Supplementary Information

The Impact of Solution Chemistry on Growth and Structural Features of Mo-substituted Spinel Iron Oxides

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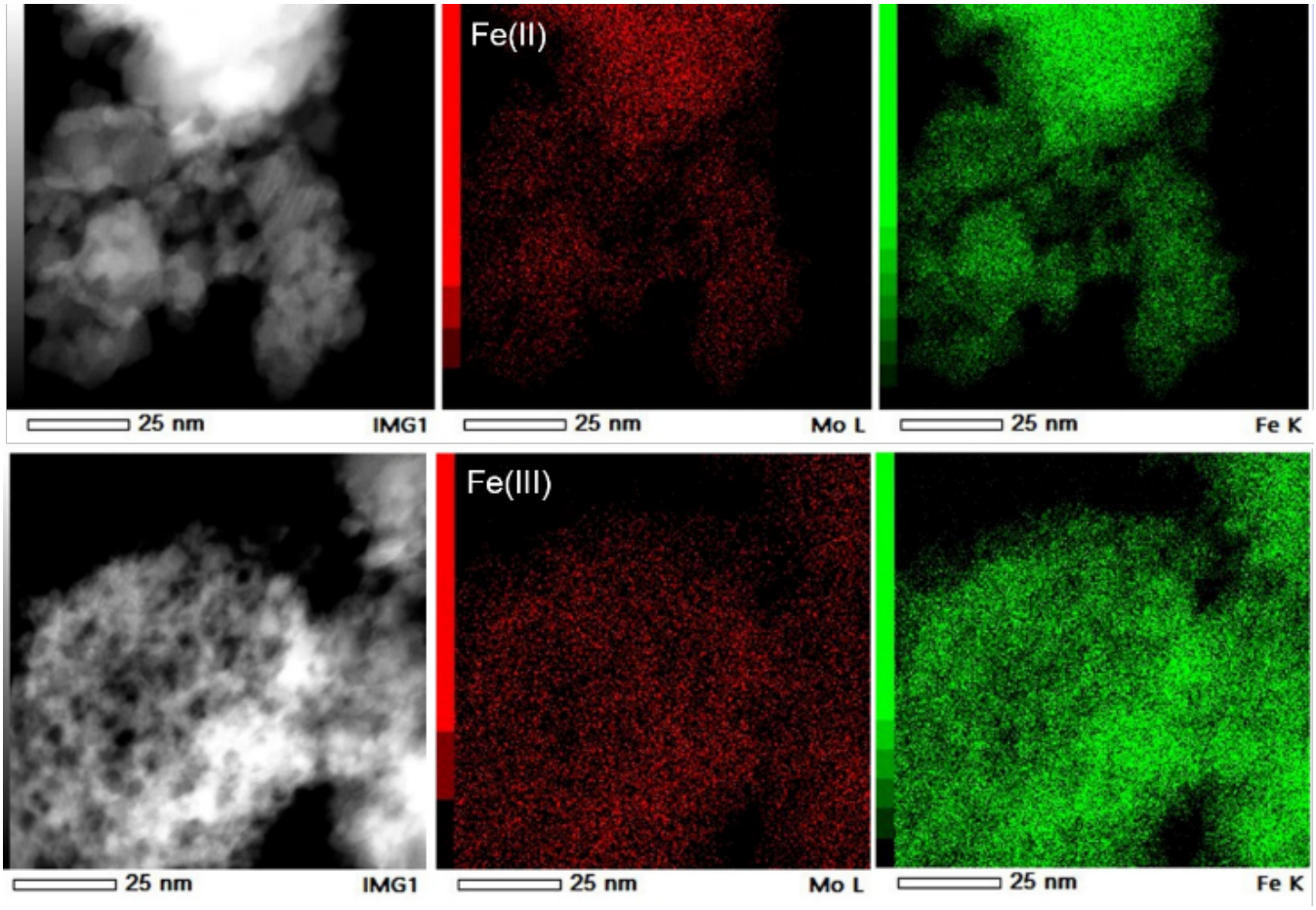

Figure S1. HAADF-STEM images of an isolated particle and corresponding EDX elemental mapping for Mo Land Fe K on the samples prepared with Fe(II) and Fe(III) precursors.

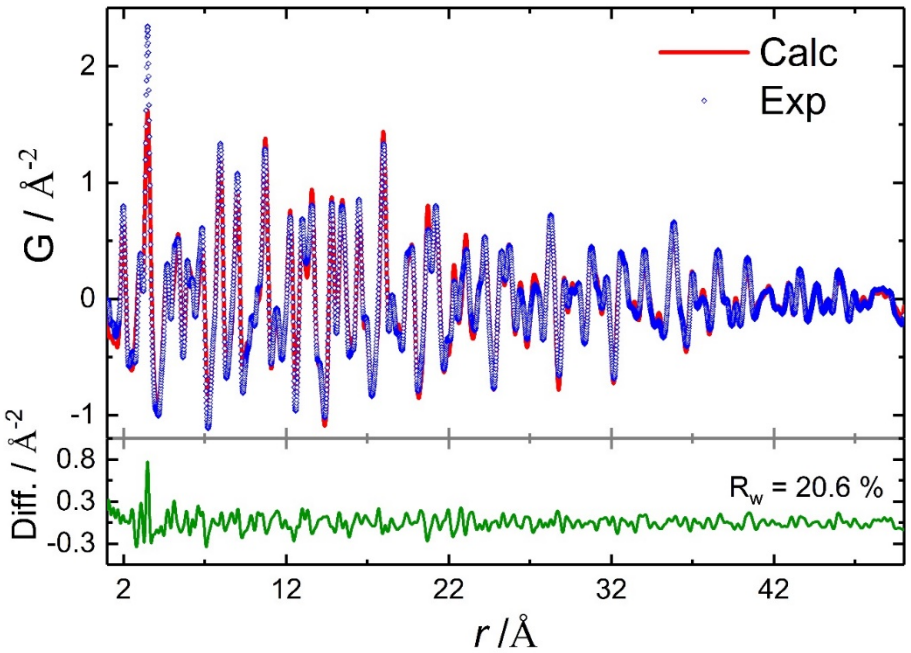

Figure S2. Refinement of the PDF data of the sample prepared with Fe(II) using a two-phase model based on *Fd-3m* and *P4₃32* space groups.

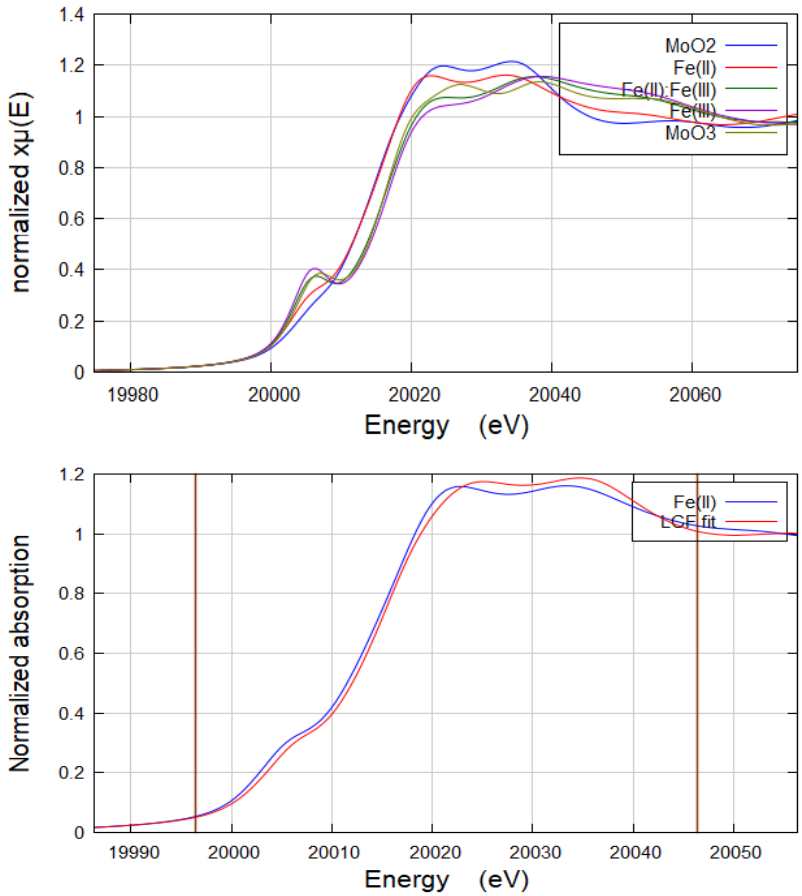

Figure S3. Top: comparison of the XANES signatures of the three samples obtained with different Fe precursors with the experimental spectra of MoO_2 and MoO_3 references. Bottom: linear combination fit of the XANES spectrum of the sample obtained starting from Fe(II) carried out using the spectra of MoO_2 and MoO_3 as references for Mo(IV) and Mo(VI), respectively, which provides a Mo(IV)/Mo(VI) ratio of content of about 3.

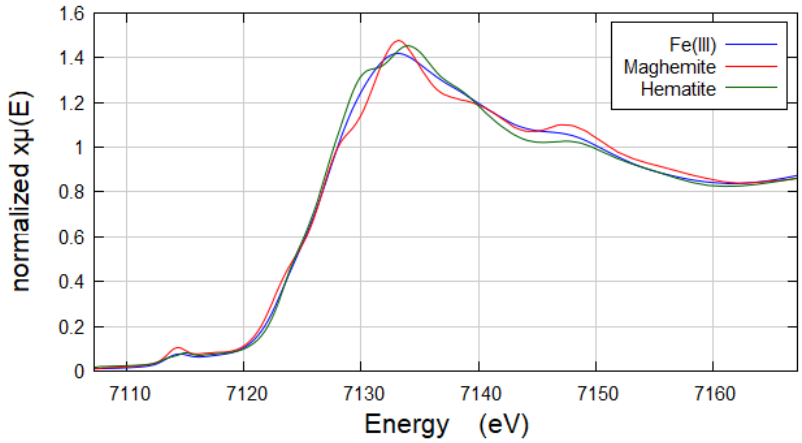

Figure S4. Comparison of the XANES signatures of the sample obtained with the Fe(III) precursor with the experimental spectra of hematite and maghemite references.

Mo and Fe K-edge XAS fitting procedure

The two series of spectra were fitted in the R space in the range 1.0-3.5 Å using the following approach for both Mo and Fe K-edge spectra:

- The first shell, between 1 and 2 Å, was divided in two contributions. The first contributions, including 4 oxygen neighbors, was set at a distance of about 1.8 Å, whereas the second one, including 6 oxygen neighbors, was set at a distance of 2.0 Å. The sum of the relative intensities of the two contributions was set equal to the value of the amplitude factor S_0^2, which was previously determined to be 0.8 and 0.75 for the Mo and Fe K-edge spectra by fitting the experimental spectrum of a reference material (crystalline MoO_3 and α-Fe_2O_3, respectively) measured in the same conditions. The σ^2 Debye-Waller factor was fitted to an identical value for both contributions.
- The second shell, between 2 and 3.5 Å was fitted in a simplified manner considering only the contributions of two Fe neighbors at different distances. Considering that, in the theoretical spectrum of spinels, octahedral iron centers are surrounded by 6 Fe neighbors at about 3 Å and 6 more at 3.45 Å, whereas tetrahedral iron centers are only surrounded by 12 neighbors at 3.45 Å, the relative intensity of the first contribution was set equal to that of octahedral Fe-O_4 sites, and that of the second contribution to the weighted average between the intensities of octahedral and tetrahedral first-shell Fe-O_n sites. The σ^2 Debye-Waller factor was fitted to an identical value for both contributions.

The results of the fittings are shown in Figure S5 and S6, and the corresponding fitting parameters reported in Tables S1 and S2 for the Mo and Fe K-edges, respectively.

Sample precursors	Site	S_0^2	%	R / Å	σ^2
Fe(II)	Mo-O_4	0.31(4)	39(5)	1.72(3)	0.003(2)
	Mo-O_6	0.49(4)	61(5)	1.99(3)	
	Mo-Fe_6	0.49(4)	-	3.14(4)	0.006(2)
	Mo-Fe_{12}	0.4(1)	-	3.46(4)	
Fe(II):Fe(III)	Mo-O_4	0.68(6)	85(8)	1.74(4)	0.005(3)
	Mo-O_6	0.12(6)	15(8)	2.03(4)	
	Mo-Fe_6	0.12(6)	-	3.17(7)	0.006(5)
	Mo-Fe_{12}	0.07(5)	-	3.51(7)	
Fe(III)	Mo-O_4	0.77(2)	95(3)	1.75(1)	0.005(3)
	Mo-O_6	0.03(2)	5(3)	2.05(3)	
	Mo-Fe_6	0.03(2)	-	2.82(5)	0.006(5)
	Mo-Fe_{12}	0.02(2)	-	3.3(1)	

Table S1. Fitting parameters obtained by refining the Mo K-edge EXAFS spectra of the samples prepared using different iron precursors.

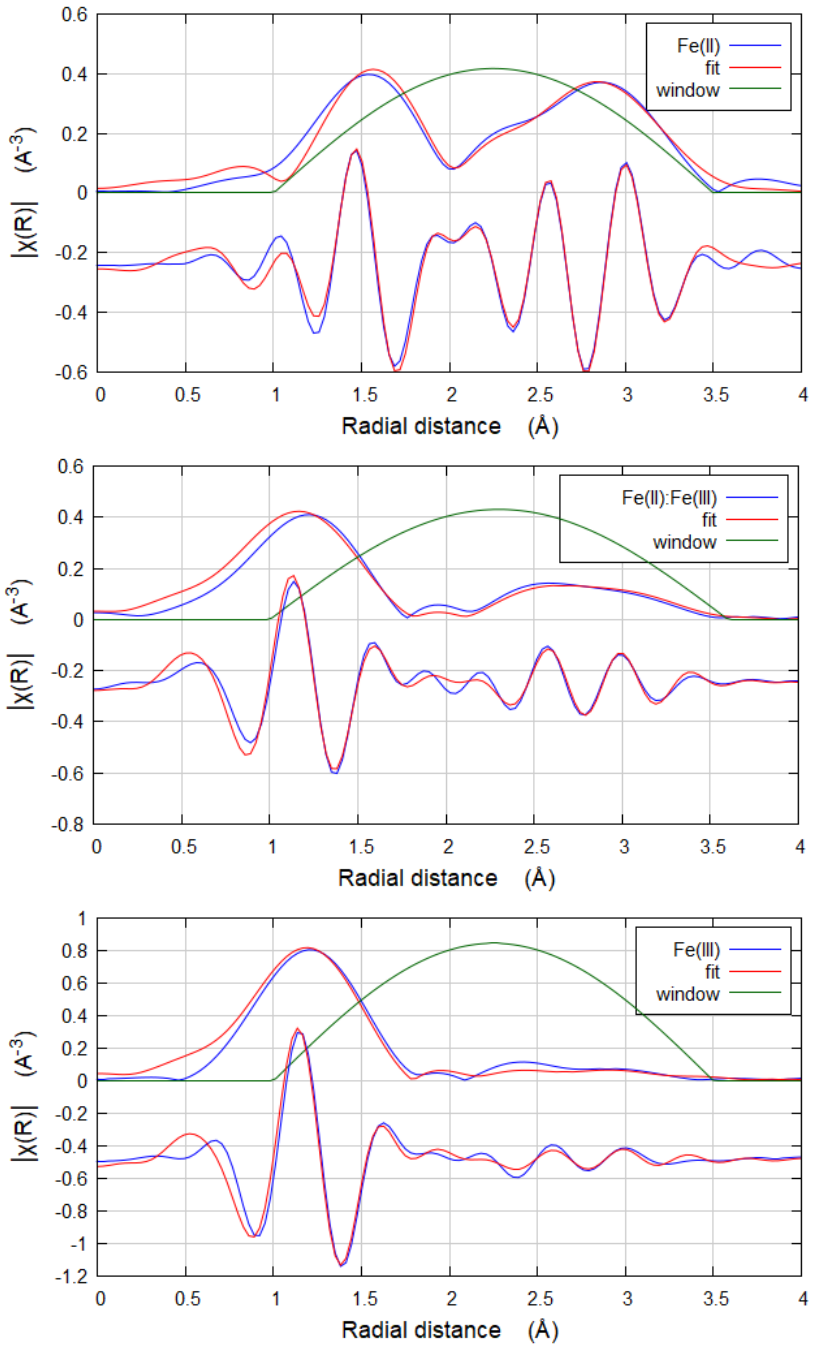

Figure S5. Fits of the Mo K-edge EXAFS spectra of the samples prepared using different iron precursors (left).

Sample precursors	Site	S_0^2	%	R / Å	σ^2
Fe(II)	Fe-O_4	0.37(7)	49(9)	1.89(2)	0.008(2)
	Fe-O_6	0.38(7)	51(9)	1.99(2)	
	Fe-Fe_6	0.38(8)	-	2.98(2)	0.012(3)
	Fe-Fe_{12}	0.56(8)	-	3.44(2)	
Fe(II):Fe(III)	Fe-O_4	0.33(6)	44(8)	1.89(3)	0.007(2)
	Fe-O_6	0.42(6)	56(8)	1.97(2)	
	Fe-Fe_6	0.42(6)	-	2.99(2)	0.015(3)
	Fe-Fe_{12}	0.53(6)	-	3.41(3)	
Fe(III)	Fe-O_4	0.23(7)	34(9)	1.89(3)	0.008(2)
	Fe-O_6	0.52(7)	66(9)	1.96(2)	
	Fe-Fe_6	0.52(7)	-	3.02(2)	0.018(3)
	Fe-Fe_{12}	0.49(7)	-	3.39(3)	

Table S2. Fitting parameters obtained by refining the Fe K-edge EXAFS spectra of the samples prepared using different iron precursors.

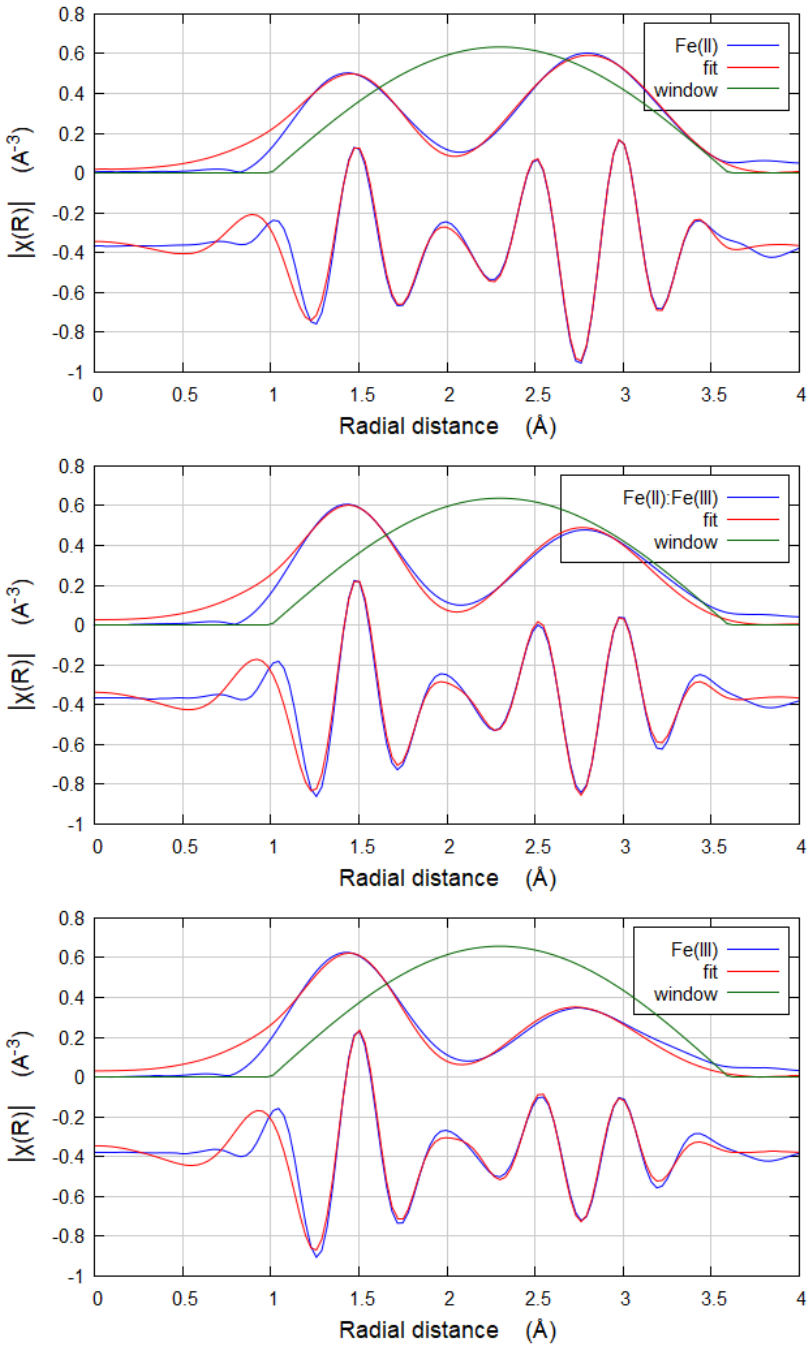

Figure S6. Fits of the Fe K-edge EXAFS spectra of the samples prepared using different iron precursors.

Sample precursors	Site	B_{hf} (T)	Δ (mm/s)	δ (mm/s)	Area (%)
Fe(II)	Fe(III)	-	0.62(2)	0.33(1)	15(2)
	$Fe^{2.5+}$ sextet	40(1)	0.00	0.88(2)	20(2)
	Fe(III) distr.	30-48	0.00	0.35(2)	65(3)
Fe(II):Fe(III)	Fe(III) T_d	-	0.48(5)	0.25(1)	16(2)
	Fe(III) O_h	-	0.65(4)	0.33(2)	15(3)
	Fe(III) distr.	30-48	0.00	0.33(1)	69(3)
Fe(III)	Fe(III)	-	0.68(1)	0.34(1)	100

Table S3. ^{57}Fe hyperfine parameters obtained by fitting the 57Fe Mössbauer spectra at room temperature of the samples prepared using different iron precursors.

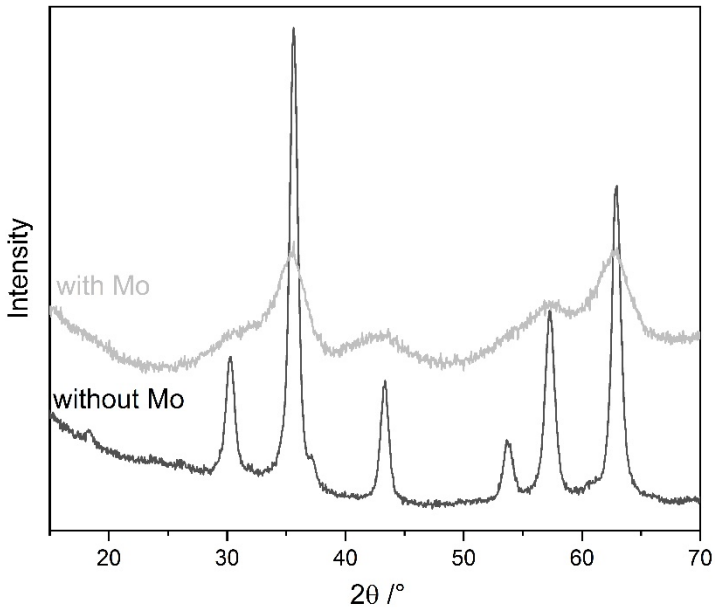

Figure S7. XRD patterns of the samples prepared with and without Mo. The samples were synthetized using an equimolar ratio of Fe(II) and Fe(III).