

## Characterization of micro and mesoporous Fe(III) materials utilizing organic template followed by carboxylates exchange

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### Introduction

Arsenic contamination in drinking water is serious worldwide environmental problem and recent regulation of the concentration is 10 ppb. Sorption method is most economic way to remove arsenic [1]. In this work, micro and mesoporous Fe<sup>III</sup> materials were prepared utilizing organic template followed by smaller carboxylates (formate, acetate, and propionate) exchange. The transformation in the synthesis was characterized using Fe K-edge synchrotron XAFS.

### Experimental section

50 ml of Fe<sup>III</sup>Cl<sub>2</sub> was mixed with 10 ml of Na dodecylsulfate (0.07 M) followed by the addition of 10 ml of H<sub>2</sub>O<sub>2</sub> (0.25 M). The solution was stirred for 1h and filtered. Obtained FeO<sub>x</sub>(OH)<sub>y</sub> composite was mixed with Na formate, acetate, or propionate (0.05 M for each) in ethanol. Obtained anion-exchanged FeO<sub>x</sub>(OH)<sub>y</sub> and ethanol-washed FeO<sub>x</sub>(OH)<sub>y</sub> in the absence of carboxylate was heated in N<sub>2</sub> gas flow [1]. Fe K-edge XAFS spectra were measured at beamline 12C and 10B in transmission mode at 20 – 290 K for FeO<sub>x</sub>(OH)<sub>y</sub> samples evacuated at 290 K and filled in a cell equipped with Kapton windows.

### Results and discussion

The EXAFS spectra were measured for FeO<sub>x</sub>(OH)<sub>y</sub> composite, acetate-exchanged FeO<sub>x</sub>(OH)<sub>y</sub>, the one heated at 423 K, ethanol-washed FeO<sub>x</sub>(OH)<sub>y</sub>, and the one heated at 473 K. In all the Fourier-transform spectra [1], strong peak appeared at 1.5 – 1.6 Å (phase shift uncorrected) due to the Fe-O bond. A medium peak at 2.7 – 2.8 Å (phase

shift uncorrected) was clearly observed due the Fe•••Fe interaction.

For crystallines α-Fe<sub>2</sub>O<sub>3</sub>, α-FeO(OH), and γ-FeO(OH), the Fe-O bond distance was between 2.0305 – 2.034 Å and the coordination number  $N_{\text{Fe-O}}$  was 6 for the octahedral [FeO<sub>6</sub>] coordination (Table 1). Obtained Fe-O bond distance FeO<sub>x</sub>(OH)<sub>y</sub> composite and the derivative microporous Fe<sup>III</sup> materials were between 2.043 – 2.088 Å, slightly relaxed from those for standard compounds (Table 1). Associated  $N_{\text{Fe-O}}$  values fell within 4.6 – 6.0. Relatively smaller value (4.6) given for acetate-exchanged FeO<sub>x</sub>(OH)<sub>y</sub> may be because of less complete array of [FeO<sub>6</sub>] units due to highly dispersed microporous nature and/or surface reduction by acetate or ethanol. The  $R_{\text{Fe•••Fe}}$  values also elongated (3.213 – 3.245 Å) compared to the value for γ-FeO(OH) (3.066 Å). These values were within the range of Fe•••Fe distance for edge-shared [FeO<sub>6</sub>] units (2.97 – 3.28 Å) [2]. Obtained  $N_{\text{Fe•••Fe}}$  values (1.8 – 3.1), suggesting highly dispersed, unsaturated nature of microporous Fe<sup>III</sup> materials.

In summary, Fe K-edge analyses demonstrated that Fe<sup>III</sup> materials studied consisted of edge-shared [FeO<sub>6</sub>] octahedral units and the unsaturated nature.

### References

- [1] Y. Izumi, D. Masih, K. Aika, Y. Seida, *Micropor. Mesopor. Mater.* **2006**, in press.
- [2] Y. Izumi, D. Masih, K. Aika, Y. Seida, *J. Phys. Chem. B.* **2005**, *109*(8), 3227 – 3232.

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**Table 1:** Best Fit Results of Fe K-edge EXAFS for FeO<sub>x</sub>(OH)<sub>y</sub> Composite and the Derivative Porous Materials<sup>a</sup>

Sample	<i>k</i> -range for fit (Å <sup>-1</sup> )	<i>R</i> -range for fit (Å)	Fe-O				Fe•••Fe				Goodness of Fit
			<i>N</i>	<i>R</i> (Å)	Δ <i>E</i> <sub>0</sub> (eV)	Δσ <sup>2</sup> (Å <sup>2</sup> )	<i>N</i>	<i>R</i> (Å)	Δ <i>E</i> <sub>0</sub> (eV)	Δσ <sup>2</sup> (Å <sup>2</sup> )	
FeO <sub>x</sub> (OH) <sub>y</sub> composite	3.7 – 12.0	1.11 – 3.13	6.0 (±0.8)	2.070 (±0.013)	-1.0 (±1.0)	-0.0002 (±0.0007)	1.8 (±0.2)	3.245 (±0.003)	-1.0 (±0.5)	0.0009 (±0.0003)	198
Acetate-exchanged FeO <sub>x</sub> (OH) <sub>y</sub>	3.7 – 12.0	1.14 – 3.08	4.6 (±0.6)	2.065 (±0.005)	0.0 (±1.1)	-0.0009 (±0.0004)	2.5 (±0.4)	3.213 (±0.020)	0.4 (±3.4)	0.0022 (±0.0007)	141
Acetate-exchanged FeO <sub>x</sub> (OH) <sub>y</sub> heated at 423 K	3.7 – 11.6	1.09 – 3.15	5.6 (±0.5)	2.043 (±0.005)	1.9 (±0.9)	0.0010 (±0.0002)	3.1 (±0.2)	3.241 (±0.013)	-2.1 (±2.0)	0.0049 (±0.0003)	264
Ethanol-washed FeO <sub>x</sub> (OH) <sub>y</sub>	3.7 – 11.9	1.11 – 3.10	5.1 (±1.6)	2.088 (±0.027)	-7.0 (±3.5)	-0.0027 (±0.0031)	2.6 (±0.1)	3.233 (±0.011)	-0.3 (±1.4)	0.0047 (±0.0005)	136
α-Fe <sub>2</sub> O <sub>3</sub> <sup>b</sup>			6	2.0305			7	3.1293			
α-FeO(OH) <sup>b</sup>			6	2.021			2	3.015,			
							6	3.390			
γ-FeO(OH) <sup>b</sup>			6	2.034			6	3.066			

<sup>a</sup> Values in parenthesis are estimated fit errors. <sup>b</sup> See the references 17 and 18 of ref. 1.