

Variations in bonding of iron in porous ferrisilicates

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Abstract Bonding strengths of iron species in different micro- and mesoporous ferrisilicates are deduced from analysis of changes in recoilless fractions extracted from various series of in situ spectra. The recoilless fractions for extra-framework ions in microporous Fe-LTA may depend strongly on the conditions. In Fe-FER, containing both framework and extra-framework types of iron, modest changes were detected. In mesoporous Fe-MCM-41 samples variations of the bonding strengths were revealed which can apparently be correlated with the partly amorphous structure of the pore walls in these substances.

Keywords Recoilless fractions · Porous ferrisilicates · Bonding strength · In situ spectra

1 Introduction

Probability of the Mössbauer effect is strongly connected to the possible vibration states of the Mössbauer nucleus inside the solid lattice. The strength of the bonding of iron in the lattice may also depend on the oxidation state, coordination etc. Thus, beside evaluation of usual basic parameters (isomer shift, quadrupole splitting) valuable additional informations can be extracted from the analysis of data related to the changes in the recoilless fractions of components. The value of the recoilless fraction (f_A) can explicitly be described e.g. in the frame of the Debye model of lattice vibrations, where a characteristic temperature (Θ_D) may be used to estimate the

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strength of bonding of the studied species in the crystal structure [1]. Θ_D is calculated usually from the temperature dependence either of the spectral area or the isomer shift (second order Doppler shift). Relative measurements can also be used, e.g. by comparing the relative areas of a reference and the studied substances mixed within a single sample [2].

Investigation of data related to the recoilless fractions of different species present in the in situ Mössbauer spectra of metallic components of supported FeRh/SiO₂ catalysts was proposed already in 1984 [3]. In particular, identification of catalytically active surface components was attempted by this way—the surface component was supposed to exhibit loose bond, i.e. stronger temperature dependence in its signal intensity. In contrast, the component originated from inside of the bulk metallic particle (thereby hardly participating in the surface catalytic process), was supposed to display less expressed temperature dependence in its intensity [3]. Existence of ionic tin species on the surface of supported bimetallic Pt-Sn catalysts was also detected in analogous studies later [4].

Application of in situ measuring technique [5] is particularly advantageous for comparison of sequential spectra collected on the same sample in a course of series of treatments. Since the measuring geometry is the same for each steps, simple comparison of normalised spectral areas may provide information on the changes of f -factors.

This type of additional analysis of data is also worth to carry out on in situ spectra of porous ferrisilicates. In particular, two main locations are distinguished for iron located in crystalline microporous zeolite analogue structures, namely framework (FW) and extra-framework (EFW) ones. It can be expected that the bonding strengths for FW and EFW sitings are different, and this feature can occasionally be correlated in the changes of the respective recoilless fractions. Completion of this assumption had already been investigated on Fe-FER sample containing iron in significant amount ($\text{Si/Fe} = 16$), located both in FW and EFW sites. Actually, no significant difference was observed for the different sitings, the relative spectral intensities did not depend strongly on the partition of iron among FW and EFW sites. An estimation could also be provided for the average value of Debye temperature from comparison of relative intensities of 300 and 80 K spectra. Namely, by approaching the $f_A(T)$ dependence with a linear straight line in the $200 < \Theta_D < 350$ K region [3], Θ_D can be estimated from the slopes determined from the ratio of the normalised spectral areas of the 300 and 80 K spectra. $\Theta_D \sim 260$ K was proposed for Fe-FER by using this approximation [6].

Similarly, distinction in locations and bondings of iron in mesoporous ferrisilicates can also be assumed, since the pore wall in these materials is partly amorphous [7], thereby the bonding in the more crystalline part may differ from that which can be observed on iron species located in primarily amorphous regions of the pore walls.

In the recent communication completion of these presumptions are investigated by comparing different types of samples. First, series of spectra collected on iron located in EFW sites in microporous LTA samples with low iron content ($\text{Si}/^{57}\text{Fe} \sim 200$) are compared. Then, data collected on the previously mentioned microporous Fe-FER sample are shortly recalled. The third series of spectra was obtained on mesoporous Fe-MCM-41 prepared in hydrothermal synthesis starting with an aqueous, sodium silicate silicon source and with low iron content ($\text{Si}/^{57}\text{Fe} \sim 140$). In the last series spectra collected on Fe-MCM-41 prepared from tetraethyl-orthosilicate silicon source with various iron contents ($\text{Si/Fe} = 16, 20, 50$) are presented and compared.

2 Experimental

2.1 Samples

Two samples (Fe-LTA and Fe-MCM-41) were prepared by using the Mössbauer-active ^{57}Fe isotope. The other two samples were prepared from natural iron source, in which the content of the ^{57}Fe isotope is only 2.8 %.

Fe-LTA samples were synthesized by crystallisation from a precursor slurry containing the elementary sodalite building blocks. ^{57}Fe was used for iron source, thus low iron content samples ($\text{Si}/^{57}\text{Fe} \sim 200$) could be prepared, providing spectra with good signal to noise ratios. Further details are described in [8].

Fe-FER samples were prepared by hydrothermal synthesis using regular iron and silicon sources and pyrrolidine template resulting in samples with $\text{Si}/\text{Fe} = 16$ ratio [9].

Fe-MCM-41 sample was prepared with low iron content ($\text{Si}/^{57}\text{Fe} = 140$) in hydrothermal synthesis by using sodium silicate solution and cetyltrimethylammonium bromide (CTMABr) template [10].

Fe-MCM-41(S) samples of spherical morphology with different iron contents ($\text{Si}/\text{Fe} = 15, 20$ and 50) were prepared by hydrolysing tetraethylorthosilicate silicon source and using CTMABr template [11].

2.2 In situ treatments and Mössbauer measurements

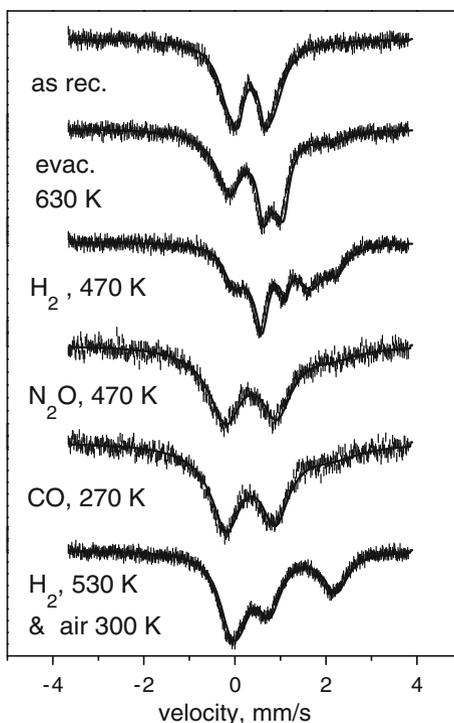
Treatments of samples were performed in an in situ cell, providing conditions to perform treatments at different temperatures in reducing or oxidizing atmospheres or for evacuation, as well as for recording spectra at various temperatures (from liquid nitrogen, 80 K, to 600 K) [5]. An important condition is that the geometry of the measurement is not changed within one series of subsequent treatments and measurements, thus normalised intensities of different spectra can directly be compared. In a simple way, I/BL values are used to characterise the relative spectral intensities, that is the value of the intensity of spectrum (spectral area, I) related to the total area under the corresponding base line (BL). The nominal error of the I/BL values is small (ratio of spectral areas). It can amount to a few per cent in the practice, still negligible when comparing I/BL data obtained on different porous ferrisilicates.

3 Results and discussion

3.1 Fe-LTA ($\text{Si}/^{57}\text{Fe} \sim 200$)

A series of treatments and in situ measurements was performed on an Fe-LTA ($\text{Si}/^{57}\text{Fe} \sim 200$) sample. The sample was prepared by recrystallisation, resulting in dominant EFW siting of iron. LTA structure is a tight pore system with typical pore diameters of 0.4 nm, and iron ions were expelled from the FW sites to EFW ones during recrystallisation [8]. Combinations of evacuation, reduction, oxidation were applied in various temperatures and atmospheres. Some selected spectra are shown in Fig. 1, corresponding data of decompositions are collected in Table 1. The detailed description and evaluation of the regular Mössbauer parameters are presented in [12]. Here the attention is mostly focussed on the I/BL values collected in the last

Fig. 1 300 K spectra fe-LTA sample ($\text{Si}/^{57}\text{Fe} \sim 200$) in a series of treatments (as indicated)



column (spectral area related to the base line). This quantity is proportional to the mean of the recoilless fractions of components.

Changes in the environment and bonding states of EFW iron ions are apparently reflected in I/BL data. The sample collects moisture during open air storage after calcination. The adsorbed water is removed with the 630 K evacuation from the coordination sphere of iron [13], there is a slight drop in the I/BL value. A modest temperature reduction converts the ferric EFW iron to ferrous one, with modest change in the I/BL. Possibly ($-\text{OH}$) groups may form in the vicinity of iron. Oxidation with atomic oxygen formed from decomposition of N_2O at 470 K results in a significant, bare ferric ions are formed. The oxidation state and environment of iron cannot be changed with the exchange of the atmosphere from N_2O to hydrogen at room temperature, in correspondence, I/BL value does not change either. An evacuation, and storage in hydrogen (which contains traces of water) restores the starting I/BL value with ca. 10 % accuracy. In short, comparison of I/BL values clearly demonstrate that removal and readsorption of water may provide certain strengthening in the bond of EFW iron ions to the zeolite framework. Comparison of the two I/BL extremes in Table 1 (4.5/6.9) reveal ca. 33 % difference in the I/BL which is certainly a noticeable value.

3.2 Fe-FER ($\text{Si}/\text{Fe} = 16$)

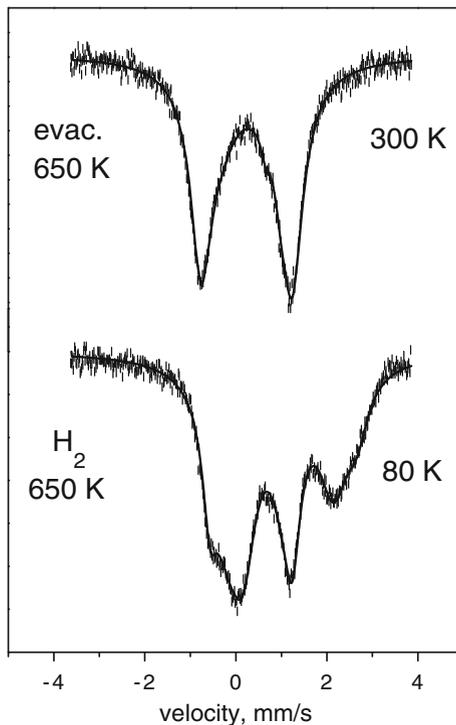
Two spectra are shown in Fig. 2 to illustrate the differences to relate with those of LTA sample. Namely, comparison of spectra of Fe-FER recorded after evacuation at

Table 1 Mössbauer parameters and I/BL data collected from decompositions of Fe-LTA spectra of Fig. 1

Treatment	Component	IS	QS	RA	I/BL
As rec. (calc.)	Fe ³⁺	0.37	0.57	17	6.37
	Fe ³⁺	0.36	0.92	83	
630 K, evac.	Fe ³⁺	0.37	0.94	58	5.97
	Fe ²⁺	0.85	0.45	25	
	Fe ²⁺	0.88	2.46	16	
470 K, H ₂	Fe ³⁺	0.26	0.75	9	6.22
	Fe ²⁺	0.85	0.51	16	
	Fe ²⁺	1.09	1.14	52	
	Fe ²⁺	1.13	2.21	23	
470 K, N ₂ O	Fe ³⁺	0.36	1.11	80	4.53
	Fe ²⁺	0.86	2.60	20	
270 K, H ₂	Fe ³⁺	0.35	1.07	73	4.67
	Fe ²⁺	0.89	2.48	37	
550 evac, RT air/(H ₂ O)	Fe ³⁺	0.33	0.86	57	6.93
	Fe ²⁺	1.16	2.10	43	

IS Isomer shift, relative to metallic α -iron, mm/s; QS quadrupole splitting, mm/s; RA relative spectral contribution, %, I/BL: Intensity of full spectrum related to the base line, %

Fig. 2 Typical spectra selected from a longer series of treatments of Fe-FER (Si/Fe = 16) [8]. Evacuated at 630 K and recorded at 300 K (top), treated in hydrogen at 630 K and recorded at 80 K (bottom)



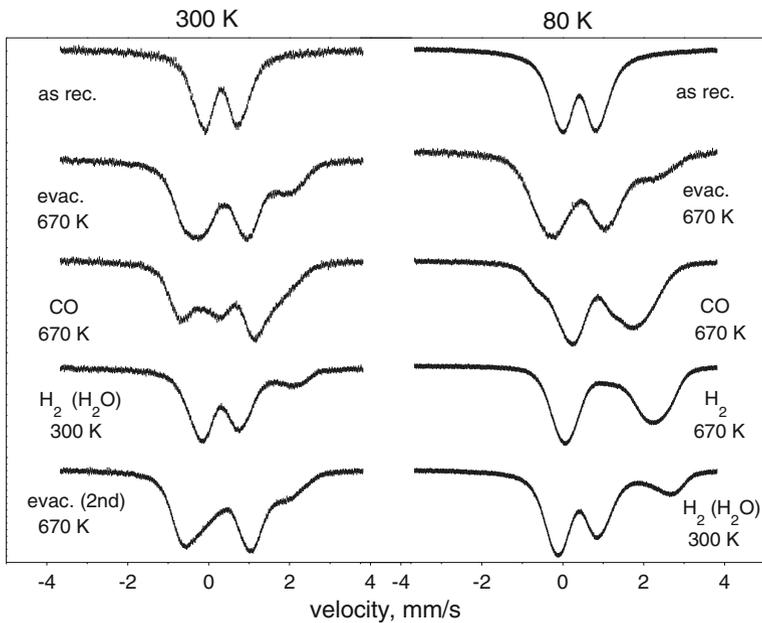


Fig. 3 Series of spectra recorded on the Fe-MCM-41 sample ($\text{Si}^{57}\text{Fe} \sim 140$) in the sequence of the marked treatments, measured both at 300 K (left) and 80 K (right)

Table 2 I/BL data collected from 300 and 80 K spectra of Fe-FER reported in [9]

Treatment	I/BL 300 K	I/BL 80 K
As received (calc.)	0.304	0.458
Evacuation / 650 K	0.322	
Hydrogen / 650 K		0.531
Hydrogen (repetition)	0.337	0.530
Evacuation / 650 K	0.333	
Hydrogen / 300 K	0.346	0.546

I/BL: Intensity of full spectrum related to the base line, %

620 K (Fig. 3a) and obtained after a reducing treatment in hydrogen at 620 K (Fig. 3b) clearly shows that both FW (Fe^{3+}) and EFW (Fe^{2+}) ions exist in the Fe-FER sample after hydrogen treatment, whereas the same treatment converts almost all the Fe^{3+} ions to EFW Fe^{2+} in the case of LTA. Detailed description and interpretation of spectra from whole series of in situ treatments and measurements on the Fe-FER can be found in [9]. It is also worth mentioning that existence of dinuclear $\text{Fe}_{\text{FW}}\text{-O-Fe}_{\text{EFW}}$ pairs can also be proposed based on the simultaneous presence of FW and EFW types of iron. I/BL data collected from 80 and 300 K spectra of Fe-FER are presented in Table 2.

Clear distinction of data collected at 300 and 80 K is apparent at the first sight. In contrast to the previous case of LTA here the comparisons of I/BL data obtained on Fe-FER at a constant temperature (either at 300 or at 80 K) do not exhibit marked differences. A slight monotonous increase of data can be observed with the progress of treatments. Thus, data of Table 2 can be summarised that in case of higher iron

Table 3 Mössbauer parameters and I/BL data collected from decompositions of Fe-MCM-41 spectra of Fig. 3

Temp. Treatm.	meas. Comp.	300 K				77 K			
		IS	QS	RI	I/BL	IS	QS	RI	I/BL
As rec (calc)	Fe ³⁺	0.35	0.68	40		0.46	0.63	20	
	Fe ³⁺	0.37	1.12	60		0.46	1.05	80	
					1.91				4.10
Evac 670 K	Fe ³⁺	0.28	1.68	44		0.40	1.92	25	
	Fe ³⁺	0.39	1.04	27		0.41	1.19	50	
	Fe ²⁺	1.07	2.03	30		1.22	2.32	25	
					1.21				4.22
CO 670 K	Fe ³⁺	0.23	1.76	44		0.33	1.78	9	
	Fe ²⁺	0.87	1.03	24		0.81	1.53	46	
	Fe ²⁺	0.92	1.97	32		1.14	1.66	30	
	Fe ²⁺					1.42	1.85	15	
					2.49				4.80
H ₂ 670 K	Fe ²⁺					0.84	1.14	13	
	Fe ²⁺					0.93	2.12	27	
	Fe ²⁺					1.20	2.25	31	
	Fe ²⁺					1.50	2.34	29	
									6.11
H ₂ (stored) 300 K	Fe ³⁺	0.34	0.78	39		0.39	0.88	32	
	Fe ³⁺	0.33	1.31	38		0.43	1.37	37	
	Fe ²⁺	1.07	2.22	23		1.34	2.37	22	
	Fe ²⁺					1.49	2.75	9	
					2.59				5.34
Evac. 670 K	Fe ³⁺	0.24	1.86	29					
	Fe ³⁺	0.27	1.35	36					
	Fe ²⁺	0.84	1.30	15					
	Fe ²⁺	1.02	2.17	20					
					2.89				

IS Isomer shift, relative to metallic α -iron, mm/s; *QS* Quadrupole splitting, mm/s; *RI* Relative spectral contribution, %, *I/BL* Intensity of full spectrum related to the base line, %

contents and combination of FW and EFW sitings of iron the recoilless fractions do not vary noticeably, the mean bonding strengths of iron species are similar, regardless to the actual treatments.

3.3 Fe-MCM-41 (Si/⁵⁷Fe ~ 140)

Mesoporus ferrisilicates were analysed in the next turn of study. In mesoporous structures the characteristic channel diameter is ca. 3–5 nm, this size is larger with ca. one order of magnitude than the pore size of microporous substances. On the other side, the extent of crystallinity in the pore walls is less expressed in mesoporous materials, a fraction of them is amorphous occasionally [7]. In the first stage a low iron content sample (Si/⁵⁷Fe ~ 140) was synthesized in hydrothermal way from a hydrous sodium silicate silicon source [10].

300 K spectra collected after different treatments are presented in Fig. 3 (left side). In order to obtain more information on the changes of the recoilless fractions

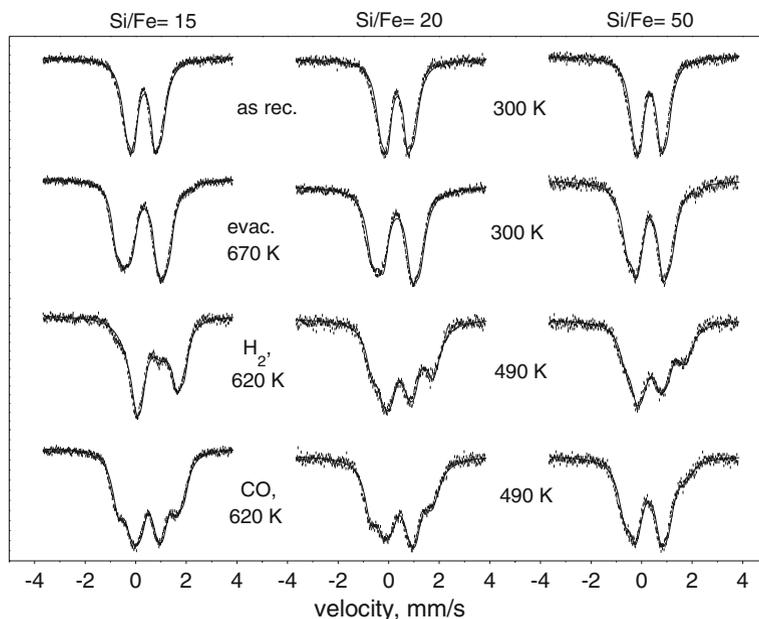


Fig. 4 Series of spectra measured on the Fe-MCM-41 (S) samples (Si/Fe = 15, 20 and 50) after treatments as indicated. Spectra were collected at 300 K (top two rows) and at 490 K (bottom two rows)

80 K spectra were also recorded (Fig. 3—right side). Corresponding data of the decompositions are collected in Table 3.

The interpretation and evaluation of 300 K spectra with emphasis on the reversible redox $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$ processes is described in [10]. Here the attention is focussed primarily on the I/BL data. The loose bonding and the partially amorphous structure in the pore walls is clearly reflected in the comparison of 300 and 80 K spectra. The temperature dependence is expressed, the ratio of I/BL response factors of the 80 and 300 K data for the corresponding pairs of spectra is always larger than 2. With a rough estimation [3] this ratio may correspond to $\Theta_D \sim 200$ K. This value is significantly smaller than Θ_D found for FW/EFW iron ions in the microporous Fe-FER with the suggested 260 K value as mentioned earlier. The smaller Θ_D corresponds to significantly weaker bond of Fe in MCM-41. Thus, most of the iron ions is probably not linked tetrahedrally to O-Si bonds, but some of them may be connected to dangling -OH, providing only a weaker link to the pore walls.

3.4 Fe-MCM-41(S) (Si/Fe = 16, 20 and 50)

MCM-41 can also be synthesized by using other silicon source, e.g. tetraethyl orthosilicate instead of the hydrous sodium silicate. Interestingly, the morphology can also be specific in this instance—well developed spheric particles may form [11]. Samples with different iron contents (nominal Si/Fe = 15, 20, and 50) were synthesized by this way and were evacuated then 300 K spectra were collected. Further on the samples were also treated in hydrogen and carbon monoxide to mimic

Table 4 Mössbauer parameters and I/BL data collected from decompositions of Fe-MCM-41 (S) spectra of Fig. 4

Treatment	Comp	IS	QS	RI	I/BL 300K	I/BL 490K
Si/Fe = 15						
As rec calc. (m: 300 K)	Fe ³⁺	0.33	1.34	60	1,349	
	Fe ³⁺	0.34	0.82	40		
Evac. 660 K. (m: 300 K)	Fe ³⁺	0.14	1.83	27	1,499	
	Fe ³⁺	0.17	1.34	28		
	Fe ^{2+/3+}	0.54	1.50	42		
	Fe ²⁺	1.09	2.20	3		
H ₂ 620 K (m: 490 K)	Fe ^{2+/3+}	0.41	1.22	41	1,499	
	Fe ²⁺	0.92	1.42	38		
	Fe ²⁺	0.96	1.91	21		
CO 620 K (m:490 K)	Fe ³⁺	0.19	1.77	29	0.828	
	Fe ³⁺	0.31	1.04	32		
	Fe ²⁺	0.82	1.56	24		
	Fe ²⁺	1.08	1.65	15		
Si/Fe = 20						
As rec. (calc.) (m:300 K)	Fe ³⁺	0.34	1.28	63	1,044	
	Fe ³⁺	0.34	0.78	37		
Evac. 660 K (m: 300 K)	Fe ³⁺	0.29	1.84	56	1,276	
	Fe ³⁺	0.34	1.11	44		
H ₂ 620 K (m: 490 K)	Fe ³⁺	0.17	1.68	21	0.815	
	Fe ³⁺	0.27	1.01	37		
	Fe ²⁺	0.91	1.69	42		
CO 620 K (m:490 K)	Fe ³⁺	0.18	1.78	32	0.869	
	Fe ³⁺	0.30	1.02	35		
	Fe ²⁺	0.91	1.62	34		
Si/Fe = 50						
As rec (calc) (m:300 K)	Fe ³⁺	0.34	1.26	63	0.632	
	Fe ³⁺	0.34	0.79	37		
Evac. 660 K (m: 300 K)	Fe ³⁺	0.30	1.70	48	0.682	
	Fe ³⁺	0.33	1.02	49		
	Fe ²⁺	1.12	2.17	4		
H ₂ 620 K (m:490 K)	Fe ³⁺	0.18	1.72	15	0.478	
	Fe ³⁺	0.27	0.98	50		
	Fe ²⁺	0.88	1.70	35		
CO 620 K (m:490 K)	Fe ³⁺	0.19	1.73	38	0.480	
	Fe ³⁺	0.26	1.00	49		
	Fe ²⁺	0.83	1.85	12		

IS Isomer shift, relative to metallic α -iron, mm/s; QS Quadrupole splitting, mm/s; RA Relative spectral contribution, %, I/BL Intensity of full spectrum related to the base line, %

reducing catalytic experimental conditions of different extent. In situ Mössbauer spectra were recorded in these reactant gases as well at modest reaction temperatures (Fig. 4). Decompositions of spectra have been performed, the corresponding data are compiled in Table 4.

The temperature dependence of I/BL values is again obvious, the I/BL values obtained from 490 K measurements are always significantly smaller, than those extracted from 300 K spectra in all the three Si/Fe ratios. Further on, it is also clear, as expected, that I/BL values depend proportionally on the iron contents. It is also worth to note that treatments in hydrogen result in smaller I/BL values than obtained in CO. This feature is primarily expressed for the Si/Fe = 15 and 20 samples. The extent of Fe³⁺ to Fe²⁺ reduction in hydrogen (RI values in Table 4) is also prevailing in these samples, resulting probably in formation of Fe²⁺(OH) entities with loose bonds, similarly to the previous MCM-41 (Si/⁵⁷Fe = 140) sample. In CO the formation of Fe(OH) is less expected, iron ions can be fixed more strongly in the pore walls. This phenomenon is less characteristic for the low iron content (Si/Fe = 50) sample, iron in low concentration can probably be more embedded into the pore wall.

4 Conclusions

Comparison of relative intensities of spectra may provide information on the relative changes of the mean recoilless fractions in series of in situ treatments. These changes are correlated with changes of the bonding conditions of the Mössbauer active nucleus to the actual solid structure.

The completion of this general statement was studied in particular for micro- and mesoporous ferrisilicates. Noticeable differences were found in the related I/BL values of EFW ions in microporous Fe-LTA (Si/⁵⁷Fe = 200) indicating the changes in the bond strength. The changes in I/BL values were less expressed in microporous Fe-FER containing iron in higher amount (Si/Fe = 16) and located in both FW and EFW positions. Bonding of iron in mesoporous MCM-41 structures is more loose in average. This finding corresponds to the expectations, since the pore walls in these substances are less crystalline and are partly amorphous. From comparison of 300 and 80 K spectra of Fe-MCM-41 (Si/⁵⁷Fe = 140) $\Theta_D \sim 200$ K was estimated. Changes of bond strengths depending on various treatments can also be evidenced for the low iron content Fe-MCM-41 and Fe-MCM-41 (S) samples with higher iron contents as well.

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