

Redox properties of iron in porous ferrisilicates

K. Lázár¹, G. Pál-Borbély², Á. Szegedi², P. Fejes³, F. Martínez⁴,



¹ Institute of Isotopes, HAS, Hungary, ² Chem. Res. Cent, HAS, Hungary, ³ Dept. of Appl Chem., University of Szeged, Hungary, ⁴ Dept. of Chem. Eng., Univ. Rey Juan Carlos, Madrid, Spain,

Aim: To demonstrate that several properties of porous ferrisilicates are influenced by redox processes taking place on iron ions (implications for catalytic processes are also considered)

Scheme:

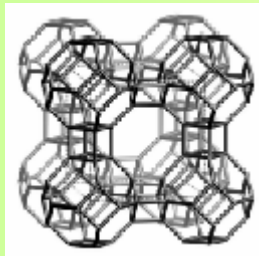
1. Introduction: structures (distinction of micro- and mesoporous systems, ferrisilicates)
2. Microporous systems (1): Framework/extra-framework siting
3. Microporous systems (2): Migration of extra-framework ions
4. Microporous systems (3): Stabilization of Fe²⁺ in oxidizing atmosphere
5. Mesoporous systems (1): Redox processes in the partly amorphous pore wall of MCM-41
6. Mesoporous systems (2): Iron leaching from the embedded bulk Fe₂O₃ ; SBA-15
7. Conclusions

1. Introduction: micro- and mesoporous structures:

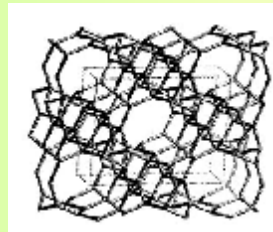
Microporous structures: 3 D crystallinity, ~ 0.5 nm pores (in average)

Primary building unit: $[\text{SiO}_{4/2}]$ tetrahedron

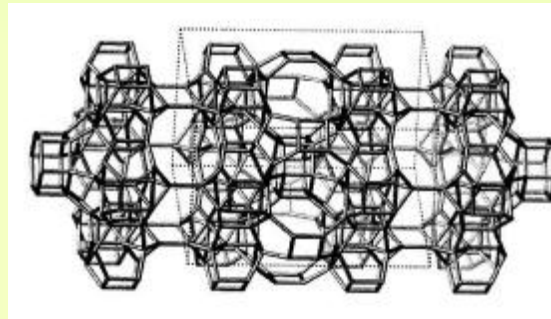
LTA



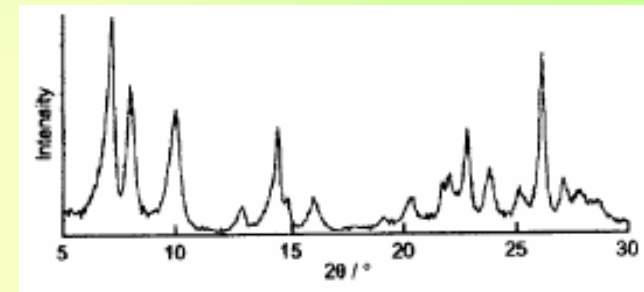
ZSM-22



MCM-22



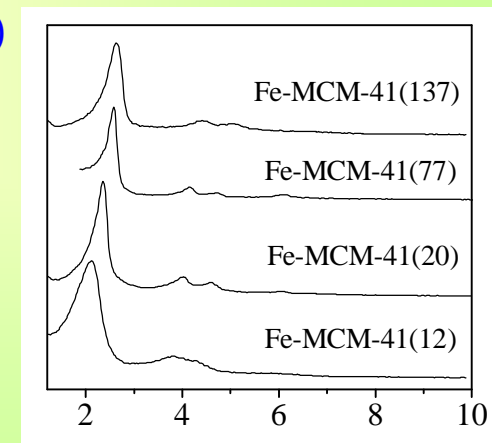
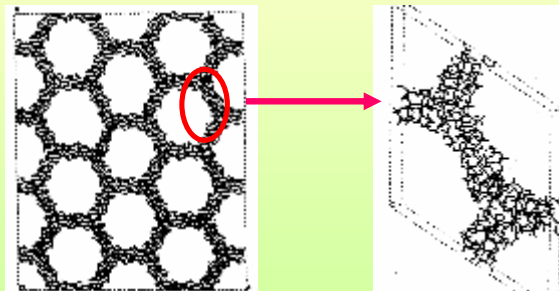
XRD of MCM-22



Mesoporous structures:
crystallinity is hardly displayed
partly amorphous pore walls
(~ 5 nm)

For catalytic applications
the mesoporous structures
are advantageous

XRD (low 2θ)
→

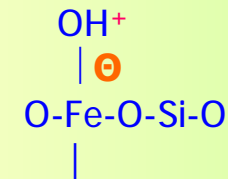


1. Introduction (2) - Ferrisilicates:

Replacement of the central Si ion to Fe: $[\text{Si}^{(4+)}\text{O}_{4/2}] \Rightarrow [\text{Fe}^{(3+)}\text{O}_{4/2}]^{\ominus}$

Charge compensation should be fulfilled: \Rightarrow Bronsted centre

Ionic radii (pm): Si^{4+} : 42, Al^{3+} : 51, Fe^{3+} : 64



1. Introduction (3): Mössbauer spectroscopy

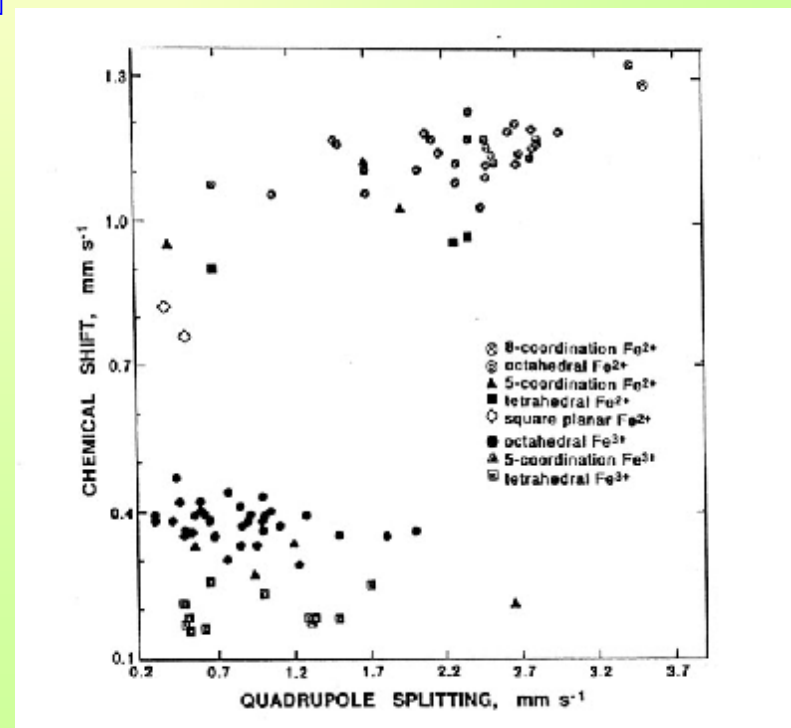
Local method (detects the primary coordination around Fe)
Positions can clearly be distinguished

Sym/QS: IS: (mm/s)

Fe^{3+} :	\uparrow / \downarrow	0.25 - 0.35
Fe^{2+} :	\uparrow / \uparrow	0.8 - 1.2

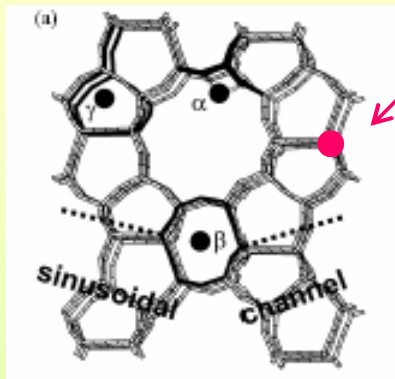
Pertinent remark:
Single ions (vs. small oxide particles)

R. Burns: Hyp. Int. 91 (1994) 739. \rightarrow



2. Microporous (1): Distinction of FW/EFW sitings

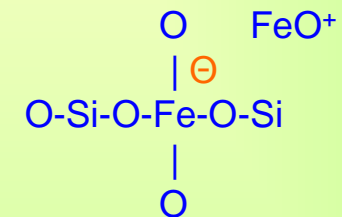
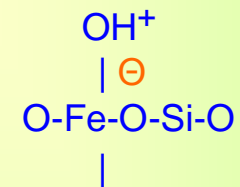
Framework (FW) and extra-framework (EFW) positions



FW: \Rightarrow Bronsted centre

EFW: \Leftarrow charge compensation
in α, β, γ sites

FW and EFW (eg. FeO^+ , FeOH^+) combined:



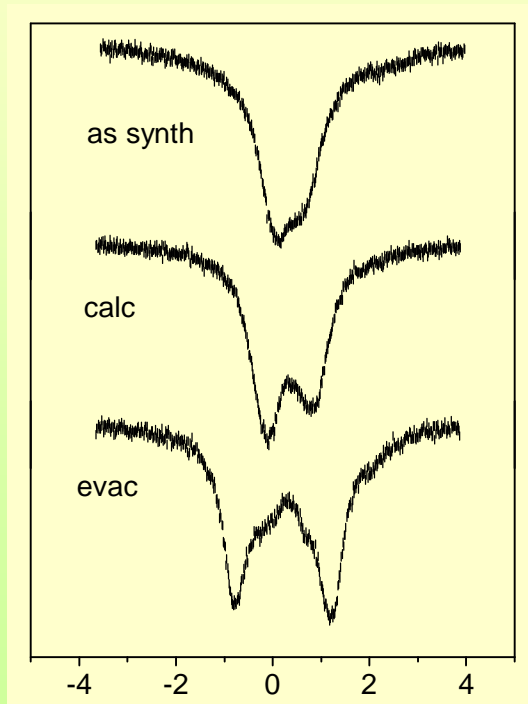
Further option: removal of FW Fe^{3+} , conversion to EFW
ionic radii: (pm) Si^{4+} : 42, Fe^{3+} : 64, Fe^{2+} : 74

FW and EFW can be distinguished in the Mössbauer spectra

2. Microporous (1): FW \leftrightarrow EFW redox (2)

Identification of the various Fe³⁺ components (QS):

FW (assymmetric, Bronsted) Si-O-Fe(OH)-O-Si : 1.7 - 2.0 mm/s
 FW (H₃O⁺, Na⁺, FeO⁺, Fe(OH)⁺) less distorted : 1.2 – 1.4 mm/s
 EFW: usually tends to complete octahedral sym : 0.8 – 1.2 mm/s
 (water chemisorption around the FW and EFW (α, β, γ) sites)

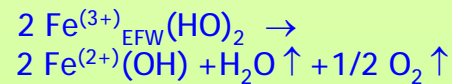


Stages:

1) Synthesis - with template

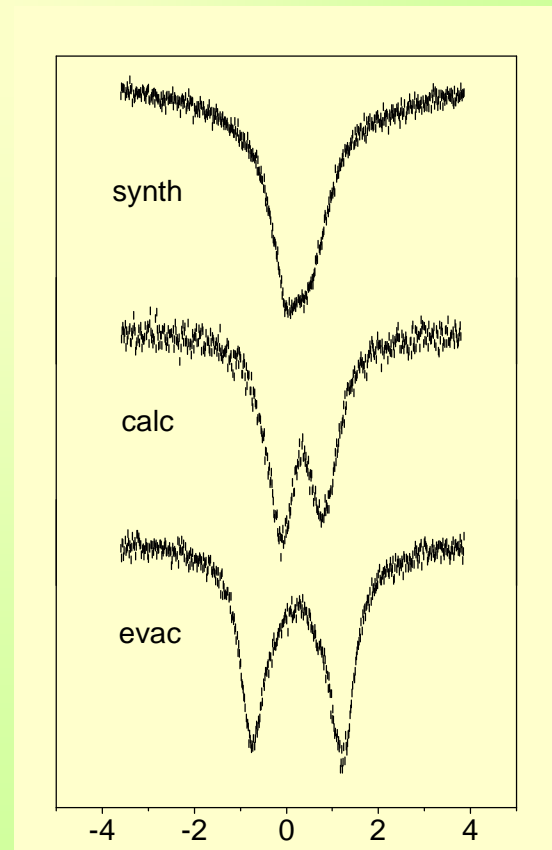
2) Calcination
& H₂O (upon storage)

3) evacuation (650 K, 10⁻² Pa),
E.g:



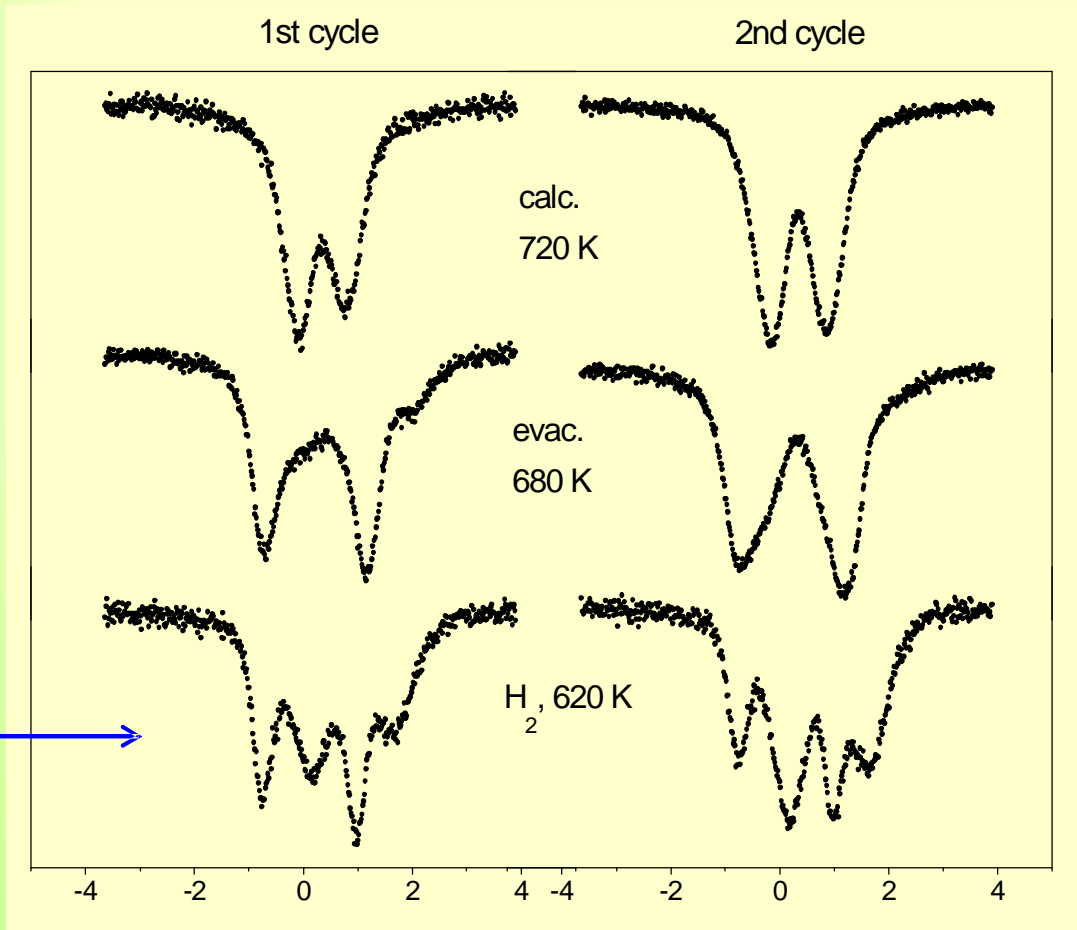
← Fe-MCM-22 Fe-FER →

⇒ Simple evacuation: Fe³⁺ → Fe²⁺



2. Microporous (1). FW \leftrightarrow EFW redox (3)

Next step: Exposure to reaction mixture i.e. \sim H₂



Observations:

- At the start: FW substitution dominates,
 - in H₂: Fe³⁺ \rightarrow Fe²⁺
i.e. FW \rightarrow EFW removal,
reduction of FW Fe³⁺
in part („FW is reduced”)
 - repetition (2nd cycle)
shows the higher EFW,
 - Fe_{FW}-O-Fe_{EFW} pairs
are probably formed
- \Rightarrow Fe³⁺ and Fe²⁺ may exist together,
redox processes mostly on EFW

2. Microporous (1) FW/EFW (4) data for MCM-22

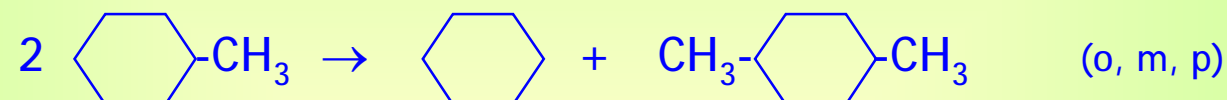
Treatm/(T_m).	Comp.	1 st cycle			Repeated cycle		
		<i>IS</i>	<i>QS</i>	<i>RI</i>	<i>IS</i>	<i>QS</i>	<i>RI</i>
Calc.	Fe ³⁺	0.29	0.58	27			
(T _m : 300 K)	Fe ³⁺				0.36	0.73	35
	Fe ³⁺	0.36	1.02	73	0.36	1.26	65
Evacuation at 690	Fe ³⁺ FW	0.24	1.92	56	0.26	2.05	51
	Fe ³⁺	0.33	1.22	28	0.32	1.27	47
(T _m : 300 K)	Fe ²⁺ EFW	1.14	1.86	16	1.14	2.26	2
H ₂ at 620 K	Fe ³⁺				0.06	0.23	8
	Fe ³⁺ FW	0.13	1.73	39	0.12	1.76	30
(T _m : 490 K)	Fe ³⁺	0.34	0.50	17			
	Fe ²⁺ EFW	0.92	1.57	44	0.95	1.40	62

2. Microporous (1) FW / EFW: Reactions on Fe-MFI: role of different acidities (Bronsted vs. Lewis)

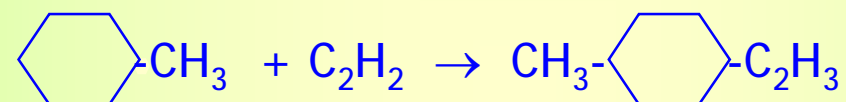
Acid-base reactions:

Si/Fe= 67, 35, 27.5

1. Disproportionation of toluene:



2. Alkylation:



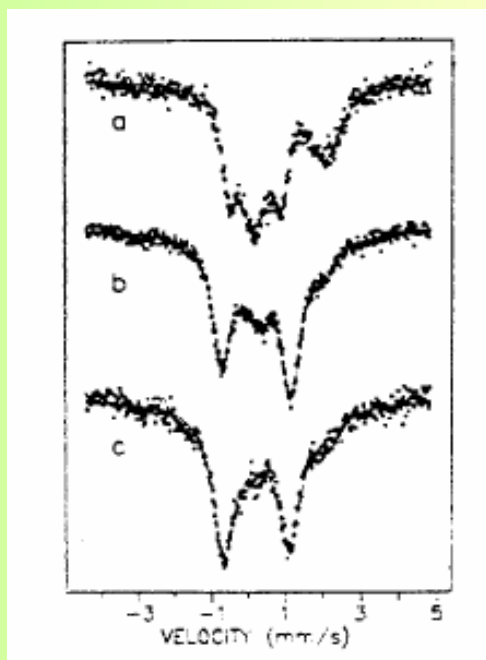
Iron wt %	Alk / (g cat) ⁻¹	Alk / (Fe at) ⁻¹	Disp / (g cat) ⁻¹	Disp / (Fe at) ⁻¹
1.5	4.8	3.2	1.8	1.2
2.8	9.0	3.2	3.6	1.3
3.6	10.7	3.0	5.3	1.5

Conv. (Fe at)⁻¹ approx. equal
 \Rightarrow activity is correlated to
 number of Fe atoms

2. Microporous (1) FW /EFW : Reaction on MFI: In situ Mössbauer spectra

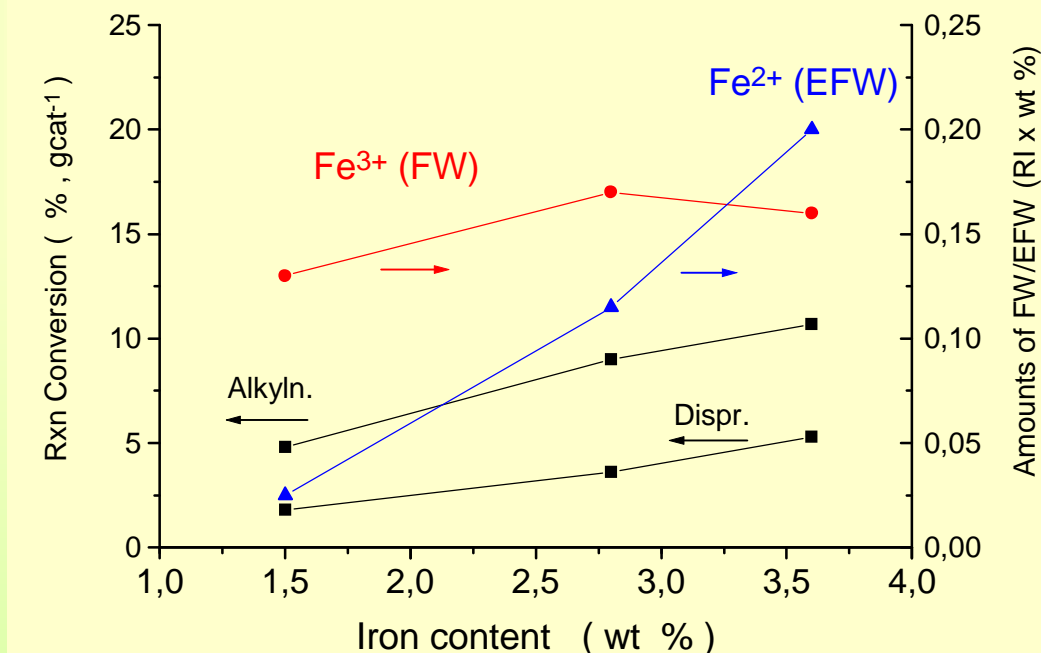
FW: Fe(III)-Td and EFW: Fe(II)

In H₂ (after 620 K /H₂):



r= Si/Fe	Comp.	IS	QS	RI
27.5	Fe(III)-Td	0.15	1.24	44
	Fe(II)-Td	0.66	0.70	9
	Fe(II)-Oh	1.01	1.76	26
	Fe(II)-Oh	1.19	2.25	21
35.0	Fe(III)-Td	0.25	1.92	59
	Fe(II)-Td	0.66	0.66	20
	Fe(II)-Oh	1.03	2.10	21
67.0	Fe(III)-Td	0.23	1.76	85
	Fe(II)-Oh	1.13	2.06	15

2. Microporous. (1) Participation of FW and EFW iron in the reactions



Both acidities play role:

The conversion is more closely related to FW than to EFW type:

$$\text{conv.}_{FW} \gg \text{conv.}_{EFW}$$

The similar statement holds for the acid strength:

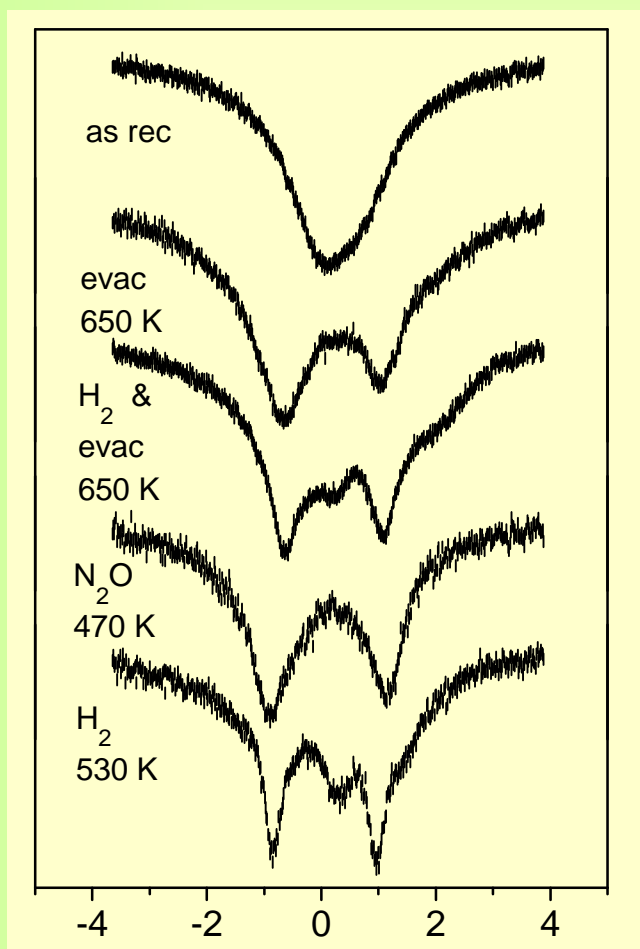
$$\text{acidity}_{FW} \gg \text{acidity}_{EFW}$$

Conclusions on (FW/EFW):

- FW / EFW iron may exist together,
- $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ proceeds mostly on EFW,
- reactions may proceed on both: FW: Si-O-Fe(OH)-O-Si Bronsted and EFW Fe²⁺, Fe³⁺ Lewis)

3. Microporous (2) Migration and change of EFW ions - MFI

FeZSM-5 (Si/Fe ~ 200)



Sequential spectra - various stages:

- as rec: mixed EFW ions: NH_4^+ , Na^+ , H_3O^+
- evac: $\text{NH}_4^+ \rightarrow \text{NH}_3 \uparrow + \text{H}^+$, $\text{H}_3\text{O} \rightarrow \text{H}_2\text{O} \uparrow + \text{H}^+$
- H_2 : $\text{Fe}_{\text{EFW}}^{3+} \rightarrow \text{Fe}_{\text{EFW}}^{2+}$, $\text{Fe}_{\text{FW}}^{3+}$ maintained
- N_2O : $\text{Fe}_{\text{EFW}}^{2+} \rightarrow \text{Fe}_{\text{EFW}}^{3+}$, large QS \Rightarrow distorted
- H_2 again: sharper lines, distorted Fe^{2+} and Fe^{3+}
 $\text{Si-O}(\text{Fe}_{\text{FW}}\text{OH})\text{-OSi}$,

Interpretation:

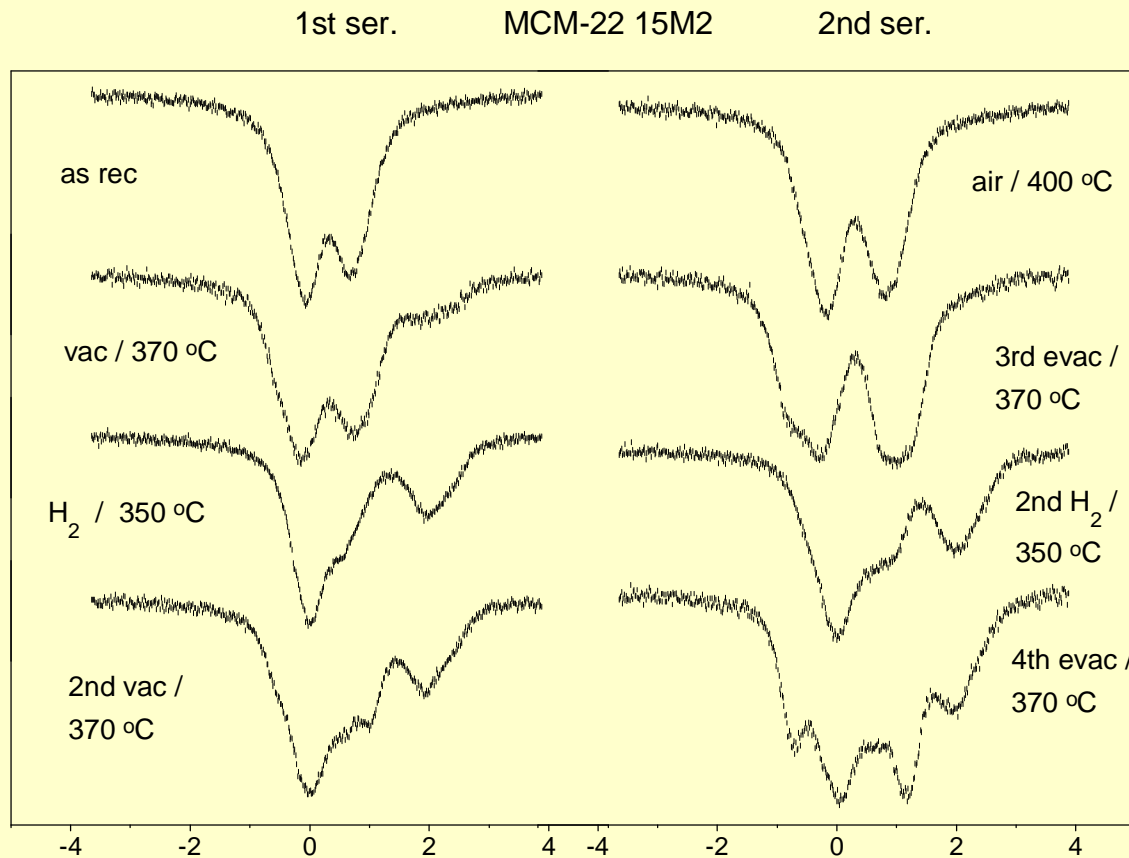
The mixture of EFW ions at the starting state

- is converted to H^+ Bronsted form -
 $\text{O-Si-O-Fe}(\text{OH})\text{-O-Si}$, and
- on the EFW Fe ions reversible $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$
 may proceed (oxide particles are absent)

\Rightarrow Migration and redistribution of EFW ions may take place

3. Microporous (2): migration of EFW (2)

Another MCM-22 sample (Si/Fe ~ 20) sequential spectra



1st series:
similar as previously,
Na⁺, H₃O⁺ removal,
the oxidation & reduction
cycle rearranges the EFW
ions:

2nd series:

- Fe_{FW}-O-Fe_{EFW} due to the larger concentration of Fe
- The formation of Si-O-Fe(OH)-O-Si centres is expressed upon the 2nd H₂ treatment,
- simultaneously neutral FeO is also formed, and is trapped in the cages

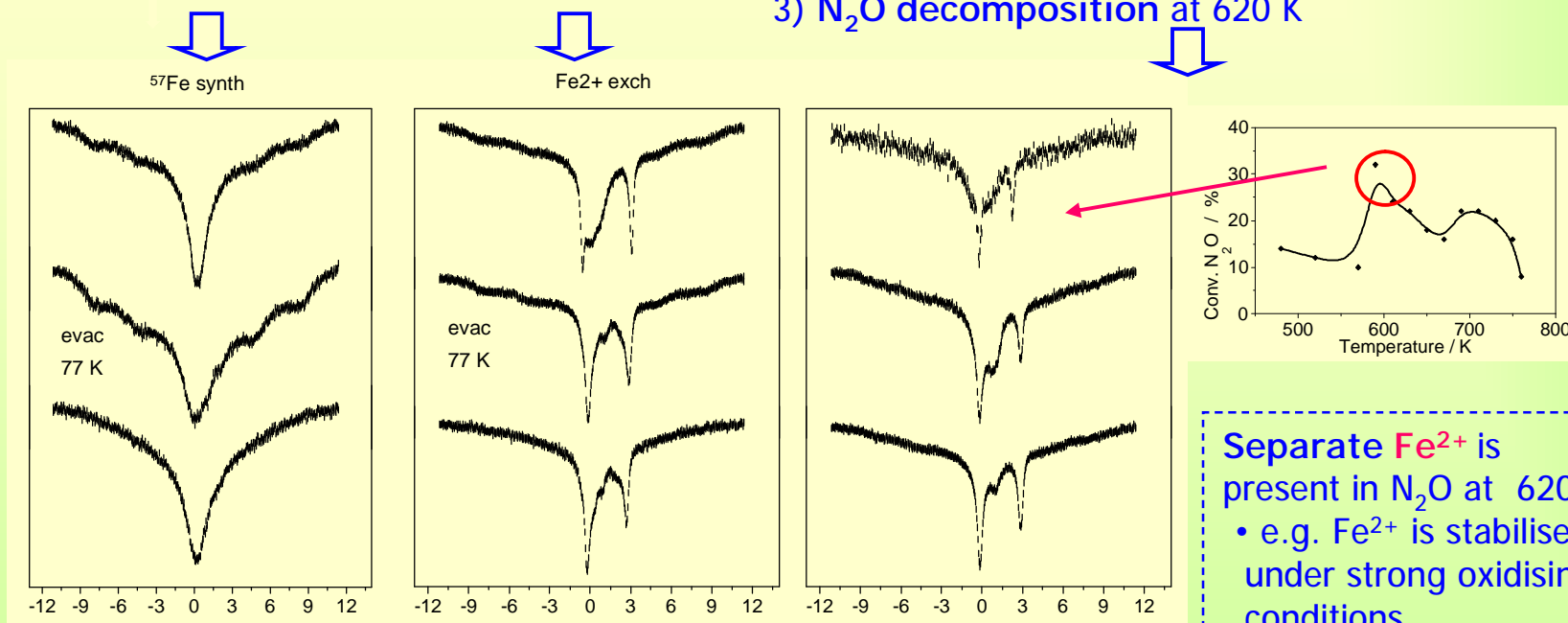
4. Microporous (3): Stabilisation of Fe²⁺ in oxidizing atmosphere

Distinguished interest: N₂O + Ferrisilicate:

i/ activated „α”-oxygen (e.g. benzene to phenol), ii/N₂O (greenhouse gas) decomposition

1) FW Fe³⁺ Si/Fe ~ 200, 2) Additional EFW Fe²⁺ : by ion exchange (NH₄-Z + FeCl₂) → Fe-Z + NH₄Cl ↑

3) N₂O decomposition at 620 K



Superparamagnetic Fe³⁺

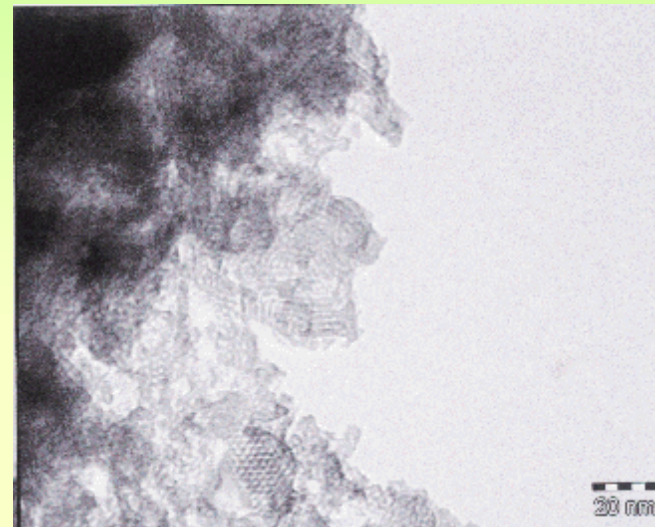
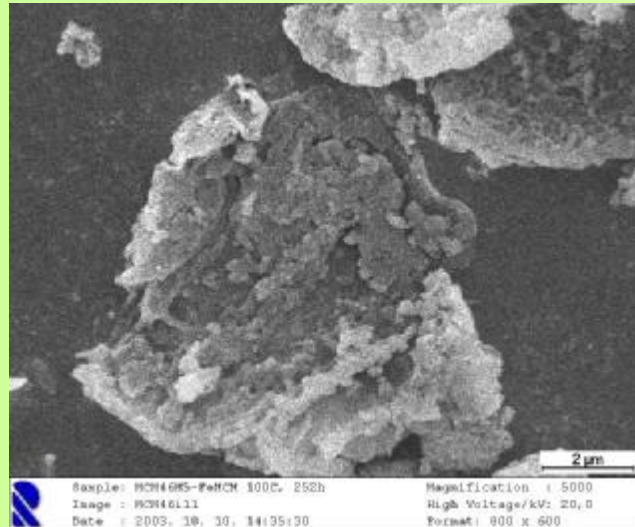
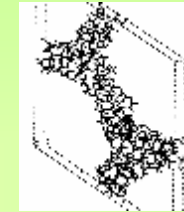
+ diamagnetic Fe²⁺ ⇒ stable in reaction

Separate Fe²⁺ is present in N₂O at 620 K

- e.g. Fe²⁺ is stabilised under strong oxidising conditions
- the Fe²⁺ and Fe³⁺ species are independent

K. Lázár, A. Wootsch, o. Pozdnyakova, P. Fejes Hyp. Int, 2006 in press

5. Mesoporous (1) : MCM-41 two different syntheses compared



1. Hydrothermal:

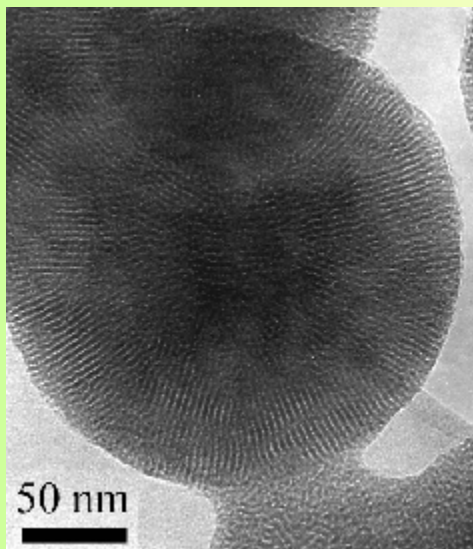
370 K / 170 h (Si/Fe= 100)

SiO₂ : Fe₂SO₄ : NaOH :
Na₂SO₄ : C₁₆TMABr (H₂O)

2. Methanolic soln.

ambient T, 24 h (Si/Fe=20)

TEOS : C₁₆TMABr : MeOH
: NH₃ (H₂O)



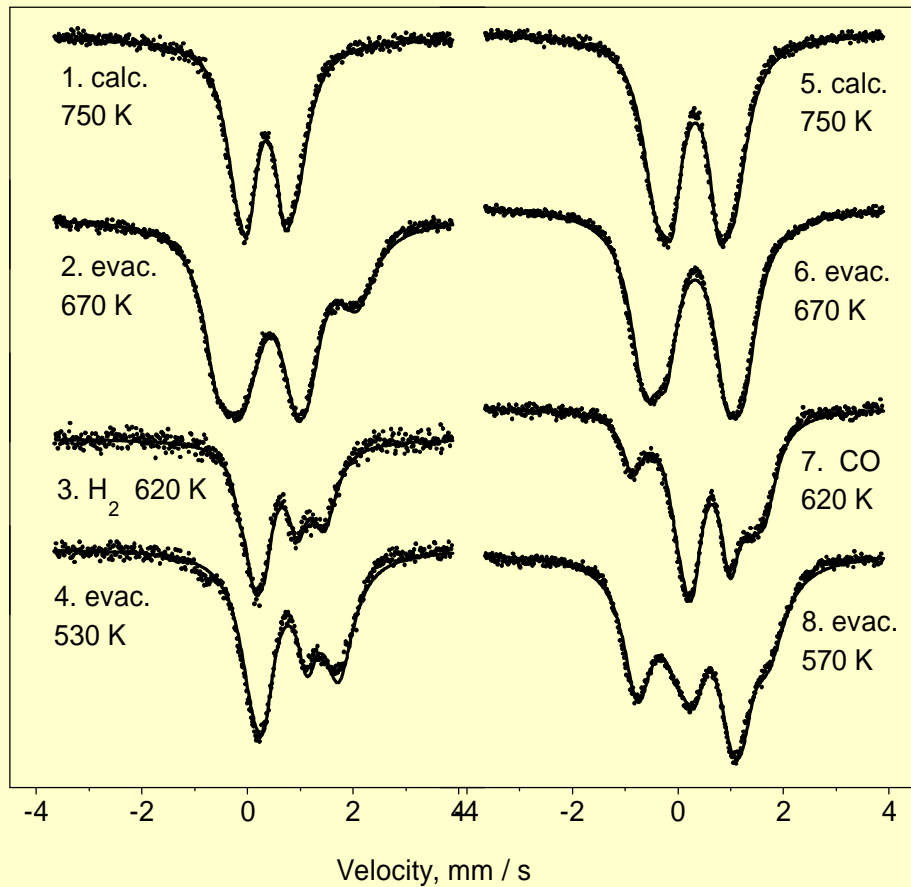
TEOS/RT ↑ Hydrothermal: Fe/Si = 20

←

	SiO ₂ / hydroth	TEOS/RT
d ₁₀₀ (nm)	3.38	3.47
a ₀ (nm)	3.90	4.01
Φ _{BJH} (nm)	2.43	2.31
WTH(1) (a ₀ - Φ _{BJH})	1.47	1.70
V _p (cm ³ /g)	0.79	0.62
W _d (nm)	3.27	3.20
WTH(2) (a ₀ - W _d)	0.63	0.81

5. Mesoporous (1): Redox processes in the pore walls of MCM-41

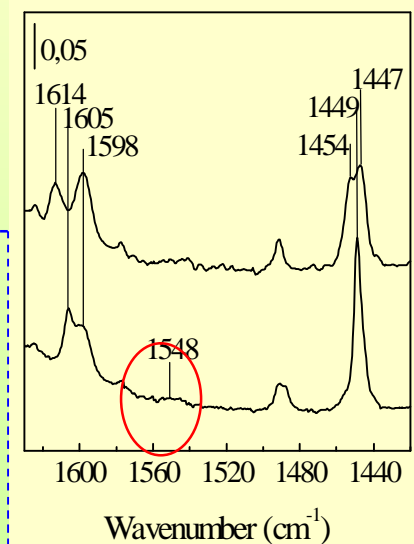
MCM-41: (Si/Fe ~ 140) - hydrothermal



- Coordinations identified:
 $\text{Fe}^{3+}_{\text{Oh}}$, $\text{Fe}^{3+}_{\text{d-Tetr}}$, $\text{Fe}^{2+}_{\text{Oh}}$, $\text{Fe}^{2+}_{\text{Td}}$, $\text{Fe}^{2+}_{\text{d-Td}}$
- The $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ redox conversion is reversible (at 620 K).
- The $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ reduction is complete in H₂, whereas only partial in CO (620 K)
- The Fe^{3+} of large QS does not show Bronsted acidity (infrared): →

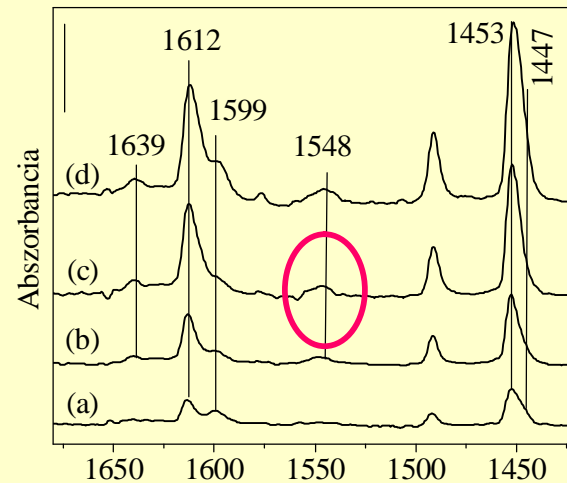
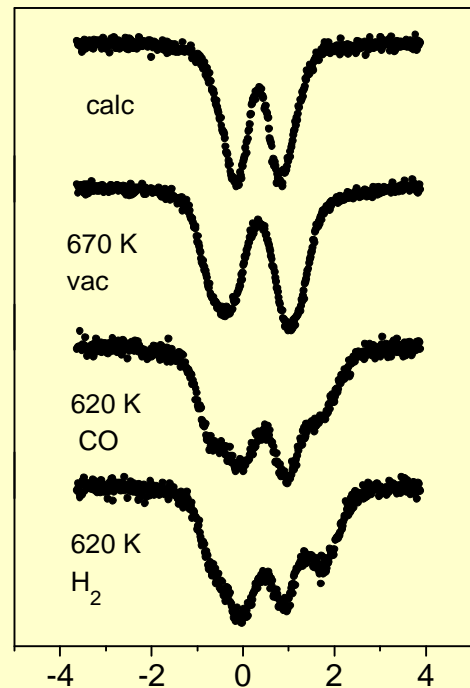
Amorphous feature is reflected in:

- full $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ reversibility,
- Fe^{2+} stabilized in the pore walls
- Bronsted acidity is practically lost



5. Mesoporous (1) MCM-41 pore wall stability (methanolic synthesis)

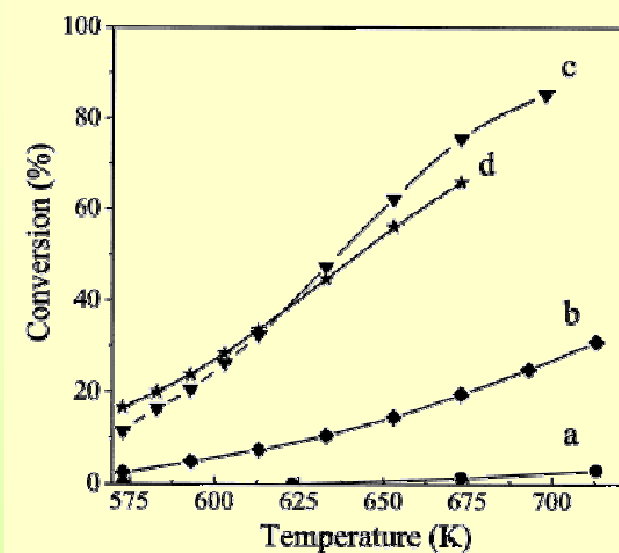
Pyridine chemisorption



Si/Fe: a) 113, b) 52, c) 24, d) 15

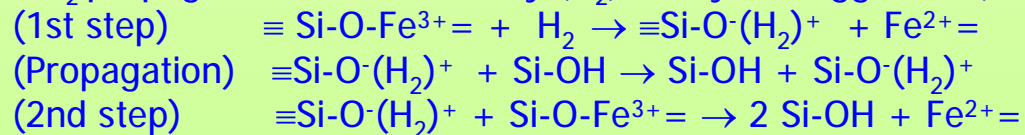
strong Lewis, weak Bronsted character

CO oxidation



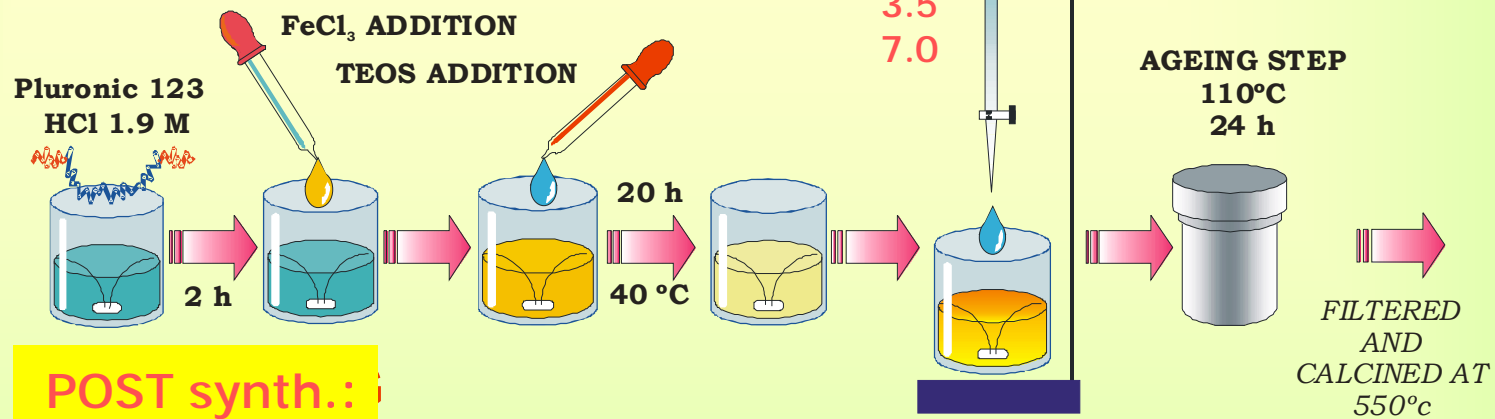
Si/Fe: a) ∞ ; b) 77; c) 20; d) 12

Partly amorphous structure \Rightarrow expressed participation of silanolic Si-OH groups can be proposed in H_2 propagation of reduction by $(H_2)^+$ may be suggested (since the structure is rich in -OH groups):

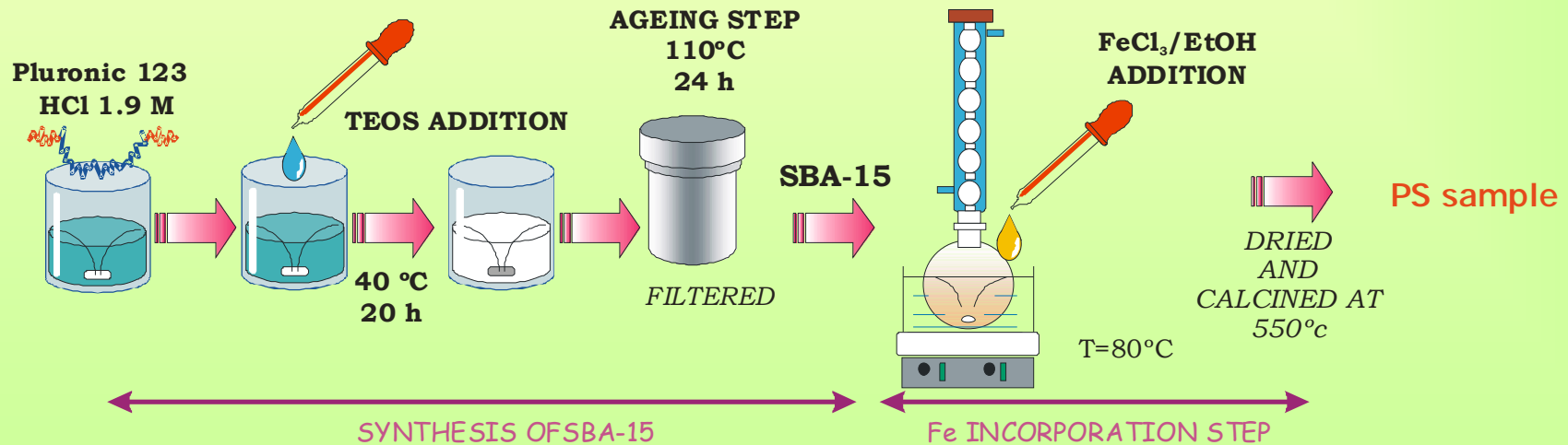


6. Mesoporous (2): Fe-SBA-15 samples

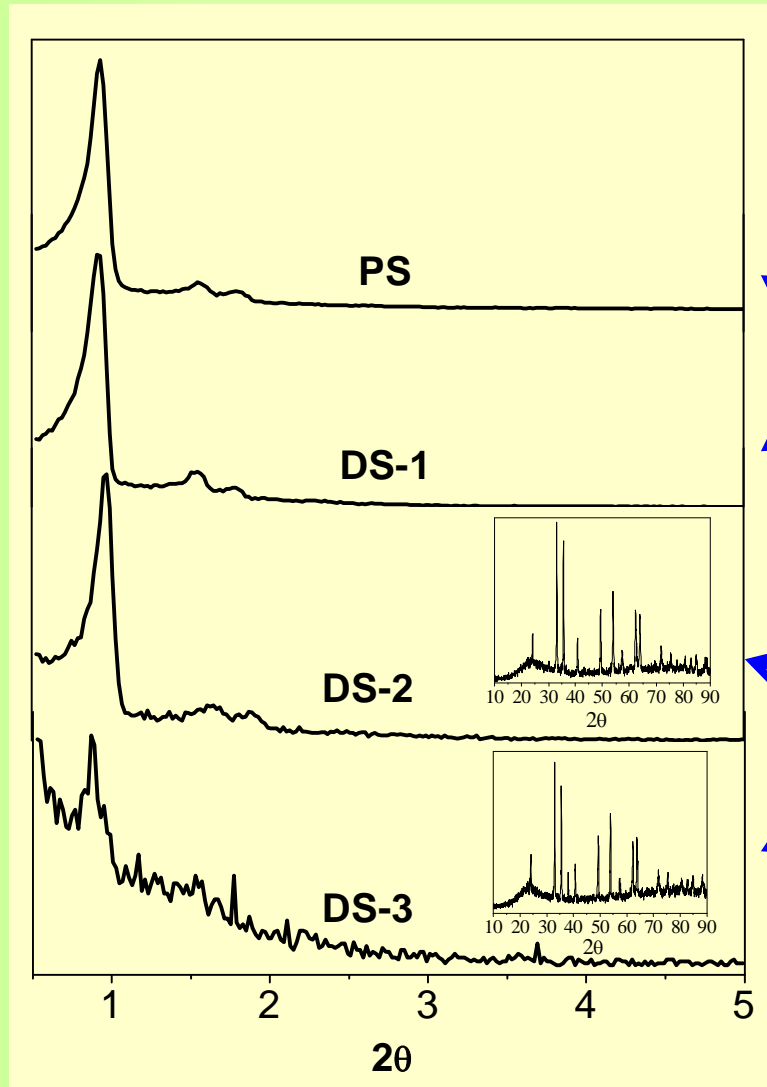
DIRECT synth.:



POST synth.:

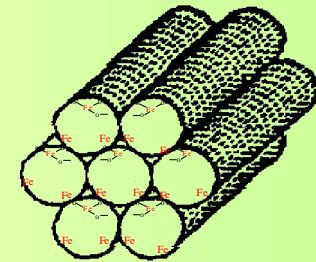


6. Mesoporous (2) Fe-SBA-15(2) – crystallinity and iron oxide particles

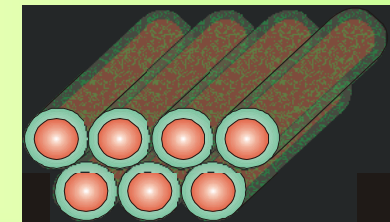


Fe-SBA-15 MATERIALS

Mesoporous SBA-15
 $a_0 \sim 10$ nm

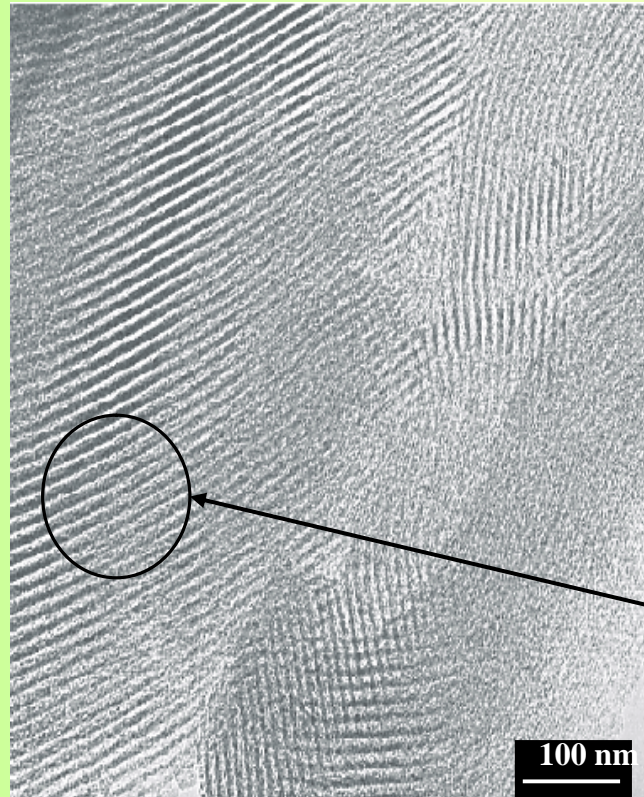


(Insert:)
Hematite, $\alpha\text{-Fe}_2\text{O}_3$,
in the range of
 $10^\circ < 2\theta < 90^\circ$



6. Mesoporous (2) - Fe- SBA-15 Transmission electron microscopy and EDX

DS-1

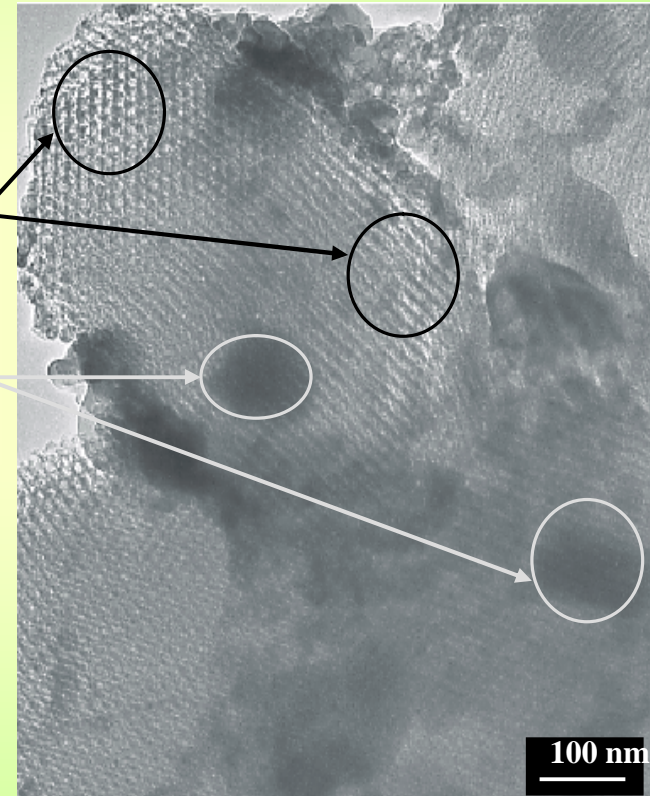


**HIGLY ORDERED
REGIONS: Fe wt %: 3.6**

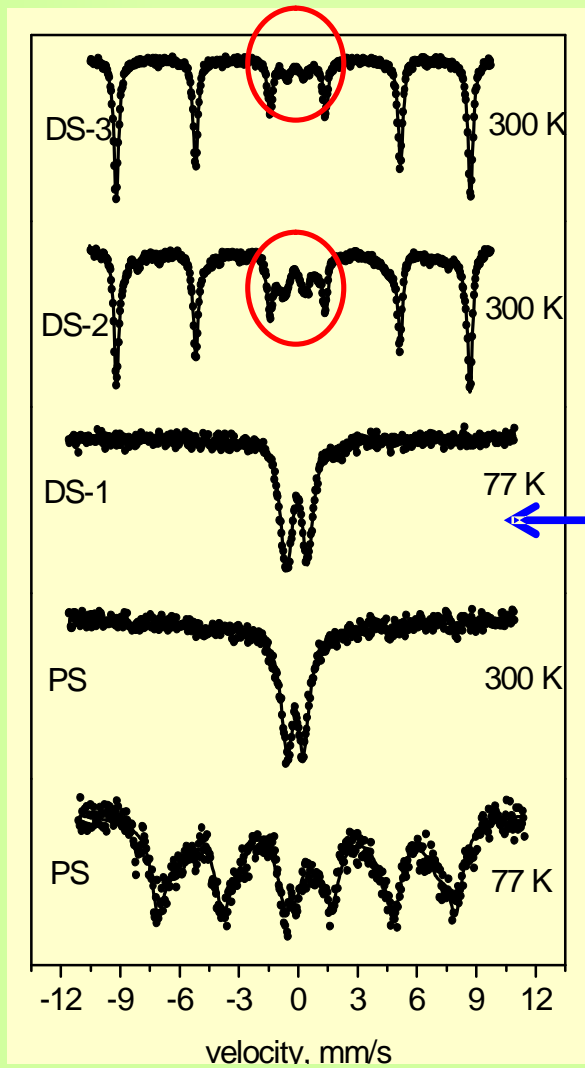
**DARKER AREAS
Fe wt %: 85**

**MESOSCOPIC ORDER
Average iron wt %: 1,4**

DS-2



6 Mesoporous (2) Fe-SBA-15 Mössbauer characterization



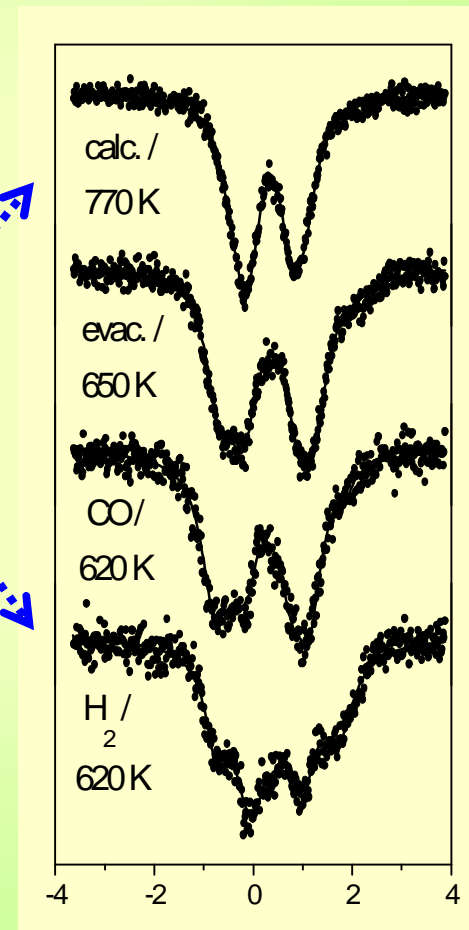
Sextets: Hematite
 (Fe : 22 and 16 %)
 d ~ 100 nm particles
 across the pores
 centre: ionic components

Mostly single,
 separated

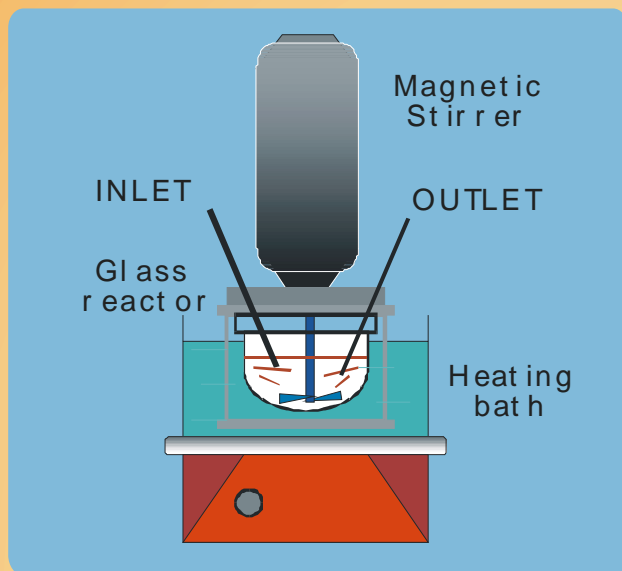
ions, Fe ~ 1 %

Sextet from
 intrapore particles,
 Fe 2.2 % , d < 5 nm

Mostly ionic: DS-1
 (under various cond.)



6. Mesoporous (2) - FeSBA-15 catalysis: wet peroxide oxidation of phenol

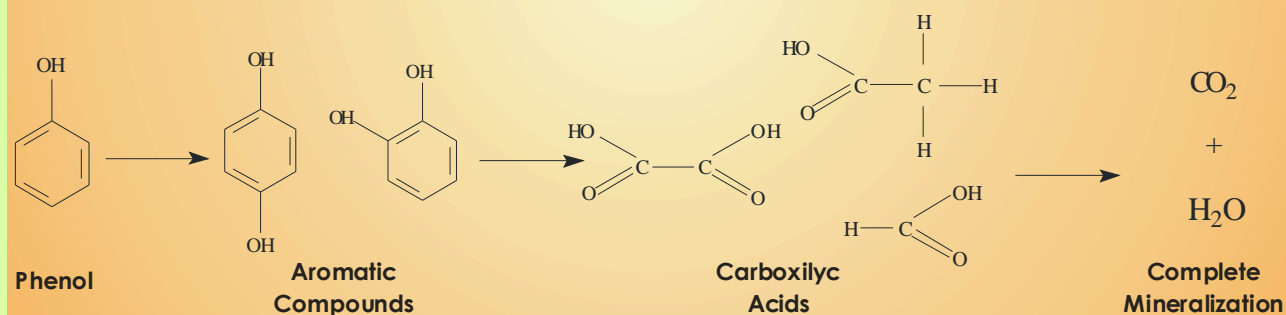


REACTION CONDITIONS

T= 100°C
 P= 7 bar.
 Stirring: 350 r. p. m.

Aqueous Solution
 [Phenol]₀= 1.0 g/L
 [Catalyst]= 0.6 g/L
 [H₂O₂]₀= 5.0 g/L

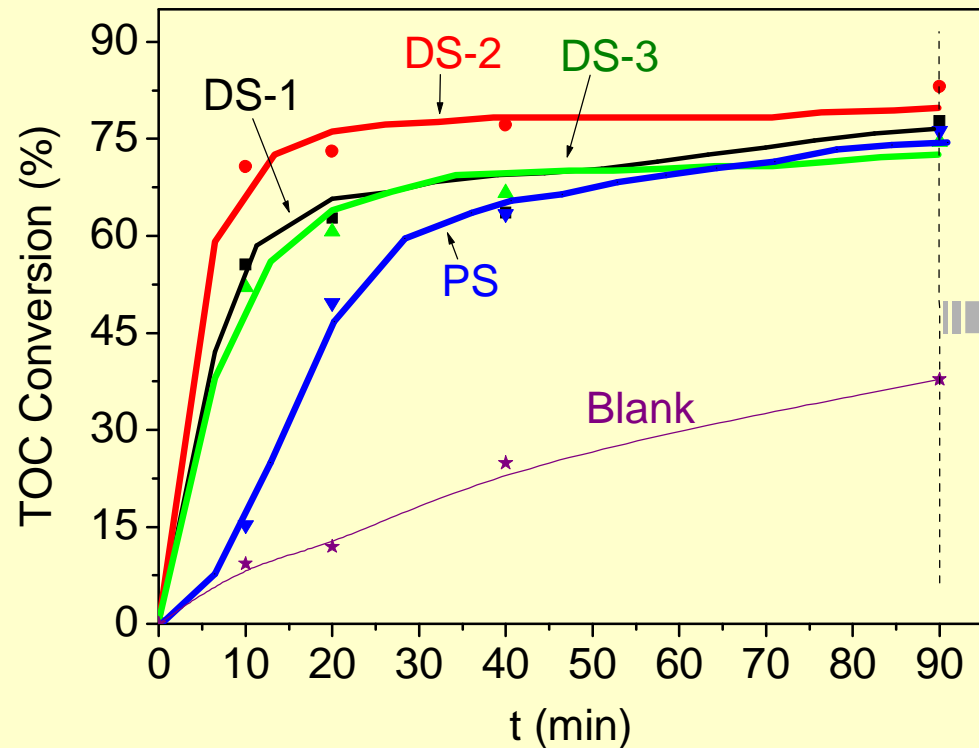
SIMPLIFIED REACTION PATHWAY FOR PHENOL OXIDATION



ANALYTICAL TECHNIQUES

TOC REMOVAL	→	TOC ANALYZER
PRODUCTS DISTRIBUTION AND H ₂ O ₂ CONVERSION	→	HPLC
LEACHING OF IRON SPECIES	→	ICP-AES

6. Mesoporous (2) Fe-SBA-15 catalysis: activity and stability

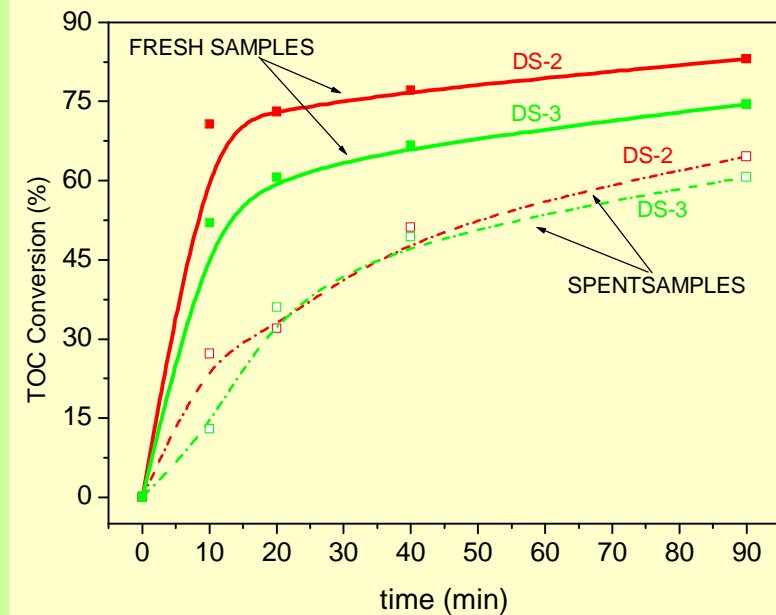


Expressed iron leaching:
Lost iron, relative % (90 min.)

DS-1	DS-2	DS-3	PS
79	8	5	70

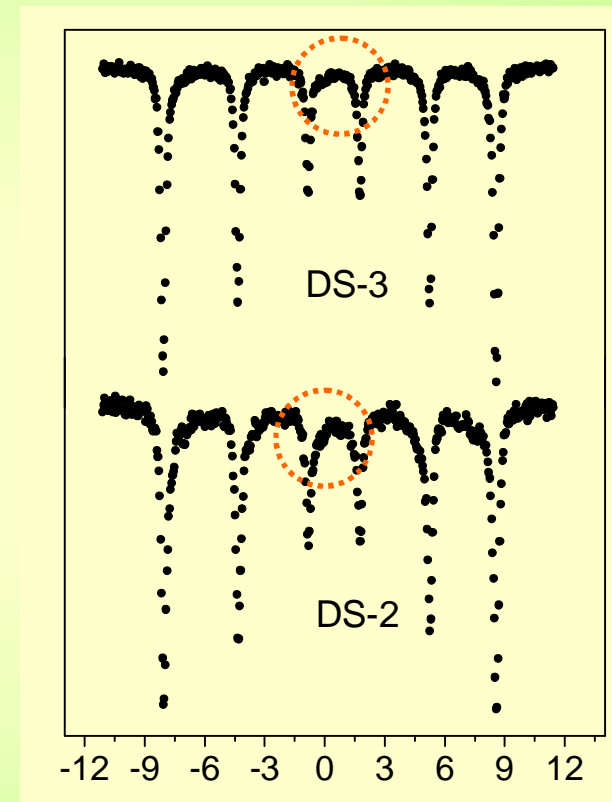
(The absolute amounts are similar:
ca. 1 wt % at DS-s, and 1.5 at PS)

6. Mesoporous (2) Fe-SBA-15 activity and stability of reused iron-containing samples



- The ionic contribution is missing from the centre of Mössbauer spectra:
⇒ the leached iron is mostly of ionic character,
- The catalytic activity reaches to a similar level at the end both at iron rich DS-2, DS-3 and at iron depleted DS-1:
⇒ the catalytic activity is related to the isolated ionic component

Spent samples (rich in iron):



7. Conclusions

Occurrence and role of redox processes in porous ferrisilicates have been demonstrated:

- 1) Determining role of the structure is shown
(3D microporous vs. partly amorphous pore walls in the mesoporous hosts)
- 2) In microporous hosts the FW / EFW distinction is clear.
 - FW is Bronsted acidic, whereas EFW is of Lewis character,
 - $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ primarily proceeds on EFW ions,
 - migration/redistribution of EFW ions can be traced under reaction conditions
 - particular species, (e.g. Fe^{2+}) with enhanced activity can be stabilized (e.g. in N_2O)
- 3) In mesoporous host the pore wall is partly amorphous, thus the FW / EFW distinction is less suitable.
 - $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ may proceed on iron located in the pore walls.
 - the distorted Fe^{3+} (large QS) exists, however, does not exhibit Bronsted acidity
 - catalytic activity in redox processes can be attributed to iron of ionic dispersion