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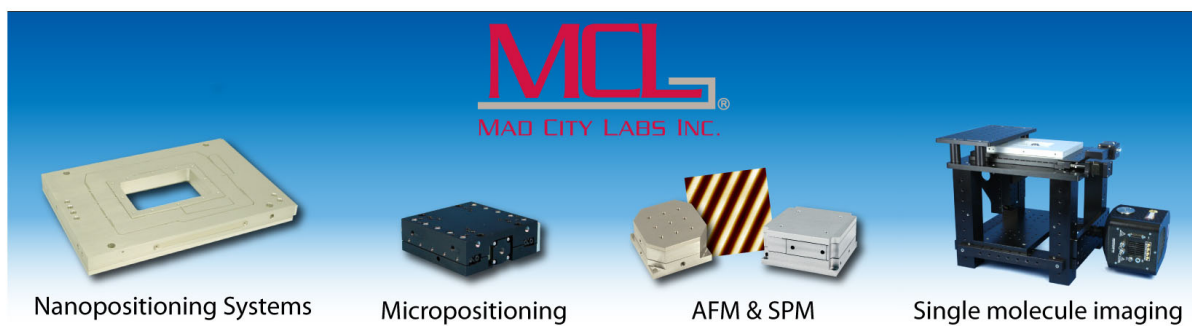
Mössbauer cell for low-temperature studies of catalysts under reaction conditions

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Mössbauer spectroscopy is an essential tool to investigate the structure of Fe supported catalysts and their changes, when they are used in the Fischer-Tropsch synthesis. A cell, that allows keeping the samples in the same atmosphere of the reduction treatment, was designed in order to characterize the Fe species without changing the working atmosphere avoiding the oxidation. It allows to measure at low temperatures in a helium closed-cycle refrigerator. Besides, this cell is useful to perform Mössbauer measurements on the used catalysts, preserving the oxidation of its species, using an inert atmosphere. In this work, we describe the details of this new cell and, as an example of its utility, we present the results obtained with a system of 12 nm iron oxide nanoparticles supported on a mesoporous silica matrix. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4913382]

I. INTRODUCTION

Metal nanoparticles (NPs) increase the activity, and selectivity of supported catalysts in many reactions, i.e., in the Fischer-Tropsch synthesis (FTS), which is widely used to convert a mixture of CO and H_2 into hydrocarbons. To understand some of the remaining unanswered questions about the mechanism of FTS, it is necessary to prepare semi-model catalysts with supported NPs of homogeneous size. Recently,[1] we prepare iron oxide NPs with a controlled average size and a very narrow size distribution, in order to obtain catalytic solids to be useful as a semi-model catalysts to study the effect of the "structure sensitivity" in FTS.[2,3]

Mössbauer spectroscopy has proved to be a unique technique that can give account of all iron species taking part in the FTS. It has been applied for many years to the study of the active sites of Fe and Fe-oxide NPs in this synthesis. With this aim, it is essential not to perturb the environment in which the reaction has taken place due to the high reoxidation capability of the very small particles. To that end, some time ago[4] we developed an acrylic cell coupled with a glass furnace that allowed keeping the reaction atmosphere after reduction and use of the catalysts at atmospheric pressure. However, FTS at atmospheric pressure is not a realistic condition since the industrial operative conditions use high pressure. Therefore, it is important to measure the activated sample and the used catalyst in the FTS at pressures up to 20 atm avoiding their contact with air.

In this paper, we report important improvements of the previous design. Thus, acrylic and glass were replaced by materials with higher mechanical and thermal resistance (aluminium and stainless steel). This allows working at higher pressures (up to 4 atm) and temperatures (1073 K). These characteristics increase the field of applications in different systems, and the handling of the samples is easier than the preceding cell. A new application of the cell, adding a new step to the process, allows to carry out Mössbauer measurements on the catalysts used in the FTS at 20 atm at cryogenic temperatures, preserving iron species. This is important because it helps to understand the different catalytic results in connection with the structural properties of the catalyst.

As an example of the use of this new equipment, we show the results obtained for a system of 12 nm Fe NPs supported on an ordered mesoporous silica matrix (SBA-15) after reduction and use in FTS at 20 atm.

II. EXPERIMENTAL

A. Cell design

Since the pre-treated solids under study can re-oxidize easily, the Mössbauer spectra, at different temperatures, must be taken in a cell with a controlled atmosphere. The cell is attached to a stainless steel tubular reactor where the pre-treatment of the sample, inside a holder, is done. This holder was specifically designed to be housed into the cell that is placed in the Mössbauer spectrometer. Fig. 1 displays a diagram of the apparatus.

In Fig. 1, arrows indicate the gas flow direction. Two "on-off" valves (A) control gases input and output. An electric furnace (B) is located at the central part of the tube (C) which allows maintaining the set temperature for a given heat treatment. A conventional programmable controller measures and monitors the temperature. A chromel-alumel thermocouple located inside the thermocouple sheath (D) is at the center of the oven.

Fig. 2 shows several pictures of part of the reactor, the oven, and the cell. The sample is placed in a sample holder (E)

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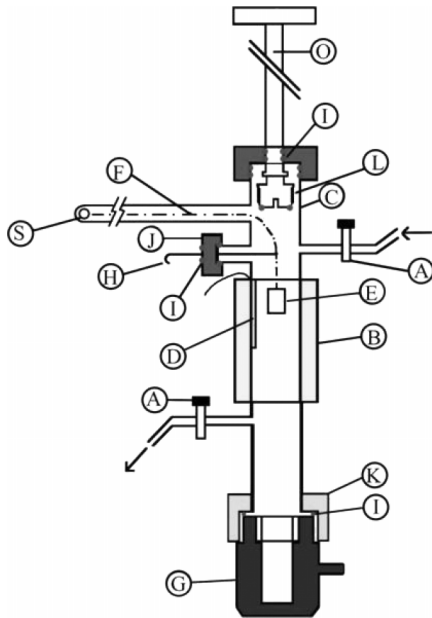
FIG. 1. Scheme of the apparatus: A, on-off valves; B, electric oven; C, central stainless steel tube; D, thermocouple sheath; E, sample holder; F, silver chain; G, aluminum cell with acrylic windows; H, aluminum tool to center the silver chain; I, Viton® O-rings; J, housing O-rings; K, part of the threaded cell; L, aluminum screw cap; O, aluminum tool; S, internal magnet.

which is made up of a 1 μm thick aluminum foil supported by the aluminum piece shown in photograph of Fig. 2(d). The sample holder is attached to one end of a silver chain (F) and the other end of the chain is attached to an internal magnet (S).

Thus, by using an external magnet, the sample may be located into the isothermal zone of the oven (to perform the heat treatment) or placed inside the cell (G) and carried afterwards to the cryogenic system to acquire the Mössbauer spectrum. An aluminum tool (H) slides through two Viton® O-rings (I) locating the sample in the center of tube.

An aluminum part (K), placed at the bottom of the central tube, permits securing the cell (G) via an internal thread. The piece (K) has acrylic windows for visual observation of the sample holder to be able to place it properly inside the cell (G). A Viton® O-ring (I) makes the system tight. While the heat treatment is carried out with the sample inside the isothermal section of the oven, air blowers help keep cool the sections of the device, which lie outside the furnace so that the O-rings and acrylic window are not damaged.

When the selected heat treatment is completed, an external magnet pulls on the internal magnet (S) attached to the sample holder and drives it from the isothermal zone into the cell. Subsequently, the silver chain is removed and the aluminum tool (H) is pulled back. The aluminum cap of the cell (L), which is clamped to an aluminum tool (O) by a key, is slid down, and screwed tightly onto the cell. Throughout these stages, the gas used for the treatment is kept flowing. The internal pressure is set using a back pressure valve located at the exit of the system.

On one of the lateral faces of the cell, a male thread allows to attach the cell to the copper "cold finger" of the cryogen. This cell face is thoroughly flat and polished in order to achieve an accurate thermal contact with the "cold finger." Mössbauer spectra of NaFeP$_2$O$_7$ were recorded at different temperatures to calibrate the cell with an internal standard. This substance is adequate for calibration because its magnetically split spectra have a significant thermal dependence below 29 K.[5] The actual sample temperature was obtained comparing our hyperfine magnetic field values below 29 K with that obtained in Ref. 5. Figure 3 shows that, within the range 13–25 K, the temperature difference between the sample and the cold finger sensor is about 2 K. However, at 13 K, this difference is negligible.
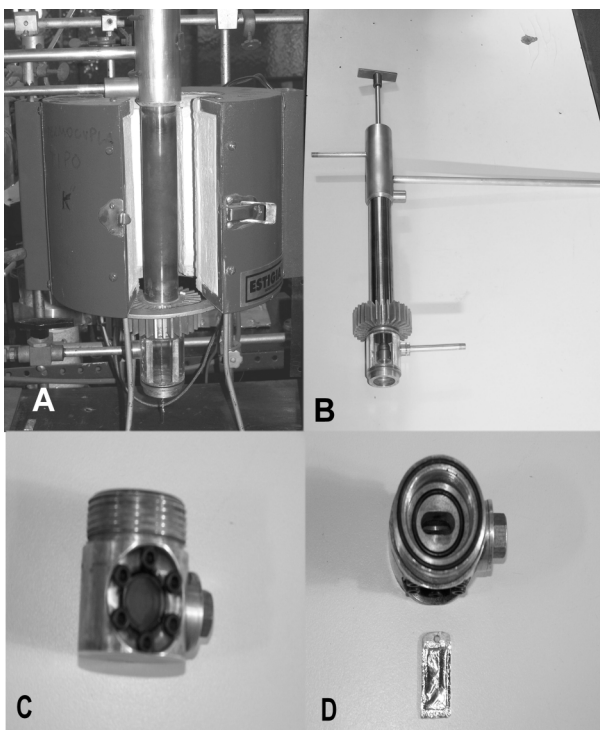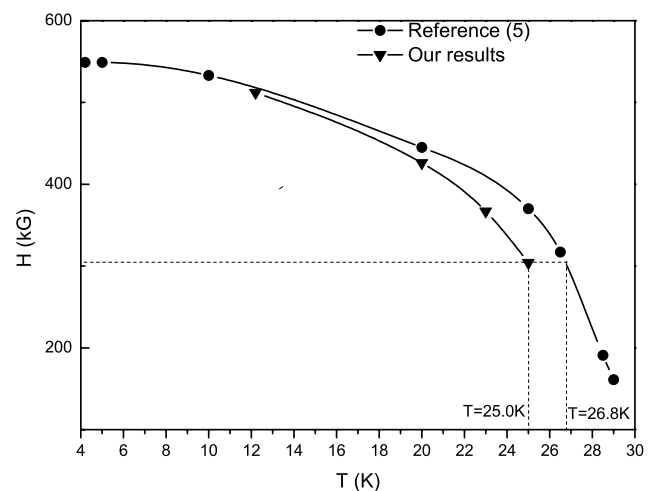

FIG. 2. (a) Reactor mounted inside the oven. (b) Reactor mounting entirely outside the oven. (c) Detail of the acrylic window. (d) Cell and sample holder, which is inserted inside the cell for transport and Mössbauer measurements.

FIG. 3. Hyperfine fields of NaFeP$_2$O$_7$ vs. temperature inside the cell in comparison with bibliographic results.[5]

B. Characterization of Fischer-Tropsch catalysts

The following is an example of one of the many applications of the controlled atmosphere cell described above. We will show its capability to characterize by Mössbauer spectroscopy iron catalysts activated and used in FTS. In order to show the efficiency of the cell, previously, we display the spectra of the NPs pre-synthetized before support impregnation.

C. Catalyst preparation

The chosen support for iron NPs was SBA-15. This material is a mesoporous solid of amorphous SiO_2 walls that has a regular hexagonal array of channels with diameters that can be tailored to lie between 5 and 30 nm. The huge surface area and both, its thermal and hydrothermal stability offer an excellent support for catalytic applications and it has already been used in many catalysts.[6,7] In the literature, the reported Fe/SBA-15 catalysts are usually prepared by impregnating the support with an appropriate solution that carries the Fe ions. To our knowledge, the example we have chosen is the first Fe/SBA-15 catalyst prepared by synthesizing first a system of 12 nm γ-Fe_2O_3 NPs of well controlled and homogeneous size[1] and later introduced into the channels of a mesoporous SBA-15 solid specially prepared with enlarged pore diameters.[8] This composite was called precursor of the catalyst.

D. "Peeling" and activation treatments

The precursor was subjected to a "peeling" process, prior to activation and reaction treatments, in order to eliminate the surfactant used in the NPs synthesis. In this way, the NPs are "naked" with its surface exposed. TGA experiments showed that heating the sample from RT to 533 K under N_2 flow (150 cm^3/min), heating rate of 10 K/min, and maintaining the sample at 533 K for one hour is enough to remove the surfactant. Then, the sample was cooled to room temperature under N_2 flow. The process was carried out at atmospheric pressure.

The activation treatment consists in heating the precursor from room temperature at 10 K/min under H_2 flow of 60 cm^3/min up to 688 K. Once this temperature is reached, the sample is quickly cooled to room temperature. The solid obtained was called c-12-Fe/SBA-15.

Both treatments were carried out in the reactor shown in Fig. 2 using small amounts of sample in order to acquire the Mössbauer spectrum of the activated catalyst in controlled atmosphere. The main advantage of the reactor is that the handling of the sample is simpler and less amount of catalyst is needed, in comparison with the treatment necessary for the used catalyst as it will be shown below.

E. Used catalyst

To identify the iron species present during the FTS, the used catalyst was characterized by Mössbauer spectroscopy, after using it 48 h in a stainless steel fixed bed reactor. The reaction conditions were a total pressure of 20 atm, H_2:CO = 2: 1 ratio (20 cm^3/min), space velocity of 828 h^{-1}, and reaction temperature of 603 K.

In order to ensure that the characterization is as representative as possible of the catalyst "working," and to prevent the contact of the catalyst with air, after 48 h of reaction, the system was cooled in synthesis gas flow. This sample was named u-12-Fe/SBA-15. Then, the reactor was isolated in this atmosphere at a total pressure of 2 atm and carried to a glove box jointly with the cell (Fig. 2(c)) for measurements in controlled atmosphere. The glove box was purged with Ar for 84 h (120 cm^3/min), with the aim to ensure that all air and moisture had been removed. The reactor was opened and the used catalyst was transferred to the Mössbauer cell under inert atmosphere. The process cannot be performed entirely in the controlled-atmosphere equipment shown in Fig. 2 because it was not designed to stand 20 atm.

F. Mössbauer analysis

Mössbauer spectra were taken in a conventional constant acceleration spectrometer of 512 channels with a 50-mCi nominal activity source of ^{57}Co in Rh matrix in transmission geometry. The temperatures from 13 to 298 K were attained by means of an Advanced Research Systems, Inc. closed-cycle cryogenic system. The Fe/SBA-15 powder absorbers were prepared with an optimum thickness of about 53 mg/cm^2 calculated with the method of Long *et al.*[9] The hyperfine parameters are the result of fitting the data using the extended Voigt-based fitting analysis of a commercial computer code.[10] Isomer shifts are calibrated against a α-Fe foil at room temperature.

III. RESULTS AND DISCUSSION

The iron species existent in the NPs were identified by means of Mössbauer measurements taken from 13 to 298 K. In addition, these yielded relevant information about their magnetic behavior.

Qualitatively, the sample displays a superparamagnetic behavior at room temperature.[11] A progressive blocking can be observed when the temperature decreases up to 50 K. At this temperature, a complete magnetic blocking is reached, as it will be described below.

Fig. 4 displays the Mössbauer spectra of the nanoparticle system taken at different temperatures and the corresponding hyperfine parameters were obtained after the fittings (not shown).

The spectrum at 13 K displays six well-defined peaks. The fitting was done with blocked sextets. The hyperfine parameters of both sextets are typical of γ-Fe_2O_3[12] and belong to Fe^{3+} ions located at tetrahedral (A) and octahedral (B) maghemite spinel sites. The fitting required a central doublet of small area that did not display any splitting. Since it has been recently found that the Fe^{3+} ions located at the surface of the NPs can form mono- and bi-dentate complexes through carboxylate groups belonging to the oleic acid (used as surfactant)[13,14] it is possible that this signal has its origin in these species.[1]

At 50 K, no relaxing signal is needed to perform the fitting. This means that below 50 K, the magnetic blocking is complete. This behavior could find its reason in the size of the 12 nm NPs and in the existence of inter-particle magnetic interactions.
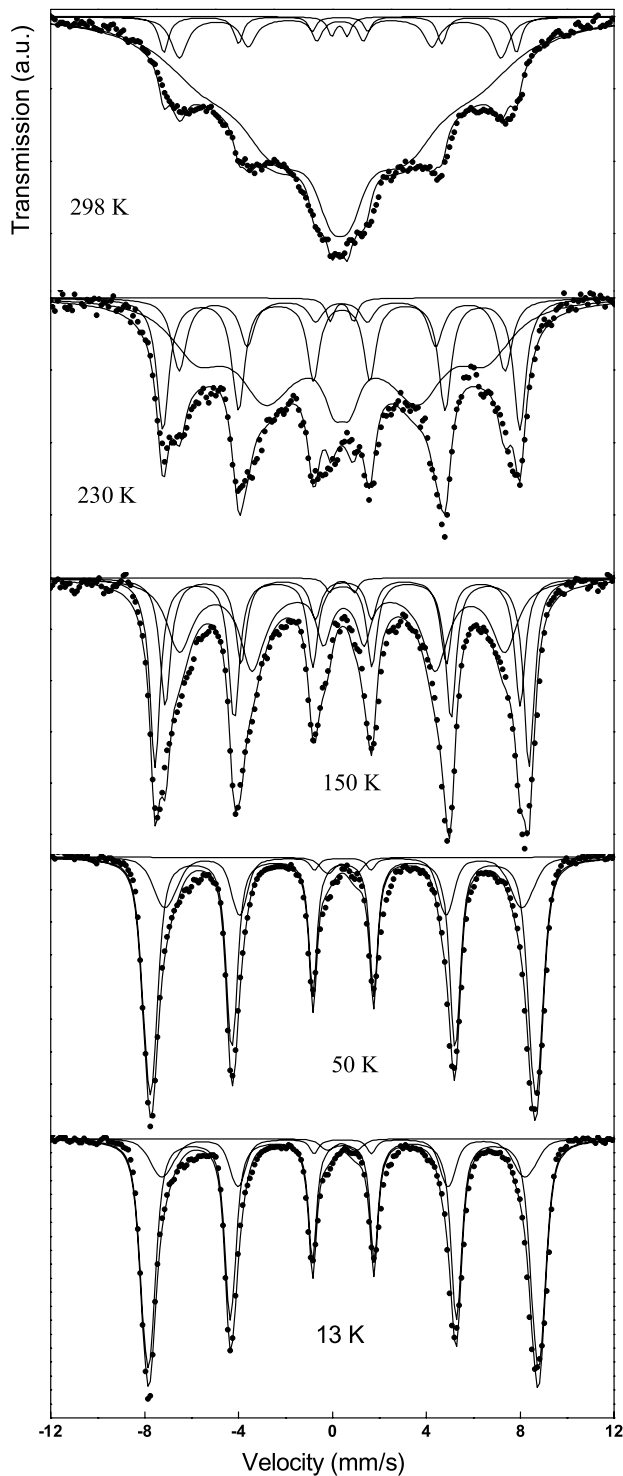
FIG. 4. NPs Mössbauer spectra at different temperatures.

The cell kept inside a hydrogen atmosphere of 1.5 atm in order to carry out the measurements at room temperature and 13 K of a fresh catalyst activated under H_2 atmosphere. Fig. 5 displays the Mössbauer spectra of this sample. At 298 K, all the spectrum peaks, located at the center, are originated by particles undergoing paramagnetic or superparamagnetic regimes. The fitting was performed assuming that a superparamagnetic signal of Fe_3O_4 can be simulated with two singlets, as in Ref. 15. The δ values used were very close to those of both A and B sites of bulk Fe_3O_4. Besides, two doublets were also needed to fit the spectrum. Their hyperfine parameters can be assigned to paramagnetic Fe^{2+} ions that have diffused into the SiO_2 walls of SBA-15 and are inside octahedral and tetrahedral sites.[16]

When the temperature decreases to 13 K, the collapsed central signal is splitted in six very broad peaks. Six sextets and two doublets were used to fit the spectrum of the activated solid. Hyperfine field distributions were needed to achieve an acceptable fitting. According to Dézsi *et al.*,[17] the sextets are originated by the different sites of a Fe_3O_4 that has undergone the Verwey transition. It is worth noting that it is not possible to fit the signals belonging to Fe_3O_4 with just two sites. This is evidence that the Verwey transition has taken place for the magnetite existing in the sample. The fitted parameters converged to very similar values to those of Ref. 17, which were obtained for Fe_3O_4 NPs of 9 nm. In addition, at this temperature, the fittings still require the two doublets assigned to paramagnetic ions of Fe^{2+} inside the SBA-15 walls.

At 150 K, the magnetic blocked fraction decreases and finally at 298 K, 85% of the sample displays a superparamagnetic regime. Besides, at this temperature, it was necessary to add two sextets corresponding to the (A) and (B) sites of γ-Fe_2O_3 to fit the spectrum. The paramagnetic doublet assigned to Fe^{3+} ions coordinated to oleic acid is also necessary to give account of the total spectral area.

The above considerations allow concluding that Mössbauer results are coherent with just γ-Fe_2O_3 as the only existing iron species in the NPs.
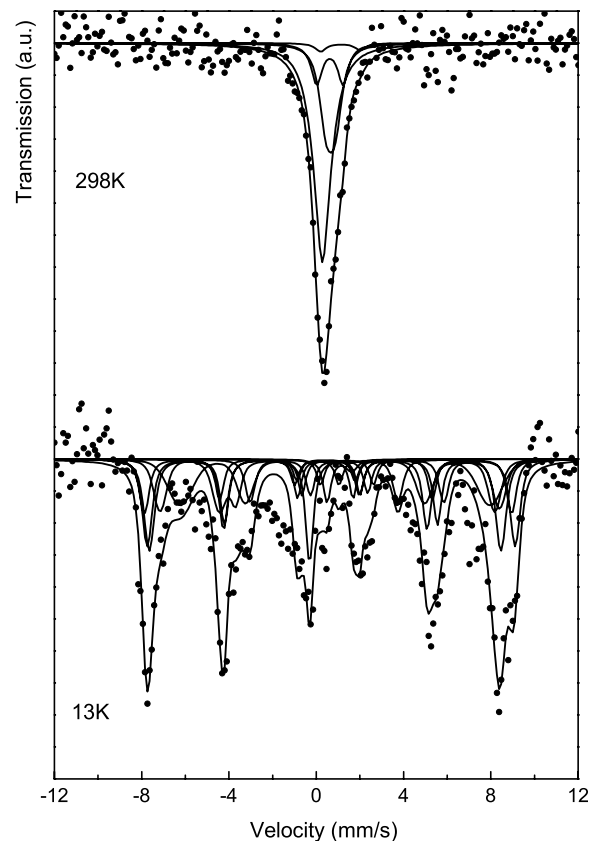

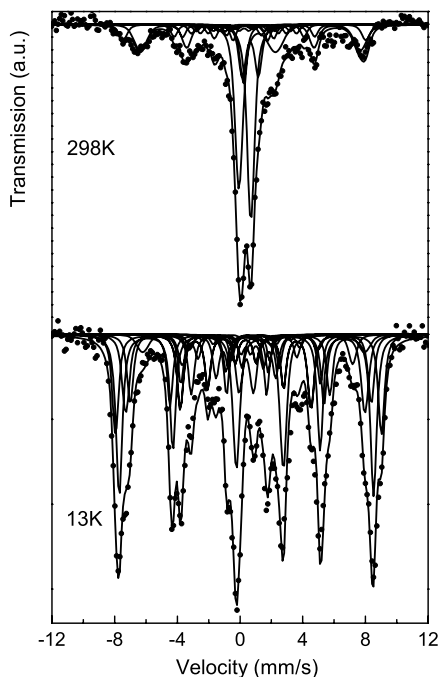FIG. 5. Mössbauer spectra of c-12-Fe/SBA-15 at 298 and 13 K.

FIG. 6. Mössbauer spectra of u-12-Fe/SBA-15 at 298 and 13 K.

The fitting of u-12-Fe/SBA-15 spectrum at 298 K was performed as follows. Superparamagnetic Fe_3O_4 was simulated using the two-singlet model of Ref. 15 with δ values very close to the A and B sites of bulk magnetite[18] in the same way that c-12-Fe/SBA-15. The two sextets of the fraction of magnetite magnetically blocked yielded hyperfine field values lower than those of bulk Fe_3O_4 because of size effects (likely, collective magnetic excitations[19]). The remaining peaks were fitted by means of the two doublets assigned to the Fe^{2+} signal arising from the ions exchanged with the SiO_2 walls, as discussed above. In addition, it was necessary to perform the fitting using five more sextets belonging to the three sites of the χ-Fe_5C_2 carbide[20] and the two sites of the ε'-$Fe_{2.2}C$ carbide.[21]

The fitting at 13 K required the presence of two doublets and ten sextets. As before, the doublets were assigned to the Fe^{2+} ions exchanged with SiO_2 walls. According to Dézsi *et al.*,[17] six sextets were assigned to the different sites existing in Fe_3O_4 that has undergone the Verwey transition. Again, it was not possible to fit in an acceptable way the Fe_3O_4 peaks with just two sites, which means that the Verwey transition has taken place. As before, the parameters converged to similar values reported in Ref. 17 for magnetite NPs of 9 nm but with slightly lower hyperfine fields. This decrease would be coherent with a model of a magnetite nanoparticle "core" of slightly smaller size than the initial nanoparticle size, likely due to the conversion of part of its mass into carbide nodules.

Finally, four sextets were assigned to sites I, II, and III of χ-Fe_5C_2 carbide[20] and to the sites I and II of ε'-$Fe_{2.2}C$ carbide.[21] Site II of χ-Fe_5C_2 carbide and site I of ε'-carbide exhibit overlapped signals with a hyperfine field of H ≈ 250 kG at low temperature. For this reason, the two carbides have been simulated with four sextets instead of five. Fig. 6 displays the Mössbauer spectra.

The controlled atmosphere of the cell allowed finding the species of the activated and used samples without any oxidation by air. Oxidation would have been a serious hindrance when dealing with systems composed of so small particles.

IV. CONCLUSIONS

Mössbauer spectroscopy is a technique especially suitable to identify the Fe species existent in the samples under study. The relative proportions of each species can be evaluated even in complex systems as the catalysts investigated in this article. The improved design of the cell allowed submitting the samples to higher temperatures and higher pressures than the previous design. The spectra measured inside the cell of controlled atmosphere demonstrate that the samples did not show any sign of oxidation. In the example chosen to illustrate its use, the cell has been essential to understand the nature of the iron species existing in the 12 nm NPs/SBA-15 system after activation treatment with hydrogen, as well as the species present in the used catalyst.

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