Redox properties of iron in porous ferrisilicates

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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)
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

Fe-MCM-41(137)
Fe-MCM-41(77)
Fe-MCM-41(20)
Fe-MCM-41(12)
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

\( \text{OH}^\oplus \)

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

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)


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

FW: \[ \Rightarrow \] Bronsted centre

EFW: \[ \Leftrightarrow \] charge compensation
in \( \alpha, \beta, \gamma \) 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 ↔ EFW redox (2)

Identification of the various Fe$^{3+}$ components (QS):

FW (assymmetric, Bronsted) Si-O-Fe(OH)-O-Si: 1.7 - 2.0 mm/s
FW (H$_3$O$^+$, 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 ($\alpha,\beta,\gamma$) sites

Stages:

1) Synthesis - with template

2) Calcination
& H$_2$O (upon storage)

3) evacuation (650 K, 10$^{-2}$ Pa), E.g:
2 Fe$^{3+}_{\text{EFW}}$(HO)$_2$ →
2 Fe$^{2+}$(OH) + H$_2$O ↑ + 1/2 O$_2$ ↑

← Fe-MCM-22 Fe-FER →

⇒ Simple evacuation: Fe$^{3+}$ → Fe$^{2+}$
Next step: Exposure to reaction mixture i.e. $\sim H_2$

Observations:
- At the start: FW substitution dominates,
- in $H_2$: $Fe^{3+} \rightarrow Fe^{2+}$ i.e. FW $\rightarrow$ EFW removal, reduction of FW $Fe^{3+}$ in part ("FW is reduced")
- repetition (2nd cycle) shows the higher EFW,
- $Fe_{FW}$-O -$Fe_{EFW}$ pairs are probably formed

$\Rightarrow Fe^{3+}$ and $Fe^{2+}$ may exist together, redox processes mostly on EFW
## 2. Microporous (1) FW/EFW (4) data for MCM-22

<table>
<thead>
<tr>
<th>Treatment/($T_m$)</th>
<th>Comp.</th>
<th>1st cycle</th>
<th>Repeated cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$IS$</td>
<td>$QS$</td>
</tr>
<tr>
<td>Calc. ($T_m$: 300 K)</td>
<td>Fe$^{3+}$</td>
<td>0.29</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$</td>
<td>0.36</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$</td>
<td>0.36</td>
<td>0.58</td>
</tr>
<tr>
<td>Evacuation at 690</td>
<td>Fe$^{3+}$</td>
<td>FW</td>
<td>0.24</td>
</tr>
<tr>
<td>($T_m$: 300 K)</td>
<td>Fe$^{3+}$</td>
<td>0.33</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$</td>
<td>EFW</td>
<td>1.14</td>
</tr>
<tr>
<td>H$_2$ at 620 K</td>
<td>Fe$^{3+}$</td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>($T_m$: 490 K)</td>
<td>Fe$^{3+}$</td>
<td>FW</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$</td>
<td></td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$</td>
<td>EFW</td>
<td>0.92</td>
</tr>
</tbody>
</table>
2. Microporous (1) FW / EFW: Reactions on Fe-MFI: role of different acidities (Bronsted vs. Lewis)

Acid-base reactions:

1. Disproportionation of toluene:

\[
2 \text{CH}_3 \rightarrow \text{CH}_3 + \text{CH}_3 \quad \text{(o, m, p)}
\]

2. Alkylation:

\[
\text{CH}_3 + \text{C}_2\text{H}_2 \rightarrow \text{CH}_3-\text{C}_2\text{H}_3
\]

<table>
<thead>
<tr>
<th>Iron wt %</th>
<th>Alk / (g cat)$^{-1}$</th>
<th>Alk / (Fe at)$^{-1}$</th>
<th>Disp / (g cat)$^{-1}$</th>
<th>Disp / (Fe at)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>4.8</td>
<td>3.2</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>2.8</td>
<td>9.0</td>
<td>3.2</td>
<td>3.6</td>
<td>1.3</td>
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<tr>
<td>3.6</td>
<td>10.7</td>
<td>3.0</td>
<td>5.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Conv. (Fe at)$^{-1}$ approx. equal activity is correlated to number of Fe atoms

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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):

<table>
<thead>
<tr>
<th>r= Si/Fe</th>
<th>Comp.</th>
<th>IS</th>
<th>QS</th>
<th>RI</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.5</td>
<td>Fe(III)-Td</td>
<td>0.15</td>
<td>1.24</td>
<td>44</td>
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<tr>
<td></td>
<td>Fe(II)-Td</td>
<td>0.66</td>
<td>0.70</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Fe(II)-Oh</td>
<td>1.01</td>
<td>1.76</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Fe(II)-Oh</td>
<td>1.19</td>
<td>2.25</td>
<td>21</td>
</tr>
<tr>
<td>35.0</td>
<td>Fe(III)-Td</td>
<td>0.25</td>
<td>1.92</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>Fe(II)-Td</td>
<td>0.66</td>
<td>0.66</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Fe(II)-Oh</td>
<td>1.03</td>
<td>2.10</td>
<td>21</td>
</tr>
<tr>
<td>67.0</td>
<td>Fe(III)-Td</td>
<td>0.23</td>
<td>1.76</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Fe(II)-Oh</td>
<td>1.13</td>
<td>2.06</td>
<td>15</td>
</tr>
</tbody>
</table>
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 Fe\( ^{2+} \), Fe\( ^{3+} \) 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$_3$O$^+$
- evac: NH$_4^+ \rightarrow$ NH$_3$ $\uparrow$ + H$^+$, H$_3$O $\rightarrow$ H$_2$O$\uparrow$ + H$^+$
- H$_2$: Fe$^{3+}_{EFW} \rightarrow$ Fe$^{2+}_{EFW}$, Fe$^{3+}_{FW}$ maintained
- N$_2$O: Fe$^{2+}_{EFW} \rightarrow$ Fe$^{3+}_{EFW}$, large QS $\Rightarrow$ distorted
- H$_2$ again: sharper lines, distorted Fe$^{2+}$ and Fe$^{3+}$
  Si-O(Fe$_{FW}$OH)-OSi

Interpretation:
The mixture of EFW ions at the starting state
- is converted to H$^+$ Bronsted form -
  O-Si-O-Fe(OH)-O-Si, and
- on the EFW Fe ions reversible Fe$^{2+}$ $\leftrightarrow$ 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\(^+\), H\(_3\)O\(^+\) 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 H\(_2\) treatment,
- simultaneously neutral FeO is also formed, and is trapped in the cages

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4. Microporous (3): Stabilisation of Fe$^{2+}$ in oxidizing atmosphere

Distinguished interest: N$_2$O + Ferrisilicate:
i/ activated „α”-oxygen (e.g. benzene to phenol), ii/N$_2$O (greenhouse gas) decomposition
1) FW Fe$^{3+}$ Si/Fe ~ 200, 2) Additional EFW Fe$^{2+}$: by ion exchange (NH$_4$·Z + FeCl$_2$) → Fe·Z + NH$_4$Cl ↑
3) N$_2$O decomposition at 620 K

Separate Fe$^{2+}$ is present in N$_2$O at 620 K
• e.g. Fe$^{2+}$ is stabilised under strong oxidising conditions
• the Fe$^{2+}$ and Fe$^{3+}$ species are independent

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

1. Hydrothermal:
   370 K / 170 h (Si/Fe= 100)
   \( \text{SiO}_2 \): Fe\(_2\)SO\(_4\) : NaOH : Na\(_2\)SO\(_4\) : C\(_{16}\)TMABr (H\(_2\)O)

2. Methanolic soln.
   ambient T, 24 h (Si/Fe=20)
   \text{TEOS} : C\(_{16}\)TMABr : MetOH : NH\(_3\) (H\(_2\)O)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SiO(_2) / hydroth</th>
<th>TEOS/RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{100}) (nm)</td>
<td>3.38</td>
<td>3.47</td>
</tr>
<tr>
<td>(a_0) (nm)</td>
<td>3.90</td>
<td>4.01</td>
</tr>
<tr>
<td>(\Phi_{\text{BJH}}) (nm)</td>
<td>2.43</td>
<td>2.31</td>
</tr>
<tr>
<td>WTH(1) ((a_0 - \Phi_{\text{BJH}}))</td>
<td>1.47</td>
<td>1.70</td>
</tr>
<tr>
<td>(\nu_p) (cm(^3)/g)</td>
<td>0.79</td>
<td>0.62</td>
</tr>
<tr>
<td>(W_d) (nm)</td>
<td>3.27</td>
<td>3.20</td>
</tr>
<tr>
<td>WTH(2) ((a_0 - W_d))</td>
<td>0.63</td>
<td>0.81</td>
</tr>
</tbody>
</table>
5. Mesoporous (1): Redox processes in the pore walls of MCM-41

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

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

Amorphous feature is reflected in:
- full Fe\textsuperscript{3+} ↔ Fe\textsuperscript{2+} reversibility,
- Fe\textsuperscript{2+} stabilized in the pore walls
- Brosted acidity is practically lost
5. Mesoporous (1) MCM-41 pore wall stability (methanolic synthesis)

Partly amorphous structure $\Rightarrow$ expressed participation of silanolic Si-OH groups can be proposed in $\text{H}_2$ propagation of reduction by ($\text{H}_2^+$) may be suggested (since the structure is rich in -OH groups):

(1st step) $\Rightarrow \text{Si-O-Fe}^{3+} + \text{H}_2 \rightarrow \text{Si-O}^+ (\text{H}_2)^+ + \text{Fe}^{2+}$
(Propagation) $\Rightarrow \text{Si-O}^+ (\text{H}_2)^+ + \text{Si-OH} \rightarrow \text{Si-OH} + \text{Si-O}^+ (\text{H}_2)^+$
(2nd step) $\Rightarrow \text{Si-O}^+ (\text{H}_2)^+ + \text{Si-O-Fe}^{3+} \rightarrow 2 \text{Si-OH} + \text{Fe}^{2+}$

Si/Fe: a) 113, b) 52, c) 24, d) 15
strong Lewis, weak Bronsted character

Pyridine chemisorption

CO oxidation

Si/Fe: a) $\infty$ ; b) 77; c) 20; d) 12
6. Mesoporous (2): Fe-SBA-15 samples

DIRECT synth.:  
Pluronic 123  
HCl 1.9 M  
2 h  
AGEING STEP  
110°C  
24 h  
FILTERED AND CALCINED AT 550°C  
DS-1 sample

POST synth.:  
Pluronic 123  
HCl 1.9 M  
AGEING STEP  
110°C  
24 h  
FILTERED  
DS-2 sample

SYNTHESIS OF SBA-15

Fe INCORPORATION STEP

PS sample

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

DIRECT synth.:  
Pluronic 123  
HCl 1.9 M  
2 h  
AGEING STEP  
110°C  
24 h  
FILTERED AND CALCINED AT 550°C  
DS-1 sample

POST synth.:  
Pluronic 123  
HCl 1.9 M  
AGEING STEP  
110°C  
24 h  
FILTERED  
DS-2 sample

SYNTHESIS OF SBA-15

Fe INCORPORATION STEP

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

**Fe-SBA-15 MATERIALS**

Mesoporous SBA-15 
\[ a_0 \sim 10 \text{ nm} \]

(Insert:)
Hematite, \( \alpha-\text{Fe}_2\text{O}_3 \),
in the range of 
\[ 10^0 < 2\Theta < 90^0 \]
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**

\[ T = 100^\circ\text{C} \]
\[ P = 7\text{ bar.} \]
Stirring: 350 r. p. m.

Aqueous Solution

\[ [\text{Phenol}]_0 = 1.0\text{ g/L} \]
\[ [\text{Catalyst}] = 0.6\text{ g/L} \]
\[ [\text{H}_2\text{O}_2]_0 = 5.0\text{ g/L} \]

**Simplified Reaction Pathway for Phenol Oxidation**

\[
\begin{align*}
\text{Phenol} & \rightarrow \text{Aromatic Compounds} \rightarrow \text{Carboxylic Acids} \\
& \rightarrow \text{Complete Mineralization} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

**Analytical Techniques**

- TOC REMOVAL
- PRODUCTS DISTRIBUTION AND \(\text{H}_2\text{O}_2\) CONVERSION
- LEACHING OF IRON SPECIES
- TOC ANALYZER
- HPLC
- ICP-AES

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
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,
   • Fe$^{3+}$ ↔ 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$_2$O)

3) In mesoporous host the pore wall is partly amorphous, thus the FW / EFW distinction is less suitable.
   • Fe$^{3+}$ ↔ 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