uptake.

The zeolite systems can undergo a dehydroxilation process when the temperature increases [19]. To study this process, TGA measurements were carried out and the weight loss with temperature was registered for ZLK and ZLH (Fig. 3). In ZLH, the water loss by dehydroxylation continues even at 923 K and the solid does not recover its original weight once exposed to air at RT. In contrast, a complete water elimination in ZLK occurs when the temperature of 494 K is exceeded. Besides, if this solid is cooled back below 494 K, the water is quickly reabsorbed and returns to its original weight. The irreversible loss of weight by thermal dehydroxylation in ZLH is 5.8 wt.%. Iron presence in Fe/ZLH reduced this quantity to 2.1 wt.% (TGA diagram is not shown). This difference could arise because Fe^{3+} are exchanged with H^+ and, consequently, a decrease of the number of neighboring hydroxyls and protons, able to generate water (Fig. 2), leads to a lower dehydroxylation in Fe/ZLH. This system seems more complex than Fe/ZLK because Fe/ZLH undergoes an irreversible thermal dehydroxilation. To verify this conclusion, O_2 chemisorption on ZLH and ZLK at 623 K was performed. ZLK does not chemisorb O_2, while an important uptake occurs on ZLH (54 ± 3 μmol O_2/g). Sites able to chemisorb O_2 at 623 K are generated through the irreversible surface dehydroxylation in ZLH. Dehydroxylation is negligible in ZLK, in agreement with the TGA results.

According to the previous description, the experimental oxygen uptake of Fe/ZLH system requires an additional correction by O_2 chemisorption at 623 K. To make this correction, we consider that Fe/ZLH dehydroxylation is 36.2% lower than the ZLH one; therefore, the O_2 chemisorption uptake would be 20 μmol O_2/g in Fe/ZLH. This value was obtained assuming that there is a linear ratio between the number of the lost hydroxyls and the chemisorbed O_2.

It can be seen that there is a good agreement between the corrected experimental value of O_2 uptake and the one calculated from Mössbauer results for Fe/ZLK. The concordance between both values in Fe/ZLH is not as good as the previous one, bearing in mind that a major number of corrections were necessary.

According to other authors [5,20], an Fe^{3+}–O^{2-}–Fe^{3+} bridge must be involved in the oxidation conditions. In Fe/ZLK, this process could occur easily because the Fe^{2+} ions are located in sites D that are accessible and close to each other. Instead, in Fe/ZLH, it seems unfavorable that two iron ions, remaining in the center of the hexagonal prism (site A), bond to an oxygen which is located inside the cancrinite cages (it cannot go into the hexagonal

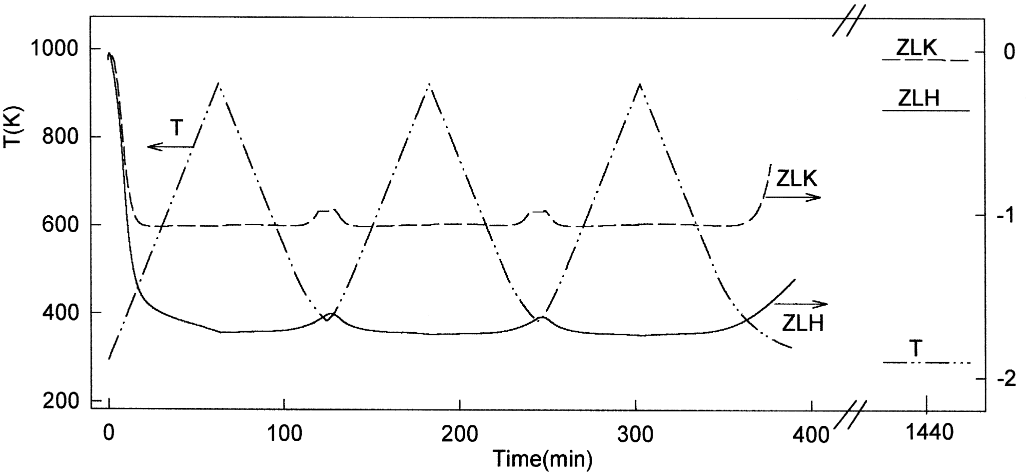

Fig. 3. Three cycles of TGA of ZLH and ZLK in He flow (10 ppm of water). The weight loss of ZLH and ZLK after 24 h of air exposition at RT is shown on the right.

prism due to its size). So, it would be necessary that two Fe^{2+} ions move from the center of the hexagonal prisms toward the windows of their corresponding prisms or toward the same cancrinite cage for the oxidation process to occur.

To verify the complete reoxidation of the samples after the treatment with O_2 at 623 K, Mössbauer spectra of reoxidized Fe/ZLK and Fe/ZLH were taken (Fig. 4). Only Fe^{3+} species were detected. Table 2 shows the hyperfine parameters of both reoxidized samples. They can be assigned to two iron species: γ-Fe_2O_3 [21] and Fe^{3+} (probably exchanged with the support and/or belonging to very small oxide microcrystals). Boudart et al. [9] have also found γ-Fe_2O_3 after reoxidation at 623 K. The γ-Fe_2O_3 presence is verified by the magnetic behavior of the samples: both of them are attracted by a magnet.

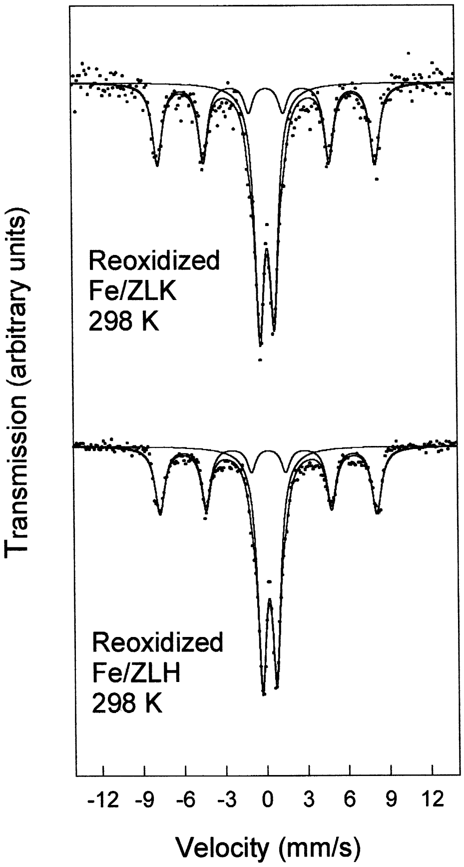

Fig. 4. Mössbauer spectra of reoxidized samples at 298 K.

Table 2
Mössbauer hyperfine parameters of the reoxidized samples

Temperature (K)	Species	Parameters	Fe/ZLK	Fe/ZLH
298	γ-Fe_2O_3	H (T)	49.3 ± 0.1	49.1 ± 0.1
		δ (mm/s)	0.34 ± 0.02	0.33 ± 0.01
		2ε (mm/s)	-0.01 ± 0.03	-0.04 ± 0.02
	Fe^{3+}	δ (mm/s)	0.34 ± 0.01	0.34 ± 0.01
		Δ (mm/s)	1.05 ± 0.02	1.04 ± 0.01

The cross-checking of VO results with the complex Mössbauer spectra of these catalysts is the only reliable method that should be used in spectra of such complexity if one has not the capability to take ‘‘in situ’’ spectra of samples with an external magnetic field. Other choices for the assignments of the iron species, different from those of Table 1, lead to unacceptable differences between both techniques.

4. Conclusions

MS at low temperatures is adequate to characterize complex supported iron systems if used jointly with the properly corrected VO.

When these techniques are applied to Fe/zeolite-L system, we found the following conclusions.

- Soft thermal treatment conditions as slow temperature raise (0.33 K/min for calcination and 2 K/min for reduction) allowed us to obtain a fraction of small iron crystals inside the zeolite channels.
- Notwithstanding the larger quantity of oxide crystals inside the zeolite structure in Fe/ZLK than in Fe/ZLH precursors (assigned to the presence of K^+ ions in the former system), after the reduction process, the iron species and their percentages were very similar in both solids. This result indicates that, during reduction, a more important crystal migration out of the pores occurs in Fe/ZLK than in Fe/ZLH.
- The Fe^{2+} ions exchanged with the zeolite are located in sites D in Fe/ZLK and in sites A in Fe/ZLH.

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