

# **Original Synthesis of Molybdenum Nitrides Using Metal Cluster Compounds as Precursors: Applications in Heterogeneous Catalysis**

Kevin Guy<sup>1,2,3</sup>, Franck Tessier<sup>1</sup>, Helena Kaper<sup>3</sup>, Fabien Grasset<sup>2,4</sup>, Noée Dumait<sup>1</sup>, Valérie Demange<sup>1</sup>  
Mitsuaki Nishio<sup>4</sup>, Yoshitaka Matsushita<sup>4</sup>, Yoshio Matsui<sup>4</sup>, Toshiaki Takei<sup>5</sup>, David Lechevalier<sup>2,4</sup>  
Caroline Tardivat<sup>3</sup>, Tetsuo Uchikoshi<sup>2,4</sup>, Naoki Ohashi<sup>2,4</sup>, Stéphane Cordier<sup>1</sup>

<sup>1</sup>Univ. Rennes – CNRS – Institut des Sciences Chimiques de Rennes, UMR 6226, 35000 Rennes, France

<sup>2</sup>CNRS – Saint-Gobain – NIMS, UMI 3629, Laboratory for Innovative Key Materials and Structures (LINK), National Institute for Materials Science, 1-1 Namiki, 305-0044 Tsukuba, Japan

<sup>3</sup>Ceramic Synthesis and Functionalization Laboratory, UMR 3080, CNRS – Saint-Gobain Research Provence, 84306 Cavaillon, France.

<sup>4</sup>Research Center for Functional Materials, National Institute for Materials Science, 305-0044Tsukuba, Japan

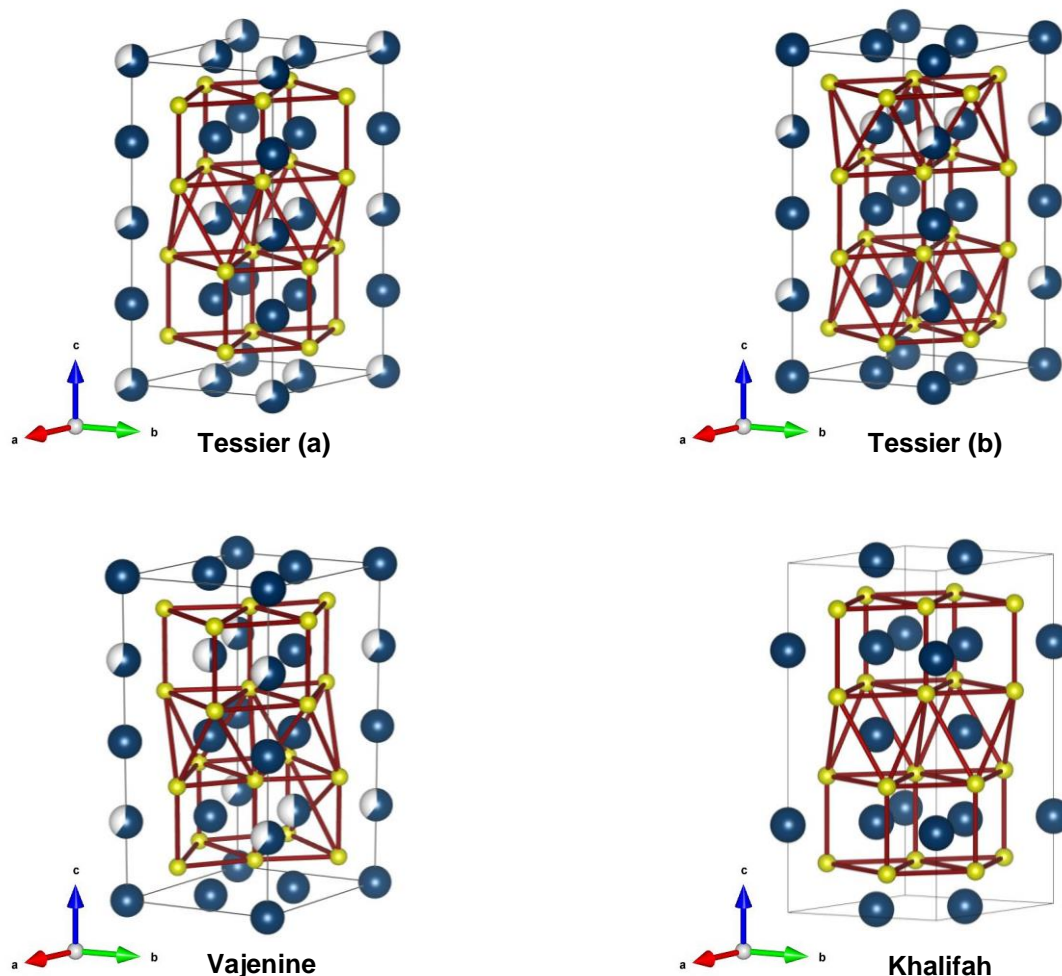
<sup>5</sup>Research Center for Materials Nanoarchitectonic, National Institute for Materials Science, 305-0044Tsukuba, Japan

## **Corresponding Authors**

[kevin.guy@univ-rennes1.fr](mailto:kevin.guy@univ-rennes1.fr)

[franck.tessier@univ-rennes1.fr](mailto:franck.tessier@univ-rennes1.fr)

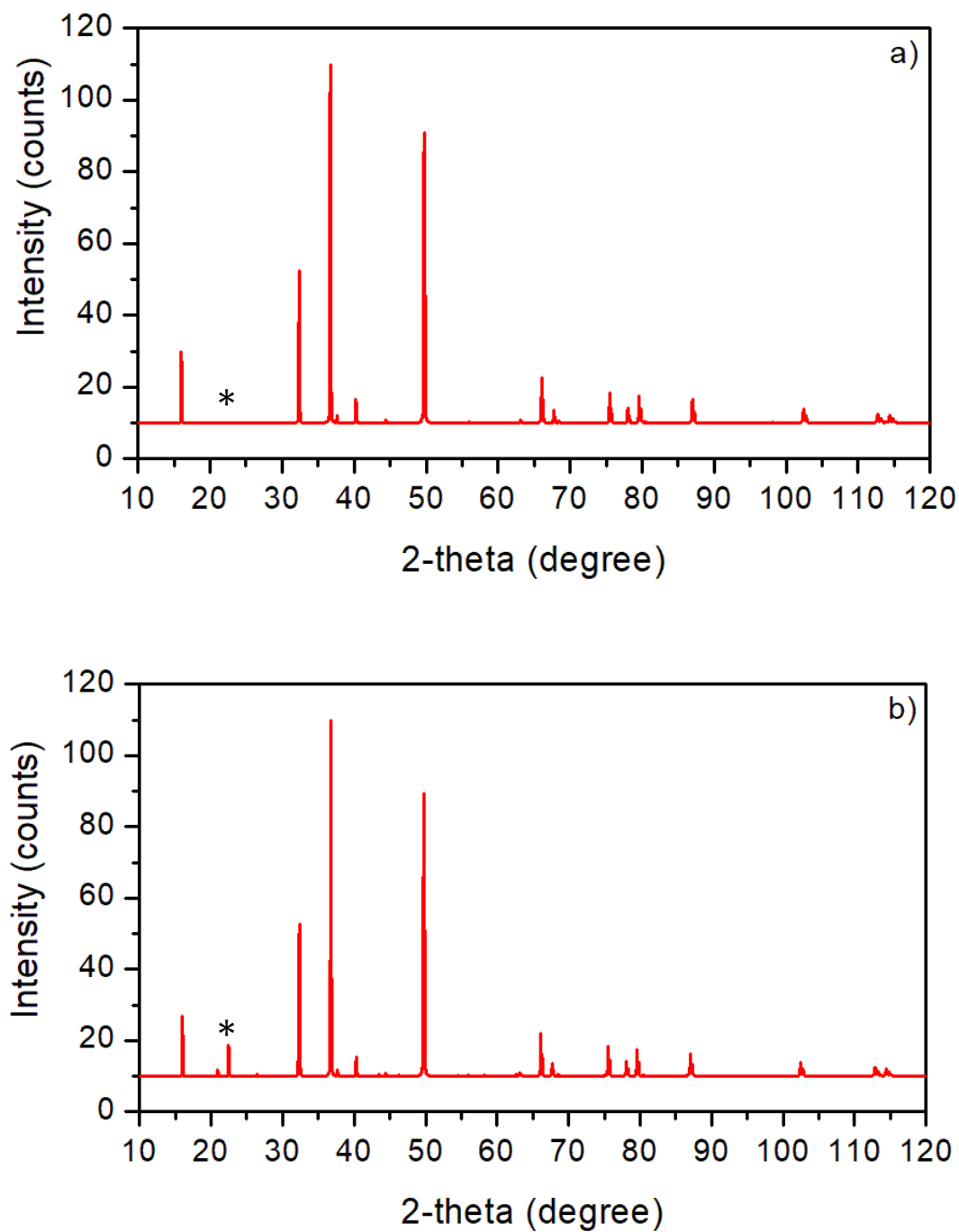
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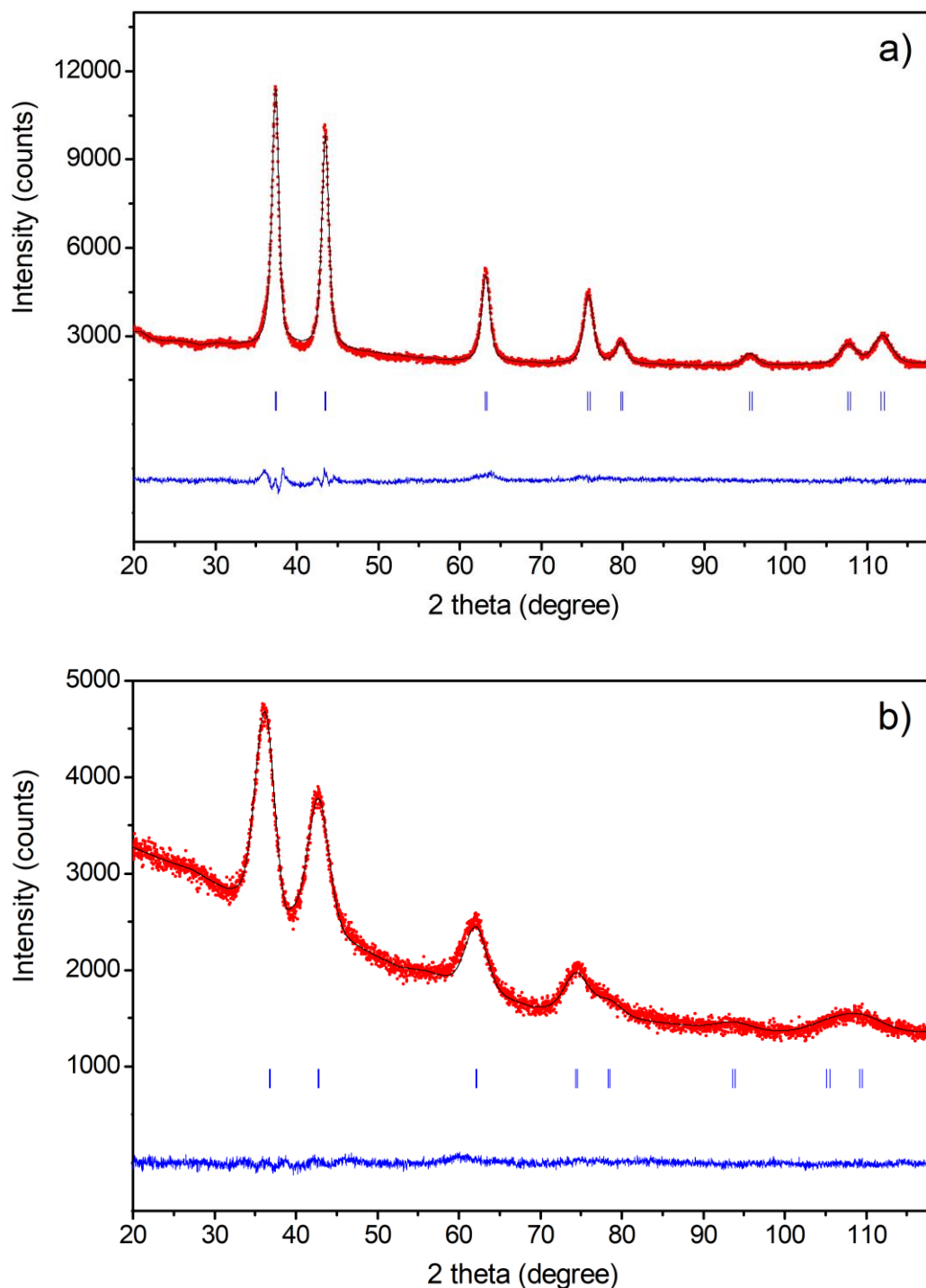
**Figure S1.** Schemes of the different structures of  $\text{Mo}_5\text{N}_6$  proposed in the literature by Tessier et al.<sup>4</sup>, Vajenine et al.<sup>2</sup> and Khalifah et al.<sup>6</sup>. Molybdenum atoms are represented in blue, nitrogen atoms in yellow and vacancies in white.

	Tessier (a)	Tessier (b)	Vajenine (c)	Khalifah (d)
$a$ (Å)	4.8960	4.8960	4.8924	4.89688
$c$ (Å)	11.0600	11.0600	11.0643	11.0754
$V$ (Å <sup>3</sup> )	229.5983	229.5983	229.3498	230.0006
Space group	$P6_3/m$	$P6_3 2 2$	$P6_3/m$	$P6_3/m c m$
Mo vacancies site	Octahedral	Octahedral	Prismatic	Octahedral

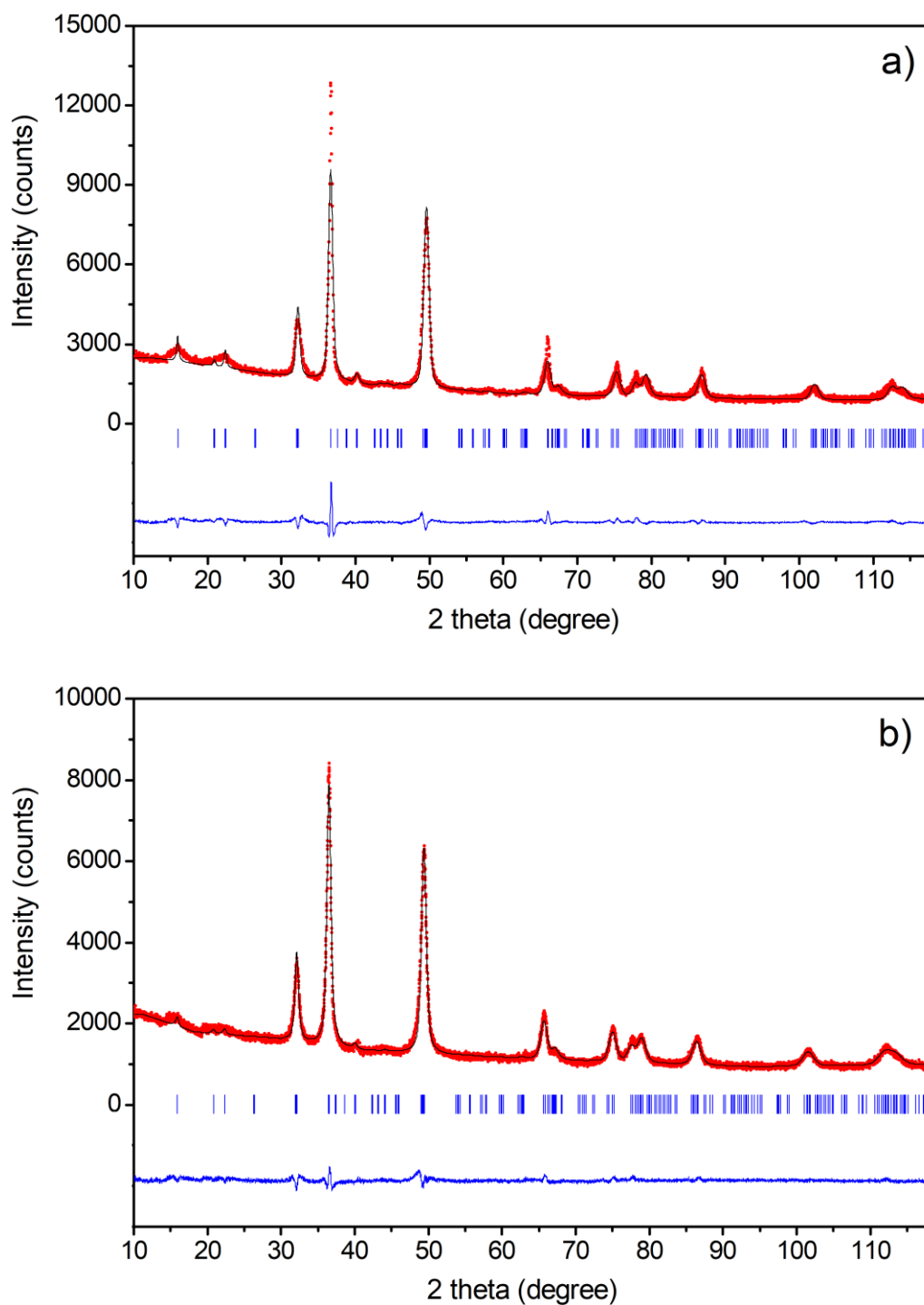
**Table S1.** Lattice parameters, space group and position of the molybdenum vacancies in the four structures of  $\text{Mo}_5\text{N}_6$  proposed in the literature.



**Figure S2.** Simulated XRD patterns, obtained with Vesta Software, for  $\text{Mo}_5\text{N}_6$  according to the model of F. Tessier (a) and the model of V. Vajenine (b). The extinction of the (101) peak is visible on the model of Tessier, annotated by (\*). The two models varies by the position of the molybdenum vacancies.



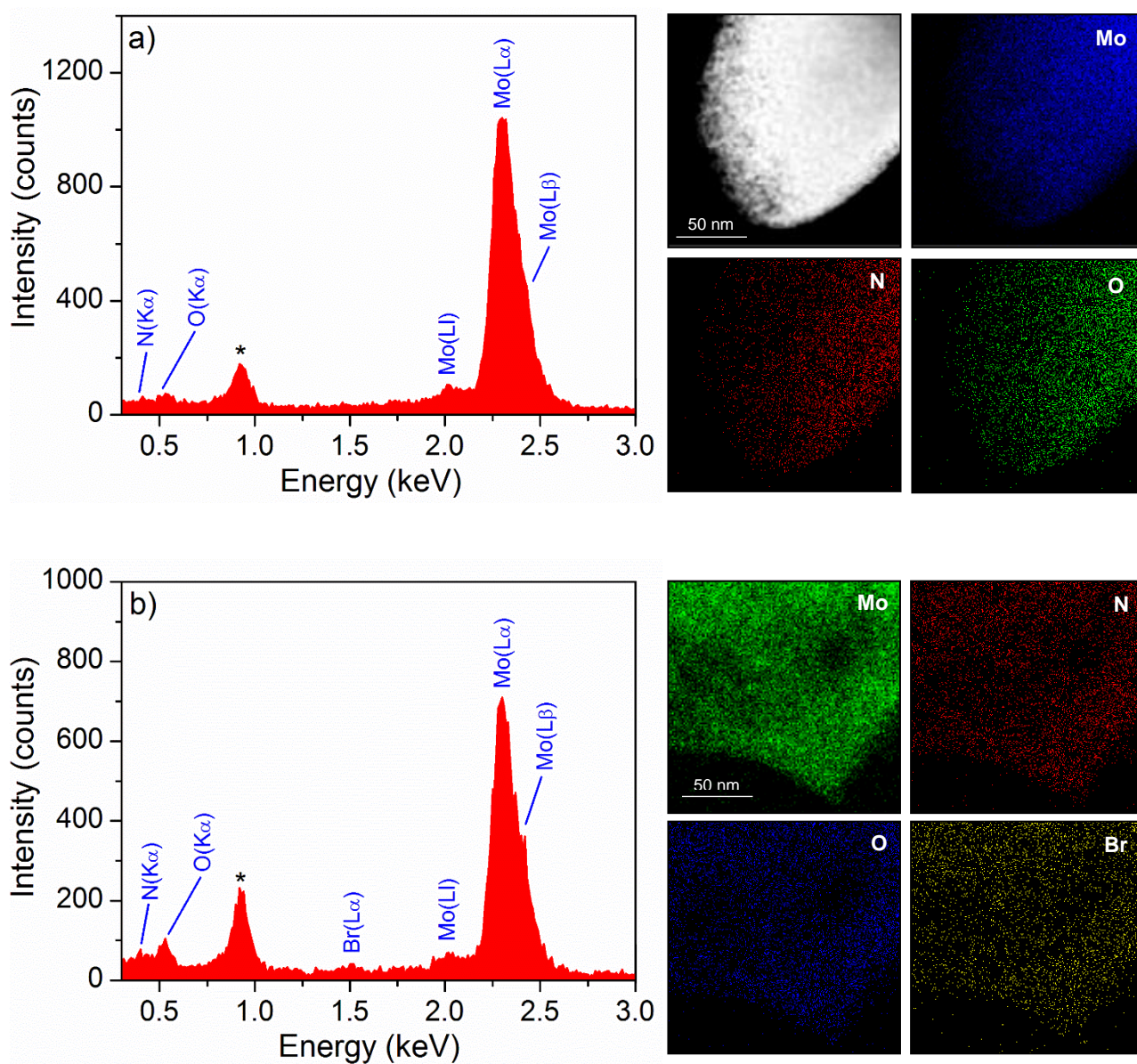
**Figure S3.a.** Rietveld refinement pattern for  $\text{Mo}_2\text{N-ref}$  (a) and TMB-450 (b): observed (red dotted line), calculated (black line) and difference X-ray powder diffraction profiles from the pattern matching plot obtained with the Full-Prof Suite Software. The vertical markers correspond to the position of the Bragg reflections.



**Figure S3.b.** Rietveld refinement pattern for  $\text{Mo}_5\text{N}_6\text{-ref}$  (a) and TMB-650 (b): observed (red dotted line), calculated (black line) and difference X-ray powder diffraction profiles from the pattern matching plot obtained with the Full-Prof Suite Software. The vertical markers correspond to the position of the Bragg reflections.

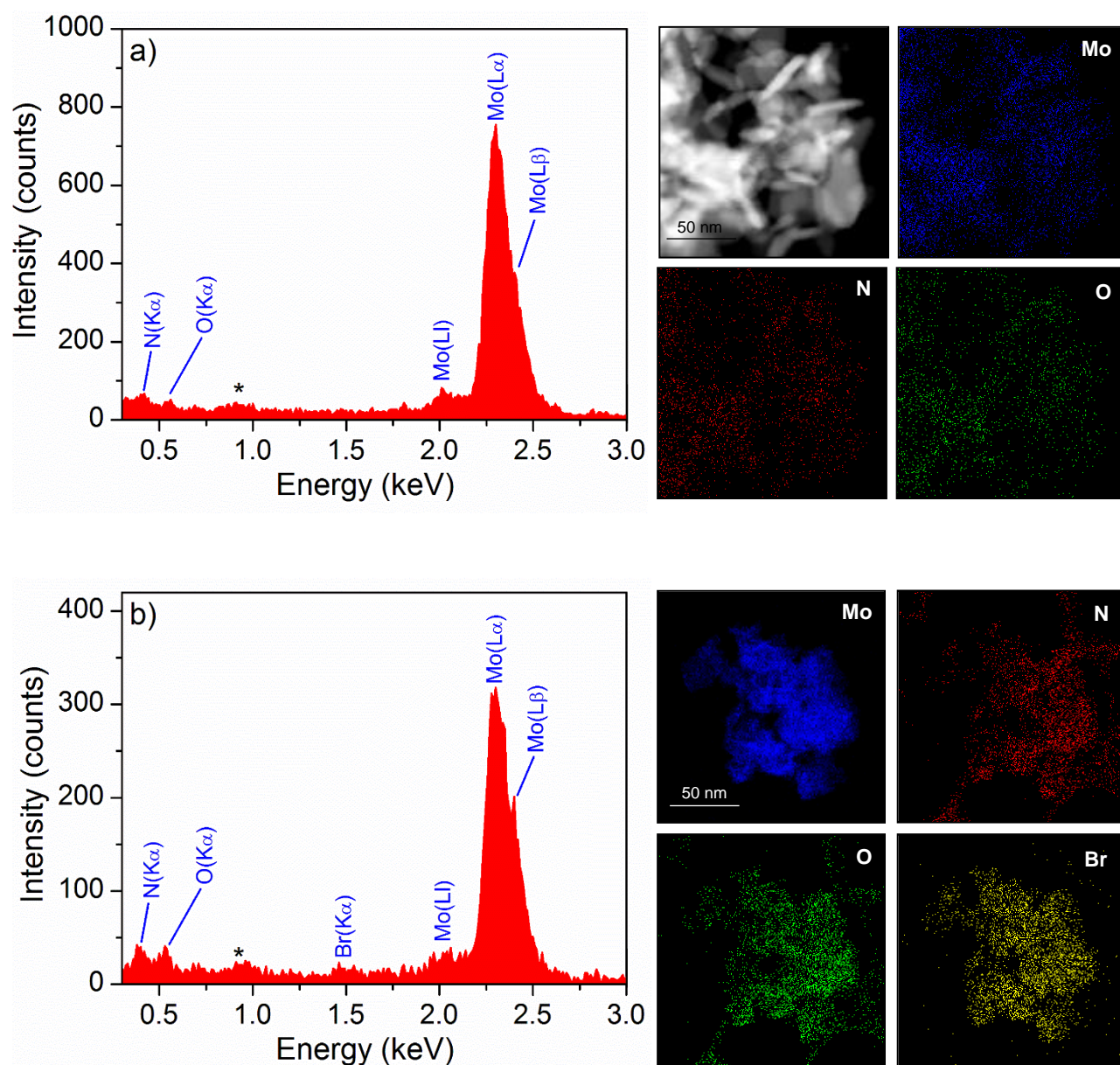
**Table S2.** Details of the Rietveld refinements and crystallites size for Mo<sub>2</sub>N-ref, TMB-450, Mo<sub>5</sub>N<sub>6</sub>-ref and TMB-650 obtained with the FullProf Suite Software. Function no. 7 is used, and the parameters U, X, Y and Gausize are refined for each sample, giving an isotropic model concerning the crystallites size and the strain.

	Mo <sub>2</sub> N-ref	TMB-450	Mo <sub>5</sub> N <sub>6</sub> -ref	TMB-650
<b>Lattice</b>				
<i>a</i> (Å)	4.1609(2)	4.2147(9)	4.90498(3)	4.9236(2)
<i>c</i> (Å)			11.1080(7)	11.1456(4)
<i>V</i> (Å <sup>3</sup> )	72.04(1)	74.87(3)	231.41(2)	233.99(2)
Space group	<i>F m -3 m</i>	<i>F m -3 m</i>	<i>P 6<sub>3</sub>/m</i>	<i>P 6<sub>3</sub>/m</i>
<b>Refinement</b>				
N0. Diffraction peaks (Kα/Kβ)	22/2	22/2	312/2	338/2
N0. Background points	18	13	12	10
N0. Refined parameters	12	12	15	15
N0. atoms	2	2	6	6
R <sub>p</sub> (%)	2.87	2.24	5.81	3.57
R <sub>wp</sub> (%)	3.67	2.89	7.86	4.57
R <sub>exp</sub> (%)	1.95	2.19	2.52	2.65
χ <sup>2</sup>	3.52	1.73	9.73	2.99
<b>Microstructure</b>				
Crystallites size (nm)	9.2(1)	3.5(1)	20.7(1)	15.4(1)
ε	0.070(3)	0.24(6)	0.0367(3)	0.047(5)



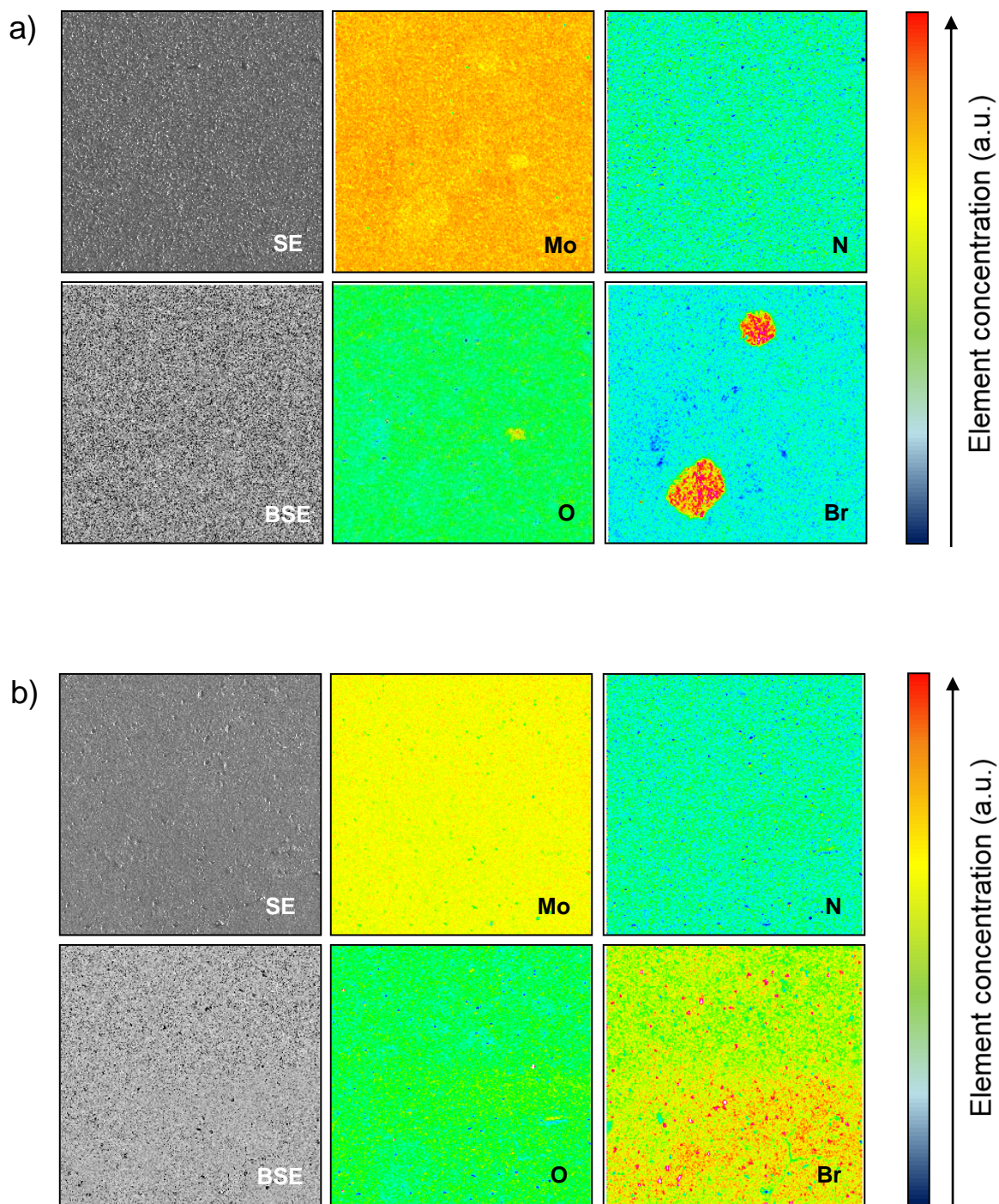
**Figure S4.a.** EDS-TEM spectra and mapping for molybdenum, nitrogen, oxygen and bromine for  $\text{Mo}_2\text{N}$  samples:  $\text{Mo}_2\text{N}$ -ref (a) and TMB-450 (b). Peaks identified as (\*) correspond to the Cu grid used for TEM analyses.



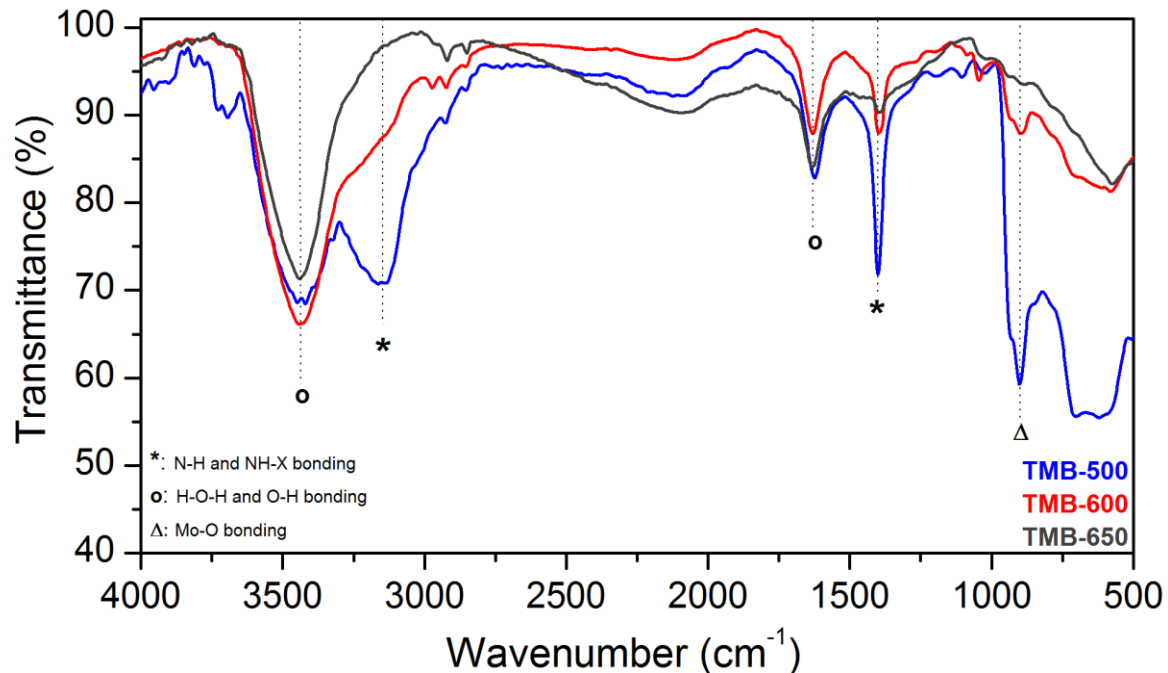


**Figure S4.b.** EDS-TEM spectra and mapping for molybdenum, nitrogen, oxygen and bromine for  $\text{Mo}_5\text{N}_6$  samples:  $\text{Mo}_5\text{N}_6\text{-ref}$  (a) and TMB-500 (b). Peaks identified as (\*) correspond to the Cu grid used for TEM analyses.

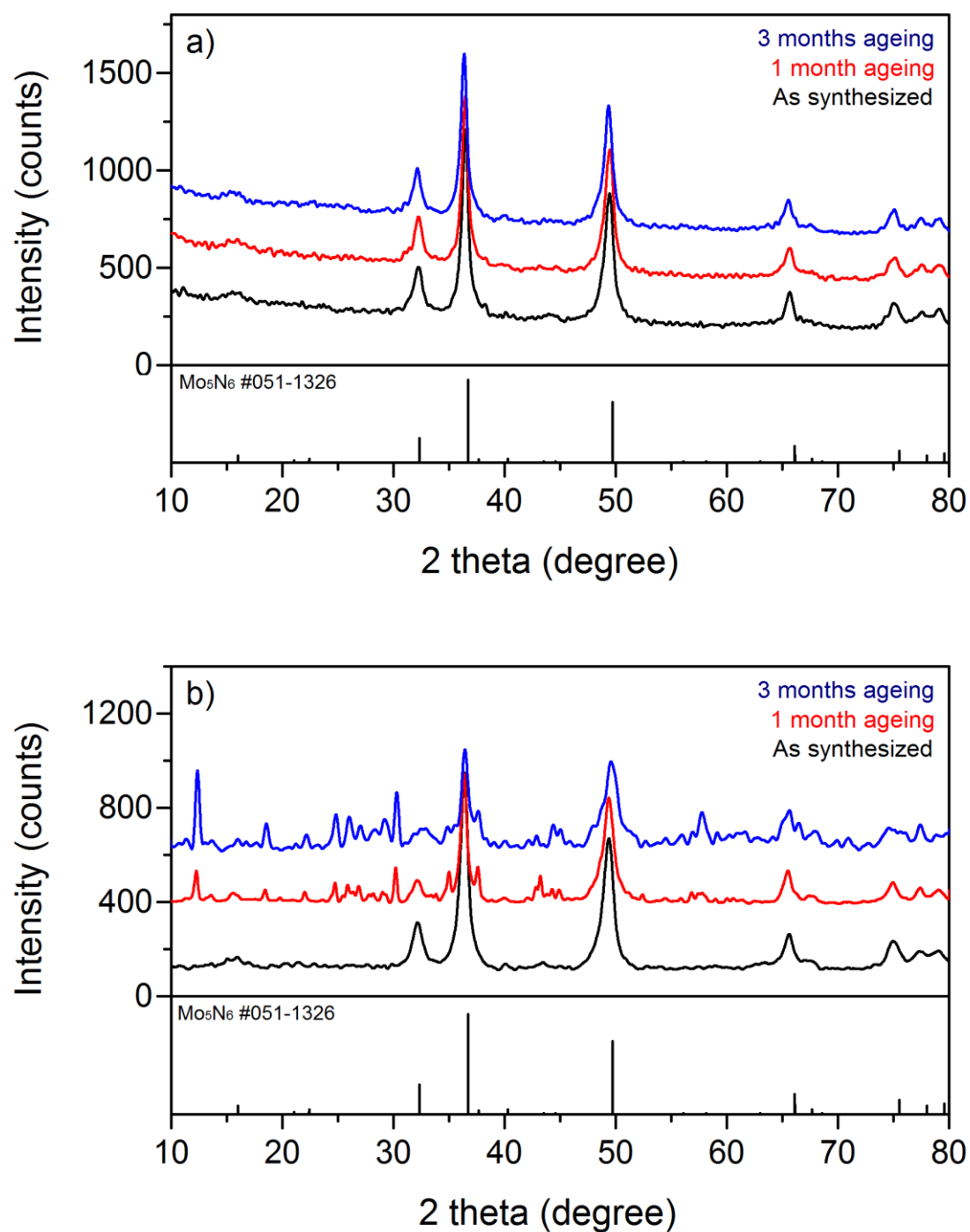




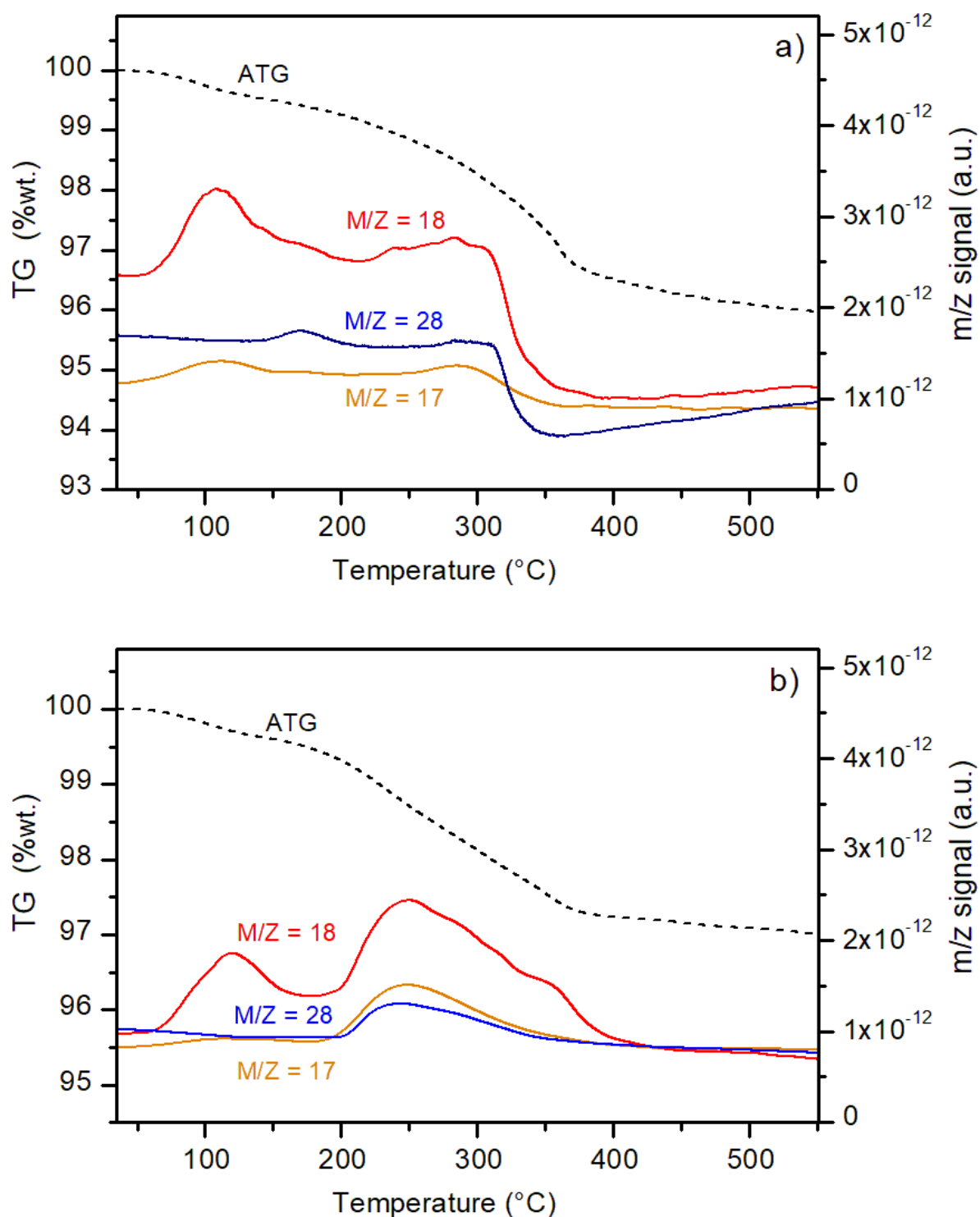
**Figure S5.** WDS-EPMA mapping for molybdenum, nitrogen, oxygen and bromine on TMB-500 (a) and TMB-450 (b). SE corresponds to secondary electron observations and BSE to backscattering electron observations.



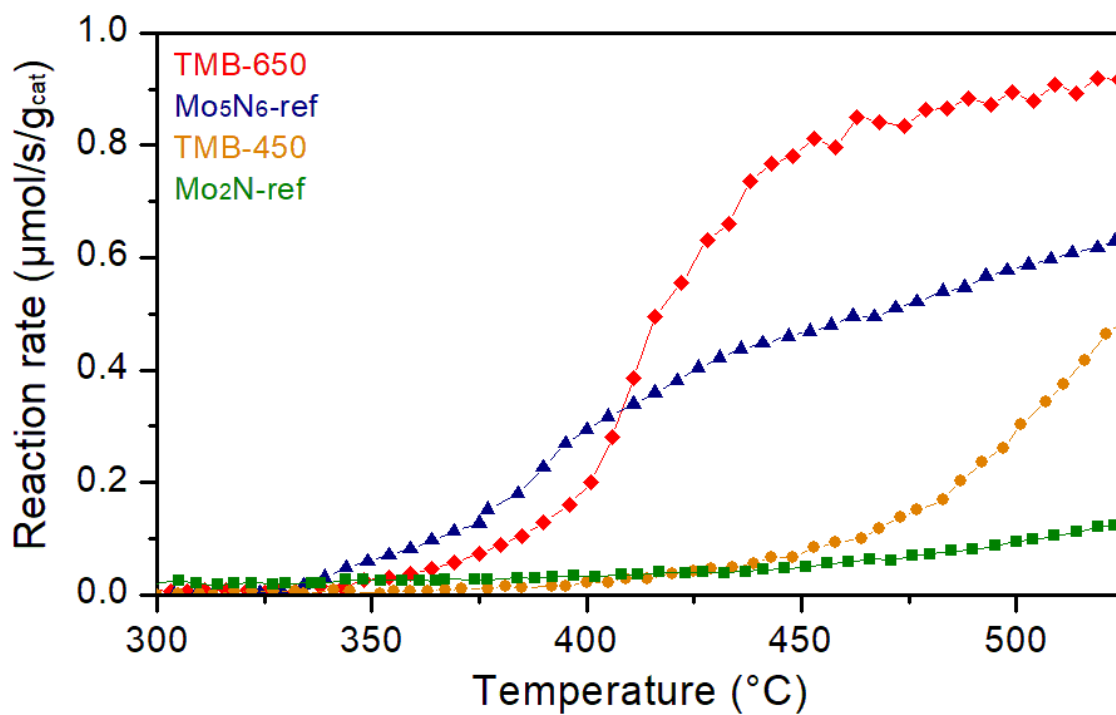
**Figure S6.** Fourier transformed infrared spectra for TMB-500, TMB-600 and TMB-650 shows the impact of the ammonolysis temperature on the presence of Mo-O, N-H and NH-X peaks. Increasing the ammonolysis temperature up to 650°C allows to prevent the formation of  $\text{NH}_4\text{Br}$ , in good accordance with the results obtained by WDS-EPMA (Figure 4 and Figure S2).



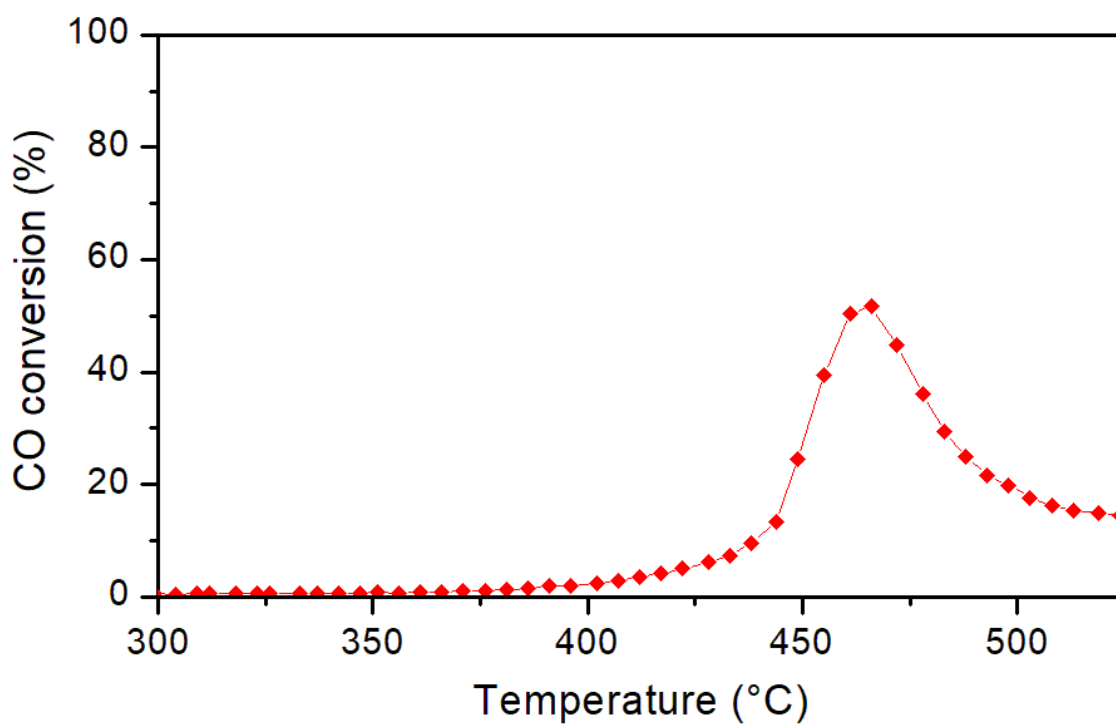
**Figure S7.** XRD patterns of TMB-650 (a) and TMB-500 (b) as synthesized, and after 1 month and three months of ageing under ambient conditions. Additional peaks observed for TMB-500 after one month and three months of ageing corresponds to the degradation of  $\text{Mo}_5\text{N}_6$  into  $\text{MoO}_2$  and  $\text{MoO}_3$ . This is due to the presence of  $\text{NH}_4\text{Br}$  on TMB-500, modifying the basicity of the surface.



**Figure S8.** ATG curves (black dotted line) coupled with mass spectroscopy. m/z = 17 (orange line), 18 (red line) and 28 (blue line) are represented. Samples  $\text{Mo}_5\text{N}_6\text{-ref}$  (a) and TMB-650 are presented (b).

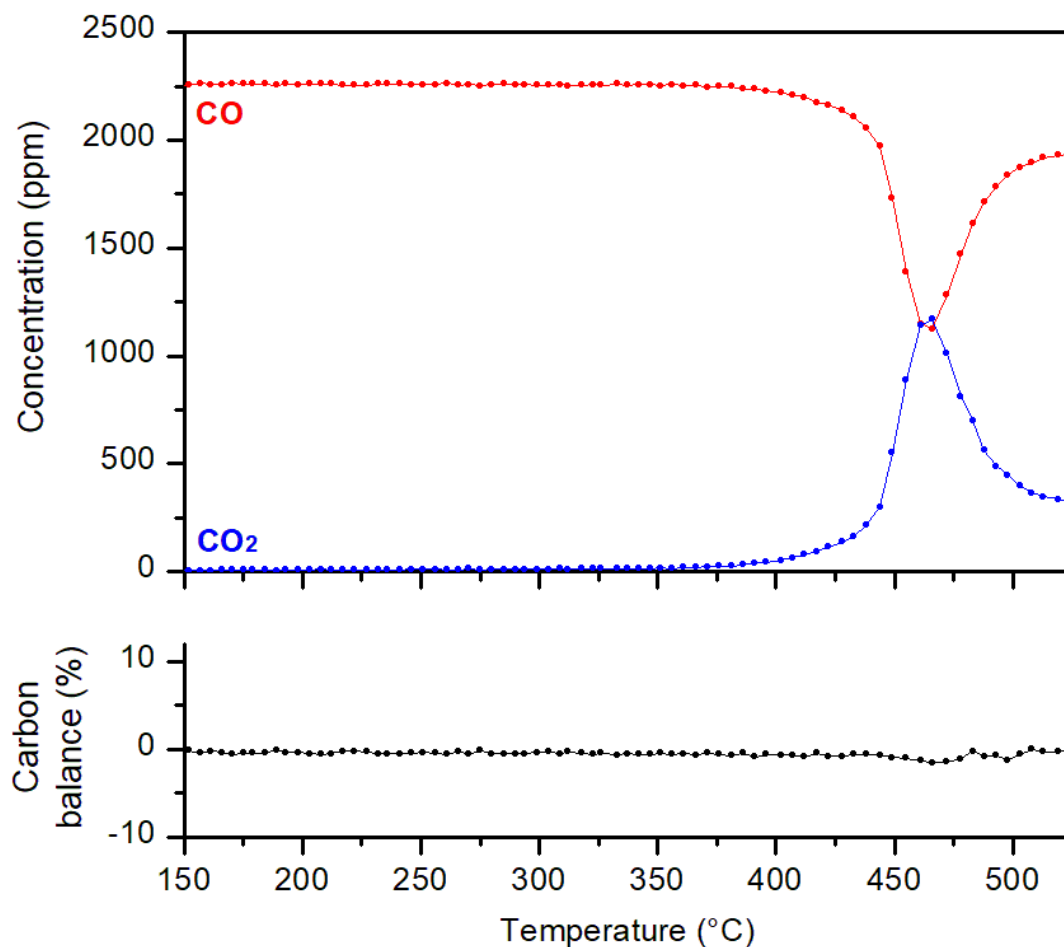


**Figure S9.** Catalytic performance of the catalysts for the WGS given in terms of normalized reaction rate, in function of the weight of Mo<sub>5</sub>N<sub>6</sub>. Light-off curves of TMB-650, Mo<sub>5</sub>N<sub>6</sub>-ref, TMB-450 and Mo<sub>2</sub>N-ref.

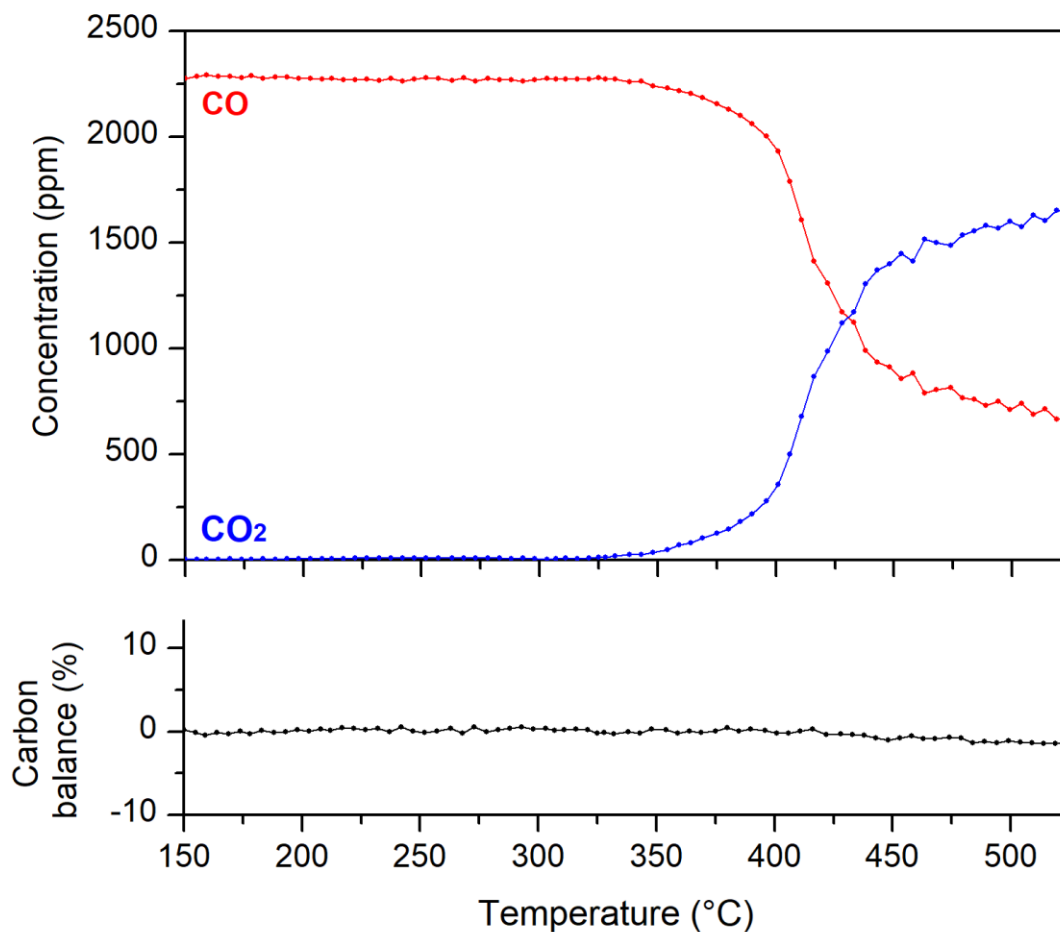


**Figure S10.** CO to CO<sub>2</sub> conversion for TMB-650 in function of the temperature, in presence of CO only.

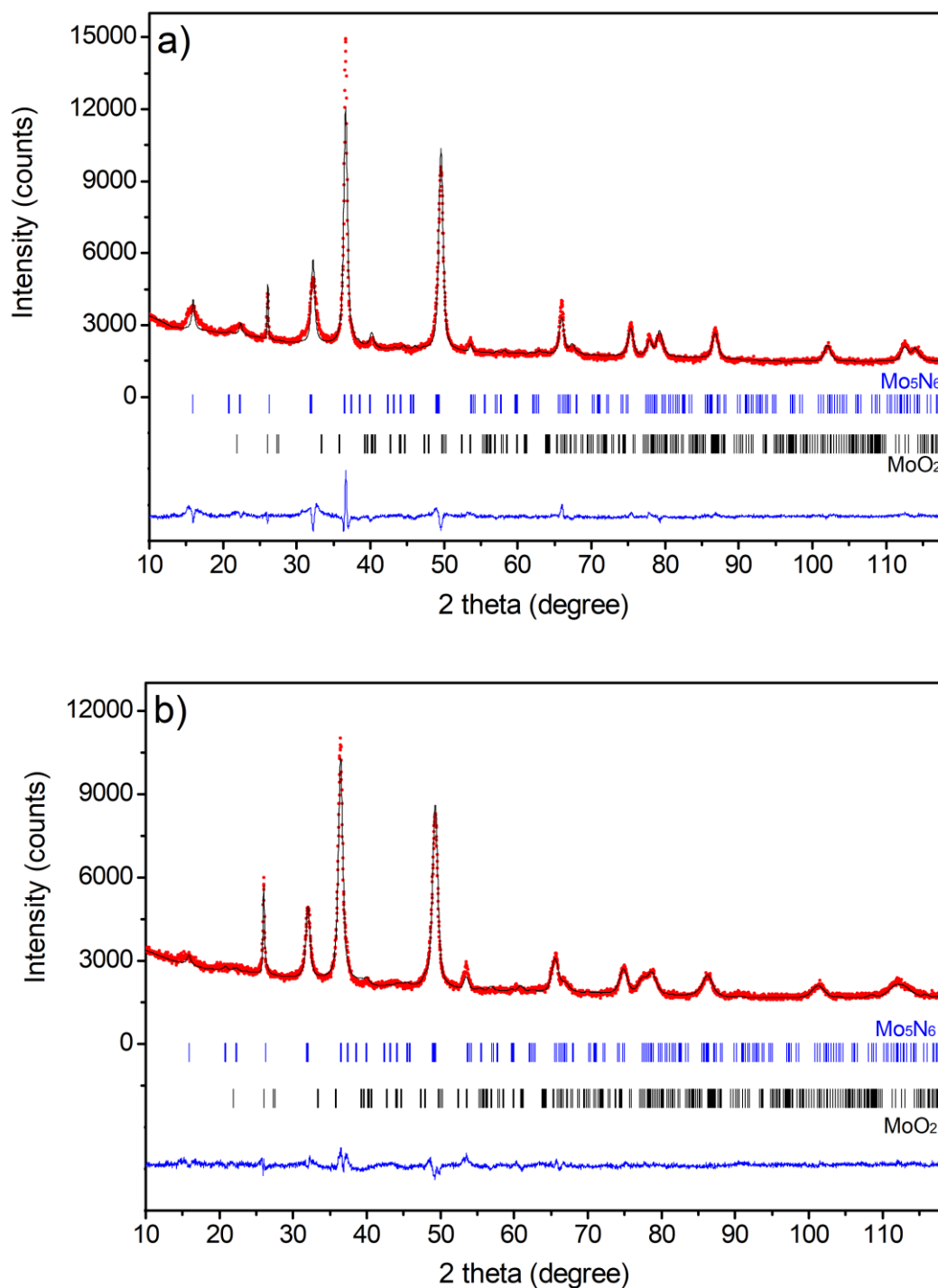




**Figure S11.** Product profile of TMB-650 during the catalytic test under CO only. Red line corresponds to the concentration of CO and blue line to CO<sub>2</sub> (in ppm), in function of the temperature. Black line shows the carbon balance as a function of the temperature (CO consumed minus CO<sub>2</sub> formed, divided by initial CO concentration).



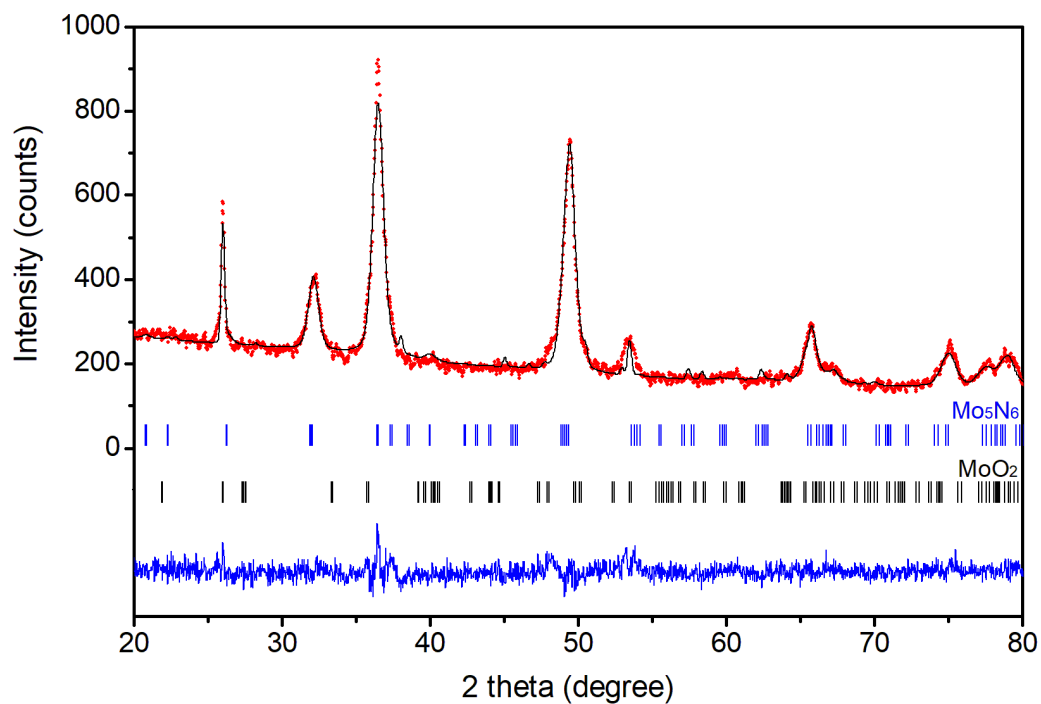
**Figure S12.** Product profile of TMB-650 during the WGSR first light-off. Red line corresponds to the concentration of CO and blue line to CO<sub>2</sub> (in ppm), in function of the temperature. Black line shows the carbon balance as a function of the temperature (CO consumed minus CO<sub>2</sub> formed, divided by initial CO concentration).



**Figure S13.** Rietveld refinement pattern for  $\text{Mo}_5\text{N}_6$ -ref (a) and TMB-650 (b) after 3 WGSR consecutive light-off: observed (red dotted line), calculated (black line) and difference X-ray powder diffraction profiles from the pattern matching plot obtained with the FullProf Suite Software. The vertical markers correspond to the position of the Bragg reflections for  $\text{Mo}_5\text{N}_6$  (blue) and  $\text{MoO}_2$  (black).

**Table S3.** Details of the Rietveld refinements and crystallites size for Mo<sub>5</sub>N<sub>6</sub>-ref and TMB-650 after 3 WGSR consecutive light-off obtained with the FullProf Suite Software. Function no. 7 is used, and the parameters U, X, Y and Gausize are refined for each sample, giving an isotropic model concerning the crystallites size and the strain.

	Mo <sub>5</sub> N <sub>6</sub> -ref	TMB-650
<b>Lattice (Mo<sub>5</sub>N<sub>6</sub>)</b>		
<i>a</i> (Å)	4.90558(2)	4.93155(2)
<i>c</i> (Å)	11.10984(6)	11.17950(6)
<i>V</i> (Å <sup>3</sup> )	231.54(2)	235.46(2)
Space group	<i>P</i> 6 <sub>3</sub> / <i>m</i>	<i>P</i> 6 <sub>3</sub> / <i>m</i>
Fraction (%wt.)	94(3)%	85(1)%
<b>Lattice (MoO<sub>2</sub>)</b>		
<i>a</i> (Å)	4.366(2)	4.603(2)
<i>b</i> (Å)	5.585(2)	5.371(1)
<i>c</i> (Å)	4.904(2)	5.042(2)
$\beta$ (°)	118.19(1)	118.11(3)
<i>V</i> (Å <sup>3</sup> )	105.41(8)	109.96(7)
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Fraction (%wt.)	6(3)%	15(1)%
<b>Refinement</b>		
N0. Diffraction peaks (K $\alpha$ /K $\beta$ )	351/2	321/2
N0. Background points	15	13
N0. Refined parameters	23	23
R <sub>p</sub> (%)	4.33	3.02
R <sub>wp</sub> (%)	5.87	3.88
R <sub>exp</sub> (%)	2.10	2.05
$\chi^2$	7.79	3.59
<b>Microstructure</b>		
Crystallites size (nm)	15.3(1)	12.7(1)
Maximum strain	0.0265(1)	0.0613(5)

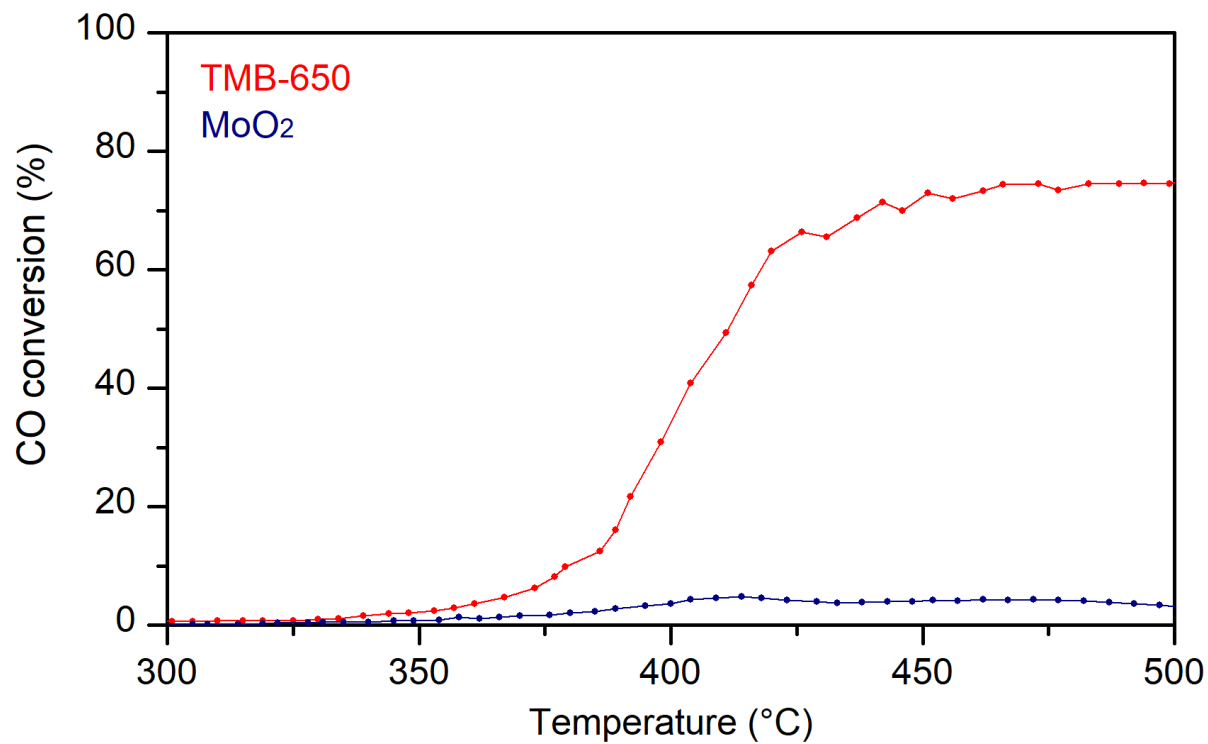


**Figure S14.** Rietveld refinement pattern for TMB-650 after hydrothermal test: observed (red dotted line), calculated (black line) and difference X-ray powder diffraction profiles from the pattern matching plot obtained with the Full-Prof Suite Software. The vertical markers correspond to the position of the Bragg reflections for Mo<sub>5</sub>N<sub>6</sub> (blue) and MoO<sub>2</sub> (black).

**Table S4.** Details of the Rietveld refinements for TMB-650 after hydrothermal test obtained with the FullProf Suite Software, using the function no. 7.

TMB-650	
<b>Lattice (Mo<sub>5</sub>N<sub>6</sub>)</b>	
<i>a</i> (Å)	4.9250(7)
<i>c</i> (Å)	11.147(2)
<i>V</i> (Å <sup>3</sup> )	234.17(6)
Space group	<i>P</i> 6 <sub>3</sub> / <i>m</i>
Fraction (%wt.)	87(3)%
<b>Lattice (MoO<sub>2</sub>)</b>	
<i>a</i> (Å)	4.308(1)
<i>b</i> (Å)	5.663(2)
<i>c</i> (Å)	4.764(2)
<i>β</i> (°)	115.34(6)
<i>V</i> (Å <sup>3</sup> )	105.06(6)
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Fraction (%wt.)	13(3)%
<b>Refinement</b>	
N0. Diffraction peaks (Kα/Kβ)	328/2
N0. Background points	9
N0. Refined parameters	23
R <sub>p</sub> (%)	6.84
R <sub>wp</sub> (%)	8.73
R <sub>exp</sub> (%)	6.40
χ <sup>2</sup>	1.86





**Figure S15.** Catalytic performances for the WGS: Light off curves of MoO<sub>2</sub> compared with TMB-650.