Supporting information

Hydrodeoxygenation of furfural to 2-methylfuran using supported molybdenum carbides: Study of the support effect

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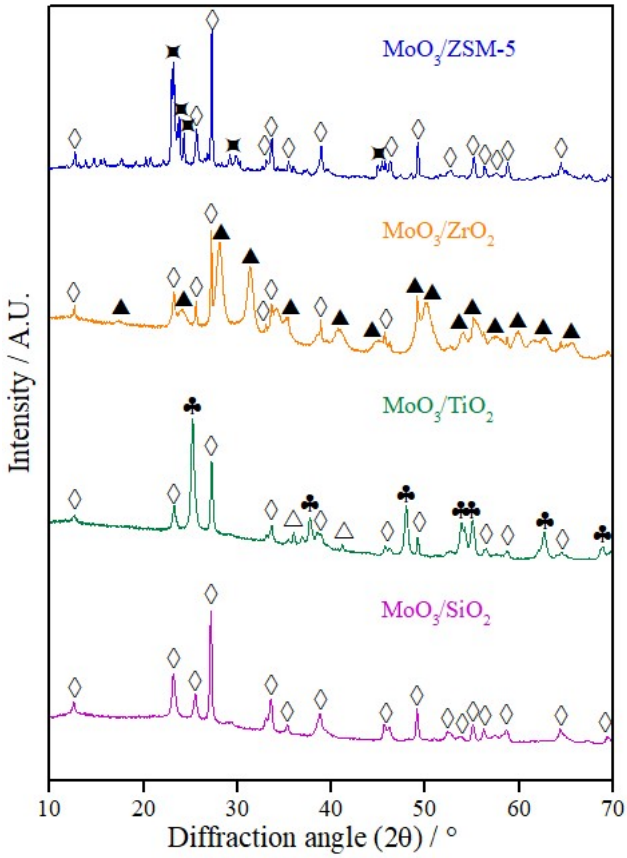


Figure S1. Diffractograms of the calcined precursors of Mo carbides supported on different materials. ◊ MoO_3, ⬀ ZSM-5, ▲ m-ZrO_2, ♣ a-TiO_2, ❒ r-TiO_2

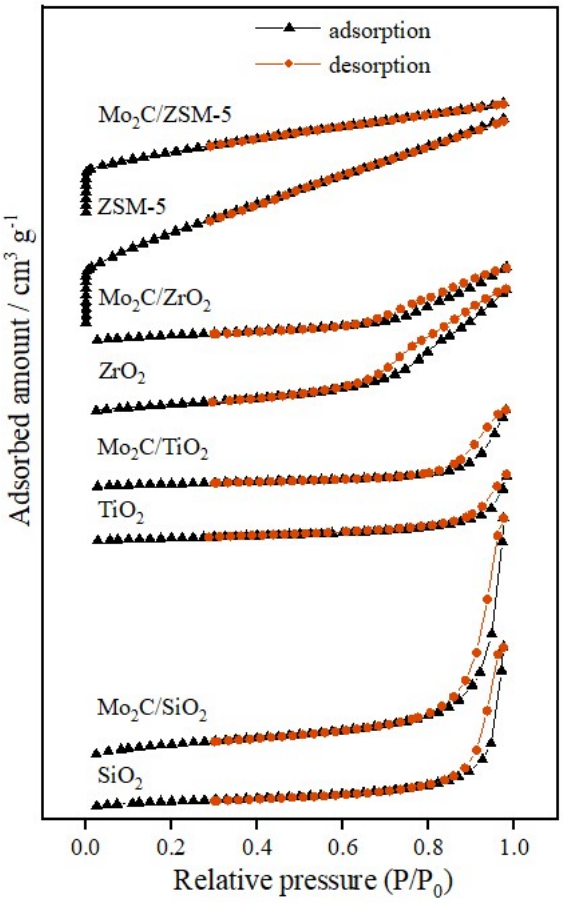


Figure S2. N_2 adsorption-desorption isotherms of the passivated Mo carbides and respective supports.

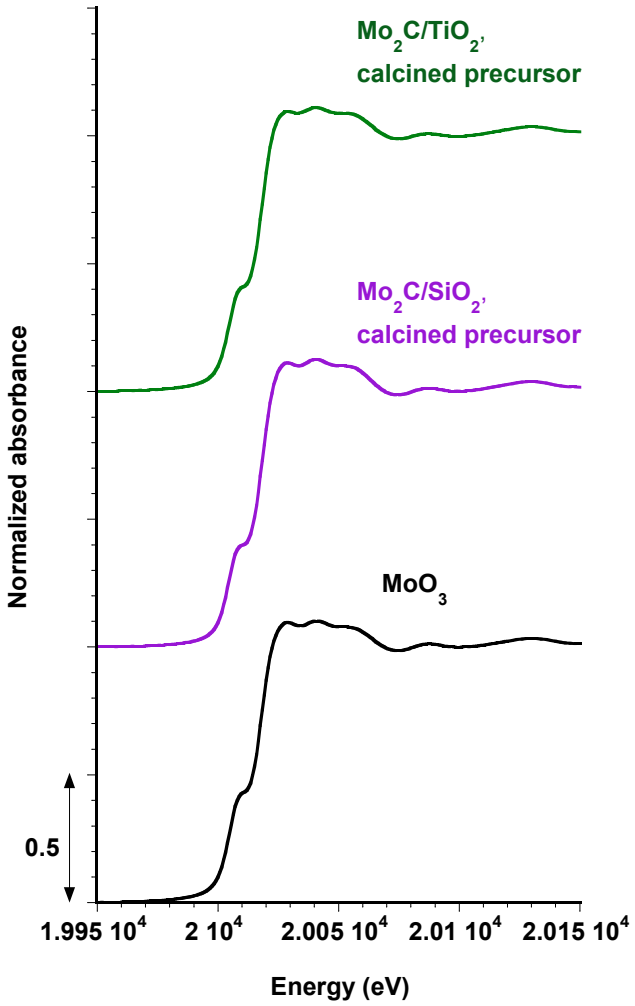


Figure S3. XANES spectra recorded at the Mo K-edge for the calcined precursors of Mo_2C/SiO_2 and Mo_2C/TiO_2. Comparison with reference MoO_3.

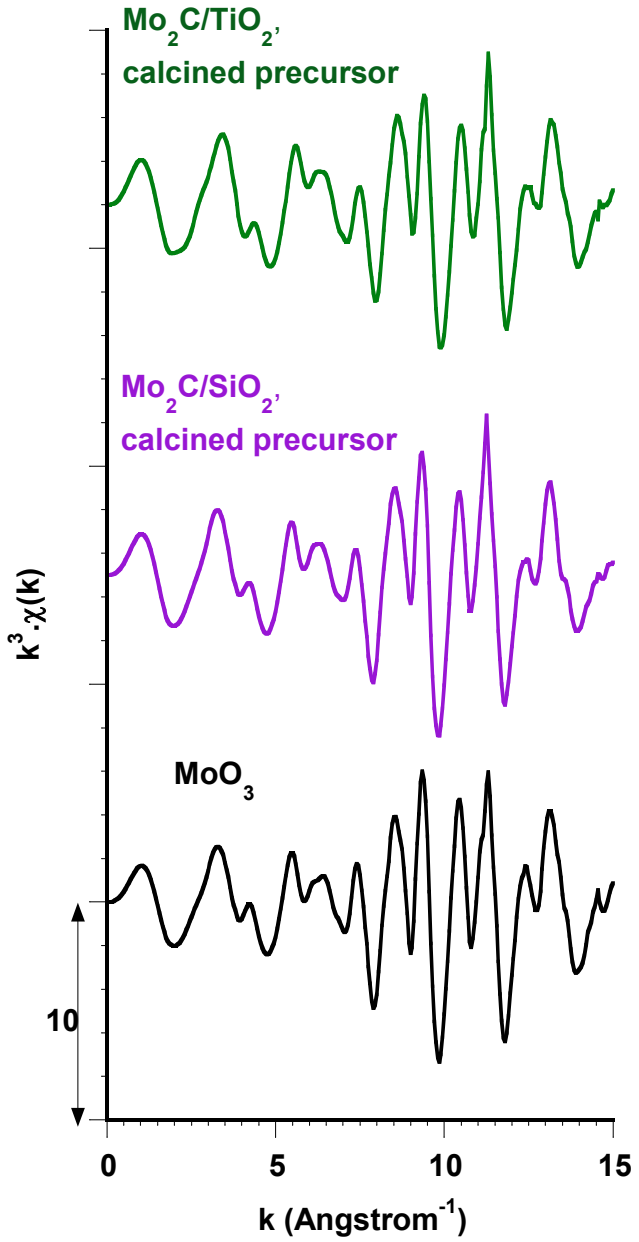


Figure S4. EXAFS signals recorded at the Mo K-edge for the calcined precursors of Mo_2C/SiO_2 and Mo_2C/TiO_2. Comparison with reference MoO_3.

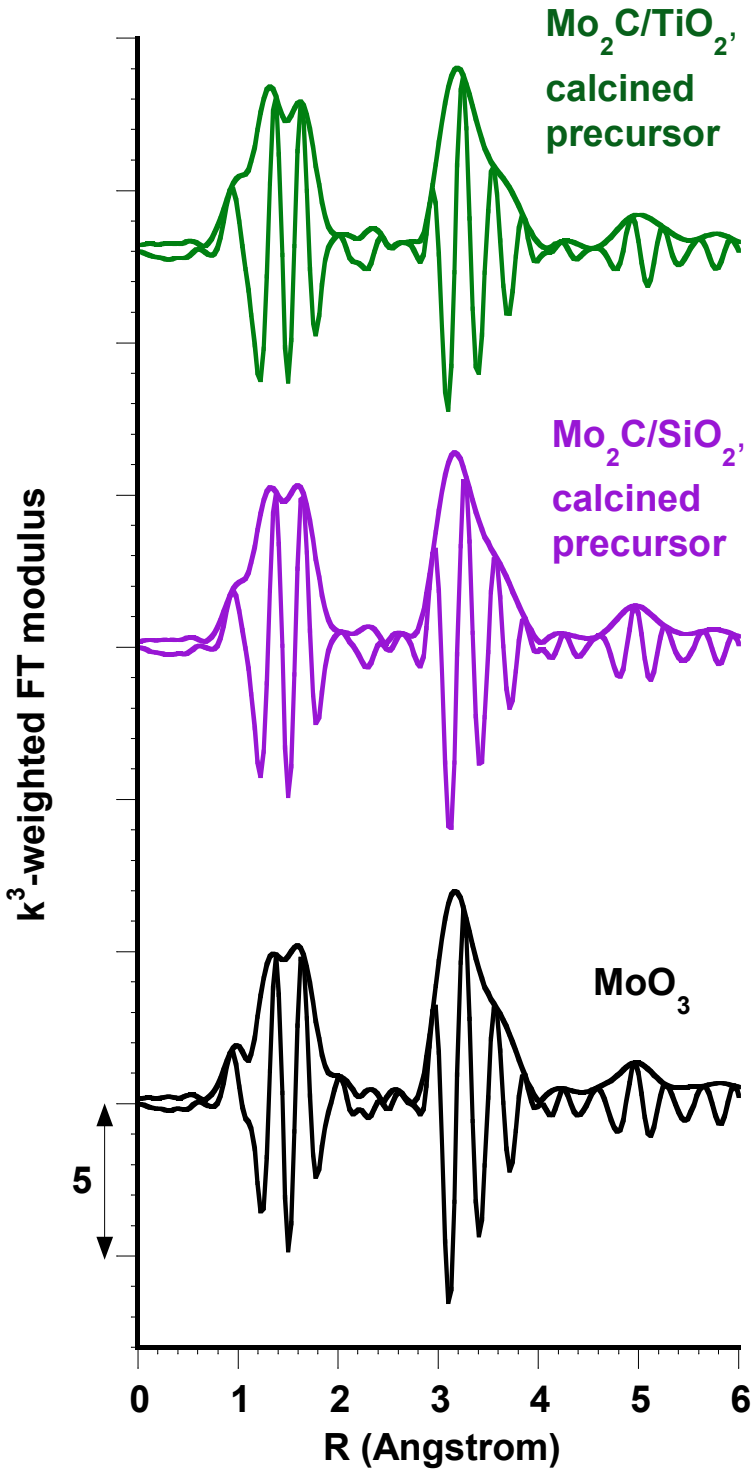


Figure S5. Fourier transforms of the EXAFS signals recorded at the Mo K-edge for the calcined precursors of Mo_2C/SiO_2 and Mo_2C/TiO_2 (k = 3.5 - 15 $Å^{-1}$). Comparison with reference MoO_3.

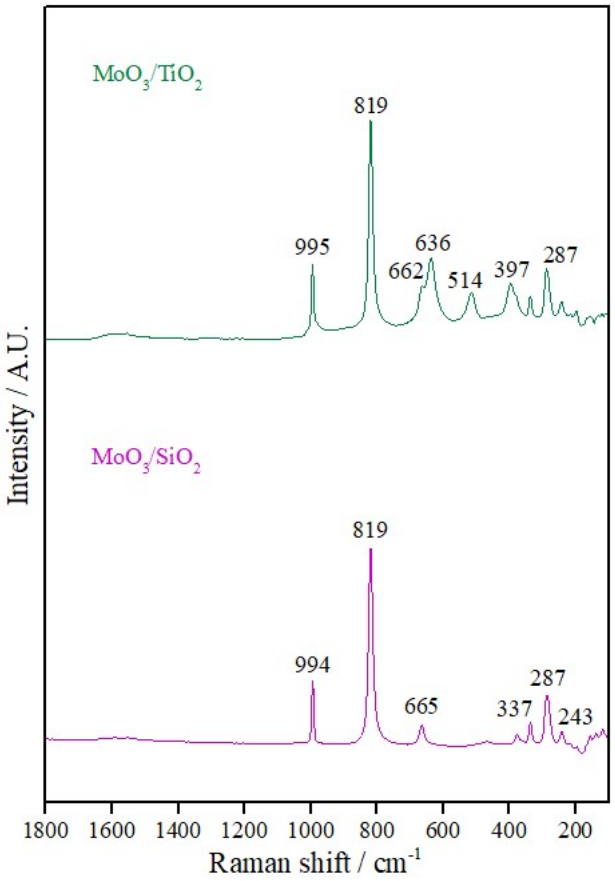


Figure S6. Raman spectra of the calcined precursors of Mo_2C/SiO_2 and Mo_2C/TiO_2 (recorded at room temperature).

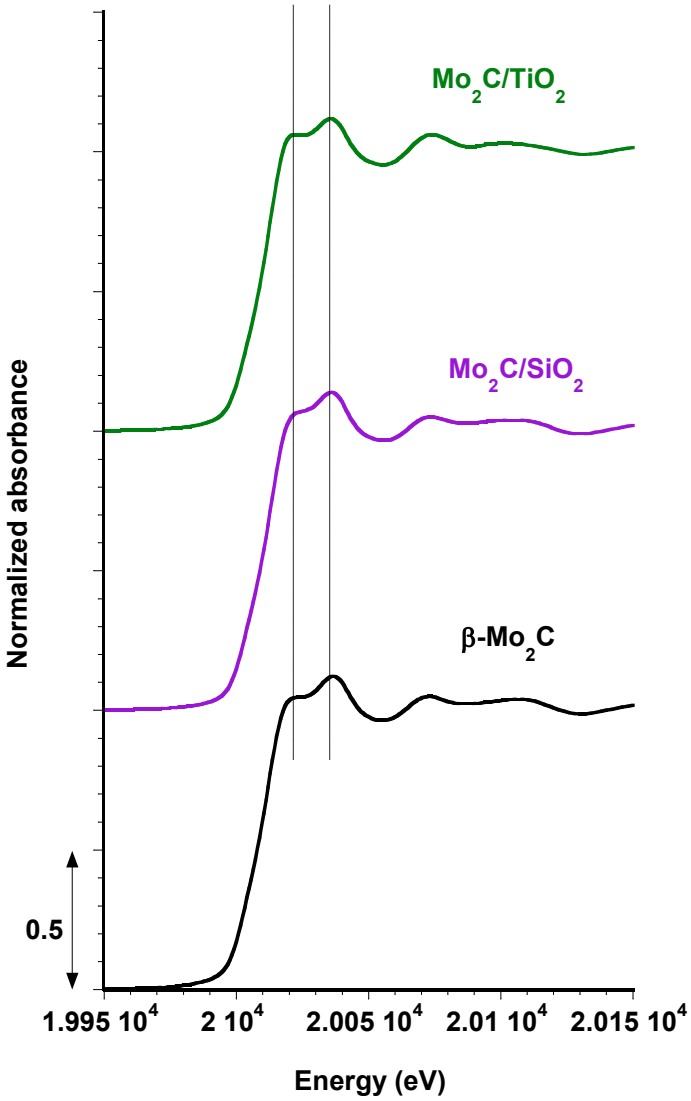


Figure S7. XANES spectra recorded at the Mo K-edge for carburized Mo_2C/SiO_2 and Mo_2C/TiO_2 (spectra recorded at room temperature).

Comparison with reference β-Mo_2C.

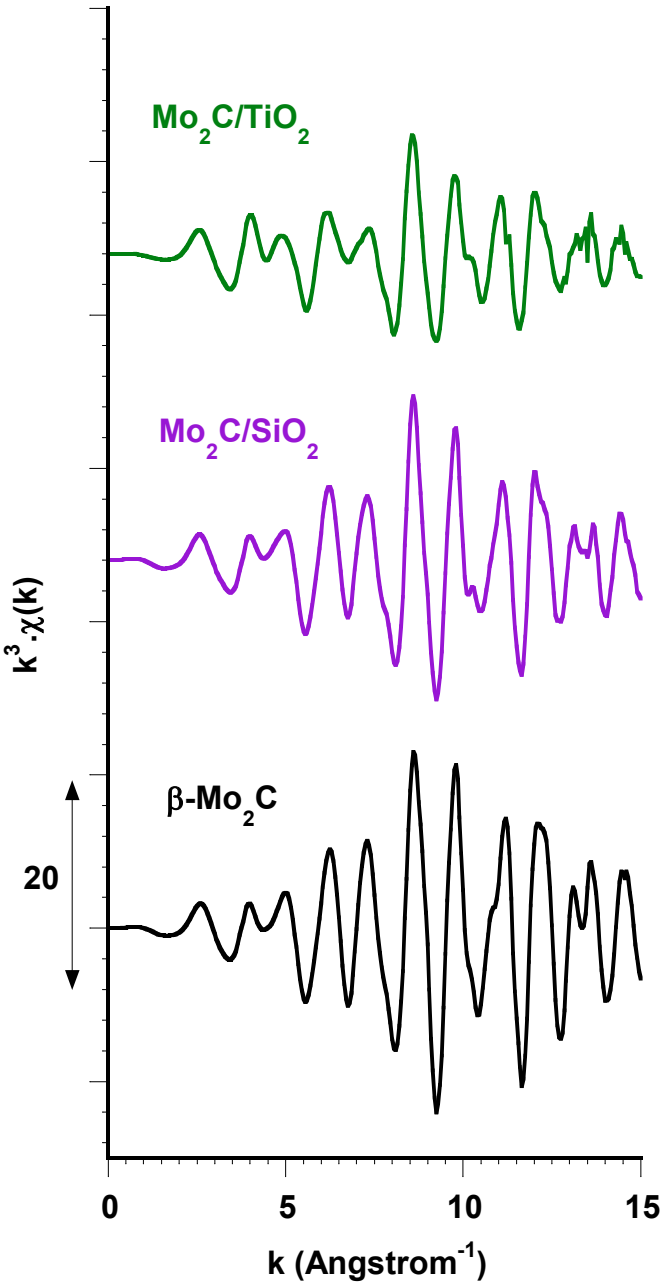


Figure S8. EXAFS signals recorded at the Mo K-edge for carburized Mo_2C/SiO_2 and Mo_2C/TiO_2 (spectra recorded at room temperature).

Comparison with reference β-Mo_2C.

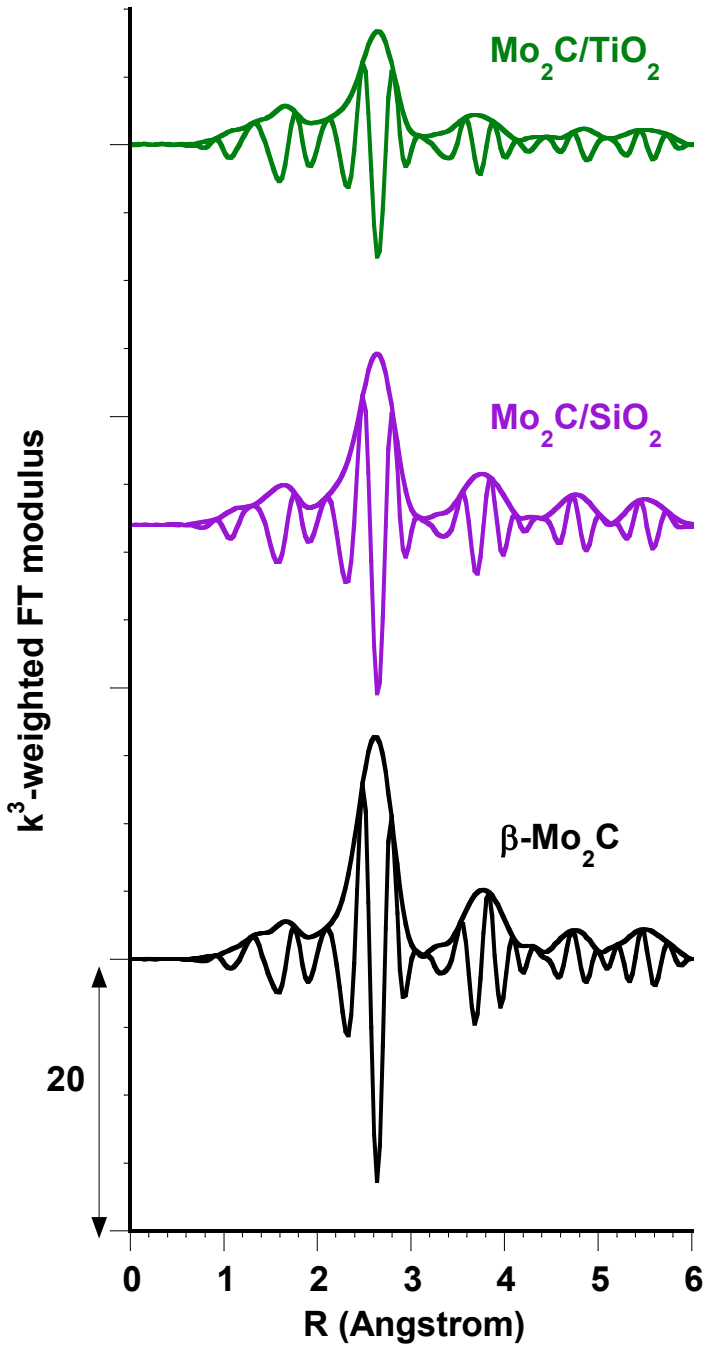


Figure S9. Fourier transforms of the EXAFS signals recorded at the Mo K-edge for carburized Mo_2C/SiO_2 and Mo_2C/TiO_2 (spectra recorded at room temperature, k = 3.5 - 15 $Å^{-1}$). Comparison with reference β-Mo_2C.

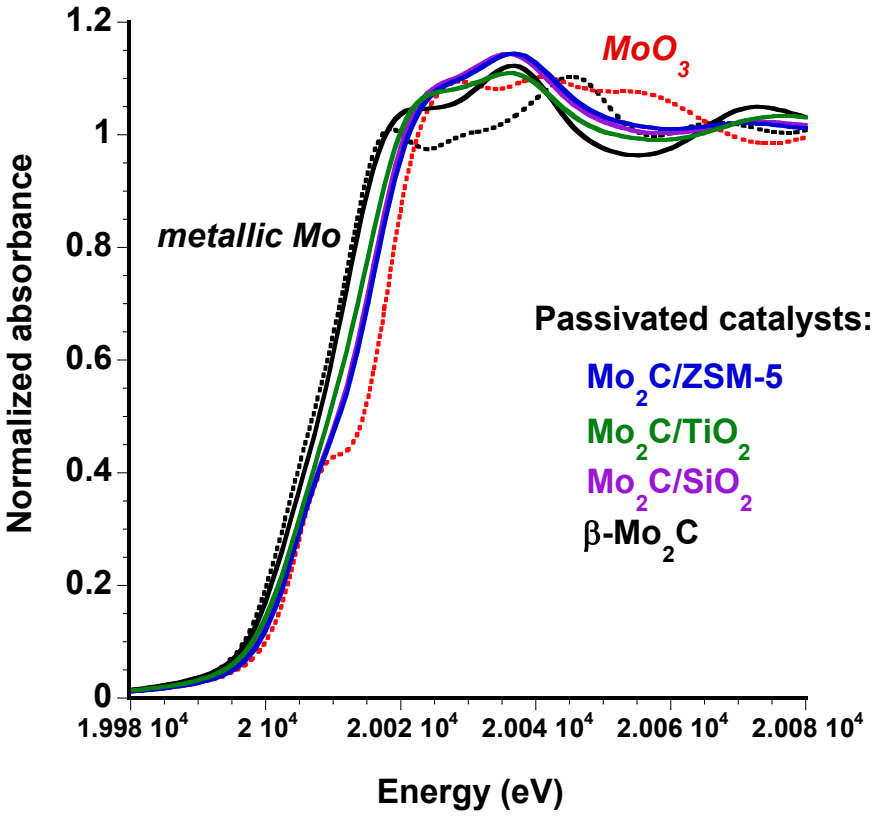


Figure S10. XANES spectra recorded at the Mo K-edge for passivated β-Mo_2C, Mo_2C/SiO_2, Mo_2C/TiO_2, and Mo_2C/ZSM-5 (spectra recorded at room temperature). Comparison with references MoO_3 and metallic Mo (dotted lines).

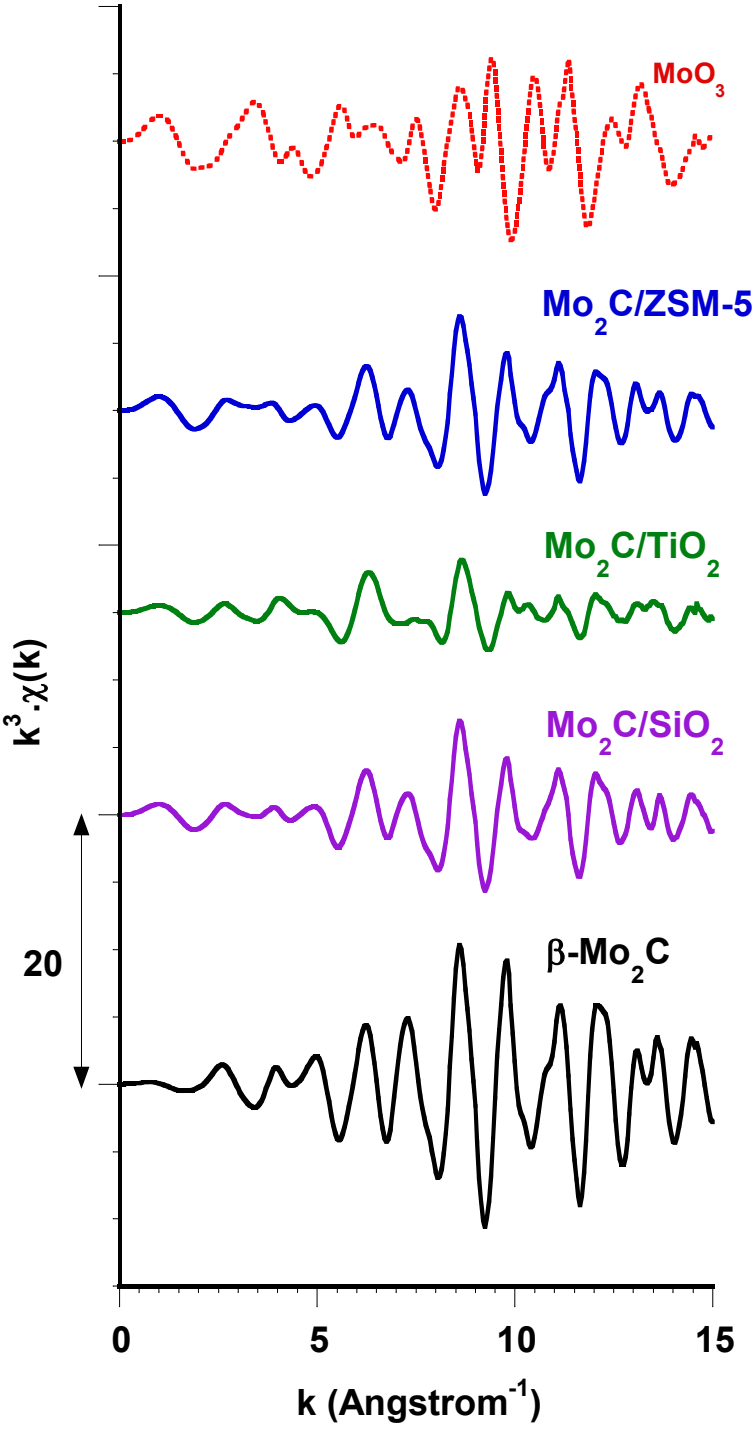


Figure S11. EXAFS signals recorded at the Mo K-edge for passivated β-Mo_2C, Mo_2C/SiO_2, Mo_2C/TiO_2, and Mo_2C/ZSM-5 (spectra recorded at room temperature). Comparison with reference MoO_3.

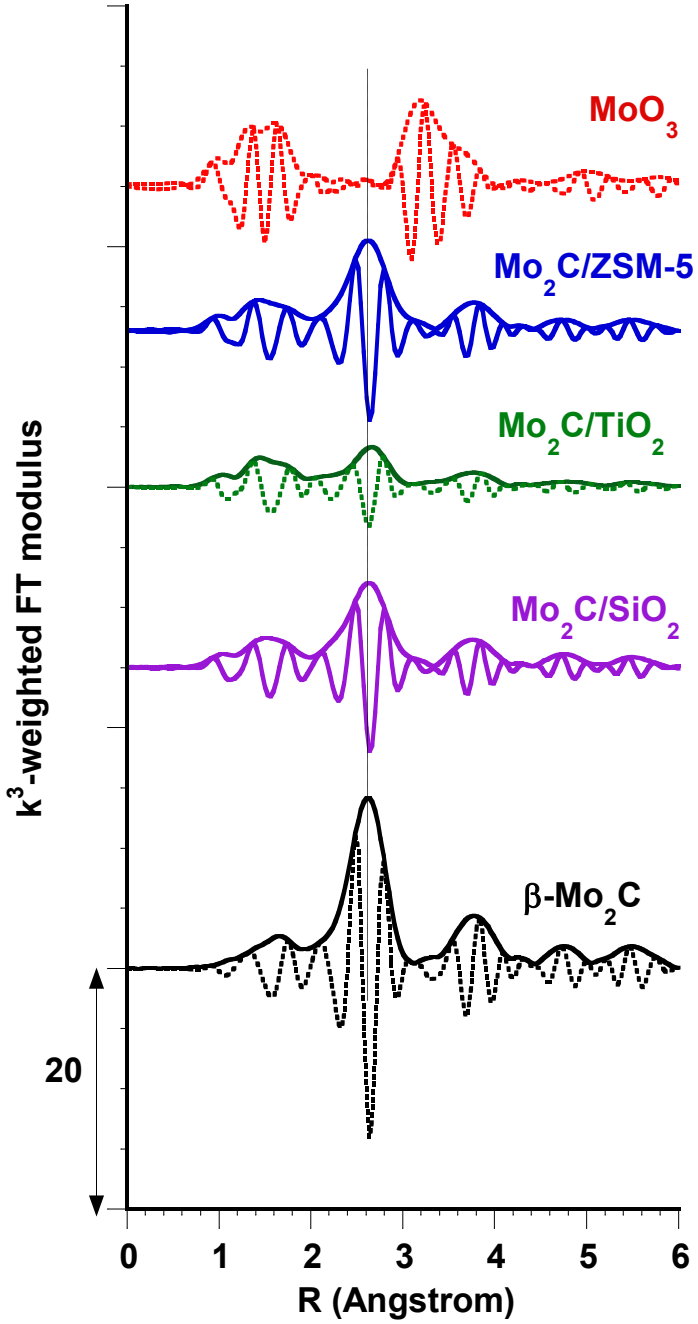


Figure S12. Fourier transforms of the EXAFS signals recorded at the Mo K-edge for passivated β-Mo_2C, Mo_2C/SiO_2, Mo_2C/TiO_2, and Mo_2C/ZSM-5 (spectra recorded at room temperature). Comparison with reference MoO_3.

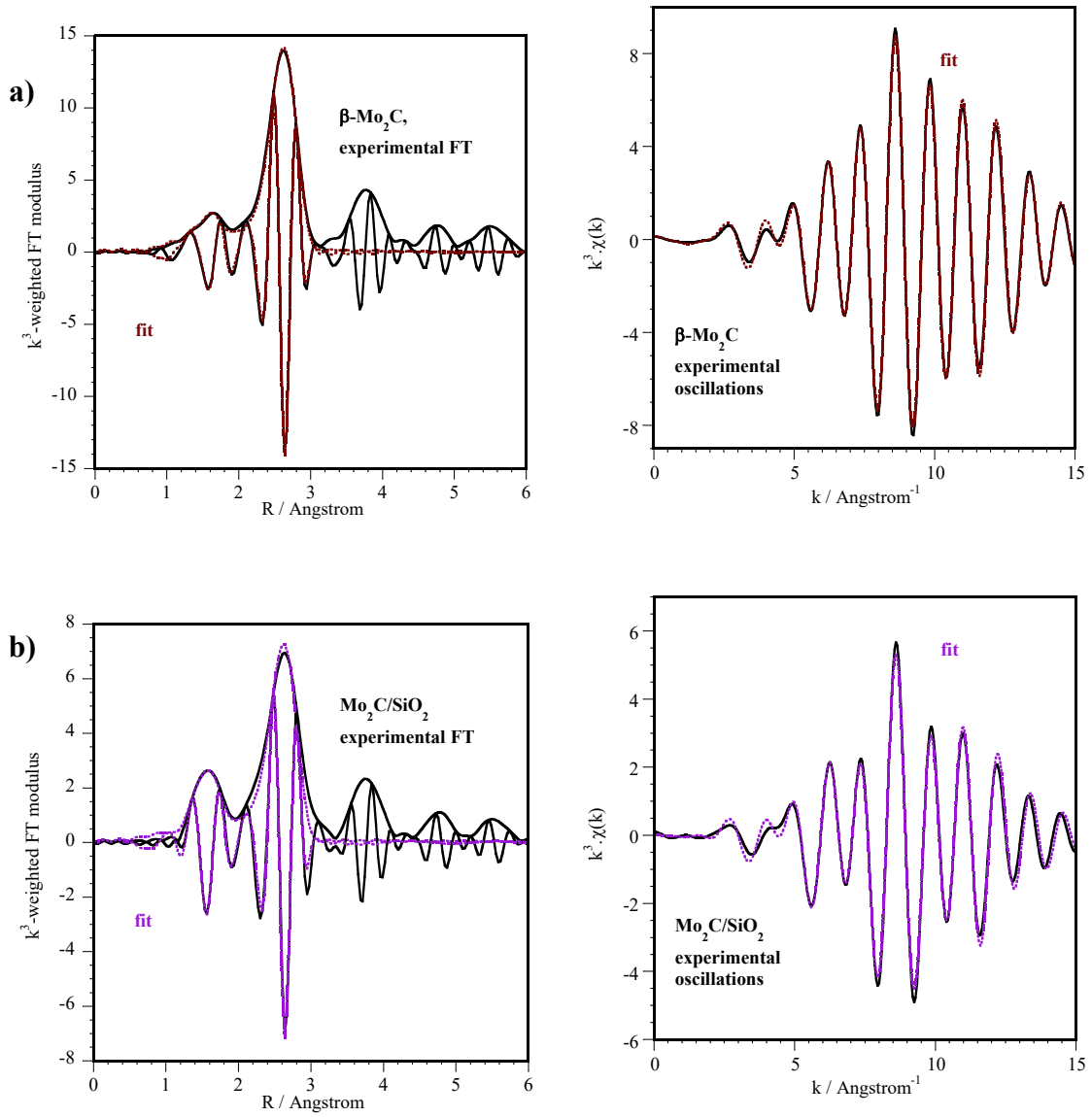
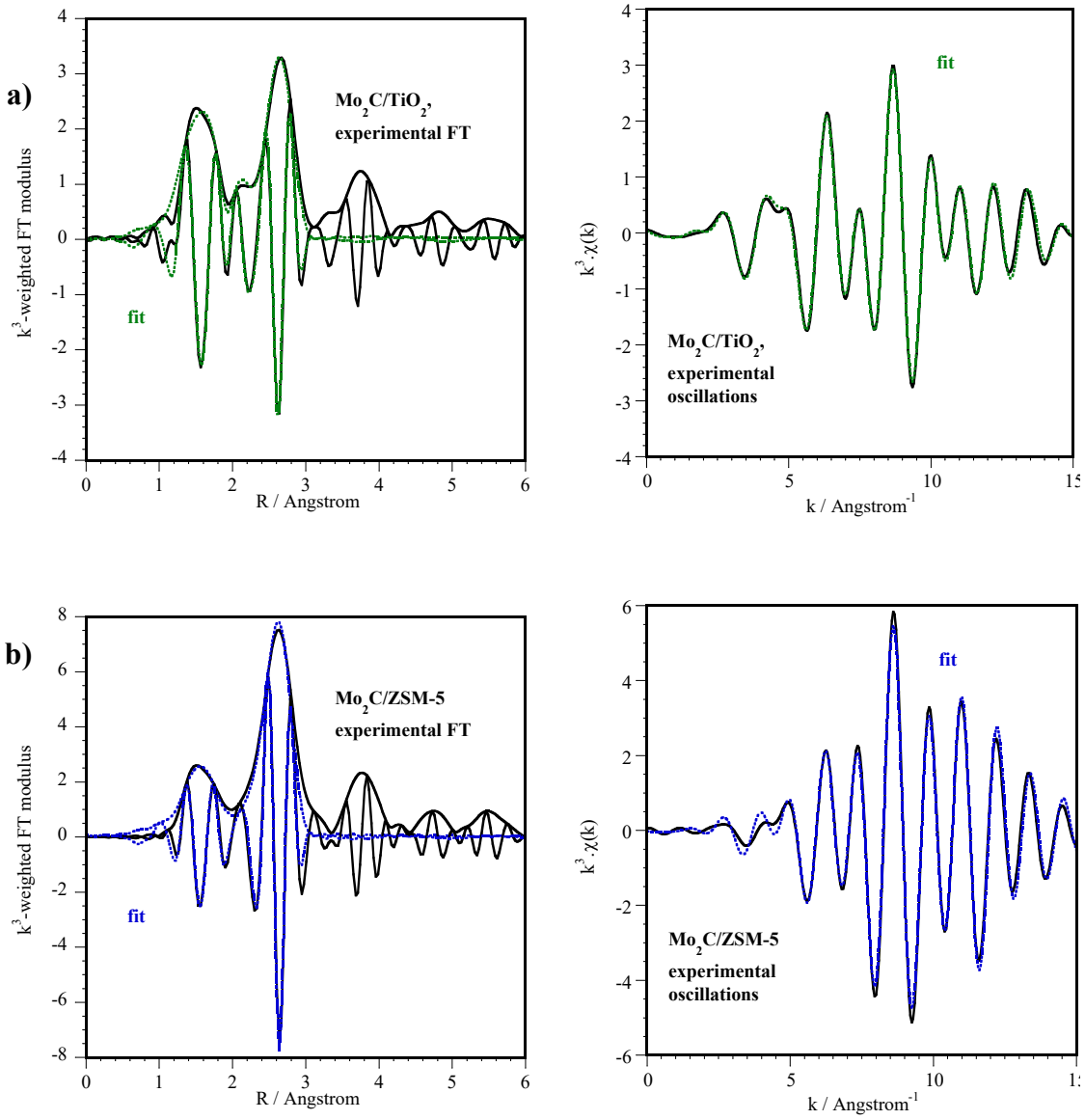


Figure S13. Analysis of the data recorded at the Mo K-edge for the passivated catalysts (spectra recorded at room temperature), using linear combinations of MCR-ALS components (see Table S1). XANES spectrum (left) and EXAFS oscillations (right), a) β-Mo_2C and b) Mo_2C/SiO_2.



Continuation of Figure S13. Analysis of the data recorded at the Mo K-edge for the passivated catalysts (spectra recorded at room temperature), using linear combinations of MCR-ALS components (see Table S1). XANES spectrum (left) and EXAFS oscillations (right), Mo_2C/TiO_2, and b) Mo_2C/ZSM-5.

Table S1. Fitted parameters at the Mo K-edge (E_0 = 20013 eV, S_0^2 = 0.98) determined from the EXAFS analysis of spectra recorded at room temperature on catalysts after passivation. k = 3.5 - 15 $Å^{-1}$. Fit of the first peak(s) from the Fourier transform between 1 and 3 Å.

Catalyst	Backscatter	N	σ^2 (Å²) x 10^3	R (Å)
β-Mo_2C	C	2.9 ± 0.9	5 ± 3	2.09 ± 0.02
	Mo	6.8 ± 0.8	6.4 ± 0.6	2.971 ± 0.005
	ΔE_0 = -4.9 eV, r-factor = 0.01493, χ^2 = 646, N_{ind} = 13, N_{var} = 7			
Mo_2C/SiO_2	O	0.9 ± 0.9	7 ± 5	1.71 ± 0.04
	C	4 ± 3	7 ± 5	2.08 ± 0.02
	Mo	4 ± 1	7 ± 2	2.97 ± 0.01
	ΔE_0 = -5.2 eV, r-factor = 0.03112, χ^2 = 1745, N_{ind} = 13, N_{var} = 9			
Mo_2C/TiO_2	O	0.8 ± 0.4	8 ± 2	1.69 ± 0.03
	C	3.7 ± 0.7	8 ± 2	2.13 ± 0.02
	Mo	0.4 ± 0.2	8 ± 2	2.52 ± 0.03
	Mo	2.1 ± 0.5	8 ± 2	2.97 ± 0.01
	ΔE_0 = -0.4 eV, r-factor = 0.01268, χ^2 = 708, N_{ind} = 13, N_{var} = 10			
Mo_2C/ZSM-5	O	0.9 ± 0.9	6 ± 4	1.71 ± 0.03
	C	3 ± 2	6 ± 4	2.10 ± 0.02
	Mo	3.9 ± 0.9	7 ± 1	2.969 ± 0.009
	ΔE_0 = -5.3 eV, r-factor = 0.02999, χ^2 = 1515, N_{ind} = 13, N_{var} = 9			

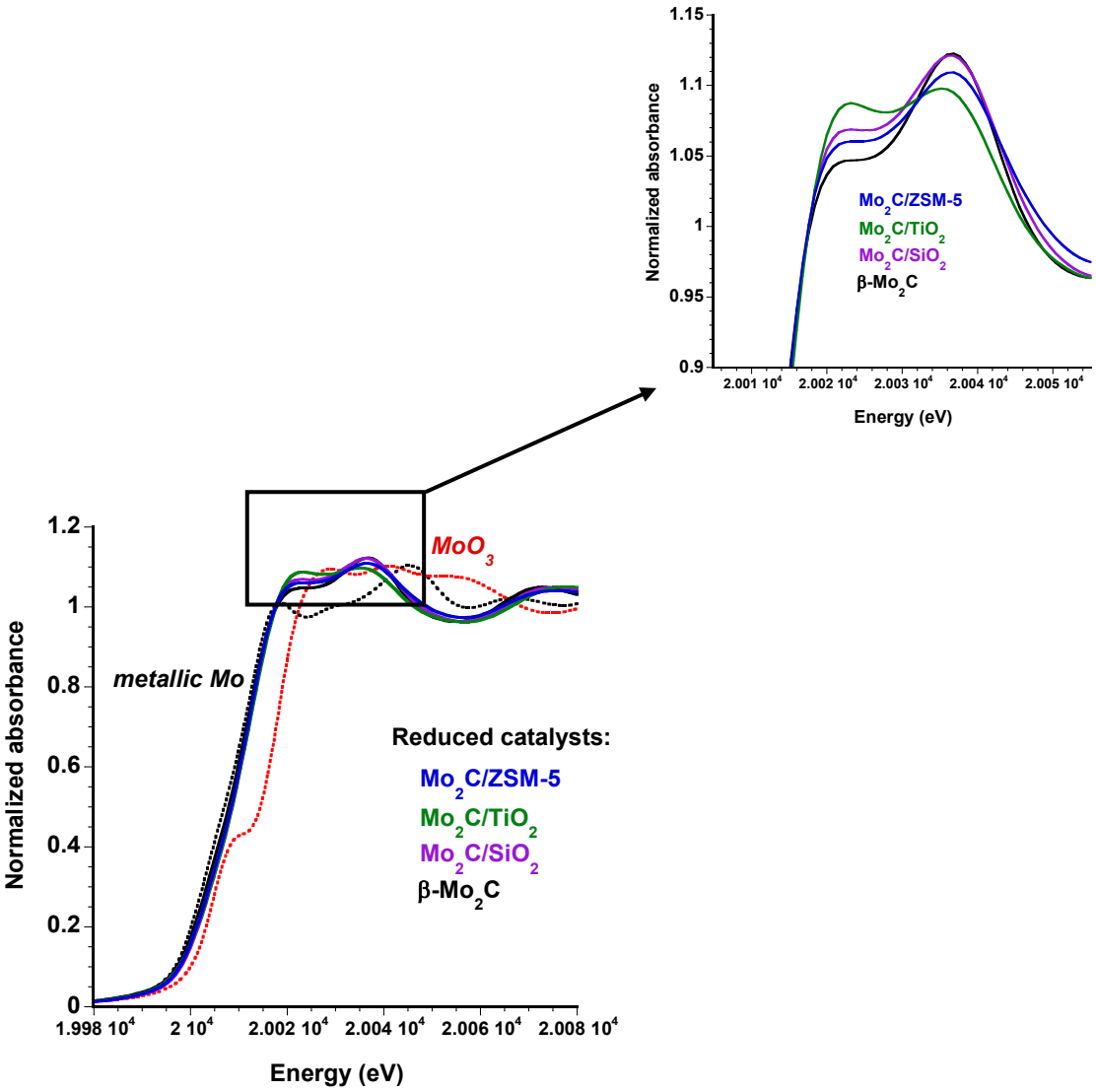


Figure S14. XANES spectra recorded at the Mo K-edge for reduced β-Mo_2C, Mo_2C/SiO_2, Mo_2C/TiO_2, and Mo_2C/ZSM-5 (spectra recorded at room temperature). Comparison with references MoO_3 and metallic Mo (dotted lines).

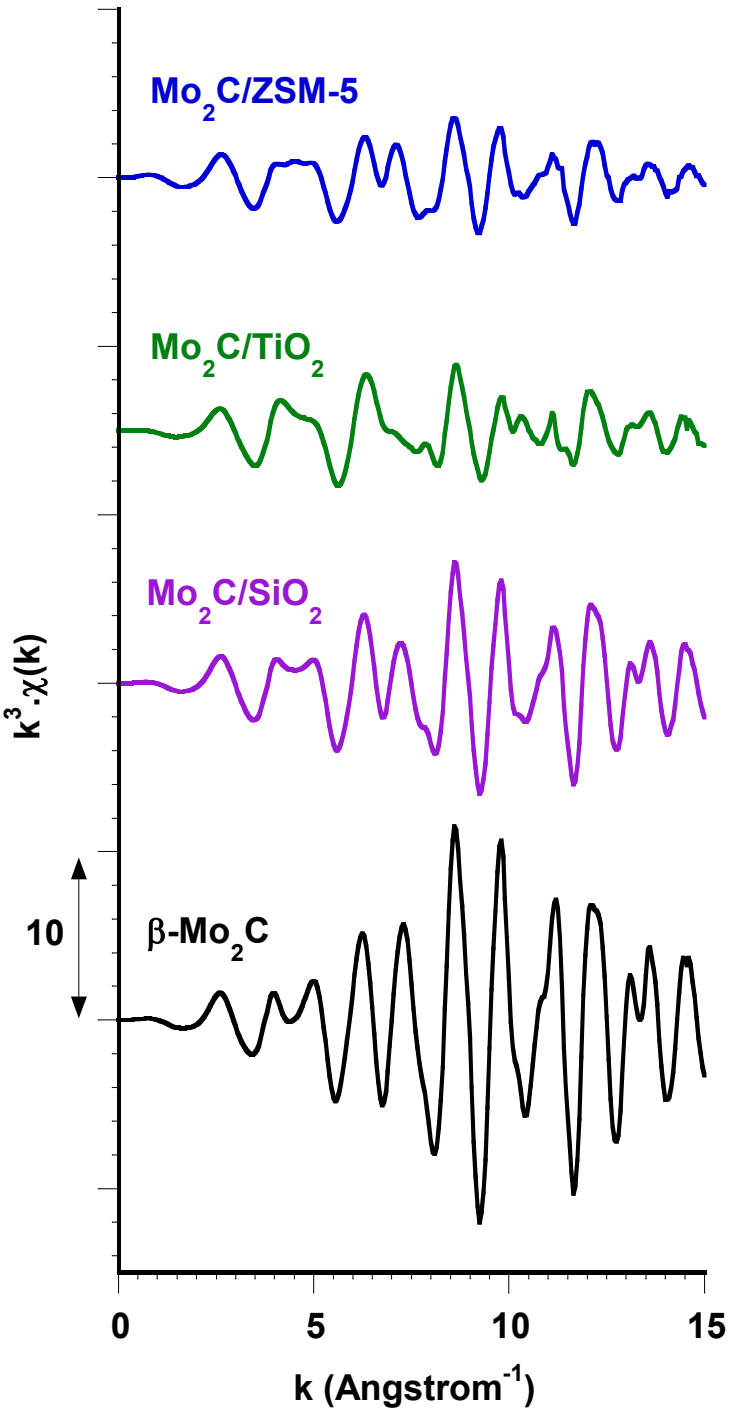


Figure S15. EXAFS signals recorded at the Mo K-edge for reduced β-Mo_2C, Mo_2C/SiO_2, Mo_2C/TiO_2, and Mo_2C/ZSM-5 (spectra recorded at room temperature).

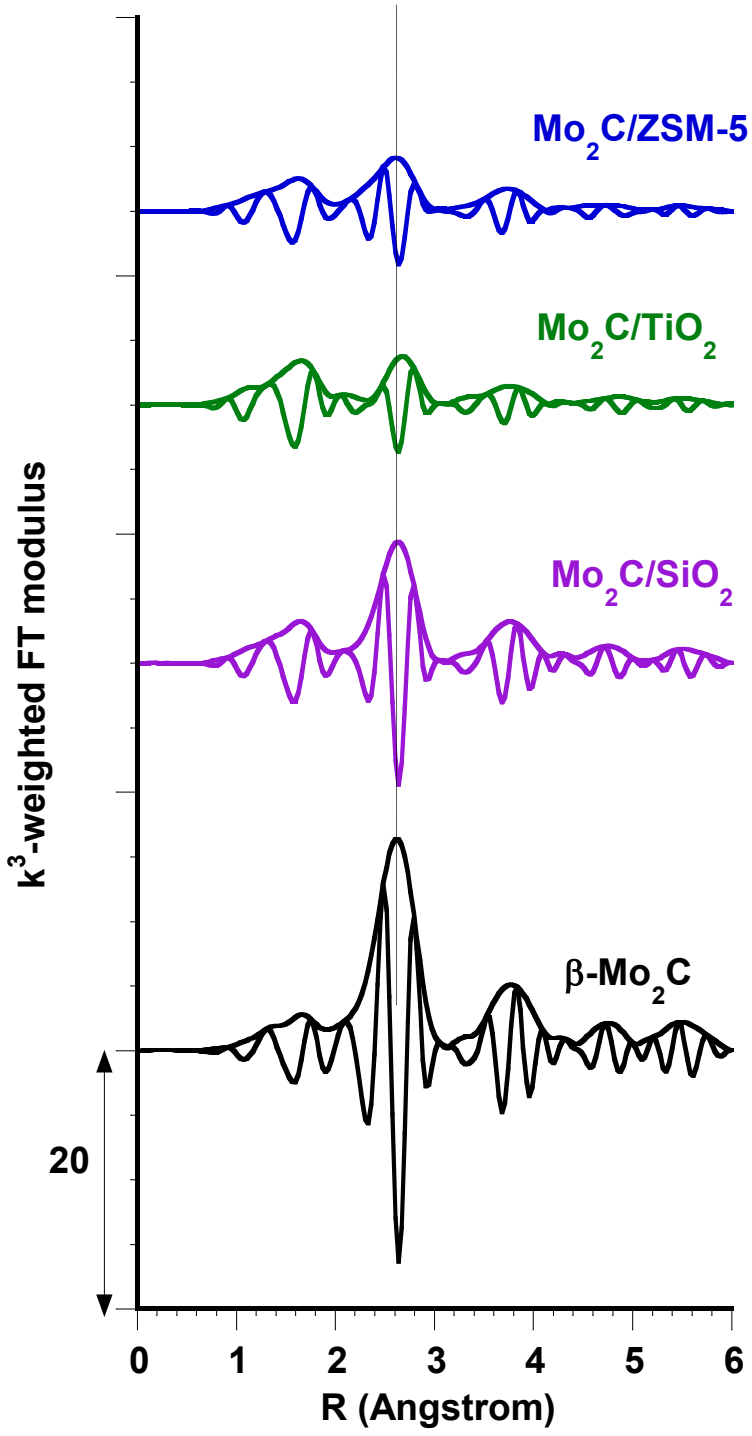


Figure S16. Fourier transforms of the EXAFS signals recorded at the Mo K-edge for reduced β-Mo_2C, Mo_2C/SiO_2, Mo_2C/TiO_2, and Mo_2C/ZSM-5 (spectra recorded at room temperature).

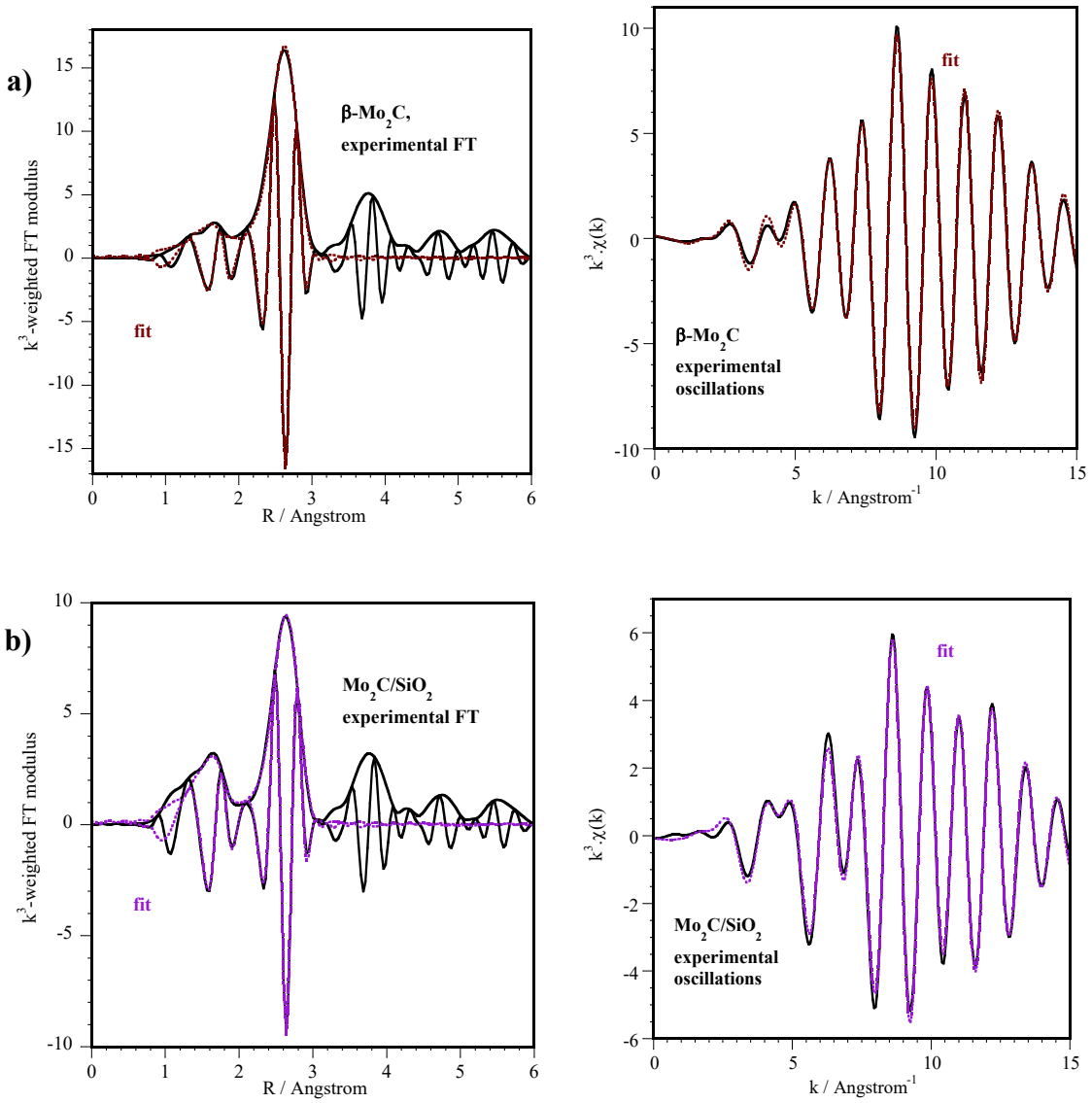
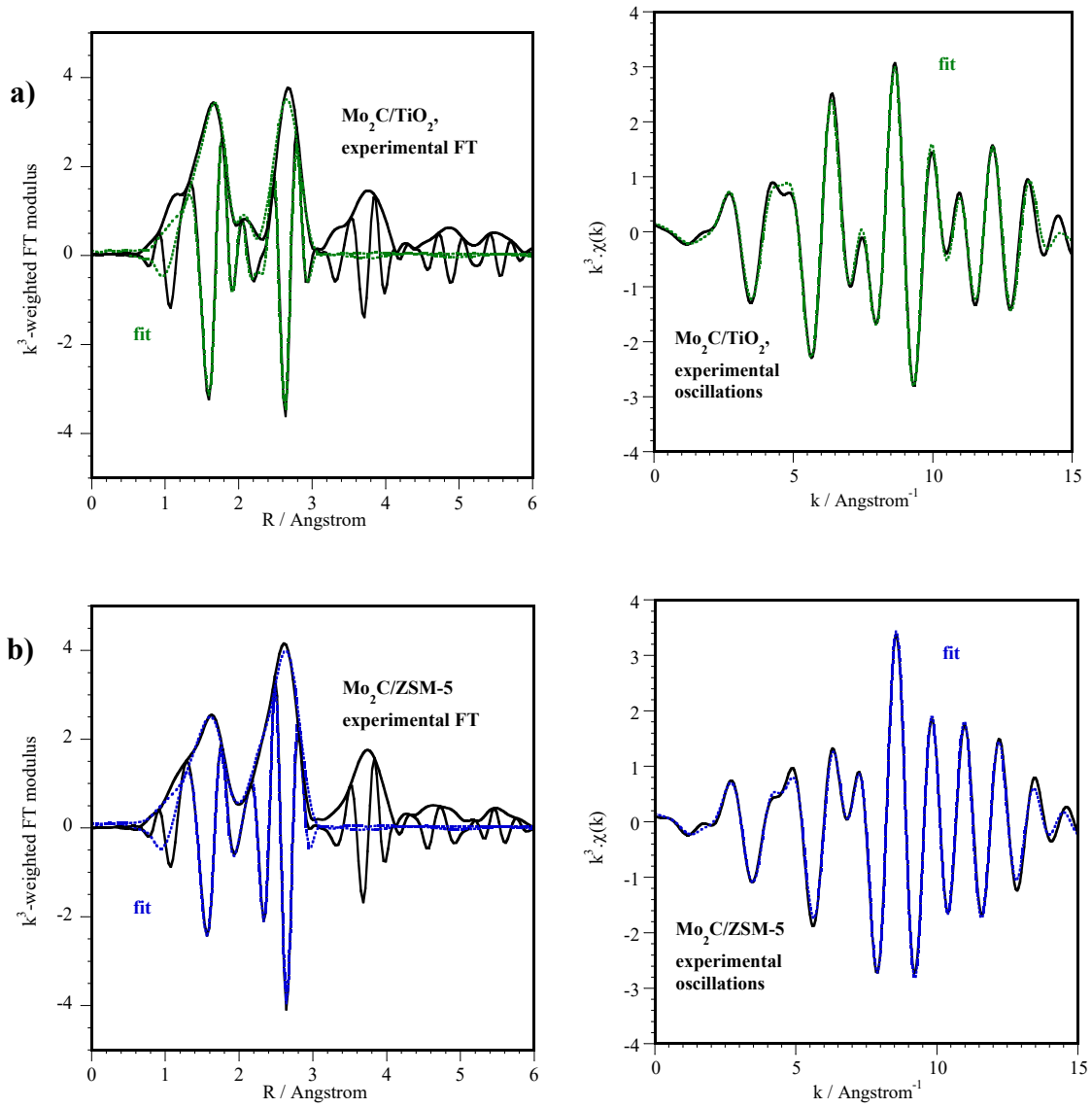


Figure S17. XAS data at the Mo K-edge of the catalysts after reduction (spectrum recorded at room temperature). Fit of the first and second shells of neighbors: Fourier transform (left) and EXAFS oscillations (right), a) β-Mo_2C and b) Mo_2C/SiO_2.



Continuation of Figure S17. XAS data at the Mo K-edge of the catalysts after reduction (spectrum recorded at room temperature). Fit of the first and second shells of neighbors: Fourier transform (left) and EXAFS oscillations (right), a) Mo_2C/TiO_2 and b) Mo_2C/ZSM-5.

Table S2. Fitted parameters at the Mo K-edge (E_0 = 20013 eV, S_0^2 = 0.98) determined from the EXAFS analysis of spectra recorded at room temperature on catalysts after passivation and reduction in H_2. k = 3.5 - 15 $Å^{-1}$. Fit of the first peak(s) from the Fourier transform between 1 and 3 Å.

Catalyst	Backscatter	N	σ^2 (Å²) x 10^3	R (Å)
β-Mo_2C	C	2.7 ± 0.9	4.1 ± 0.3	2.08 ± 0.02
	Mo	7.3 ± 0.8	5.7 ± 0.5	2.966 ± 0.005
	ΔE_0 = -5.5 eV, r-factor = 0.01575, χ^2 = 592, N_{ind} = 13, N_{var} = 7			
Mo_2C/SiO_2	C	4.1 ± 0.6	6 ± 1	2.105 ± 0.006
	Mo	4.1 ± 0.4	6.1 ± 0.4	2.976 ± 0.003
	ΔE_0 = -2.7 eV, r-factor = 0.00717, χ^2 = 202, N_{ind} = 13, N_{var} = 7			
Mo_2C/TiO_2	C	4.0 ± 0.7	5 ± 2	2.13 ± 0.01
	Mo	0.3 ± 0.2	8 ± 2	2.49 ± 0.04
	Mo	2.3 ± 0.7	8 ± 2	2.977 ± 0.009
	ΔE_0 = -0.1 eV, r-factor = 0.01630, χ^2 = 514, N_{ind} = 13, N_{var} = 9			
Mo_2C/ZSM-5	C	3.9 ± 0.7	8 ± 2	2.10 ± 0.01
	Mo	0.7 ± 0.5	9 ± 2	2.69 ± 0.02
	Mo	3.0 ± 0.9	9 ± 2	2.980 ± 0.009
	ΔE_0 = -2.9 eV, r-factor = 0.01134, χ^2 = 271, N_{ind} = 13, N_{var} = 9			