Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Mechanisms of CO Oxidation on High Entropy Spinels

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Multiplet Calculations

Multiplet calculations were performed by means of the CT4XAS code [45]:

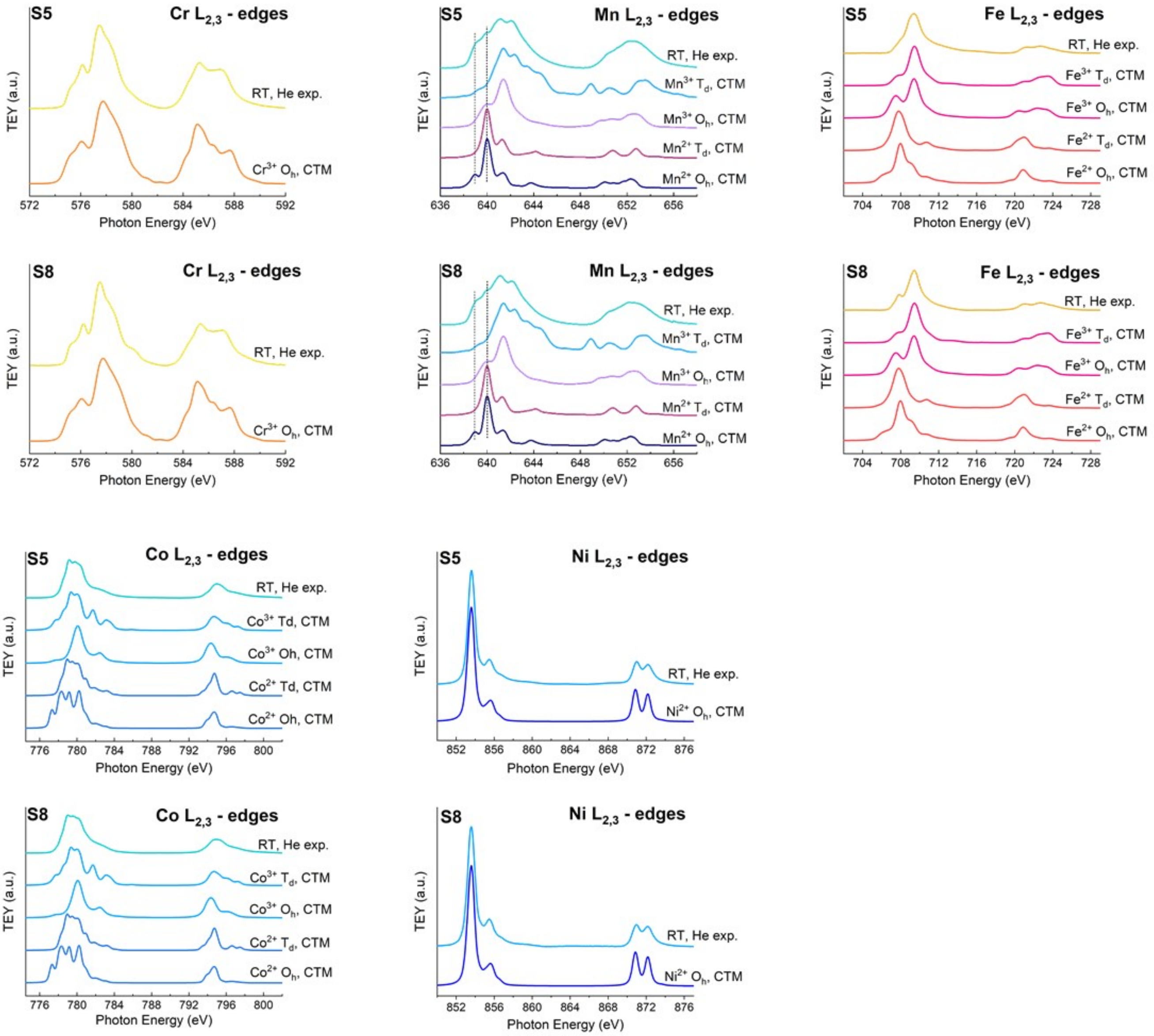

Fig. S1 $L_{2,3}$-edges XAS spectra for the S5 and S8 spinels at the different transition metals edges, along with simulated spectra using multiplet calculations. The parameters for the multiplet calculations are reported in the tables below, according to the pertinent literature in reference. For the Mn $L_{2,3}$-edges, the energies of the peaks mainly due to Mn^{2+}, whose intensity is changed during the course of the reaction, are evidenced with vertical dotted lines. Oxidation states and local symmetries are chosen according to the results of the analysis of the K-edges spectra shown in Fig. 1.

The $L_{2,3}$-edge X-ray absorption spectrum of 3*d* elements is dominated by dipole allowed electron excitations from the 2*p* core states to the 3*d* valence states. In compounds of these elements, the 3*d* states can be treated as nearly atomic levels. Thus, the near edge spectrum can be calculated simply by calculating all the probabilities of the transitions from the $3d^{n}$ initial state to the $2p^{5}3d^{n+1}$ final state ($3d^{n} \rightarrow 2p^{5}3d^{n+1}$). The calculations can be thought as performed in two steps. First, only the interactions within the absorbing atom are considered: the hole in the 2*p* states and the extra electron in the 3*d* state are strongly interacting, and this gives rise to a large number of final states (multiplets). Due to the very small core hole broadening at the 3d element $L_{2,3}$-edges, all these states are usually seen in the spectra. Then, the effect of neighboring atoms is introduced as a perturbation, including crystal field and charge transfer effect.

The CTM4XAS program requires the following sets of parameters for the calculations: a) the electronic configuration of the 3*d* metal ion (number of 3*d* electrons in the initial state); b) all the crystal field parameters (*i.e.* 10Dq for octahedral symmetry, and the additional parameters Dt and Ds for lower symmetries); c) charge transfer parameters, accounting for possible covalence of the metal-ligand bonds; d) Slater integrals reduction parameters, which account for all the electron interactions (*i.e.* 3d electrons with each other, core state with valence state, etc.).

The program is semi-empirical: this means that parameters b-c are usually adjusted until a good correspondence between experiment and theory is obtained: in the present case, literature values, as taken from the references below, have been used.

Tab. S1: Cr L edge – CTM calculation [S1]

parameters	Cr^{3+} O_h
ionic crystal field (eV)	
10Dq	2.5
Dt	0
Ds	0
Slater's integrals reduction (%)	
F_{dd}	1.0
F_{pd}	1.0
G_{pd}	1.0
charge transfer (eV)	
Δ	1
U_{dd}	0
U_{pd}	1.1
$T_{(eg)}$	0.5
$T_{(t2g)}$	0

Tab. S2: Mn L edge – CTM calculations [S2-S4]

parameters	Mn^{3+} O_h	Mn^{2+} O_h	$Mn^{2+}T_d$
ionic crystal field (eV)			
10Dq	1.8	1.4	-0.6
Dt	0.06	0.075	0
Ds	0.02	0	0
Slater's integrals reduction (%)			
F_{dd}	1.0	1.0	1.1
F_{pd}	1.0	1.3	1.5
G_{pd}	0.8	1.0	1.3
charge transfer (eV)			
Δ	0.5	/	/
U_{dd}	0		
U_{pd}	0		
$T_{(eg)}$	1		
$T_{(t2g)}$	0		

Tab. S3: Fe L edge – CTM calculations [S5-S7]

parameters	**Fe^{3+} O$_h$**	**Fe^{3+} T$_d$**	**Fe^{2+} O$_h$**	**Fe^{2+}T$_d$**
ionic crystal field (eV)				
10Dq	2	-1.4	1.4	-0.8
Dt	0	0	0.05	0
Ds	0.02	0.01	0.1	0.2
Slater's integrals reduction (%)				
F_{dd}	1.0	1.0	1.0	1.0
F_{pd}	1.0	1.2	1.2	1.0
G_{pd}	0.7	0.7	1.0	1.0

Tab. S4: Co L edge – CTM calculations [S8,S9]

parameters	**Co^{3+} O$_h$**	**Co^{3+} T$_d$**	**Co^{2+} O$_h$**	**Co^{2+}T$_d$**
ionic crystal field (eV)				
10Dq	2.6	-0.3	0.9	-0.6
Dt	0	0	0	0
Ds	0	0	0	0
Slater's integrals reduction (%)				
F_{dd}	1.0	0.4	1.0	1.0
F_{pd}	1.0	0.6	1.0	1.0
G_{pd}	1.0	1.1	1.0	1.0

Tab. S5: Ni L edge – CTM calculations [S10]

parameters	**Ni^{2+} O$_h$**
ionic crystal field (eV)	
10Dq	1.2
Dt	0
Ds	0.05
Slater's integrals reduction (%)	
F_{dd}	1.0
F_{pd}	1.0
G_{pd}	1.0

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