Supplementary information for

Structural dynamics of an iron molybdate catalyst under redox cycling conditions studied with *in situ* multi edge XAS and XRD

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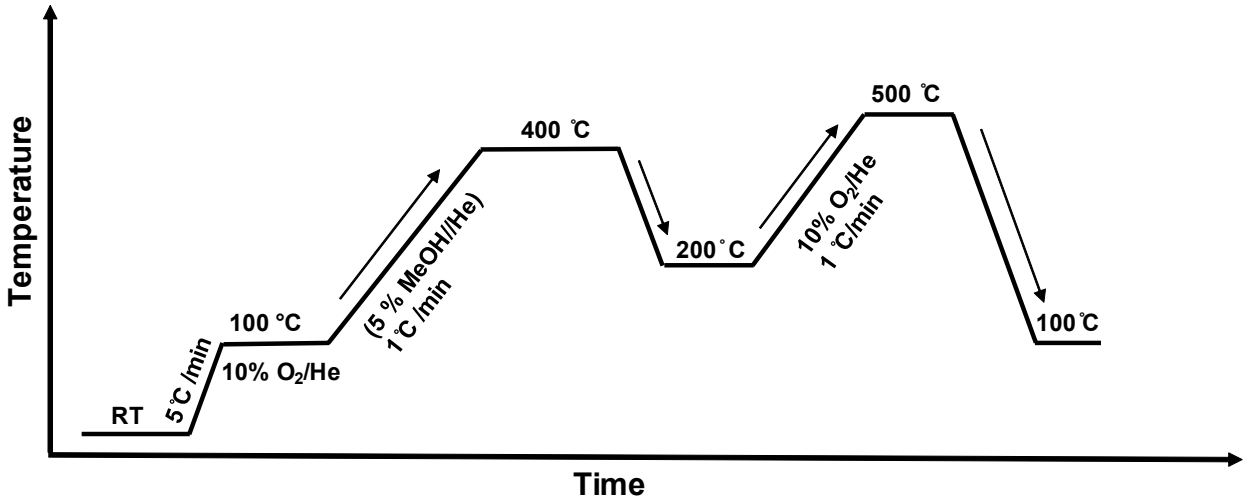

Figure S1. Overview of the experimental procedure followed during the *in situ* TPR/TPO experiment at the synchrotron.

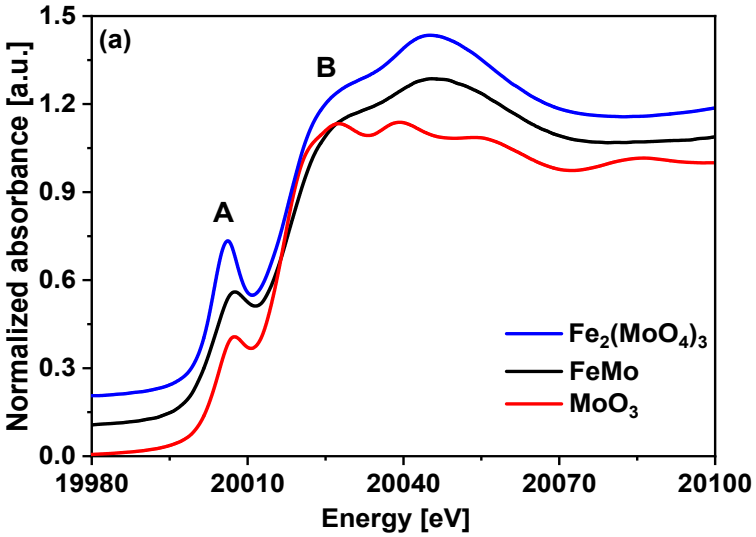

Figure S2. Normalized Mo K-edge XANES spectrum of the initial state of the FeMo catalyst measured at 100 °C in a flow of 10 % O2/He. XANES spectra of MoO3 and Fe2(MoO4)3 are shown for comparison.

Table S1: Structural parameters obtained from EXAFS fitting at Mo K-edge for initial state of the catalyst at 100 °C in 10 % O_2/He. $\Delta E_0 = 1.27$ and $\chi_v^2 = 31$.

Path	R [Å]	CN	σ^2 [Å^{-2}]	Corresponding to phase
Mo-O_1	1.76±0.01	5.0±0.4	0.0046±0.0006	$Fe_2(MoO_4)_3$ and MoO_3
Mo-O_2	2.04±0.06/2.36±0.06	1[a] /1[a]	0.0084±0.0051	MoO_3
Mo-Fe	3.50±0.02	1[a]	0.0064±0.0025	$Fe_2(MoO_4)_3$
Mo-Mo	3.73±0.03	1[a]	0.0064±0.0025	MoO_3

a – fixed during the fitting

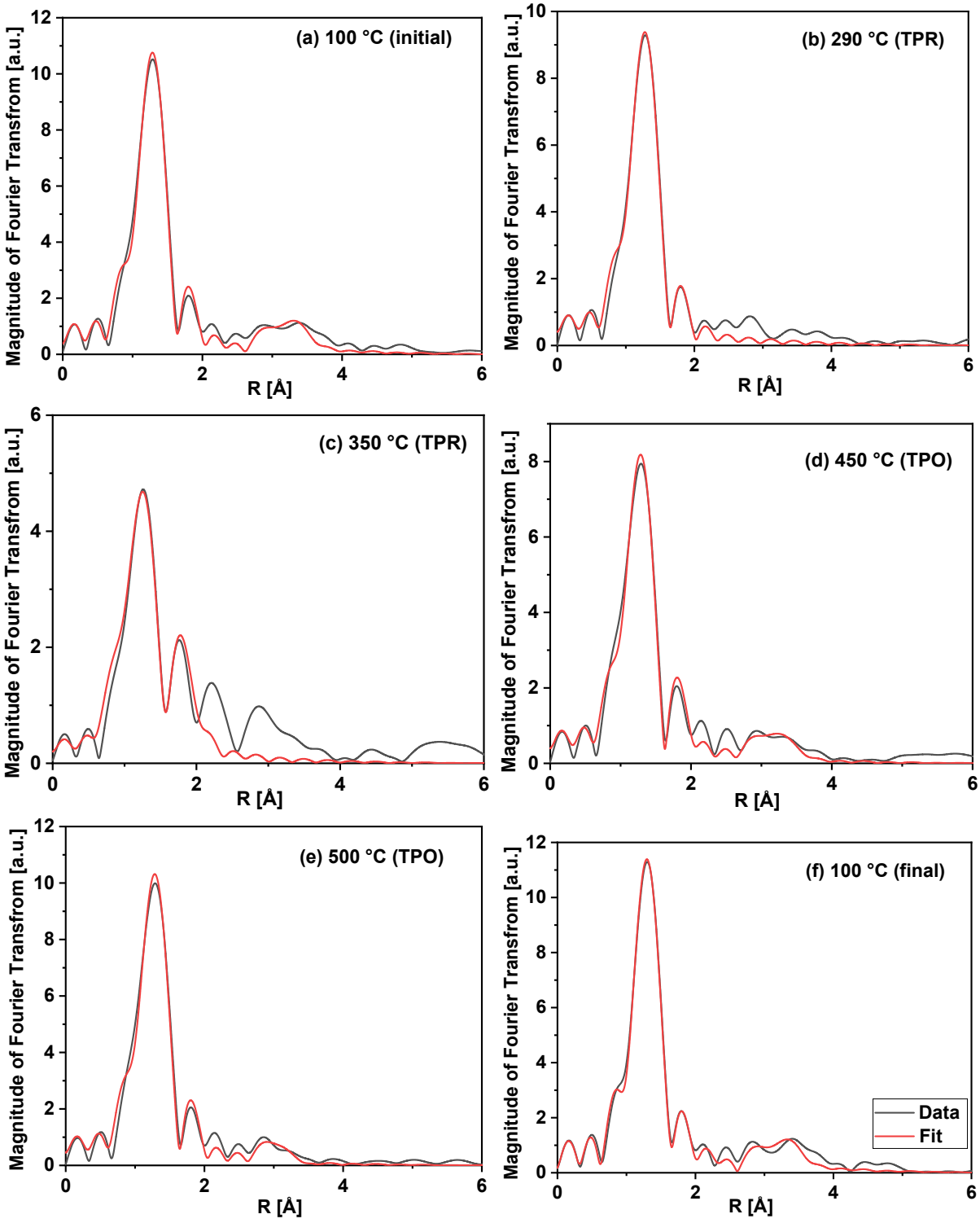

Figure S3: k^3-weighted Fourier transformed EXAFS spectra of the catalyst (FeMo) during different stages of redox cycling (black line) and the corresponding R-space fit (red line).

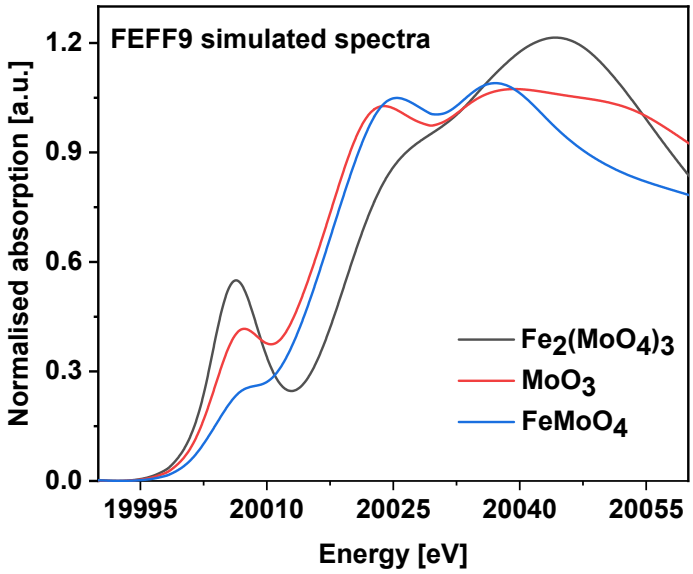

Figure S4. FEFF9 simulated XANES spectra for the Mo(VI) species.

Table S2. Structural parameters obtained from EXAFS fitting at Mo K-edge of the intermediate states of the catalyst for TPR and TPO. $\Delta E_0 = 2.3$ and $\chi_v^2 = 62$ for 290 °C (TPR), $\Delta E_0 = 4.1$ and $\chi_v^2 = 72$ for 350 °C (TPR), $\Delta E_0 = 1.9$ and $\chi_v^2 = 11$ for 450 °C (TPO).

	290 °C (TPR)			**350 °C (TPR)**			**450 °C (TPO)**		
Path	R [Å]	CN	σ^2[Å^{-2}]	R [Å]	CN	σ^2[Å^{-2}]	R [Å]	CN	σ^2[Å^{-2}]
Mo-O$_1$	1.76	4.5±0.7	0.0049	1.77	3.5±1.4	0.0084	1.77	4.4±0.3	0.0059
Mo-O$_2$	2.0/2.3	1/1	0.0138	2.0/2.3	1/1	0.0031	2.0/2.3	1/1	0.0057
Mo-Fe	3.5			3.5			3.5	1	0.0093
Mo-Mo	3.7			3.7			3.7	1	0.0093

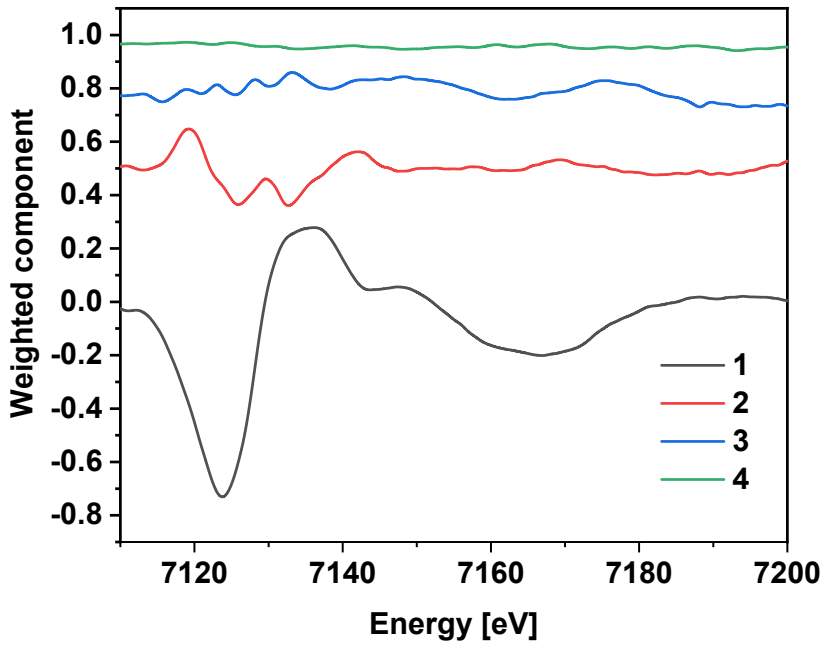

Figure S5. Components obtained from PCA weighted by eigen values for Fe K-edge XANES spectrum at 275 °C during TPR.

Table S3. Parameters of the components shown in Figure S4 obtained by PCA

Component	Eigenvalue	Variance	Cumulative variance
1	0.356124	0.071225	0.994501*
2	0.015736	0.003147	0.997648
3	0.011603	0.002321	0.999969
4	0.000156	0.000031	1.000000

*Variance from target spectrum is 0.923276

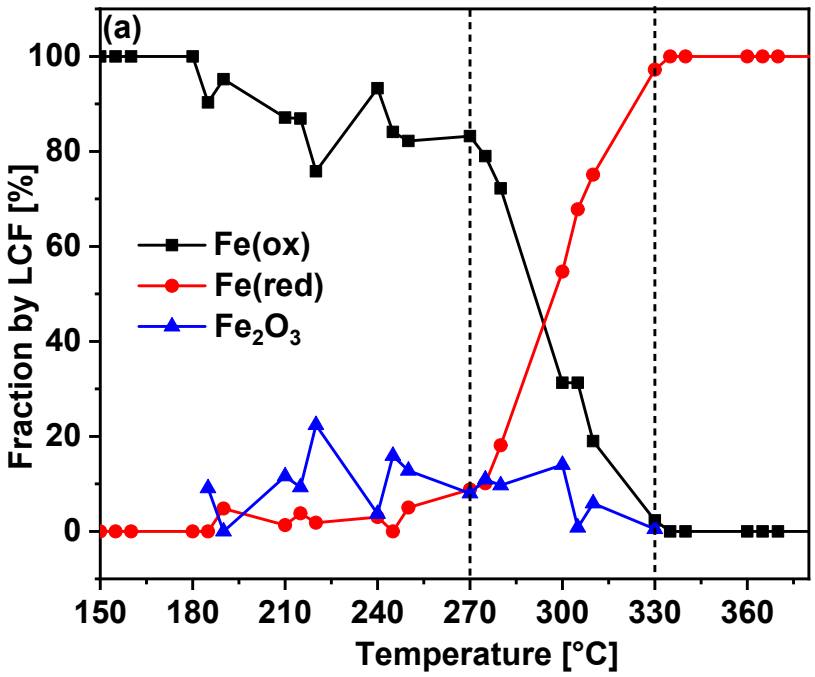

Figure S6. LCF results of Fe K-edge XANES spectra (shown in Figure 4(a)) for the catalyst during TPR under 5 % MeOH/He. Fe(ox) is the initial phase of the catalyst and Fe(red) is the final phase after TPR. Dashed lines indicate the temperatures corresponding to start and end of Fe reduction process.

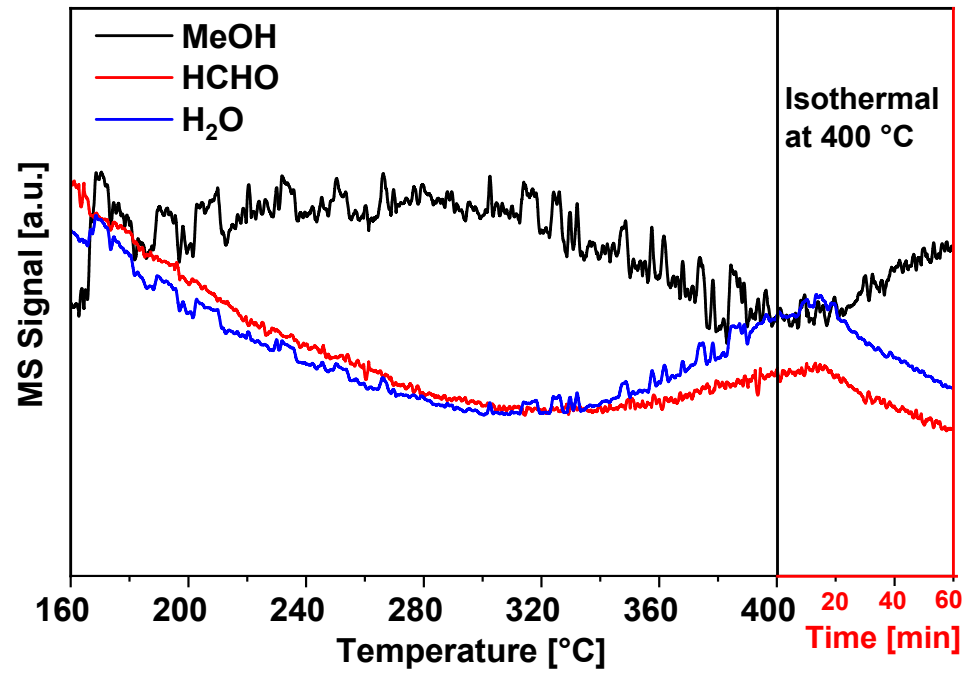

Figure S7. MS traces for heating (160 to 400 °C at 1 °C/min) under reducing conditions of 5% MeOH/He. *m*/*z* = 18 is water, *m*/*z* = 29 is formaldehyde HCHO (corrected for contribution from MeOH) and *m*/*z* = 31 is MeOH. The extended X-axis (in red) shows the isothermal period at 400 °C for the next 60 minutes.

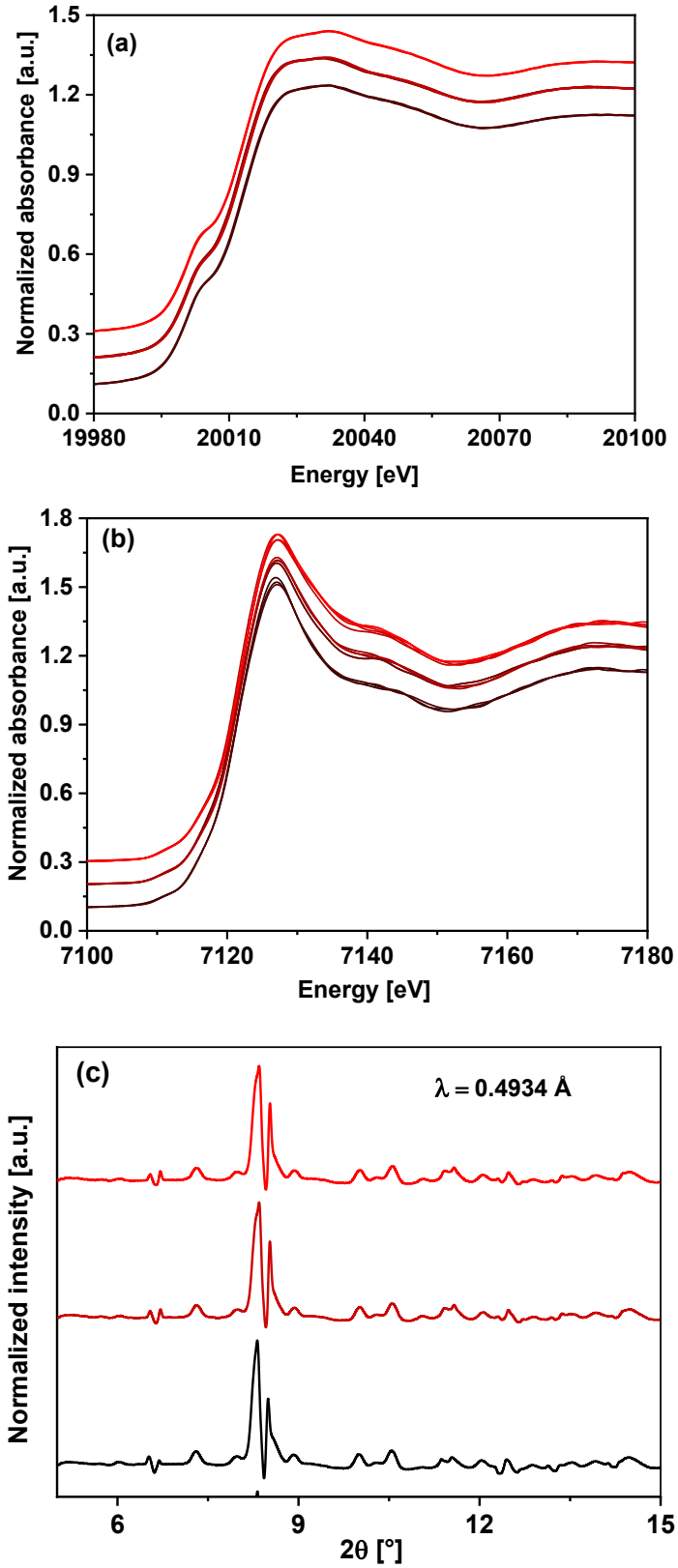

Figure S8. *In situ* (a) Mo K-edge XANES, (b) Fe K-edge XANES and (c) XRD at isothermal conditions at 400 °C in 5 % MeOH/He (black) after TPR, cooling down to 200 °C in 5 % MeOH/He (brown) and finally after change to 10 % O_2/He at 200 °C(red).

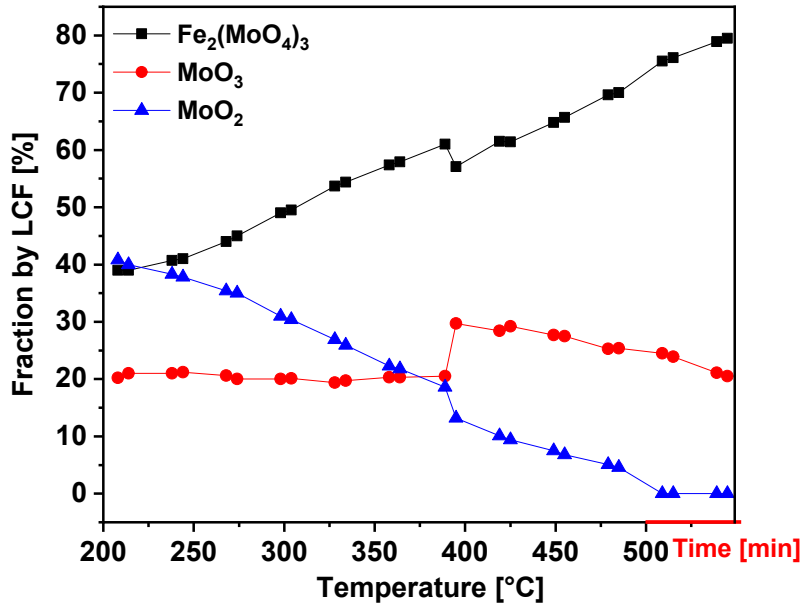

Figure S9. Complete LCF results at Mo K-edge for the catalyst during heating (1 °C/min) under 10 % O_2/He. (TPO).

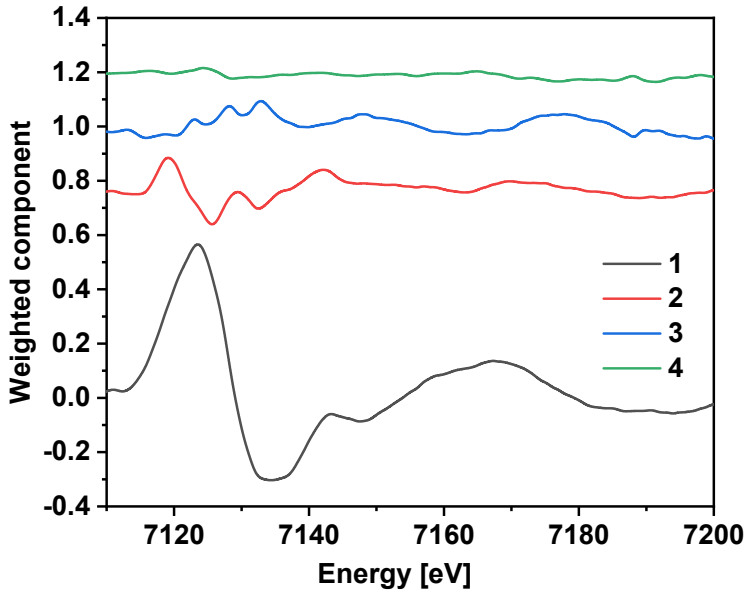

Figure S10. Components obtained from PCA weighted by eigen values for Fe K-edge XANES spectrum at 380 °C during TPR.

Table S4. Parameters of the components shown in figure S7 obtained by PCA

Component	Eigenvalue	Variance	Cumulative variance
1	0.197850	0.039570	0.996829 *
2	0.009847	0.001969	0.998798
3	0.005382	0.001076	0.999875
4	0.000627	0.000125	1.000000

*Variance from target spectrum is 0.957259