CHARACTERIZATION OF IRON SITES IN POROUS FERRISILICATES BY *IN SITU* MÖSSBAUER SPECTROSCOPY

Károly Lázár

Institute of Isotopes, Budapest, P.O.B. 77, H-1525, Hungary
E-mail: lazar@iki.kfki.hu

INTRODUCTION

The method of Mössbauer spectroscopy is a convenient tool to analyse and identify oxidation and coordination states of iron. The close vicinity of iron ions influences both the oxidation and coordination states, thus information can be extracted as for the local environment, i.e. for the structure where iron ions are located.

Among a wide variety of substances porous ferrisilicates can also be advantageously studied by the method. The porous structure allows the stabilisation of iron ion in various sites in various environments. In addition, the porous structure allows also the penetration of moisture from air through the channels and pores, and water molecules favour to adsorb on charged sites, e.g. in the vicinity of iron ions, as well. In this instance, a simple evacuation may help to restore the original structure. Since collection of Mössbauer spectra usually takes several hours, the evacuation should be maintained during the measurement, which can easily be accomplished by using *in situ* conditions for the measurement. Furhermore, the *in situ* conditions provide means to expose iron ions to various conditions, e.g. either to reducing or oxidizing ones. These various conditions may refer to various reactions – eg. the reducing ones may provide analogy to those characterising conversions of hydrocarbons, or, oxidising conditions may refer e.g. to selective oxidation reactions. In correspondence, by using the *in situ* methodology, the changes in the states of iron can further be correlated with the catalytic properties of ferrisilicates in these reactions.

In the two large groups of porous ferrisilicates, namely in the micro- and in the mesoporous ones, the structure, and consequently, the environment of iron may be different in a certain extent. Microporous structures are strictly crystalline, in three dimensions. Thus, the two sitings, the framework (FW) and the extra-framwork (EFW) ones can clearly be distinguished. The FW one is the isomorphous substitution in the tetrahedral sites in the centre of the $[FeO_{4/2}]^-$ units embedded into the structurally similar net of $[SiO_{4/2}]$ tetrahedra. In contrast, the EFW positions are the charge compensating sites in the pores, to counterbalance the charges generated at the trivalent FW sites, most frequently that of the $[AlO_{4/2}]^-$, or the previously mentioned $[FeO_{4/2}]^-$. The space restriction is less rigid for these EFW irons, thus they may occupy the most favourable position, and in correspondence, a certain variety can be observed in the symmetry of their environment. As for the mesoporous systems, their structure is less ordered in a certain extent. In contrast to the previously mentioned crystalline 3D structure of the microporous systems, mesoporous substances exhibit only two dimensional array of pores and/or channels, and the structure in their pore walls is less ordered, it can be partly amorphous.

The Mössbauer spectra of ferrisilicates is composed in most of cases from twin-peak components, namely from doublets. The position of the centre of doublets in the spectra is called isomeric shift (IS), whereas the line separation between these two peaks is the other measurable parameter, the quadrupole splitting (QS). The ferric and ferrous states can clearly be distinguished by the value of their isomeric shifts ($0.2 < IS(ferric) < 0.4$ mm/s, and $0.6 < IS(ferrous) < 1.2$ mm/s, respectively). The coordination state of the ions is primarily correlated

with the quadrupole splitting. For instance, for ferrisilicate minerals a comprehensive compilation of data can be found in [1]. Thus, on the basis of the measured IS and QS pairs of data both the oxidation and coordination states of iron can be identified with a good accuracy. In most of cases the observed spectra are composed from a few doublets, thus, in order to obtain the respective data, the spectra should be decomposed to doublets.

In the present contribution some examples are presented to illustrate the application of Mössbauer spectroscopy to identify various states of iron occuring in porous ferrisilicates. First, the features of isomorphously substituted iron in FW sites are shown in an Fe-ZSM-5. Then an example is presented to illustrate the distinctly different beaviour of EFW iron ions in an Fe-LTA. The third illustration in microporous systems is the study of the combination of these two types of iron, namely formation of dinuclear Fe$_{framework}$-O-Fe$_{extra-framework}$ pairs is discussed in an Fe-MCM-22. From studies of mesoporous ferrisilicates also three examples are presented. First, behaviour of iron in a thin-wall MCM-41 sample is shown, then the effects of the modification of the synthesis which result in the formation of thicker walls are shown, and finally, spectra of composite Fe-SBA-15/Fe$_2$O$_3$ systems with various iron contents are presented and interpreted.

EXPERIMENTAL

The studied ferrisilicate samples were synthesized by hydrothermal way or by hydrolysing tetraethylortosilicate. The Si to Fe ratio in the samples varied from 20 to 200 (at the higher ratios iron was enriched in the ^{57}Fe isotope to enhance the Mössbauer signal). Further details of the synthesis are presented in the respective publications.

The measurements were performed in an *in situ* cell. In this cell evacuation and treatments in various atmospheres can be performed up to 650 K, thus various redox conditions can be generated and the corresponding changes of iron can be detected. The sheme of the cell is shown in [2].

RESULTS AND DISCUSSION

First, an example is presented to illustrate the appearance of framework substituted iron. The sample studied is an Fe-ZSM-5 (Si/Fe ~ 200). Various treatments were performed in a series on the same sample (see Fig. 1 – from top to downward). By evacuation the chemisorbed water is desorbed − a component with apparent quadrupole splitting appears. On the third spectrum, after treatment in hydrogen, the characteristic dominating component is the doublet of the non-reduced, FW substitiuted Fe^{3+} displaying a large quadrupole splitting (QS ~ 2.0 mm/s). The large assymmetry of the environment of iron in the (SiO)$_3$≡Fe(OH)-O-Si unit is reflected in this large QS value. In this third spectrum same Fe^{2+} is also shown, exhibiting the regular ferrous isomer shift (IS ~ 1.0 mm/s). The reverse of the reducing atmosphere to oxidizing one by exposing the sample to N$_2$O results in the reoxidation of Fe^{2+} to Fe^{3+}, as shown in the fourth spectrum. The processes are reversible, after a repeated reduction in hydrogen the same state is restored in the sixth spectrum than shown in the third one. Next, after performing the treatments and storing the sample on ambient air for a few hours, some water is chemisorbed from the air, the starting state of the sample is almost restored, the shapes of the first and last spectra of the series are similar. Further details are described in [3]. The behaviour of the extra-framework ions is distinctly different from that of the framework ones. This is illustrated by a series of spectra recorded on the Fe-LTA sample (Si/Fe ~ 200). The obtained spectra shown in Fig. 2 are clearly different from those shown in Fig. 1.

Upon evacuation already an Fe^{3+} to Fe^{2+} reduction is observed for a significant part of iron (spectrum on the top). The treatment of the sample in mild reducing conditions at 570 K

results in reduction for almost all the the iron to ferrous state. A small amount of moisture present in the hydrogen changes the coordinatin around the ferrous iron (third spectrum from top). The reversal of the reducing conditions to oxidizing ones in N_2O results in complete reoxidation of the ferrous iron formed in the previous steps. Repetition of the reduction in hydrogen reverts again the oxidation state to ferrous one. Thus, as demonstrated in the Fe-LTA sample, the $Fe^{3+} \leftrightarrow Fe^{2+}$ process is completely reversible for almost the whole amount of iron. Further, variety of coordination states is available for the ferrous iron as is reflected in the noticeable changes in the value of the quadrupole splitting. Further details and interpretation are presented in [4].
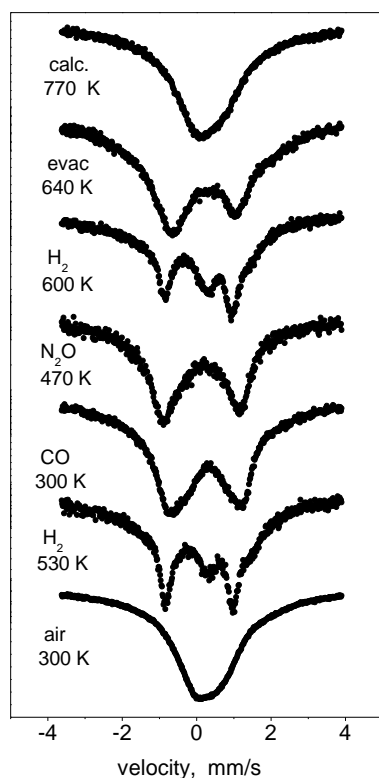

Figure 1. Sequential *in situ* Mössbauer spectra of Fe-ZSM-5 (Si/Fe ~ 200) sample recorded at room temperature after steps in a series of the marked treatments (sequence is from top to down).
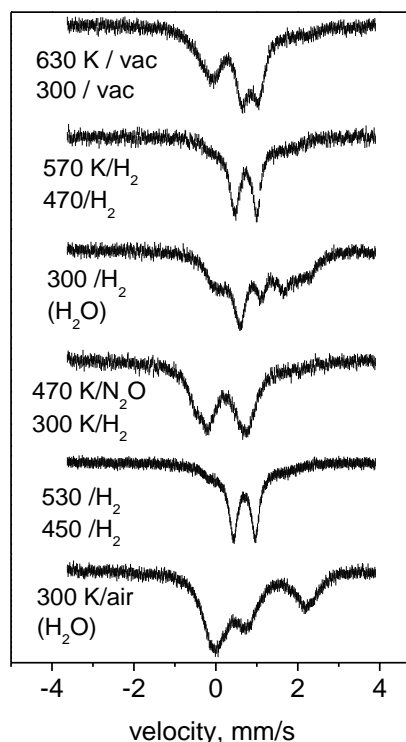
Figure 2. Sequential *in situ* Mössbauer spectra of EFW iron in Fe-LTA (Si/Fe ~ 200) sample in the series of treatments as indicated at each spectrum (from top down. First the conditions of treatments are listed, then those of the measurement.)

The third example presented for the illustration of the application of the Mössbauer technique for analysing the behaviour of iron in microporous systems is a series of spectra recorded on an Fe-MCM-22 system (Si/Fe = 20). The structure of MCM-22 is specific, it is composed from the regular array of tight narrow channels and more spacious, non-connected, ellipsoid pores. The sample was studied after the synthesis and calcination – it contained sodium in a part of the pores (Si/Na = 35) [5]. The corresponding spectra are shown in Fig. 3.

The evacuation results in an $Fe^{3+} \rightarrow Fe^{2+}$ reduction for a part of iron. The reduced form of iron is located in EFW sites and can provide also charge compensating function, eg. in the form of $Fe(OH)^+$. The quadrupole splitting exhibited by the FW iron is rather small (QS ~ 1.6 mm/s), as compared to the previusly discussed 2.0 mm/s value found on the Fe-ZSM-5. The smaller QS value can probably be attributed to the smaller distortion exerted by the

voluminous $Fe(OH)^+$ ion, the distortion in the symmetry for the FW iron is probably smaller than in the case of the Fe-ZSM-5 where the charge compensation was provided by a small proton. The case, in which the charge compensation for the FW ferric iron is provided by a nearby $Fe(OH)^+$ entity, in other terms, is equivalent with the formation of a dinuclear $Fe^{3+}_{framework}$-O-$Fe^{2+}_{extra-framework}$ pair.
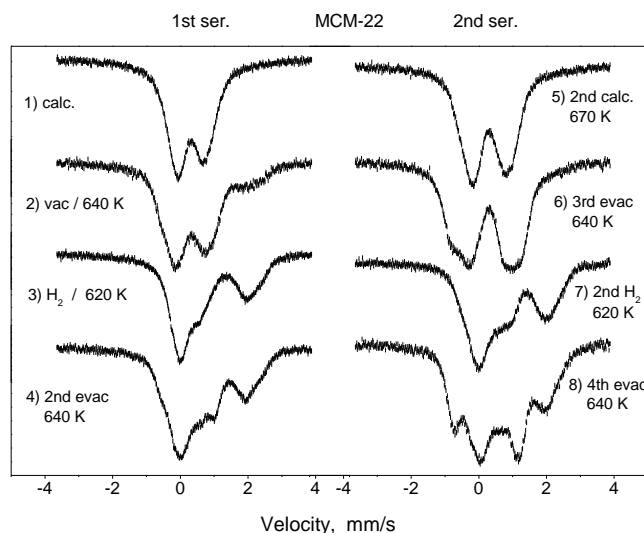

Figure 3. *In situ* Mössbauer spectra recorded on two cycles of sequential treatments of Fe-MCM-22 (Si/Fe = 20)

The second series (right side of the figure) was started with a repeated calcination which probably reoxidised the EFW ferrous $Fe(OH)^+$ to ferric FeO^+. The third evacuation resulted in the appearance of both a smaller and a larger QS for the ferric component. The second reduction in hydrogen may also result in the formation of neutral ferric FeO, which is not able to compensate the charge of the FW iron any more, and it may leave its previous environment. To provide the net neutral charge balance protons (or hydroxonium ions) may take over the role of the necessary charge compensation for a part of FW iron ions.

This presumption is probably true, since on the final spectrum recorded after the fourth evacuation the signal of the protonated $(SiO)_3\equiv Fe(OH)$-Si group exhibiting the large quadrupole splitting appears in a significant intensity. Thus the presented spectra of Fe-MCM-22 can be interpreted as attesting for dynamic formation and disruption of dinuclear centres in the sequence of redox treatments. Further details on the Fe-MCM-22 spectra are described in [5].

On the basis of the presented spectra the behaviour of iron in the microporous systems can be characterized as follows:

- The framework substituted iron in H-form, (Si-O)$_3\equiv$Fe-(OH)-O-Si, experiences a high charge assymmetry – a large QS (~ 2.0 mm/s) is detected for this FW component.

- The framework substituted species is able to retain its FW state in ferric form under modest reducing conditions (even at 620 K in hydrogen).

- Iron present in extra-framework state is more easy to reduce, most of ferric EFW irons can be reduced to Fe^{2+} at 620 K in H_2. This reduced ferrous iron easily changes its coordination, among the available positions.

- Almost all the EFW iron is accessible for the reversible $Fe^{3+} \leftrightarrow Fe^{2+}$ process.

- The FW and EFW types of iron may be combined, formation of dinuclear $Fe^{3+}_{framework}$-O-$Fe^{2+}_{extra\text{-}framwork}$ pairs can be observed among certain conditions and larger iron contents.

On mesoporous systems distinctly different fetures can be observed than on the previously discussed microporous ones. In this aspect the stucture of the pore wall plays a primary role.

This can be illustrated by comparing Fe-MCM-41 samples prepared by different synthesis methods (Fig. 4). Using sodium silicate solution and cetyltrimethylammonium bromide as a surfactant, the formed Fe-MCM-41 consists of thin pore walls of partly amorphous structure. It is clearly reflected in the in situ Mössbauer spectra in which the iron exhibits a behaviour similar to that found for EFW iron in microporous systems. Namely, a simple evacuation results in an $Fe^{3+} \rightarrow Fe^{2+}$ reduction for a significant part of iron. Furthermore, the subsequent treatment in hydrogen results in the reduction for almost all the iron to ferrous state. (The spectrum on the bottom left is composed only from ferrous components. Further details on this sample are reported in [6].) Fe-MCM-41 with thicker pore walls and regular spherical shape can be synthesized by hydrolysing tetraethylorthosilicate in methanolic solution. In this case the pore walls are more ordered, and partly crystalline. The same treatments as used for the previous sample, results in different spectra in this instance. Namely, reduction cannot be observed on a simple evacuation, and treatment in hydrogen results only in $Fe^{3+} \rightarrow Fe^{2+}$ reduction only for a part of iron. This features are closer to those observed for FW iron in the microporous systems. Further details on the synthesis and comparison are reported in [5].
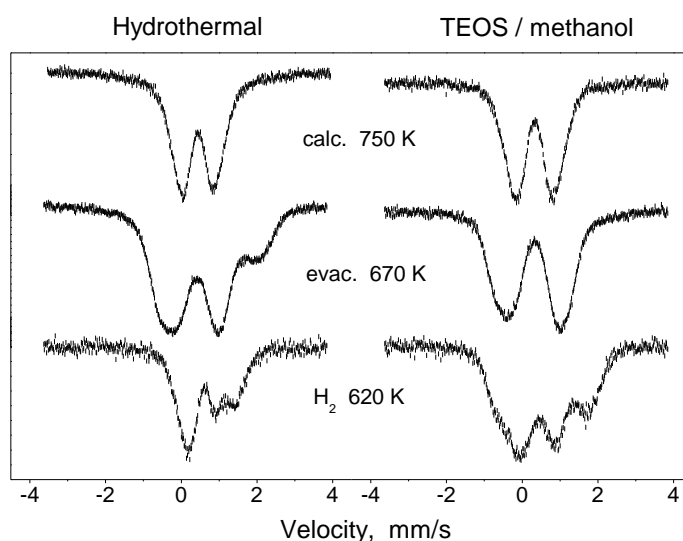

Figure 4. Series of Mössbauer spectra collected on Fe-MCM-41 samples synthesised by different procedures (hydrothermal way, left, and from methanolic solution by hydrolysing tetraethylorthosilicate, right)

Other, secondary phases can also be formed and stabilized in the host mesoporous ferrisilicates depending on the synthesis procedure. For example Fe-SBA-15 can be synthesized using Pluronic 123 in an acidic media (1 < pH). In this case ca. 1.2 wt % iron can be accommodated homogeneously in ionic form in the structure (sample DS-1). A slight modification of the conditions, namely raising the pH of the aging to 3.5 results in the increase of the iron content of the sample to 16 wt %. As the respective XRD and TEM measurements revealed Fe_2O_3 (hematite) particles are embedded in the structure (sample DS-2) [7]. The Mössbauer spectra recorded on the DS-1 nd DS-2 samples are in good

correspondence with this observation. DS-1 sample exhibits spectra similar to those of MCM-41 (TEOS / methanolic), or to those recorded for FW type iron in microporous systems (Fig. 5, right side). In the DS-2 sample most of iron is present in the form of hematite. (Hematite appears in the Mössbauer spectra in the form of a sextet composed from six lines– Fig. 5, left side, middle and bottom spectra.) These DS-1 and DS-2 samples were tested as catalysts for total oxidation of phenol in aqueous media with hydrogen peroxide. Surprisingly, in spite of the one order of magnitude difference of the iron content in them, the two samples exhibit simiar catalytic activity. Thus, the catalytic performance can probably be attributed to the ionic form of iron distributed homogeneously in the host, regardless the presence or absence of hematite. Further details are reported in [7].
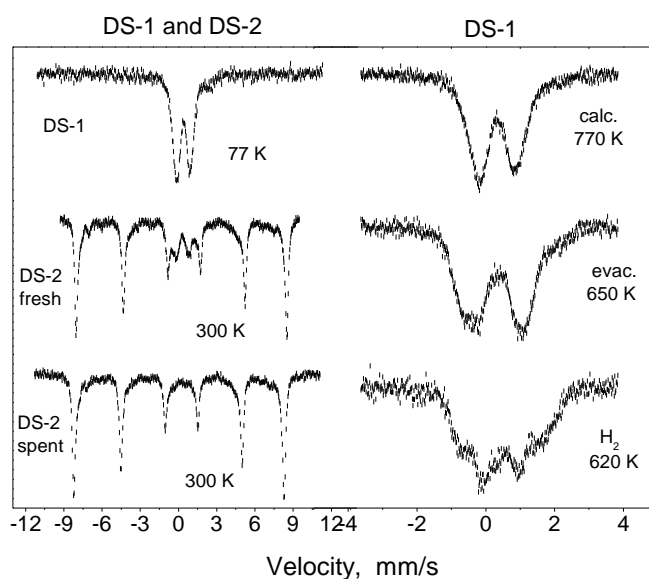

Figure 5. Mössbauer spectra of Fe-SBA-15 samples. In sample DS-1 1.2 wt % iron is distributed homogeneously in ionic form. Sample DS-2 is an Fe-SBA-15 / Fe_2O_3 composite with 16 wt % Fe.

CONCLUSIONS

The method of *in situ* Mössbauer spectroscopy was applied to study the various oxidation and coordination states of iron in porous ferrisilicates. In microporous substances the behaviour of iron located either in FW or in EFW sites can clearly be distinguished. Formation of $Fe^{3+}_{framework}$-O-$Fe^{2+}_{extra-framework}$ dinuclear entities can also be evidenced. In mesoporous ferrisilicates the structure of the pore walls plays determining role. An ordered structure may impose conditions for iron similar to FW ones, whereas a partly amorphous structure allows stabilisation of iron in less ordered ferrous states, simliar to those characteristic for EFW siting in microporous systems.

ACKNOWLEDGEMENT

REFERENCES

[1] R.G. Burns, *Hyperfine Interactions,* 1994, **91**, 739-745.

[2] K. Lázár, K. Matusek, J. Mink, S. Dobos, L. Guczi, A. Vizi-Orosz, L. Markó and W.M. Reiff, *J. Catal.,* 1984, **87**, 163-178.

[3] K. Lázár, Á. Szegedi, G. Pál-Borbély, A.N. Kotasthane and P. Fejes, *Catal. Today,* 2005, **110**, 239-246.

[4] K. Lázár, C. Vincent and P. Fejes, *Hyperfine Interactions,* 2008, **187,** 1-6.

[5] K. Lázár, G. Pál-Borbély, Á. Szegedi, P. Fejes and F. Martinez, *Czechoslovak Journal of Physics,* 2006, **56,** E109-E121.

[6] G. Pál-Borbély, Á. Szegedi, K. Lázár and H.K. Beyer, *Stud. Surf. Sci. Catal.*, 2001, **135**, 150.

[7] K. Lázár, G. Calleja, J.A. Melero, F. Martinez and R. Molina, *Stud. Surf. Sci, Catal.,* 2004, **154**, 805-812.