Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Effects of Nanoconfinement and Surface Charge on Iron Adsorption on Mesoporous Silica

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Electronic Supplementary Information

Table S1. Fluid Composition for Molecular Dynamics Simulations[a]

Charged		0.05 M		0.1 M		0.5 M	
Pore Size (nm)	H_2O[b]	Fe^{2+}	OH^-/Cl^-	Fe^{2+}	OH^-/Cl^-	Fe^{2+}	OH^-/Cl^-
2	3262	22	10	27	20	67	100
4	6219	25	16	32	30	92	150
8	11,955	30	26	42	50	142	250
Nonporous	11,969	30	26	42	50	142	250
Neutral		0.05 M		0.1 M		0.5 M	
Pore Size (nm)	H_2O[b]	Fe^{3+}	OH^-/Cl^-	Fe^{3+}	OH^-/Cl^-	Fe^{3+}	OH^-/Cl^-
2	3262	5	15	10	30	50	150
4	6223	8	24	15	45	75	225
8	11,846	13	39	25	75	125	375
Nonporous	11,955	14	42	26	78	126	378

[a] Number of species. [b] Numbers of water for 0.05 M Cl^- system. Slightly fewer waters were needed for OH^- systems and at higher concentrations.

Table S2. Fe(II) Concentrations and Adsorption Results (Charged Surface)

Pore Size (nm)	N_Fe_{tot}	$N\_Fe_{aq,init}$[a]	$[Fe]_{init}$ (mol/L)[a]	Anion	N_Fe_{ads}	Conc. Fe_{ads} ($\mu mol/m^2$)	$N\_Fe_{aq,final}$[b]	$[Fe]_{final}$ (mol/L)[b]
2	22	5	0.05	Cl^-	21.2	0.25	0.8	0.01
				OH^-	22.0	0.26	0.0	0.00
4	25	8	0.05	Cl^-	23.1	0.28	1.9	0.01
				OH^-	24.4	0.29	0.6	0.00
8	30	13	0.05	Cl^-	24.1	0.29	5.9	0.02
				OH^-	24.0	0.29	6.0	0.02
NP	30	13	0.05	Cl^-	21.3	0.26	8.7	0.03
				OH^-	27.9	0.33	2.1	0.01
2	27	10	0.1	Cl^-	25.2	0.30	1.8	0.02
				OH^-	27.0	0.32	0.0	0.00
4	32	15	0.1	Cl^-	26.7	0.32	5.3	0.04
				OH^-	30.0	0.36[c]	2.0	0.01
8	42	25	0.1	Cl^-	26.8	0.32	15.2	0.06
				OH^-	28.4	0.34	13.6	0.05
NP	42	25	0.1	Cl^-	25.0	0.30	17.0	0.07
				OH^-	29.1	0.35	12.9	0.05
2	67	50	0.5	Cl^-	39.3	0.47	27.7	0.28
				OH^-	60.1	0.72	6.9	0.07
4	92	75	0.5	Cl^-	38.8	0.47	53.2	0.35
				OH^-	55.4	0.67	36.6	0.24
8	142	125	0.5	Cl^-	39.1	0.47	102.9	0.41
				OH^-	53.9	0.65	88.1	0.35
NP	142	125	0.5	Cl^-	39.8	0.48	102.2	0.41
				OH^-	58.7	0.70	83.3	0.33
4 Neutral	15	15	0.1	OH^-	3.4	0.04[c]	11.6	0.08

[a]Number and approximate concentration of Fe(II) cations not including cations needed to balance the negative surface charge (17 Fe(II) ions). [b]Number and approximate concentration of Fe(II) cations not adsorbed to silica surfaces. [c]Comparison of adsorbed amounts for charged and neutral surfaces (4 nm, 0.1 M). For reference, adsorbed amounts for 0.1 M Fe(III) with OH^- anions at charged and neutral surfaces are 0.03 and 0.25 $\mu mol/m^2$.

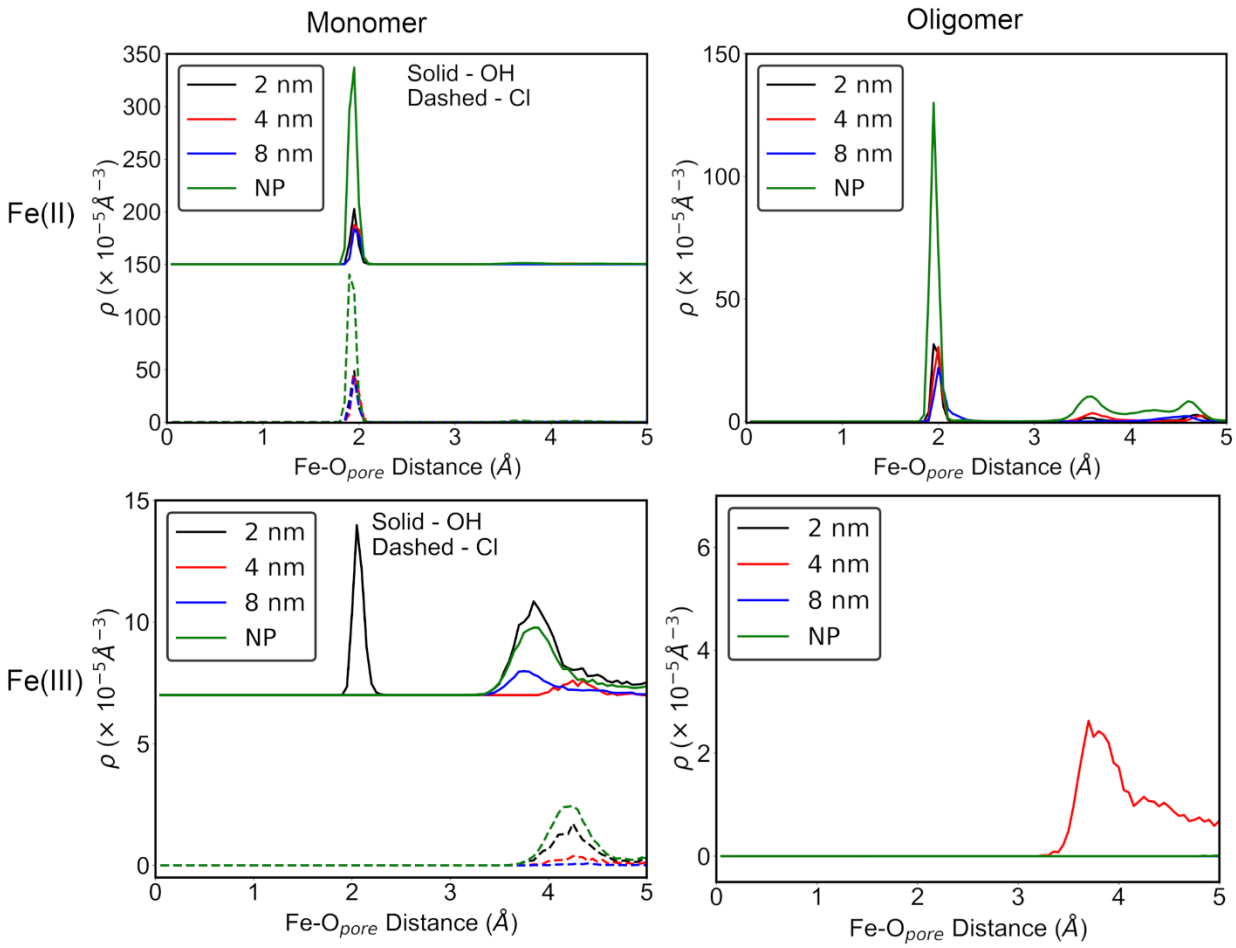

Figure S1. Atomic density profiles of the shortest distance between an iron cation and a surface oxygen atom (O_{pore}) as a function of pore size and anion (NP refers to nonporous). Results are shown for 0.05 M Fe(II) at the charged surface (top) and Fe(III) at the neutral surface (bottom). Profiles for iron oligomer adsorption (right) are shown for OH^- only since no oligomers formed in the Cl– systems.

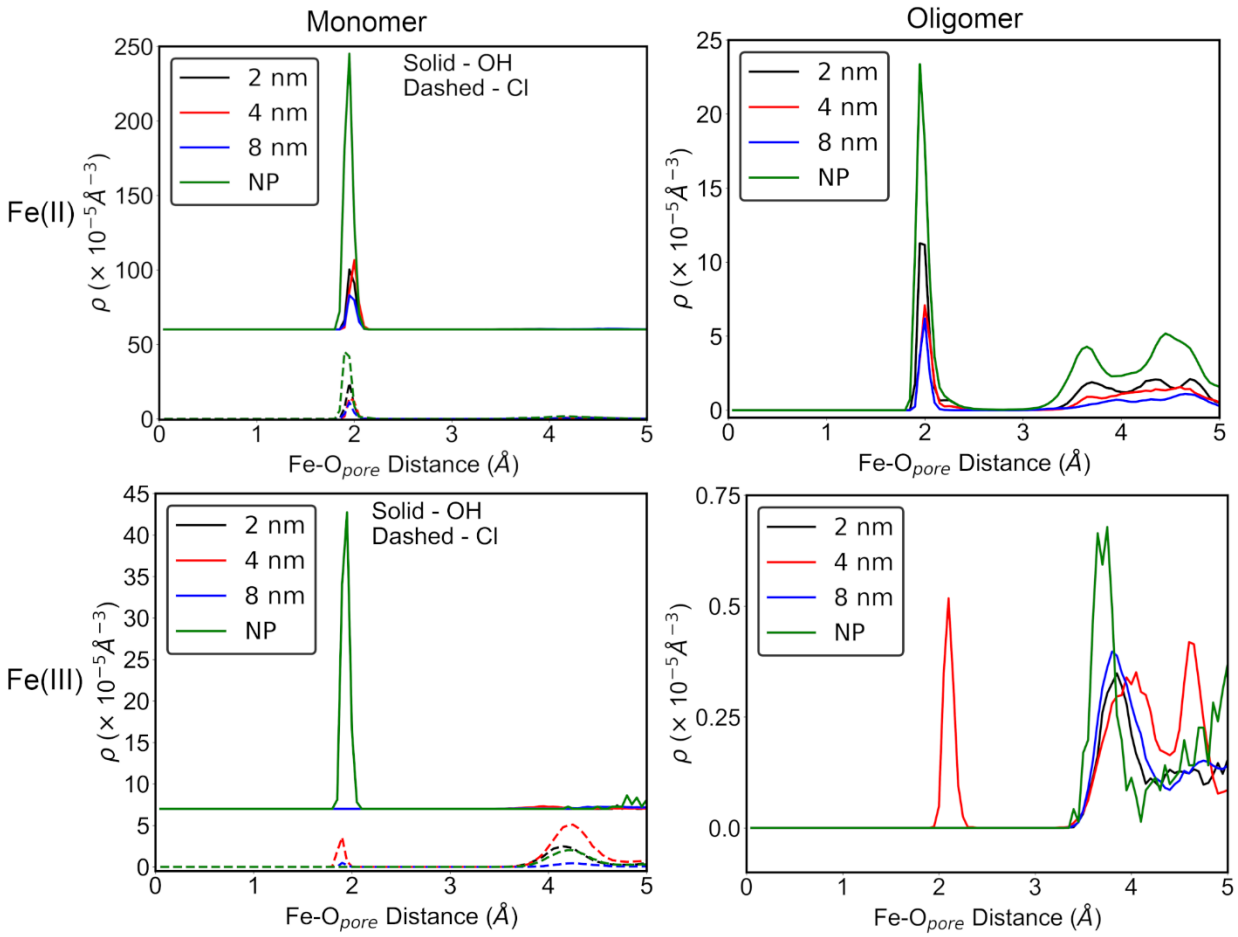

Figure S2. Atomic density profiles of the shortest distance between an iron cation and a surface oxygen atom (O_{pore}) as a function of pore size and anion (NP refers to nonporous). Results are shown for 0.5 M Fe(II) at the charged surface (top) and Fe(III) at the neutral surface (bottom). Profiles for iron oligomer adsorption (right) are shown for OH^- only since no oligomers formed in the Cl– systems.

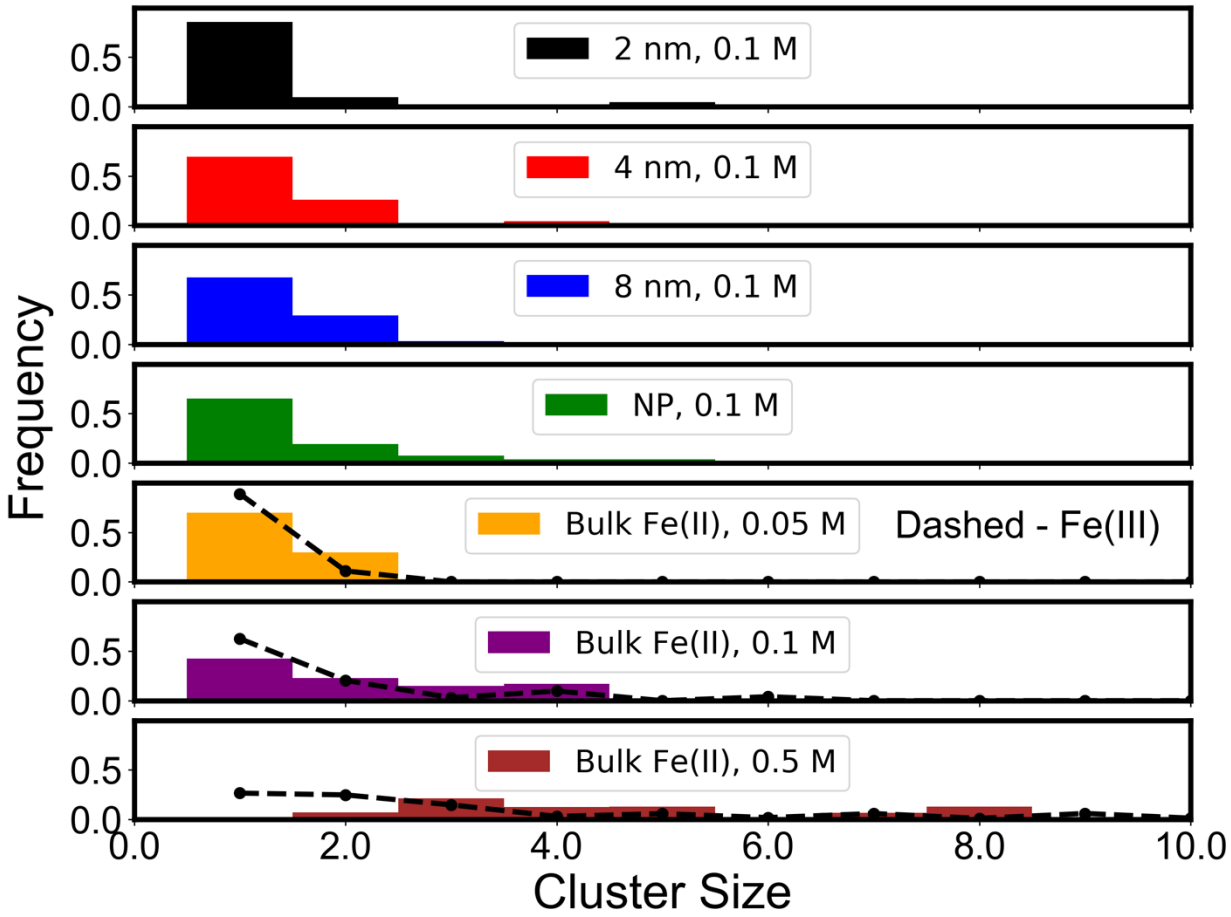

Figure S3. Histograms of Fe oligomer frequency from MD simulations of 0.1 M Fe(II) with hydroxide anions in negatively-charged porous and nonporous silica models, and bulk Fe(II) and Fe(III) solutions with hydroxide anions. Results for Fe(III) are shown as dashed lines.

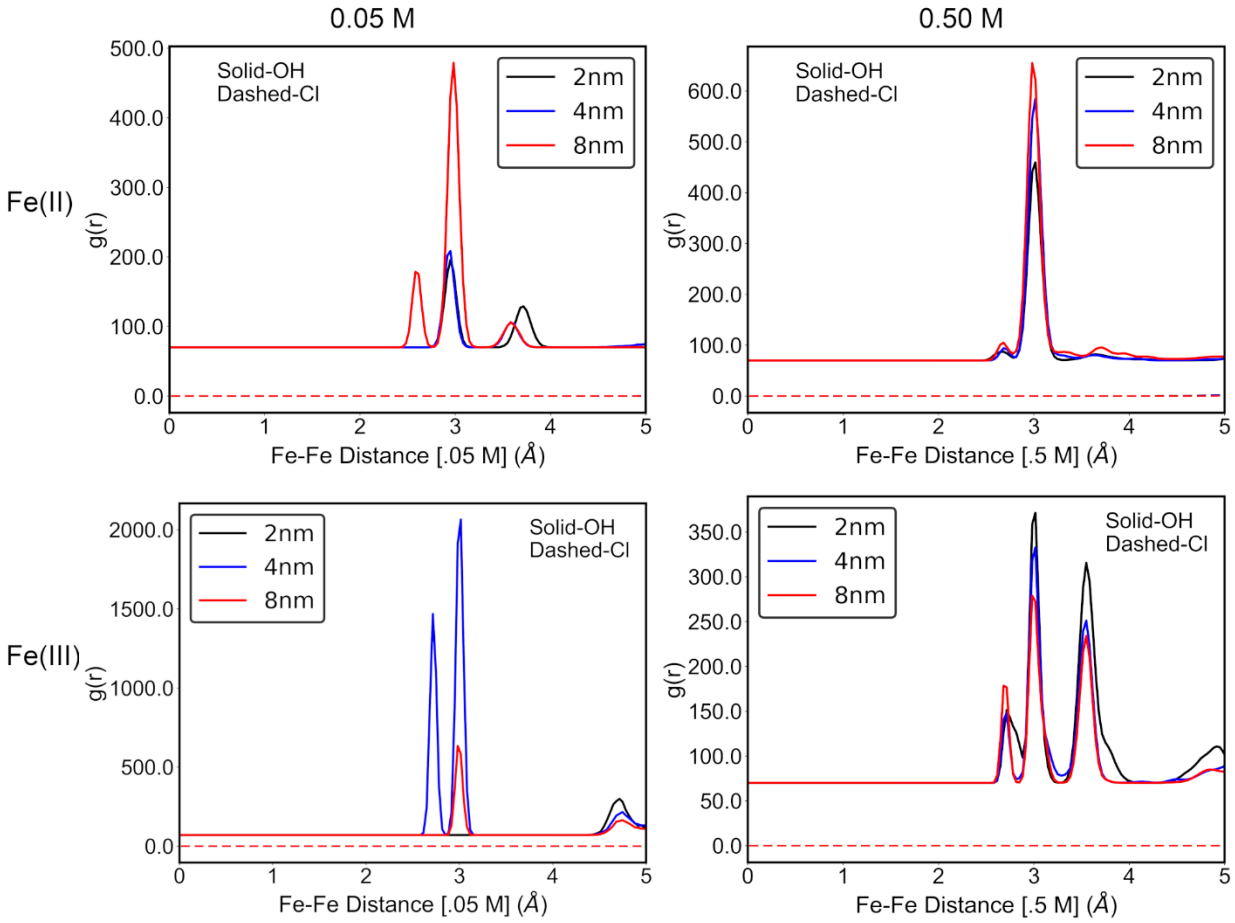

Figure S4. Fe-Fe RDFs for 0.05 M and 0.5 M OH model systems with Fe(II)-charged and Fe(III)-neutral.

MD Interaction Parameters for neutral surface (LAMMPS format with units “real”)

Masses

1 28.0855
2 15.9994
3 1.0079
4 28.0855
5 15.9994
6 15.9994
7 15.9994
8 1.00797
9 55.845
10 15.9994
11 1.00797
12 35.453

Pair Coeffs # lj/cut/coul/long

1 1.8402e-06 3.30196 # st
2 0.155416 3.16552 # oh
3 0 0 # ho
4 1.8402e-06 3.30196 # sdep (Si at SiO^- site)
5 0.155416 3.16552 # odep (O at SiO^- site)
6 0.155416 3.16552 # ob
7 0.15539 3.1656 # o* (SPC water)
8 0 0 # h* (SPC water)
9 0.0427 1.8406 # Fe2+
10 0.15539 3.1656 # OH (hydroxide O)
11 0 0 # HO (hydroxide H)
12 0.1001 4.39997 # Cl

Bond Coeffs # harmonic

1 553.935 1 # OH-HO and o*-h*

Angle Coeffs # harmonic

1 15 100 # st-oh-ho
2 45.77 109.47 # h*-o*-h*

Atom Charges

1 2.100
2 -0.950
3 0.425
4 1.960
5 -1.385
6 -1.050
7 -0.820
8 0.410
9 2.000
10 -1.410
11 0.410
12 -1.000

MD Interaction Parameters for negatively charged surface (LAMMPS format with units “real”)

Masses

1 28.0855
2 15.9994
3 1.0079
4 15.9994
5 15.9994
6 1.00797
7 55.845
8 15.9994
9 1.00797
10 35.453

Pair Coeffs # lj/cut/coul/long

1 1.8402e-06 3.30196	# st
2 0.155416 3.16552	# oh
3 0 0	# ho
4 0.155416 3.16552	# ob
5 0.15539 3.1656	# o* (SPC water)
6 0 0	# h* (SPC water)
7 0.0427 1.8406	# Fe3+
8 0.15539 3.1656	# OH (hydroxide O)
9 0 0	# HO (hydroxide H)
10 0.1001 4.39997	# Cl

Bond Coeffs # harmonic

1 553.935 1	# OH-HO and o*-h*

Angle Coeffs # harmonic

1 15 100	# st-oh-ho
2 45.77 109.47	# h*-o*-h*

Atom Charges

1 2.100
2 -0.950
3 0.425
4 -1.050
5 -0.820
6 0.410
7 3.000
8 -1.410
9 0.410
10 -1.000

Table S3. Fe distances and coordination numbers for Fe(II)-Cl system.

Fe(II) Cl	0.05 M											
Pore size	**N Fe**	**d(Fe-odep)**	**CN Fe-odep**	**d (Fe-Cl)**	**CN (Fe-Cl)**	**CN Fe-oh**	**CN (Fe-ob)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
2	22	1.96	0.91	2.55	0.27	0.00	0.00	2.12	4.82	0.00	0.00	3.27	0.91
4	25	1.94	0.92	2.54	0.16	0.00	0.00	2.12	4.92	0.00	0.00	3.27	0.92
8	30	1.94	0.77	2.53	0.34	0.00	0.00	2.11	4.89	0.00	0.00	3.27	0.77
9	30	1.95	0.67	2.53	0.40	0.00	0.00	2.11	4.93	0.00	0.00	3.27	0.67

Note: pore size 9 corresponds to nonporous

Fe(II) Cl	0.1 M											
Pore size	**N Fe**	**d(Fe-odep)**	**CN Fe-odep**	**d (Fe-Cl)**	**CN (Fe-Cl)**	**CN Fe-oh**	**CN (Fe-ob)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
2	27	1.94	0.89	2.55	0.33	0.00	0.00	2.12	4.78	0.00	0.00	3.27	0.89
4	32	1.94	0.75	2.53	0.31	0.00	0.00	2.11	4.94	0.00	0.00	3.27	0.75
8	42	1.94	0.57	2.53	0.40	0.00	0.00	2.10	4.02	0.00	0.00	3.27	0.57
9	42	1.95	0.57	2.53	0.45	0.00	0.00	2.12	4.98	0.00	0.00	3.27	0.57

Note: pore size 9 corresponds to nonporous

Fe(II) Cl	0.5 M											
Pore size	**N Fe**	**d(Fe-odep)**	**CN Fe-odep**	**d (Fe-Cl)**	**CN (Fe-Cl)**	**CN Fe-oh**	**CN (Fe-ob)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
2	67	1.94	0.45	2.55	1.04	0.01	0.00	2.11	4.50	0.00	0.00	3.27	0.45
4	92	1.94	0.32	2.53	0.97	0.00	0.00	2.11	4.71	0.00	0.00	3.27	0.32
8	142	1.96	0.20	2.53	0.88	0.00	0.00	2.10	4.91	0.00	0.00	3.27	0.20
9	142	1.94	0.22	2.53	1.00	0.00	0.00	2.11	4.78	0.00	0.00	3.27	0.22

Note: pore size 9 corresponds to nonporous

Table S4. Fe distances and coordination numbers for Fe(II)-OH system.

Fe(II) OH	**0.05 M**													
Pore size	**N Fe**	**d(Fe-odep)**	**CN Fe-odep**	**d(Fe-OH)**	**CN Fe-OH**	**CN Fe-oh**	**CN (Fe-ob)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**	**sum Fe-Fe CN**	**d(Fe-Si)**	**CN Fe-Si**
2	22	1.96	0.91	1.97	0.73	0.05	0.00	2.13	4.31	2.95, 3.70	0.18, 0,18	0.36	3.27	0.91
4	25	1.96	0.84	1.96	0.84	0.00	0.00	2.13	4.32	2.93, 3.60	0.16, 0.08	0.24	3.27	0.84
8	30	1.96	0.70	1.97	1.33	0.00	0.00	2.13	3.83	2.59, 2.99, 3.59	0.07, 0.40, 0.07	0.54	3.24	0.70
9	30	1.96	0.77	1.96	1.23	0.00	0.00	2.13	4.07	2.96	0.33	0.33	3.26	0.77

Note: pore size 9 corresponds to nonporous

Fe(II) OH	**0.1 M**													
Pore size	**N Fe**	**d(Fe-odep)**	**CN Fe-odep**	**d(Fe-OH)**	**CN Fe-OH**	**CN Fe-oh**	**CN (Fe-ob)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**		**d(Fe-Si)**	**CN Fe-Si**
2	27	1.97	0.89	1.97	1.27	0.00	0.04	2.13	3.71	2.60, 3.03	0.074, 0.67	0.74	3.27	0.89
4	32	1.97	0.72	1.97	1.47	0.06	0.00	2.13	3.68	2.97, 3.62	0.56, 0.13	0.69	3.25	0.72
8	42	1.96	0.50	1.97	1.76	0.00	0.00	2.13	3.61	2.61, 2.97	0.05, 0.52	0.57	3.24	0.50
9	42	1.96	0.50	1.98	2.16	0.00	0.00	2.13	3.38	2.62, 2.99, 3.59	0.096, 0.946, 0.084	1.13	3.26	0.50

Note: pore size 9 corresponds to nonporous

Fe(II) OH	**0.5 M**													
Pore size	**N Fe**	**d(Fe-odep)**	**CN Fe-odep**	**d(Fe-OH)**	**CN Fe-OH**	**CN Fe-oh**	**CN (Fe-ob)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**		**d(Fe-Si)**	**CN Fe-Si**
2	67	1.97	0.42	1.99	3.25	0.06	0.00	2.15	2.02	2.70, 3.00, 3.63	0.033, 2.12, 0.20	2.35	3.24	0.43
4	92	1.97	0.27	2.00	3.73	0.00	0.00	2.15	1.84	2.68, 3.00, 3.60	0.14, 2.173, 0.98	3.29	3.27	0.27
8	142	1.97	0.17	2.00	4.06	0.00	0.00	2.15	1.62	2.69, 3.02, 3.67	0.20, 2.48, 0.63	3.31	3.23	0.17
9	142	1.98	0.18	1.99	3.99	0.00	0.00	2.13	1.81	2.68, 3.02, 3.73	0.093, 2.734, 0.366	3.19	3.27	0.18

Note: pore size 9 corresponds to nonporous

Fe(II) OH	**0.1 M**	**Neutral surface**												
Pore size	**N Fe**	**d(Fe-odep)**	**CN Fe-odep**	**d(Fe-OH)**	**CN Fe-OH**	**CN Fe-oh**	**CN (Fe-ob)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**		**d(Fe-Si)**	**CN Fe-Si**
4	15	0.00	0.00	1.97	3.12	0.00	0.00	2.15	2.52	2.69, 2.97, 3.33, 3.73	0.08, 1.00, 0.19, 0.2		0.00	0.00

Table S5. Fe distances and coordination numbers for Fe(III)-Cl system.

Fe(III) Cl	**0.05 M**											
Pore size	**N Fe**	**d(Fe-Cl)**	**CN Fe-Cl**	**CN(Fe-oh)**	**f(oh_occ)**	**CN (Fe-ob)**	**f(ob_occ)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
2	5	2.40	1.40	0.00	0.00	0.00	0.00	2.01	4.60	0.00	0.00	0.00	0.00
4	8	2.38	1.13	0.00	0.00	0.00	0.00	2.00	4.88	0.00	0.00	0.00	0.00
8	13	2.39	1.31	0.00	0.00	0.00	0.00	2.01	4.69	0.00	0.00	0.00	0.00
9	14	2.39	1.29	0.00	0.00	0.00	0.00	2.00	4.71	0.00	0.00	0.00	0.00

Note: pore size 9 corresponds to nonporous

Fe(III) Cl	**0.1 M**											
Pore size	**N Fe**	**d(Fe-Cl)**	**CN Fe-Cl**	**CN Fe-oh**	**f(oh_occ)**	**CN (Fe-ob)**	**f(ob_occ)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
2	10	2.40	1.20	0.00	0.00	0.00	0.00	2.00	4.80	0.00	0.00	0.00	0.00
4	15	2.40	1.27	0.00	0.00	0.00	0.00	2.00	4.73	0.00	0.00	0.00	0.00
8	25	2.40	1.24	0.00	0.00	0.00	0.00	2.00	4.76	0.00	0.00	0.00	0.00
9	26	2.39	1.31	0.00	0.00	0.00	0.00	2.00	4.69	0.00	0.00	0.00	0.00

Note: pore size 9 corresponds to nonporous

Fe(III) Cl	**0.5 M**											
Pore size	**N Fe**	**d(Fe-Cl)**	**CN Fe-Cl**	**CN Fe-oh**	**f(oh_occ)**	**CN (Fe-ob)**	**f(ob_occ)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
2	50	2.40	1.62	0.00	0.00	0.00	0.00	2.01	4.38	0.00	0.00	0.00	0.00
4	75	2.40	1.62	0.00	0.00	0.00	0.00	2.01	4.38	0.00	0.00	0.00	0.00
8	125	2.40	1.61	0.02	0.00	0.00	0.00	2.01	4.38	0.00	0.00	0.00	0.00
9	126	2.39	1.51	0.00	0.00	0.00	0.00	2.01	4.49	0.00	0.00	0.00	0.00

Note: pore size 9 corresponds to nonporous

Table S6. Fe distances and coordination numbers for Fe(III)-OH system.

Fe(III) OH	0.05 M										
Pore size	**N Fe**	**d(Fe-OH)**	**CN Fe-OH**	**CN Fe-oh**	**f(oh_occ)**	**CN (Fe-ob)**	**d(Fe-o*)**	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
2	5	1.91	3.00	0.20	0.00	0.00	2.07	2.68, 3.00	0.14, 0.29	3.46	0.20
4	8	1.87	3.88	0.00	0.00	0.00	2.07	2.73, 3.00	0.25, 0.50	0.00	0.00
8	13	1.87	3.00	0.00	0.00	0.00	2.08	2.99	0.15	0.00	0.00
	14	1.87	3.43	0.00	0.00	0.00	2.08	2.68, 3.00	0.14, 0.29	0.00	0.00

Note: pore size 9 corresponds to nonporous

Fe(III) OH	0.1 M										
Pore size	**N Fe**	**d(Fe-OH)**	**CN Fe-OH**	**CN Fe-oh**	**f(oh_occ)**	**CN (Fe-ob)**	**d(Fe-o*)**	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
2	5	1.88	3.80	0.00	0.00	0.00	2.08	3.00, 3.60	0.6, 0.4	0.00	0.00
4	8	1.87	3.87	0.00	0.00	0.00	2.06	2.7, 3.00	0.40, 0.27	0.00	0.00
8	13	1.89	3.72	0.00	0.00	0.00	2.07	2.67, 3.00	0.08, 0.64	0.00	0.00
9	14	1.88	3.81	0.00	0.00	0.04	2.09	3.00, 3.54	0.69, 0.46	0.00	0.00

Note: pore size 9 corresponds to nonporous

Fe(III) OH	0.5 M										
Pore size	**N Fe**	**d(Fe-OH)**	**CN Fe-OH**	**CN Fe-oh**	**f(oh_occ)**	**CN (Fe-ob)**	**d(Fe-o*)**	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
2	5	1.90	5.14	0.00	0.00	0.00	2.09	2.73, 3.00, 3.55	0.28, 0.92, 1.8	0.00	0.00
4	8	1.90	4.77	0.00	0.00	0.00	2.09	2.70, 3.00, 3.54	0.17, 0.99, 1.14	0.00	0.00
8	13	1.91	4.87	0.00	0.00	0.00	2.08	2.70, 3.00, 3.55	0.27, 0.93, 1.15	0.00	0.00
9	14	1.91	4.70	0.00	0.00	0.00	2.09	2.70, 3.00, 3.55	0.17, 0.81, 1.22	0.00	0.00

Note: pore size 9 corresponds to nonporous

Fe(III) OH	0.1 M	Charged surface											
Pore size	**N Fe**	**d(Fe-odep)**	**CN Fe-odep**	**d(Fe-OH)**	**CN Fe-OH**	**CN Fe-oh**	**CN (Fe-ob)**	**d(Fe-o*)**	**CN Fe-o***	**d(Fe-Fe)**	**CN Fe-Fe**	**d(Fe-Si)**	**CN Fe-Si**
4	22	1.86	0.91	1.86	1.59	0.00	0.00	2.06	3.50	2.70	0.09	4.00	0.02