Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supporting Information

Stabilization of Intermediate Mo Oxidation states by Nb Doping Enhancing Methane Aromatization on Mo/HZSM-5 Catalysts

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Table S1: Methane conversions and major product selectivities (S > 1 %) under different MDA reaction conditions for 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5. Values are given as arithmetic means of 12 measurements over 360 min of reaction.

			mean conversions *X* and product selectivities *S* [%]						
Catalyst	**T [°C]**	**GHSV [SCC g_{cat}^{-1} h^{-1}]**	***X* [CH_4]**	***S* [C_2H_4]**	***S* [C_2H_6]**	***S* [C_6H_6]**	***S* [C_7H_8]**	***S* [$C_{10}H_{10}$]**	***S* [coke]**
6Mo	700	1600	8.42	4.30	1.81	57.23	3.31	12.36	20.17
	700	3200	6.25	7.81	2.14	60.36	4.40	8.75	15.21
	700	4800	5.06	10.80	2.19	54.38	3.35	4.16	23.91
	650	3200	4.41	5.53	2.95	53.24	3.66	7.89	25.34
	600	3200	2.75	4.83	4.11	45.01	3.27	7.08	30.15
6Mo1Nb	700	1600	8.39	4.27	1.82	57.80	3.27	12.29	19.66
	700	3200	6.43	7.58	2.16	61.01	4.44	8.97	14.49
	700	4800	5.10	10.87	2.26	58.67	3.48	4.35	19.17
	650	3200	4.51	5.33	2.91	55.74	3.66	8.39	22.63
	600	3200	2.63	4.69	4.36	49.53	3.37	8.40	23.65

Table S2: TGA/DSC measurement results of spent 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 catalysts after reaction at different reaction conditions for 360 min on stream. Mass losses refer to change in sample mass from 300-700 °C to omit adsorbed species like water.

Catalyst	T_{react} [°C]	GHSV [SCC g_{cat}^{-1} h^{-1}]	DSC peak [°C]	Mass loss [%]
6Mo	700	3200	464.7	4.25
6Mo1Nb	700	3200	469.4	4.13
6Mo	700	1600	464.1	2.21
6Mo1Nb	700	1600	468.1	1.52
6Mo	700	4800	466.9	4.07
6Mo1Nb	700	4800	467.5	4.62
6Mo	650	3200	432.6	3.37
6Mo1Nb	650	3200	443.5	2.84
6Mo	600	3200	421.4	3.22
6Mo1Nb	600	3200	428.9	2.54

Table S3: N_2 sorption characteristics (specific surface area S_{BET}, micropore area S_{micro}, external surface area S_{ext} as well as total pore volume V_{total} and micropore volume V_{micro}) for the catalysts at different stages. "Fresh" denotes samples after calcination but before reaction, "spent" after 360 min of reaction (700 °C, 3200 mL g_{cat}^{-1} h^{-1}) and "reg." after four reaction-regeneration cycles (total time on stream 24 h).

Catalyst	S_{BET} [m^2 g^{-1}]	S_{micro} [m^2 g^{-1}]	S_{ext} [m^2 g^{-1}]	V_{total} [mL g^{-1}]	V_{micro} [mL g^{-1}]
6Mo fresh	328	280	48	0.264	0.118
6Mo1Nb fresh	318	260	58	0.242	0.110
6Mo spent	273	241	32	0.200	0.096
6Mo1Nb spent	271	242	29	0.183	0.097
6Mo reg.	253	224	29	0.201	0.092
6Mo1Nb reg.	280	250	30	0.195	0.102

Table S4: Surface elemental compositions of 6Mo1Nb/HZSM-5 determined by *in situ* NAP-XPS in an atmosphere of 90 % CH_4 / 10 % N_2 (total pressure 2 mbar) unless specified otherwise. Times are measured after reaching 627 °C to represent time under reaction conditions. Values are given in at.%; Al was not considered in the quantification. Nb^{x+} refers to the Nb species with higher binding energy compared to Nb^{5+} (see also Figures 7 and S19). As reported previously, the reduced pressure employed during NAP-XPS is likely the cause of the increase in absolute surface concentration of Mo compared to our *ex situ* samples.[1, 2]

Conditions	C	Si	O	Mo^{6+}	Mo^{5+}	Mo^{4+}	Mo^{2+}	Nb^{5+}	Nb^{x+}	Nb^{4+}
127 °C, N_2	4.2	29.2	62.7	3.1	0.19	0	0	0.72	0	0
127 °C	7.4	28.0	60.6	2.4	0.82	0	0	0.75	0	0
627 °C, 0.2 h	6.3	25.9	60.3	1.6	1.4	3.9	0	0.48	0.08	0.05
627 °C, 2.2 h	9.0	25.6	56.8	1.6	0.51	6.0	1.0	0.32	0.16	0.13
627 °C, 5.4 h	9.6	23.9	54.0	1.3	0.53	6.5	3.6	0.30	0.18	0.05

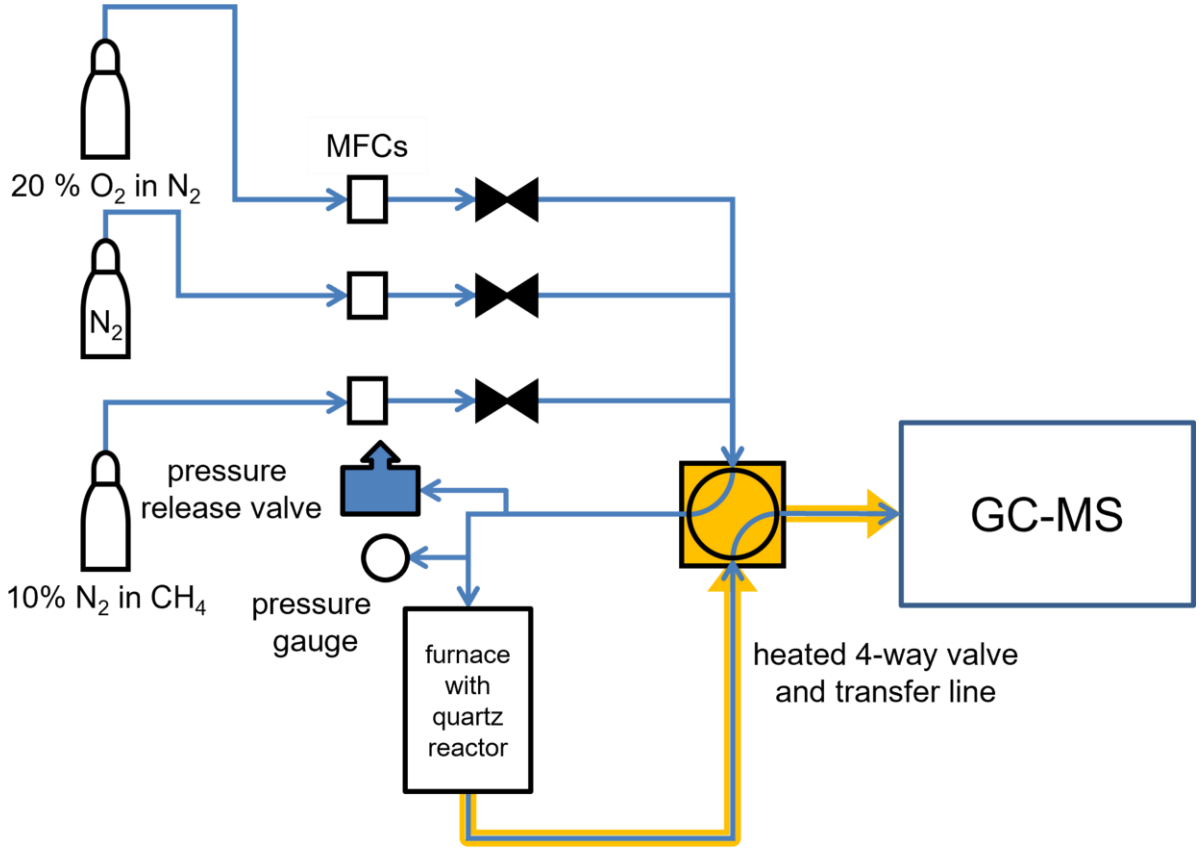

Figure S1: Experimental setup used in performing the catalytic dehydroaromatization measurements.

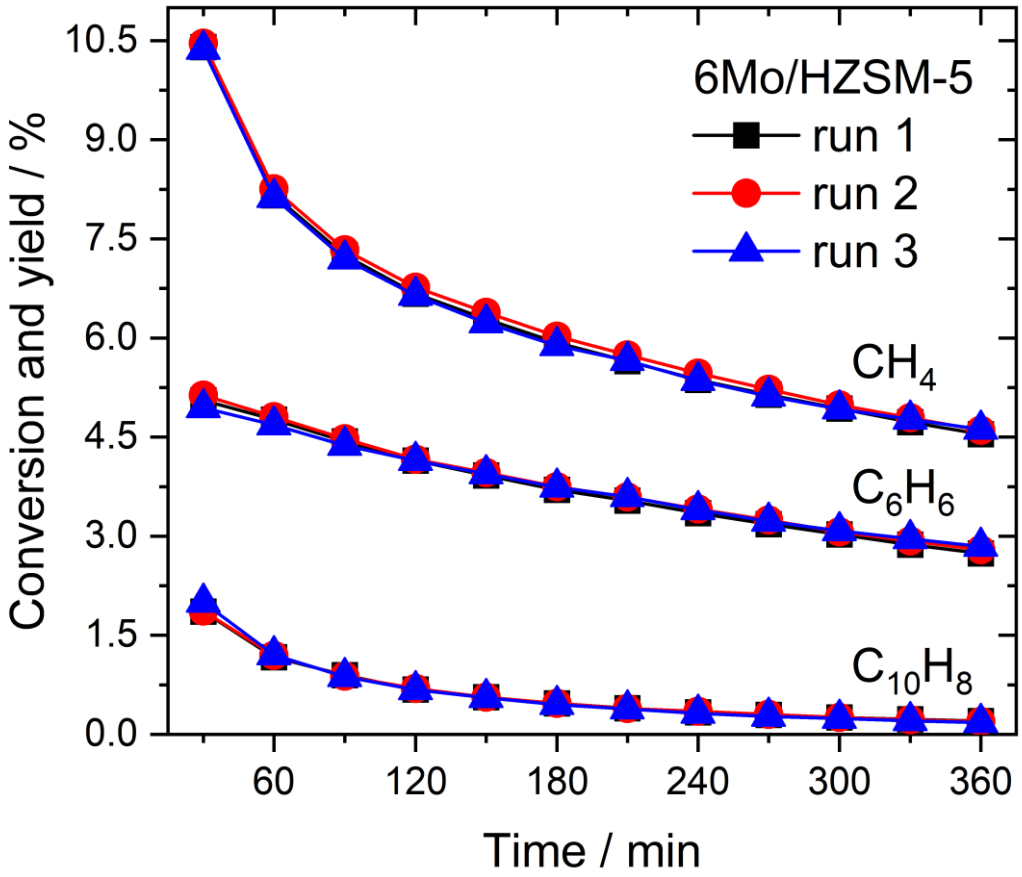

Figure S2: Methane conversions and yields of benzene and naphthalene from MDA reproducibility experiments performed on 6Mo/HZSM-5 under the same reaction conditions (300 mg catalyst, 3200 SCC g_{cat}^{-1} h^{-1}, 700 °C).

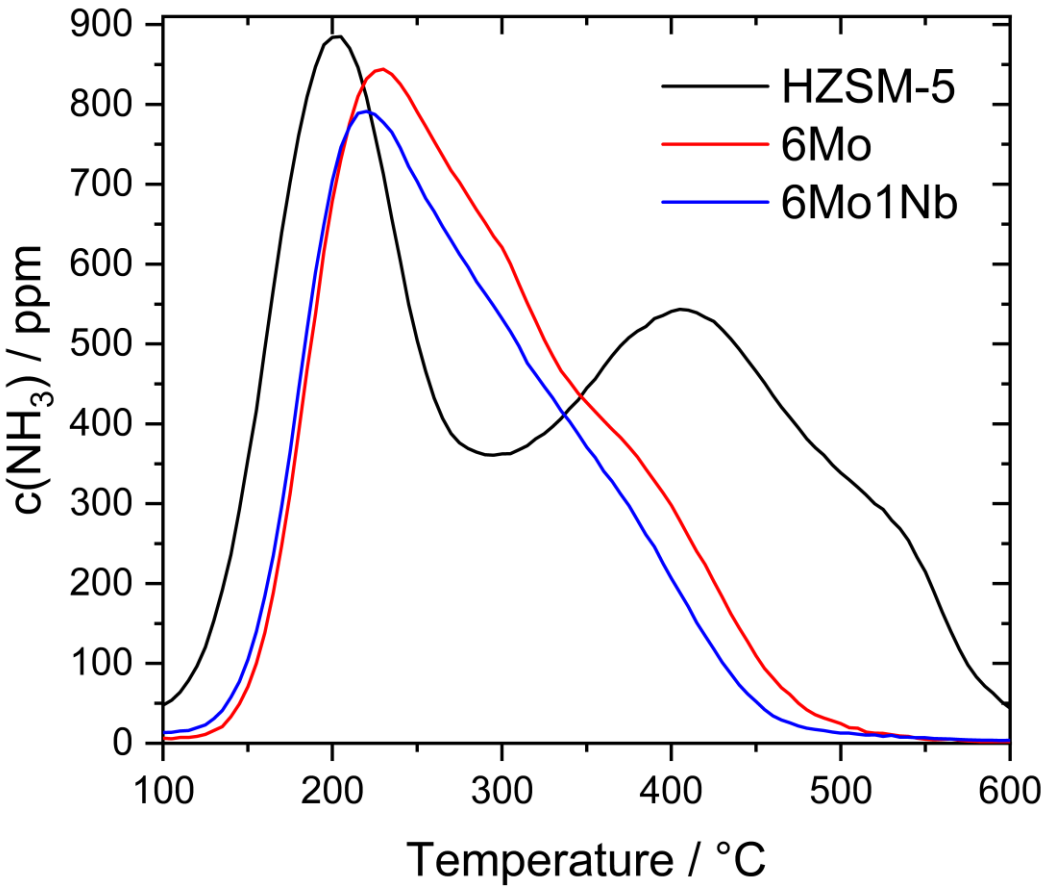

Figure S3: Temperature-programmed ammonia desorption (NH_3-TPD) measurements on the HZSM-5 support as well as the 6.3 wt.% Mo/HZSM-5 (6Mo) and 6.3 wt.% Mo + 1 wt.% Nb/HZSM-5 (6Mo1Nb) catalysts.

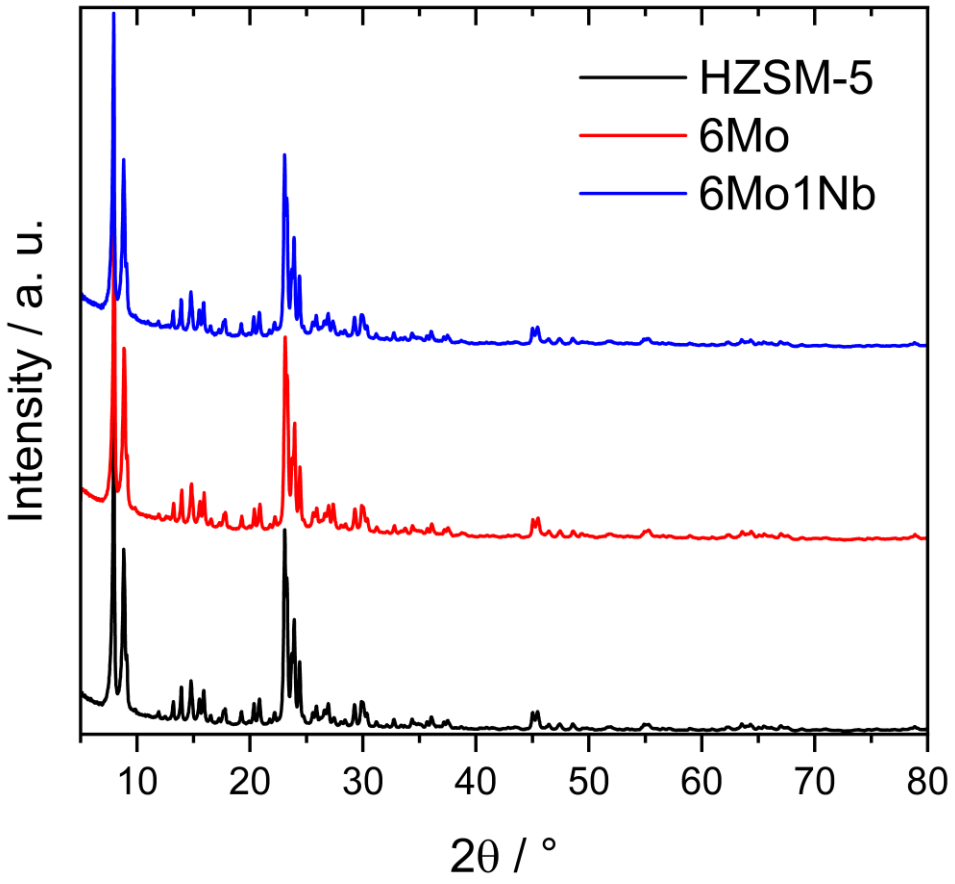

Figure S4: normalized X-ray diffraction (XRD) patterns (obtained with Cu Kα radiation) of HZSM-5 support as well as fresh 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 catalyst samples.

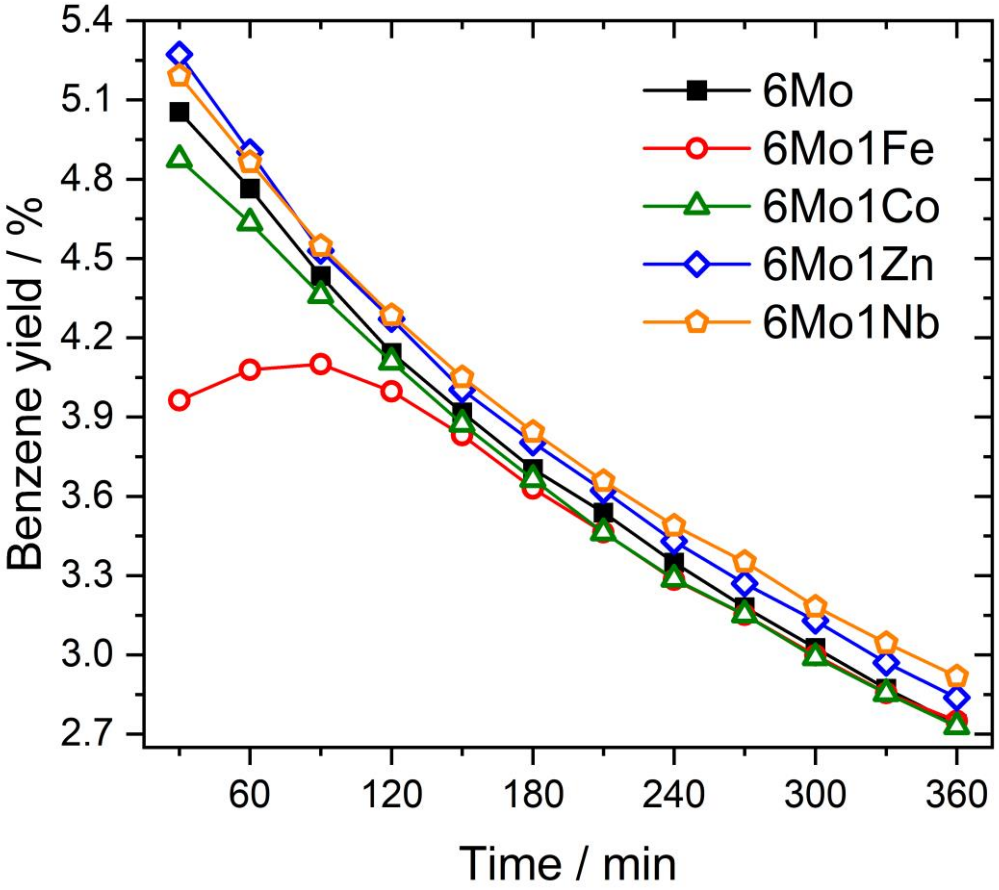

Figure S5: benzene yields over time for MDA on a selection of promoted 6Mo/HZSM-5 catalysts. Reaction conditions: 700 °C, 300 mg catalyst, 90 % CH_4 + 10 % N_2, 3200 SCC g_{cat}^{-1} h^{-1}.

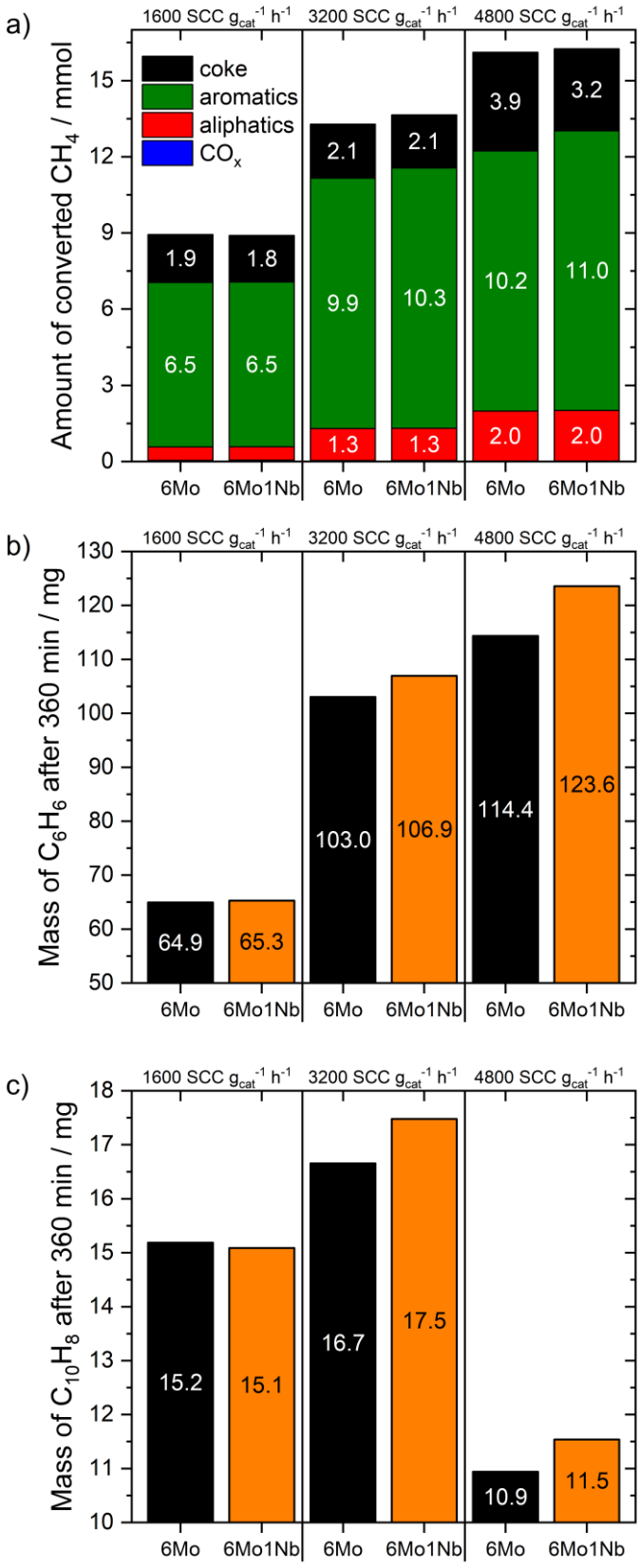

Figure S6: molar amounts of methane converted to different product categories during 360 min of MDA reaction (a) and amounts of benzene (b) and naphthalene (c) with different space velocities. Values were calculated from the yields of the respective products.

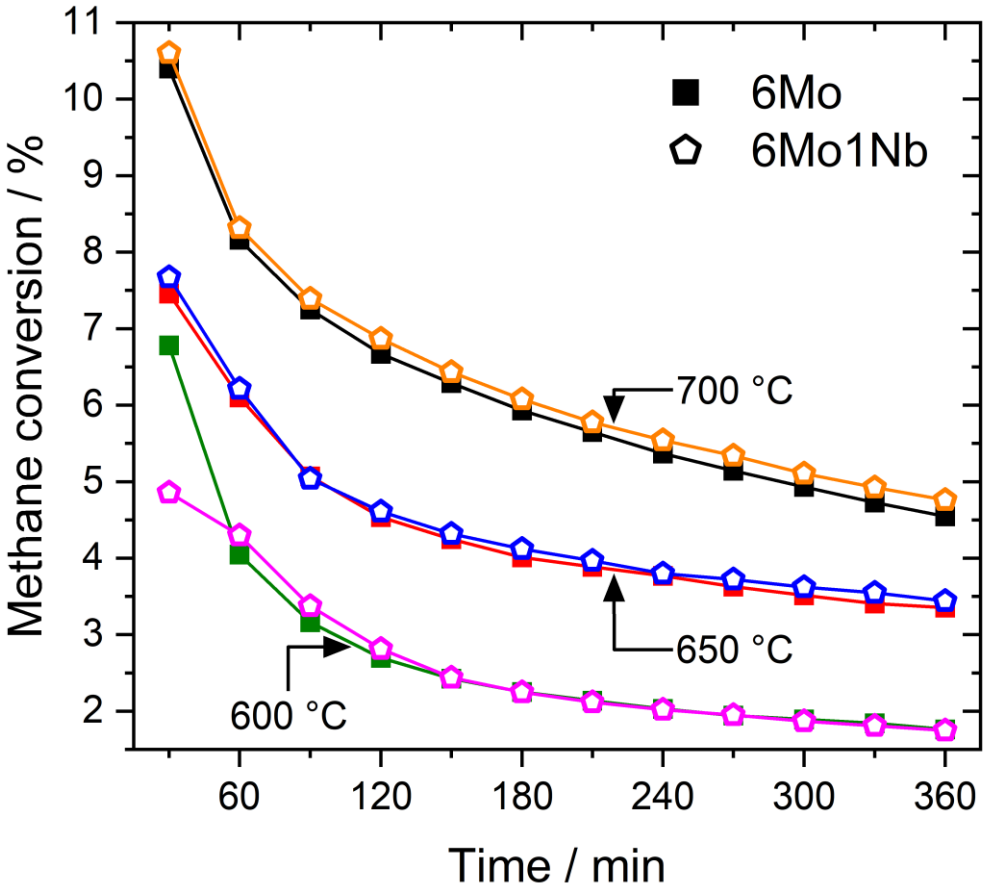

Figure S7: methane conversions over time for MDA on 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 catalysts at different temperatures. Reaction conditions: 300 mg catalyst, 90 % CH_4 + 10 % N_2, 3200 SCC g_{cat}^{-1} h^{-1}.

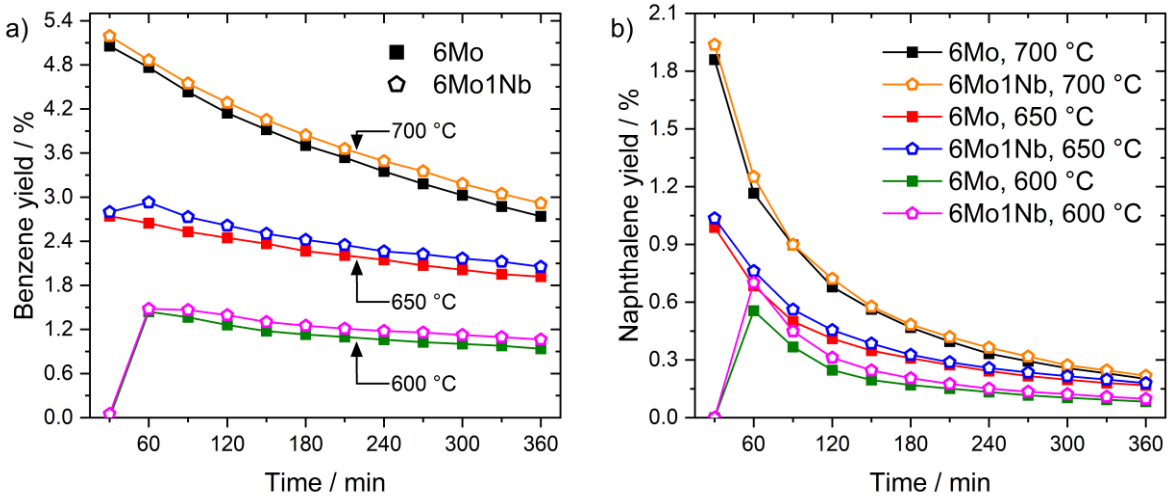

Figure S8: benzene (a) and naphthalene yields (b) over time for MDA on 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 catalysts at different temperatures. Reaction conditions: 300 mg catalyst, 90 % CH_4 + 10 % N_2, 3200 SCC g_{cat}^{-1} h^{-1}.

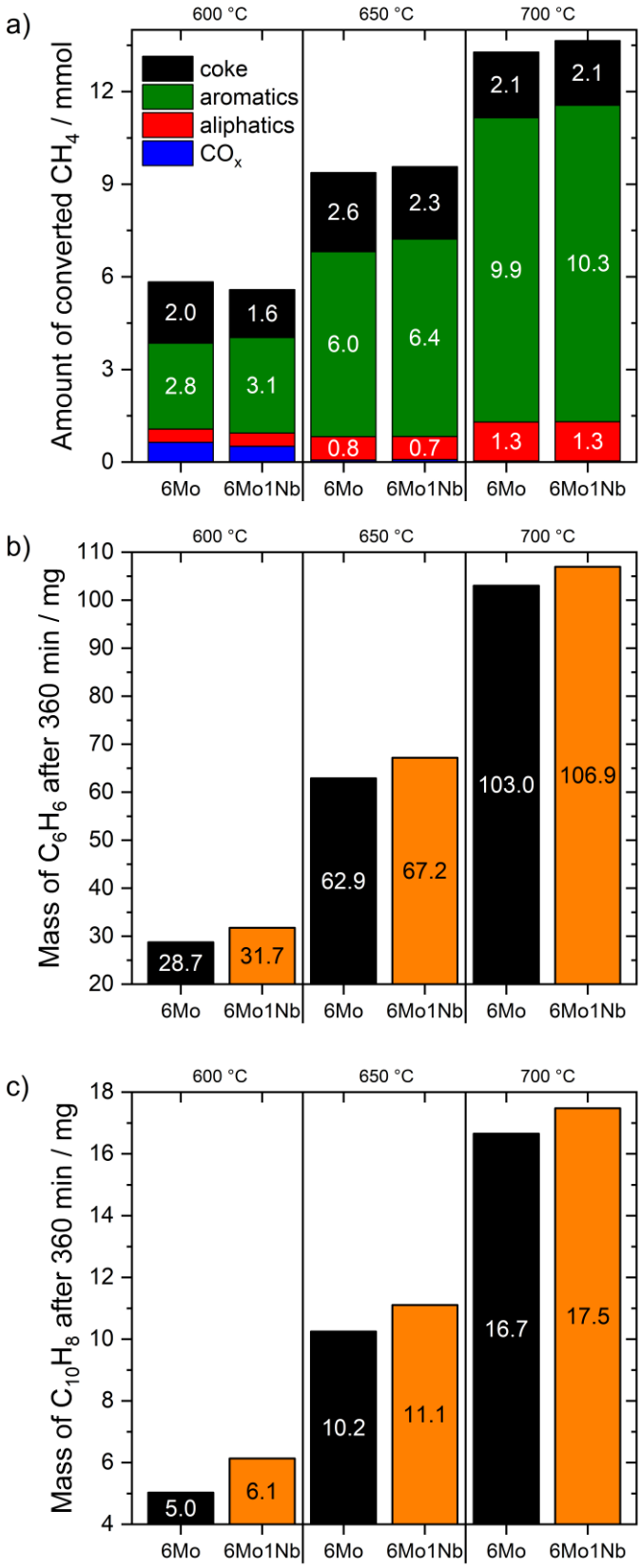

Figure S9: Molar amounts of methane converted to different product categories during 360 min of MDA reaction (a) and amounts of benzene (b) and naphthalene (c) with different reaction temperatures. Values were calculated from the yields of the respective products.

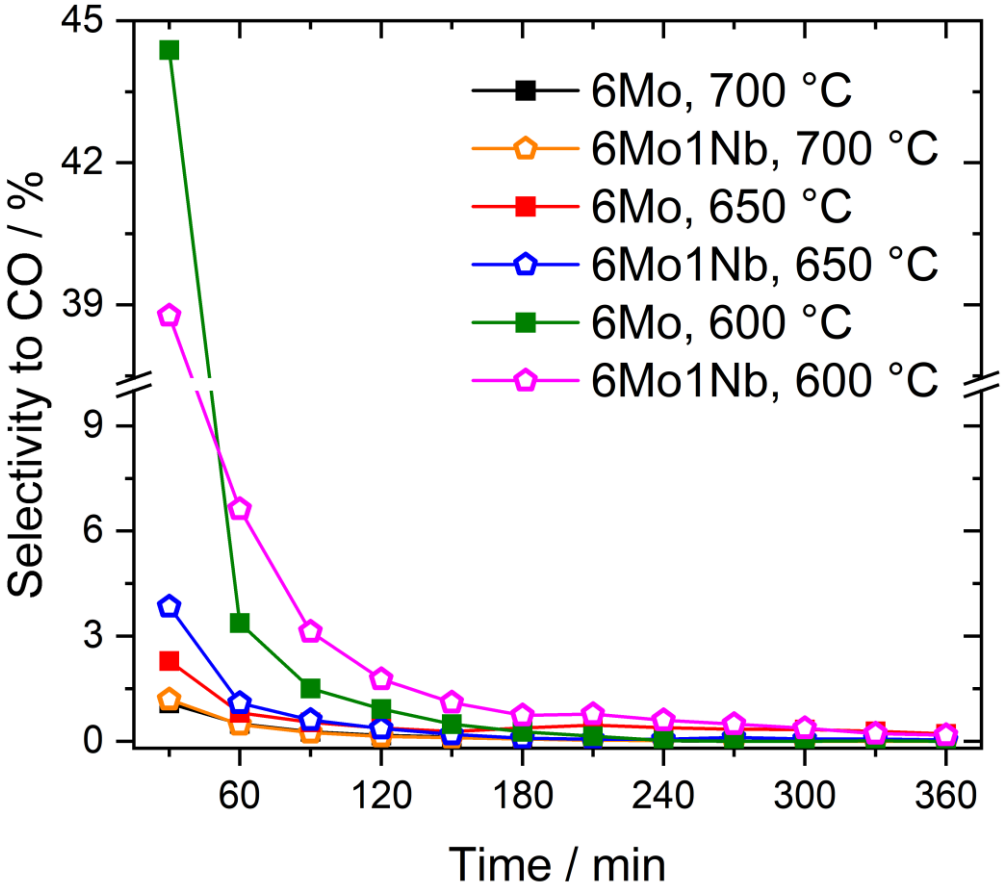

Figure S10: CO selectivities over time for MDA on 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 catalysts at different temperatures. Reaction conditions: 300 mg catalyst, 90 % CH_4 + 10 % N_2, 3200 SCC g_{cat}^{-1} h^{-1}.

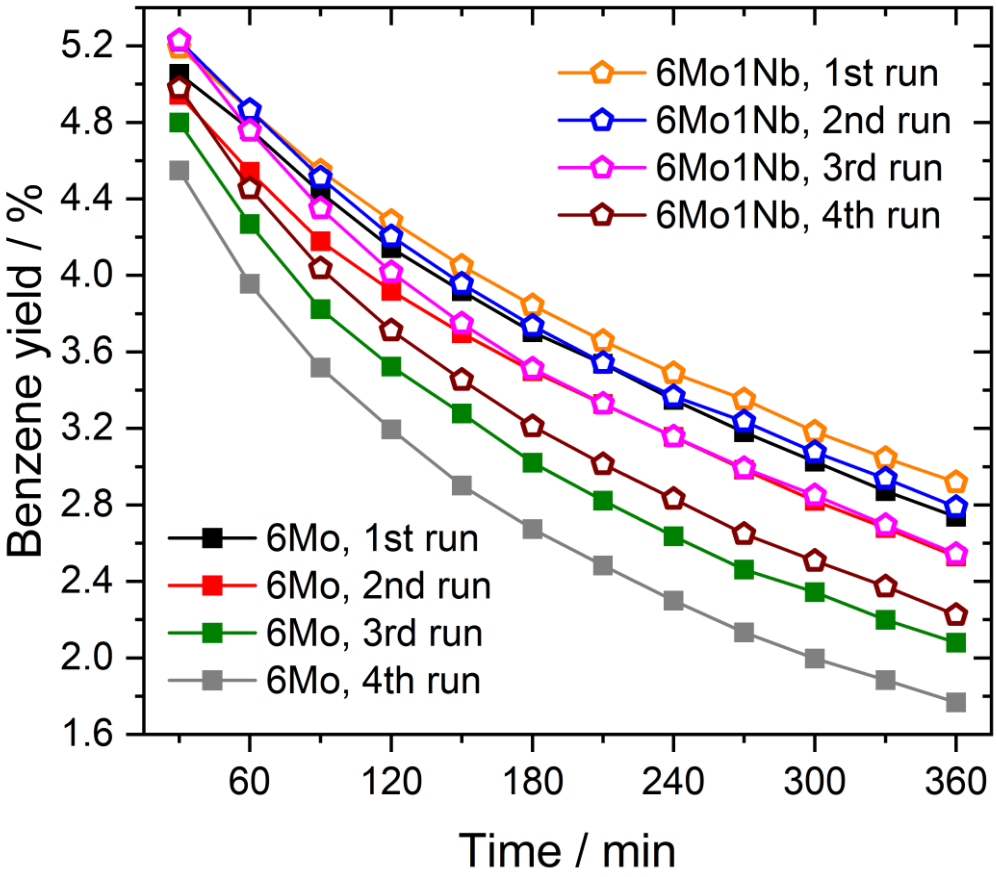

Figure S11: benzene yield over time for MDA over 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 catalysts in subsequent reaction-regeneration cycles. Reaction conditions: 700 °C, 300 mg catalyst, 90 % CH_4 + 10 % N_2, 3200 SCC g_{cat}^{-1} h^{-1}. Regeneration: 450 °C, air, 1100 SCC g_{cat}^{-1} h^{-1}, 45 min.

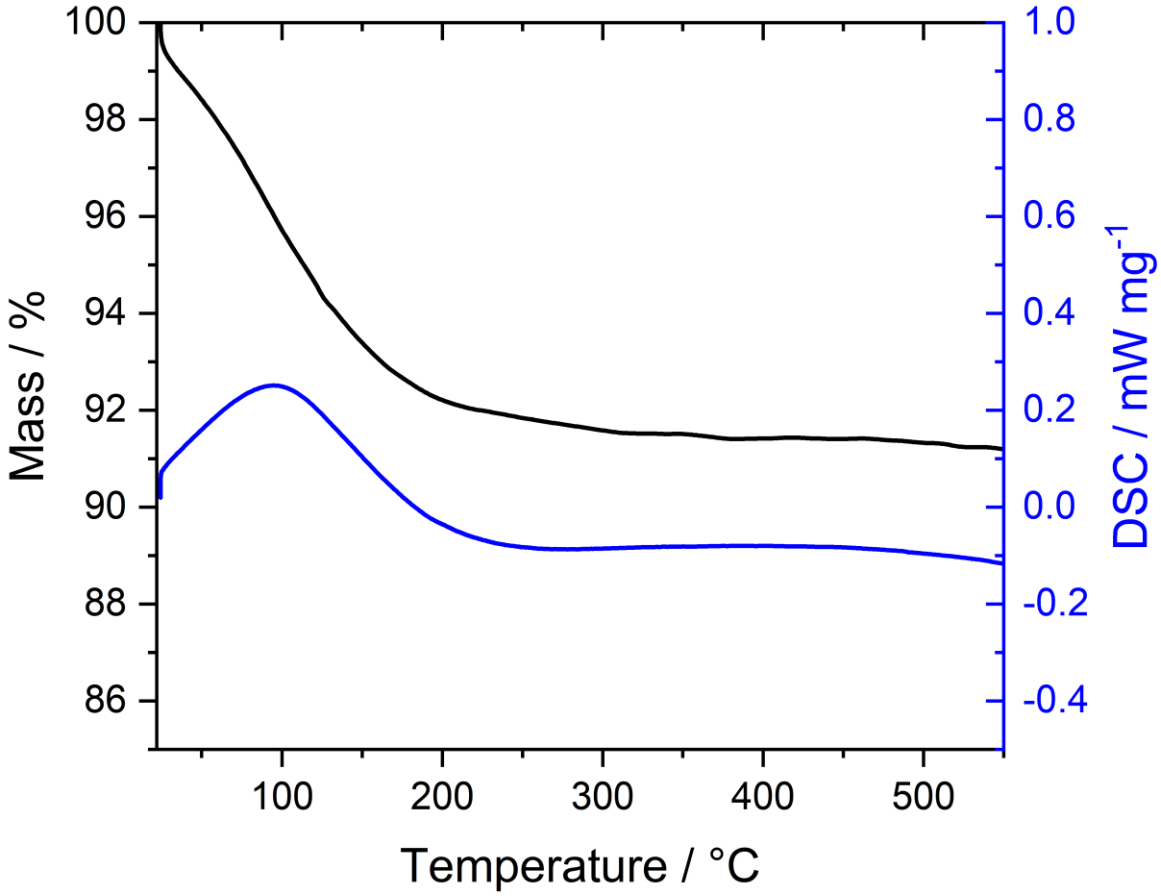

Figure S12: TGA (black) and DSC (blue) curves of fresh 6Mo/HZSM-5. The observed mass loss is related to atmospheric water adsorbed on the surface, inside the pore system and on acidic sites.[3, 4]

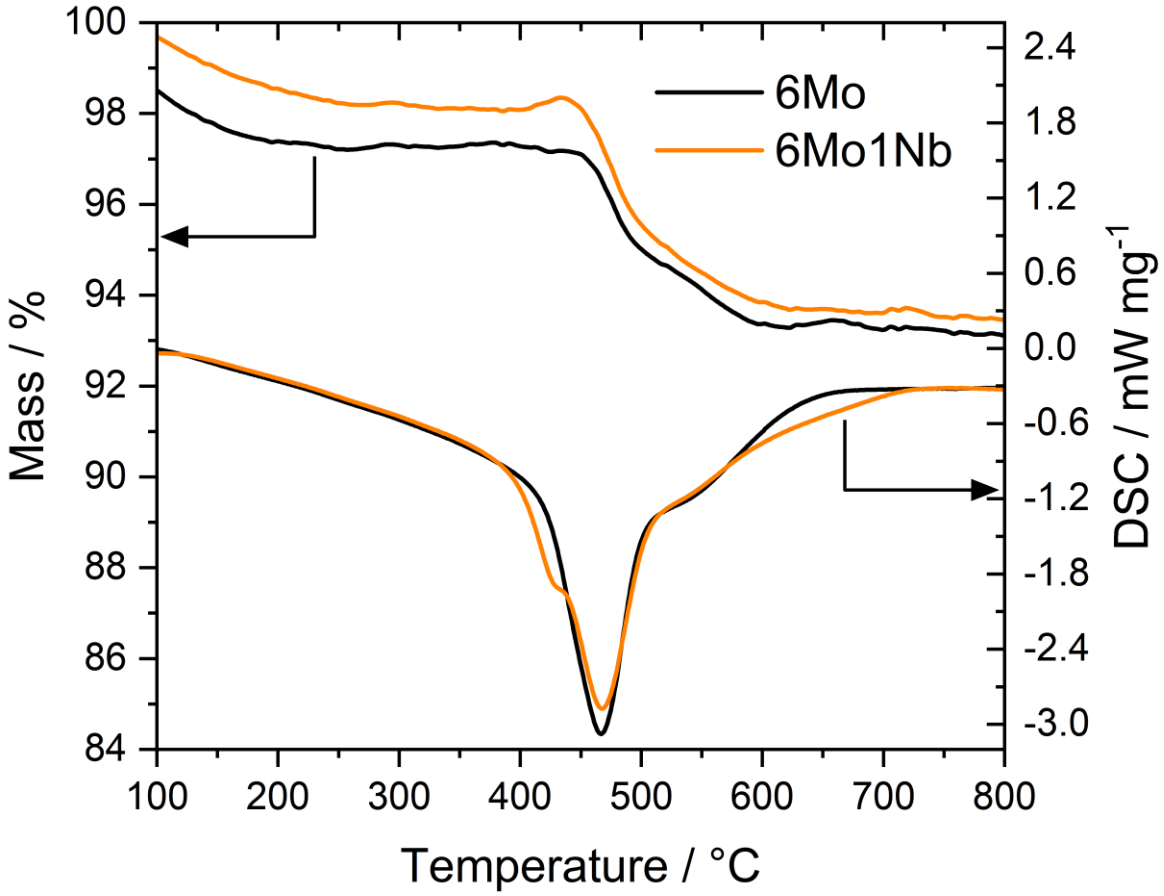

Figure S13: TGA (top curves) and DSC (bottom curves) measurements on spent 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 after reaction for 360 min. Reaction conditions: 700 °C, 300 mg catalyst, 90 % CH_4 + 10 % N_2, 4800 SCC g_{cat}^{-1} h^{-1}, 1 atm.

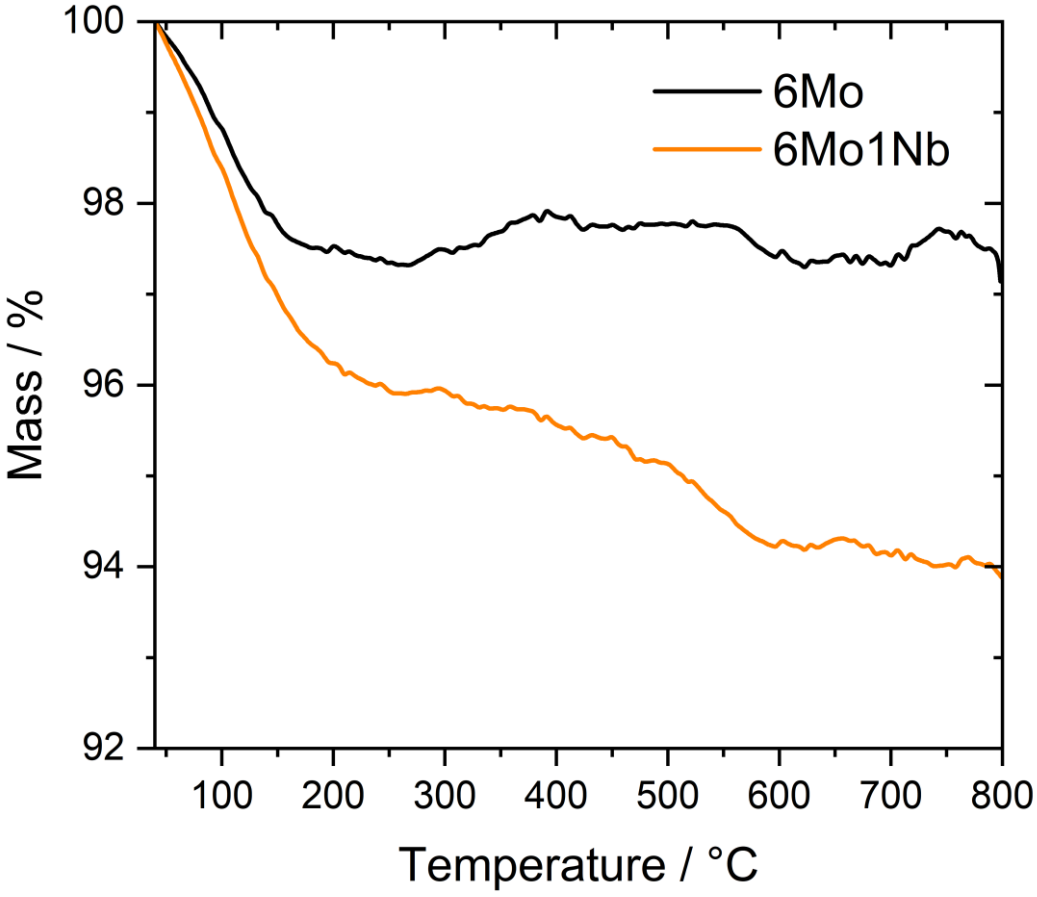

Figure S14: TGA of 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 after four reaction / regeneration cycles (total TOS 24 h). After the fourth reaction run, a final regeneration procedure was performed.

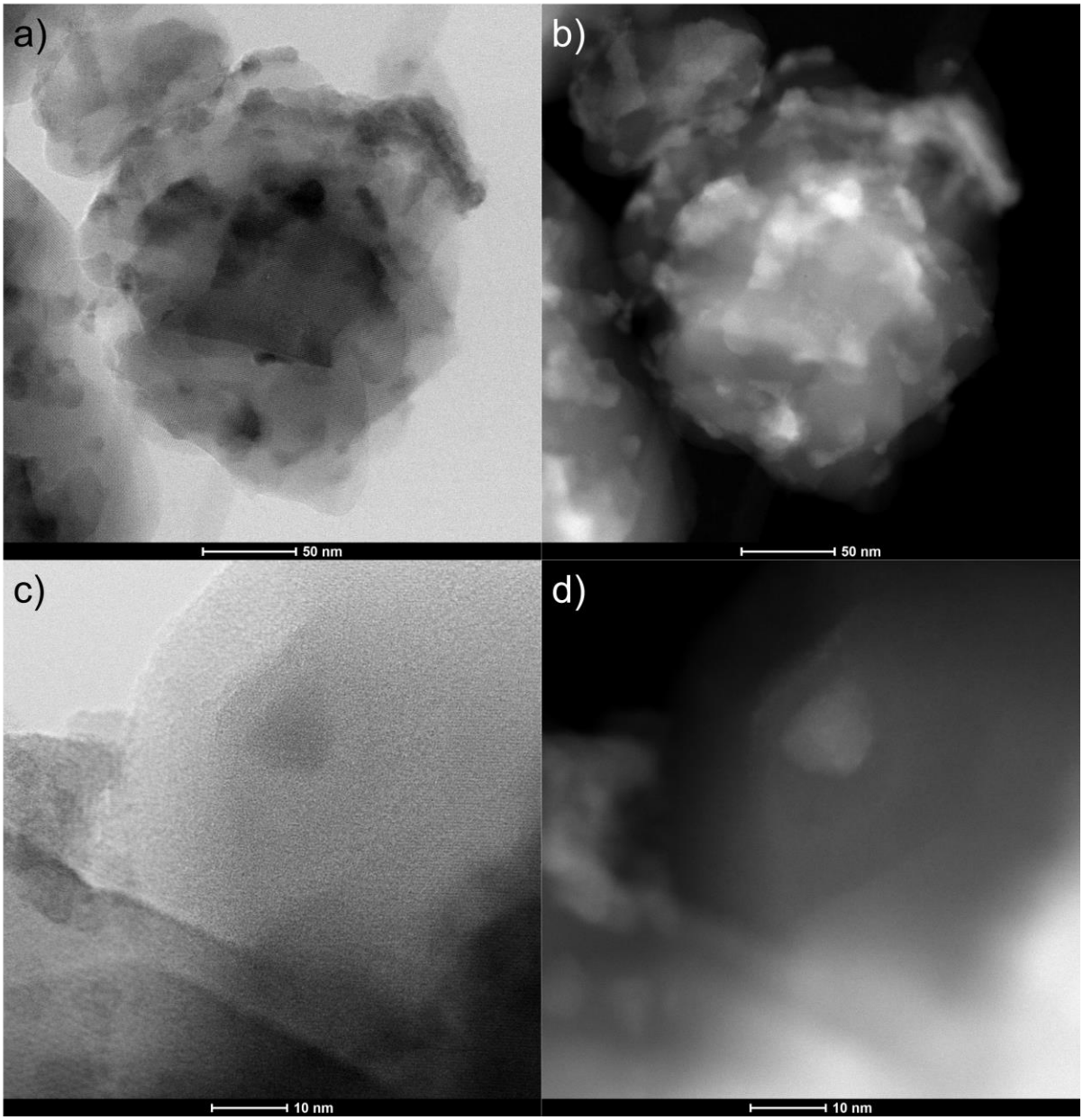

Figure S15: Additional overview STEM micrographs of the fresh (a: bright field (BF); b: dark field (HAADF)) and higher resolution images (c: BF; d: HAADF) of the fresh 6Mo1Nb/HZMS-5 catalyst.

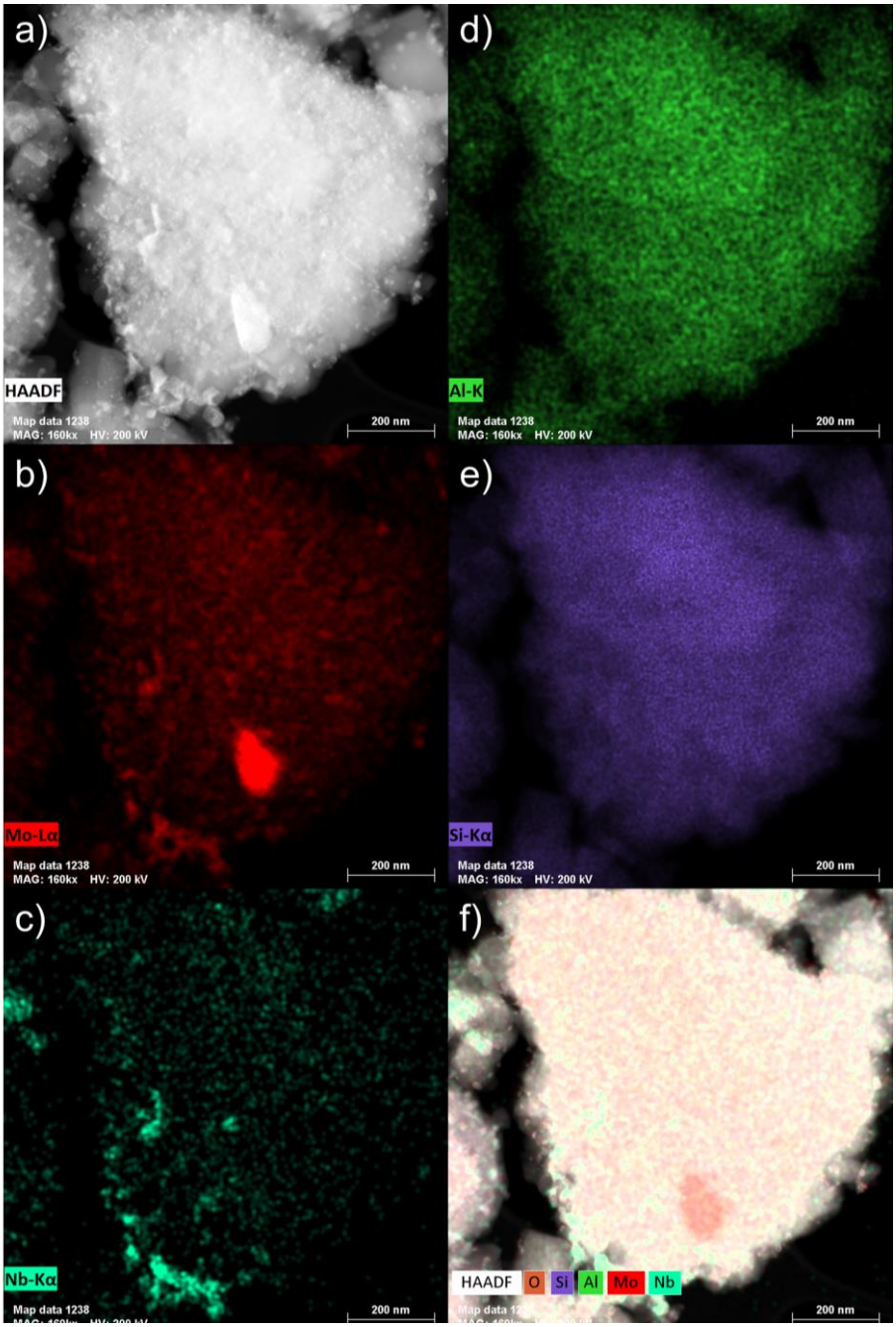

Figure S16: STEM micrograph (a) and corresponding EDS maps (b: Mo Lα; c: Nb Kα; d: Al Kα; e: Si Kα; f: overlay of O, Si, Al; Mo and Nb) of the spent 6Mo1Nb/HZSM-5 catalyst after reaction for 360 min on stream at 700 °C.

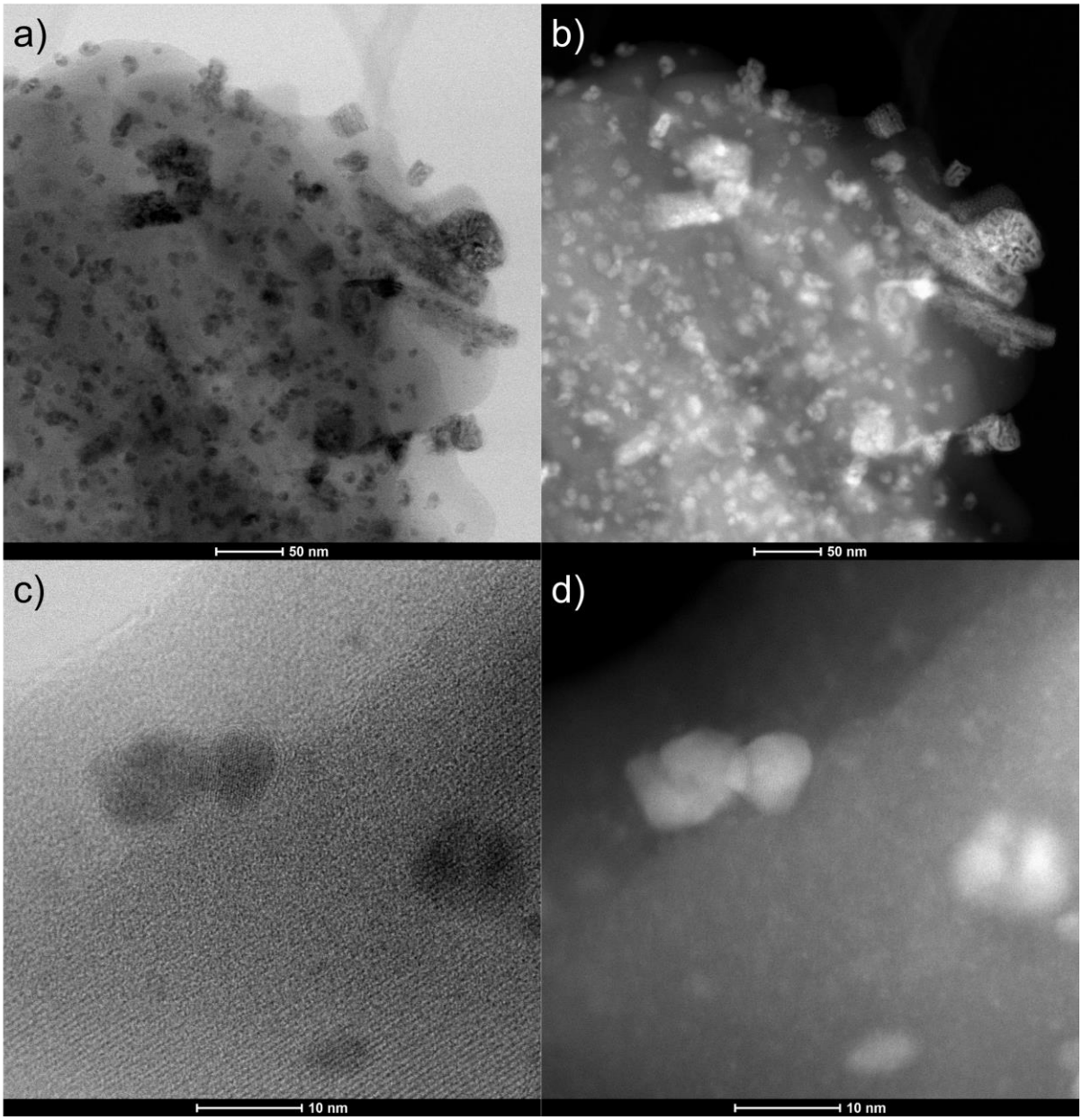

Figure S17: Additional overview STEM micrographs (a: bright field (BF); b: dark field (HAADF)) and higher resolution images (c: BF; d: HAADF) of the spent 6Mo1Nb/HZMS-5 catalyst after reaction for 360 min on stream at 700 °C.

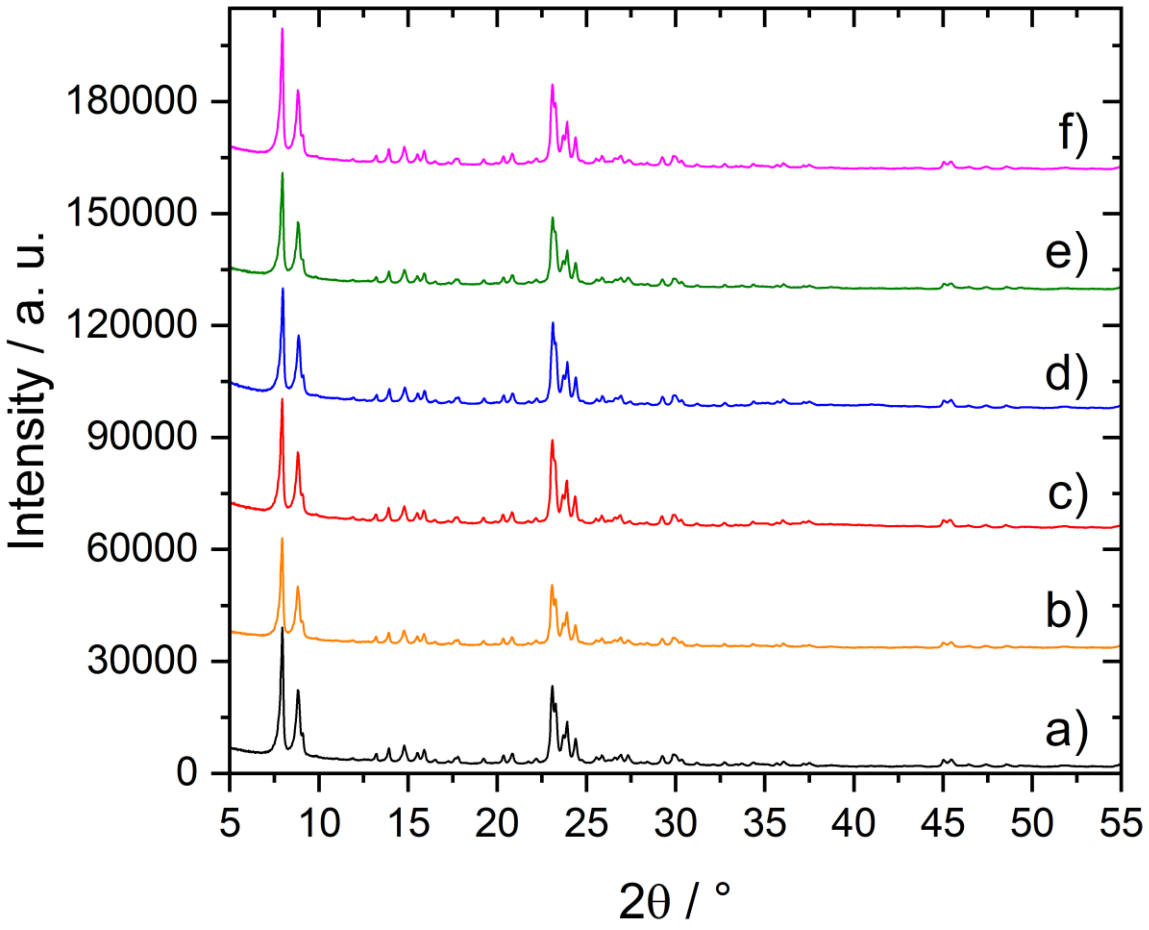

Figure S18: XRD patterns (obtained with Cu Kα radiation) of fresh 6Mo/HZSM-5 (a) and 6Mo1Nb/HZSM-5 (b), spent 6Mo/HZSM-5 (c) and 6Mo1Nb/HZSM-5 (d) as well as regenerated 6Mo/HZSM-5 (e) and 6Mo1Nb/HZSM-5 (f) catalyst samples. Intensities were not normalized.

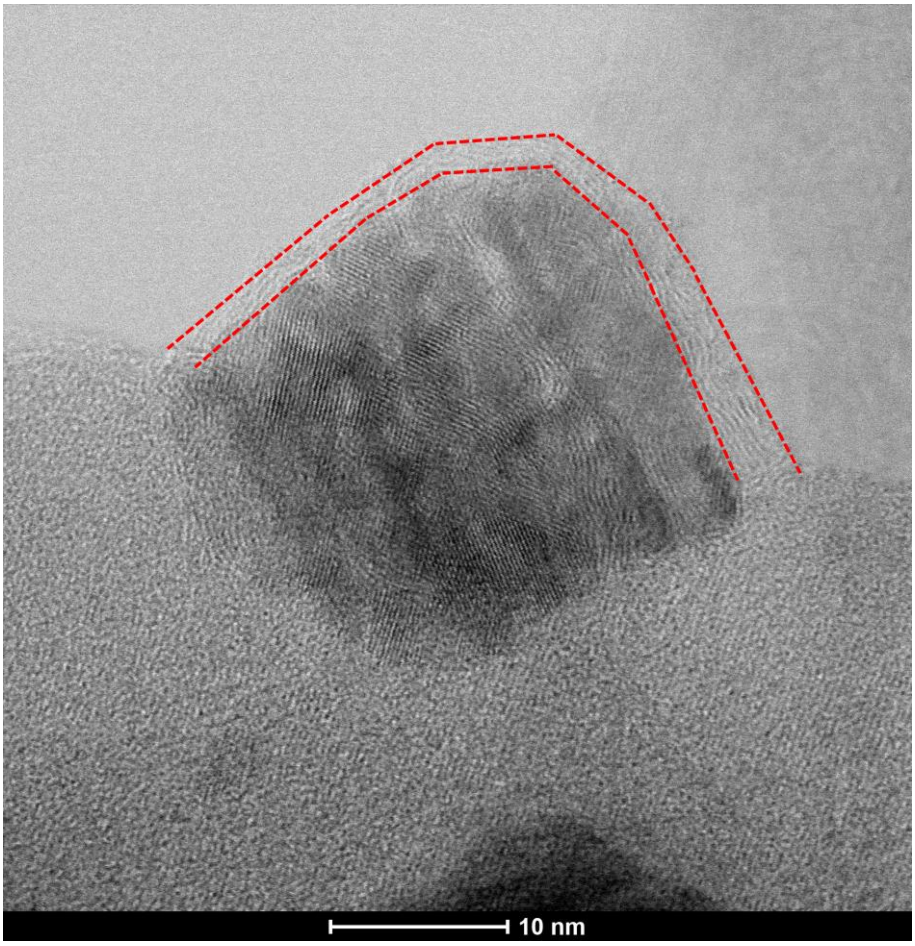

Figure S19: High resolution BF-STEM micrograph of the spent 6Mo1Nb/HZMS-5 catalyst showing the overgrowth of a thin carbon layer on the surface of MoNb nanoparticles (see additional discussion on the evaluation in Ref. [1]).

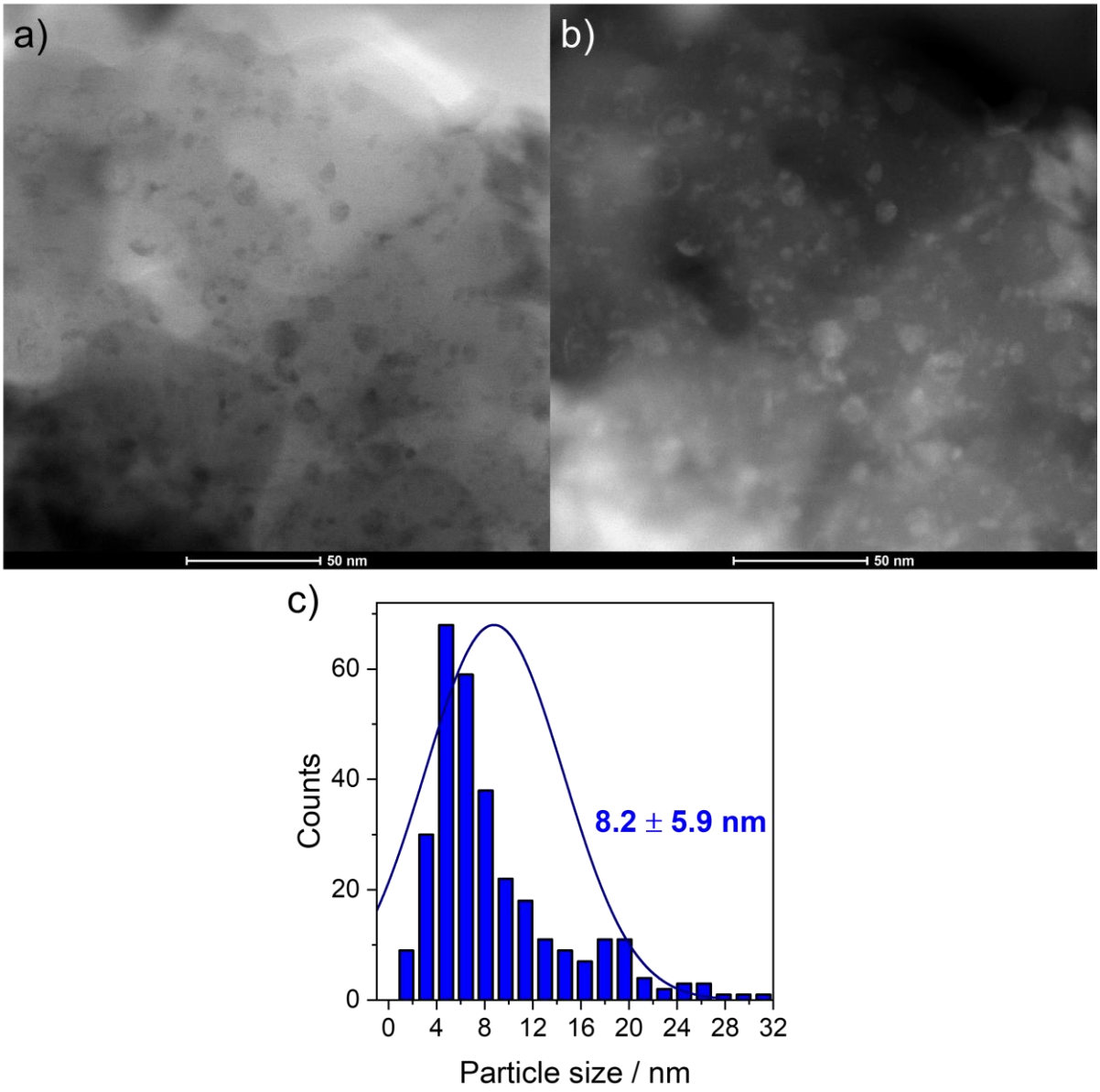

Figure S20: STEM micrographs of the regenerated 6Mo1Nb/HZMS-5 catalyst (a: bright field (BF); b: dark field (HAADF)), and (c) the corresponding particle size distribution.

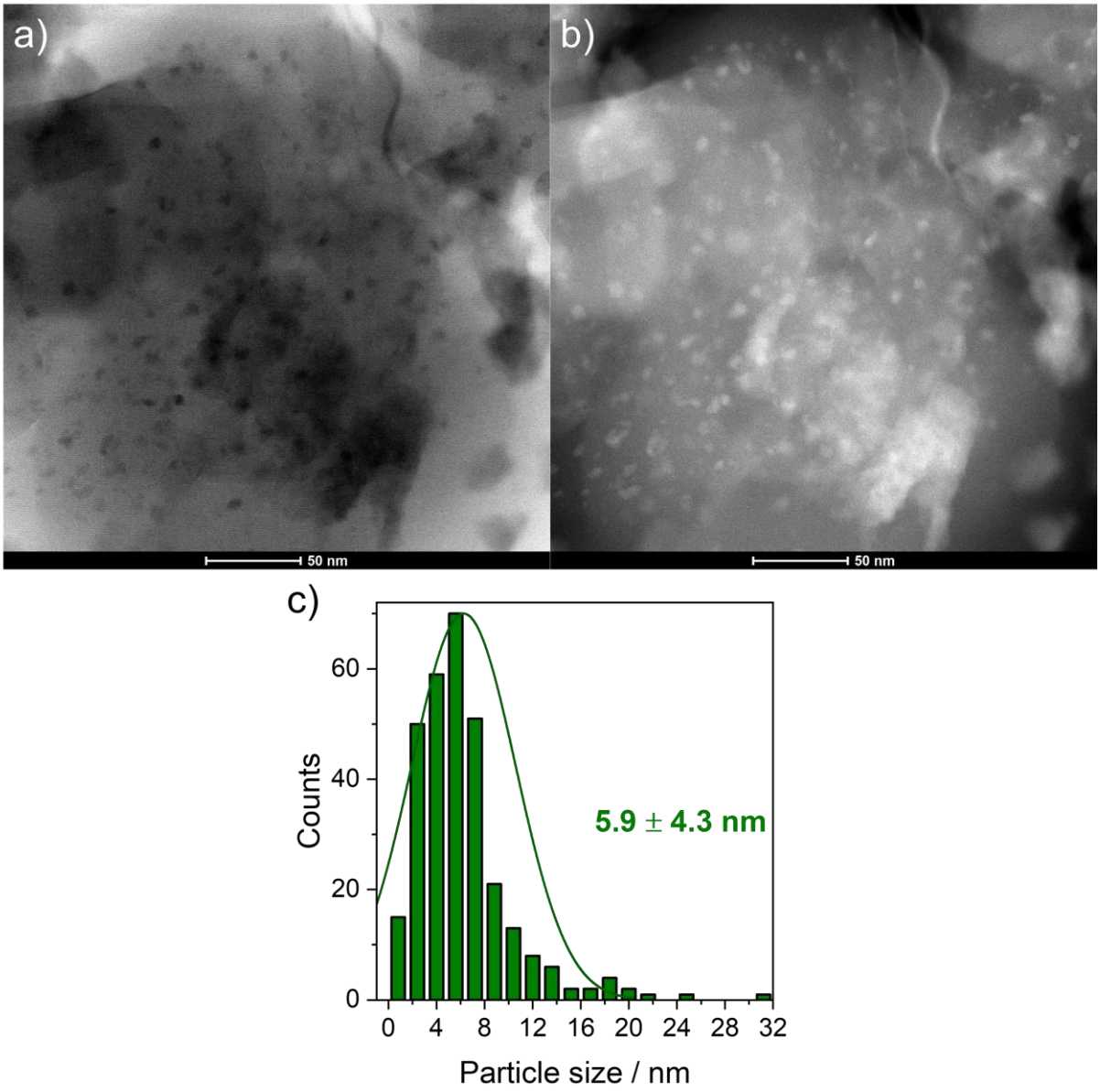

Figure S21: STEM micrographs of the regenerated 6Mo/HZMS-5 catalyst (a: bright field (BF); b: dark field (HAADF)), and (c) the corresponding particle size distribution.

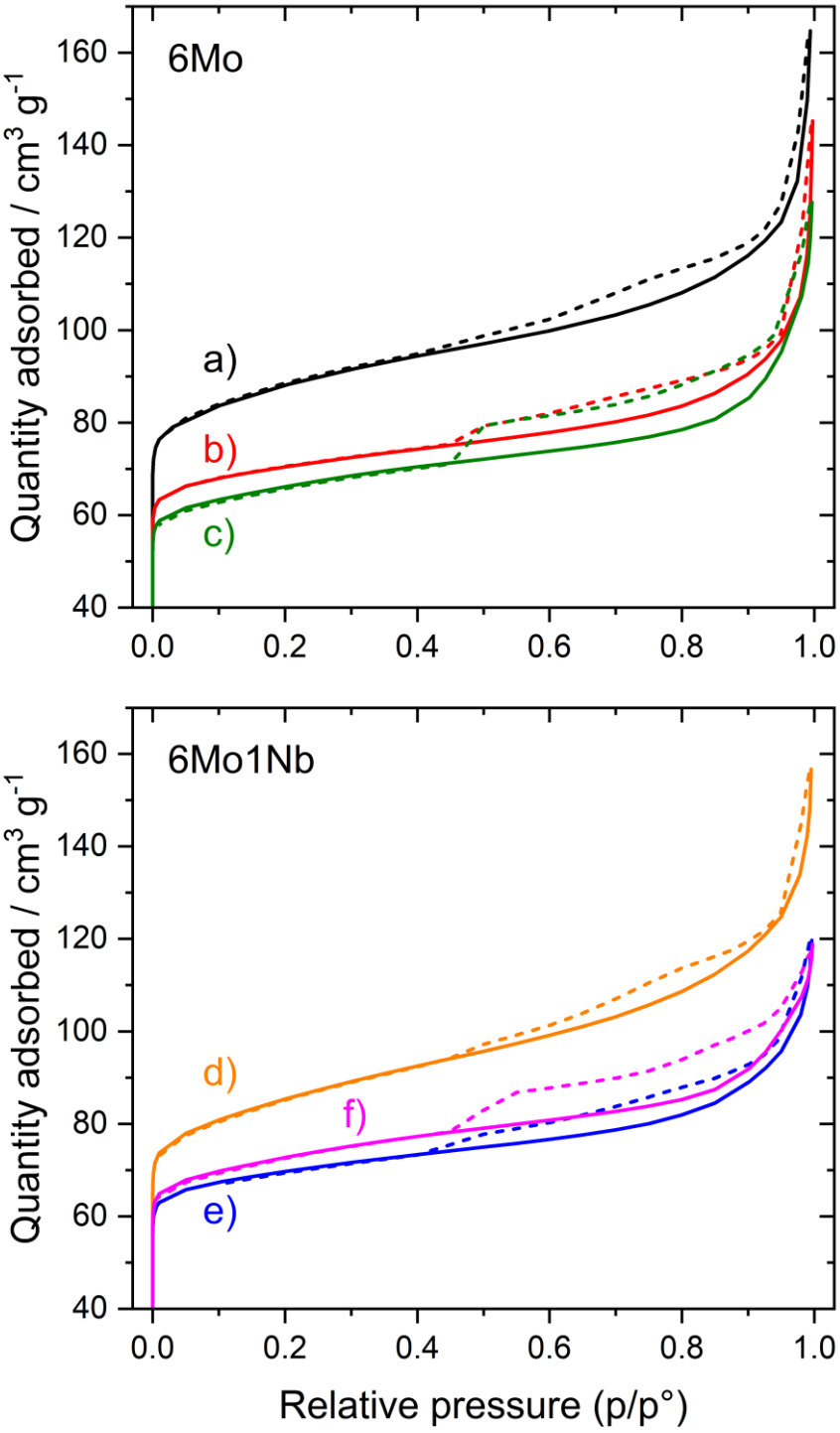

Figure S22: N_2 sorption isotherms recorded according to the BET method. Top: fresh (a), spent (b) and regenerated (c) 6Mo/HZSM-5; bottom: fresh (d), spent (e) and regenerated (f) 6Mo1Nb/HZSM-5. Calculated characteristics like specific surface areas and micropore volumes are given in Table S3.

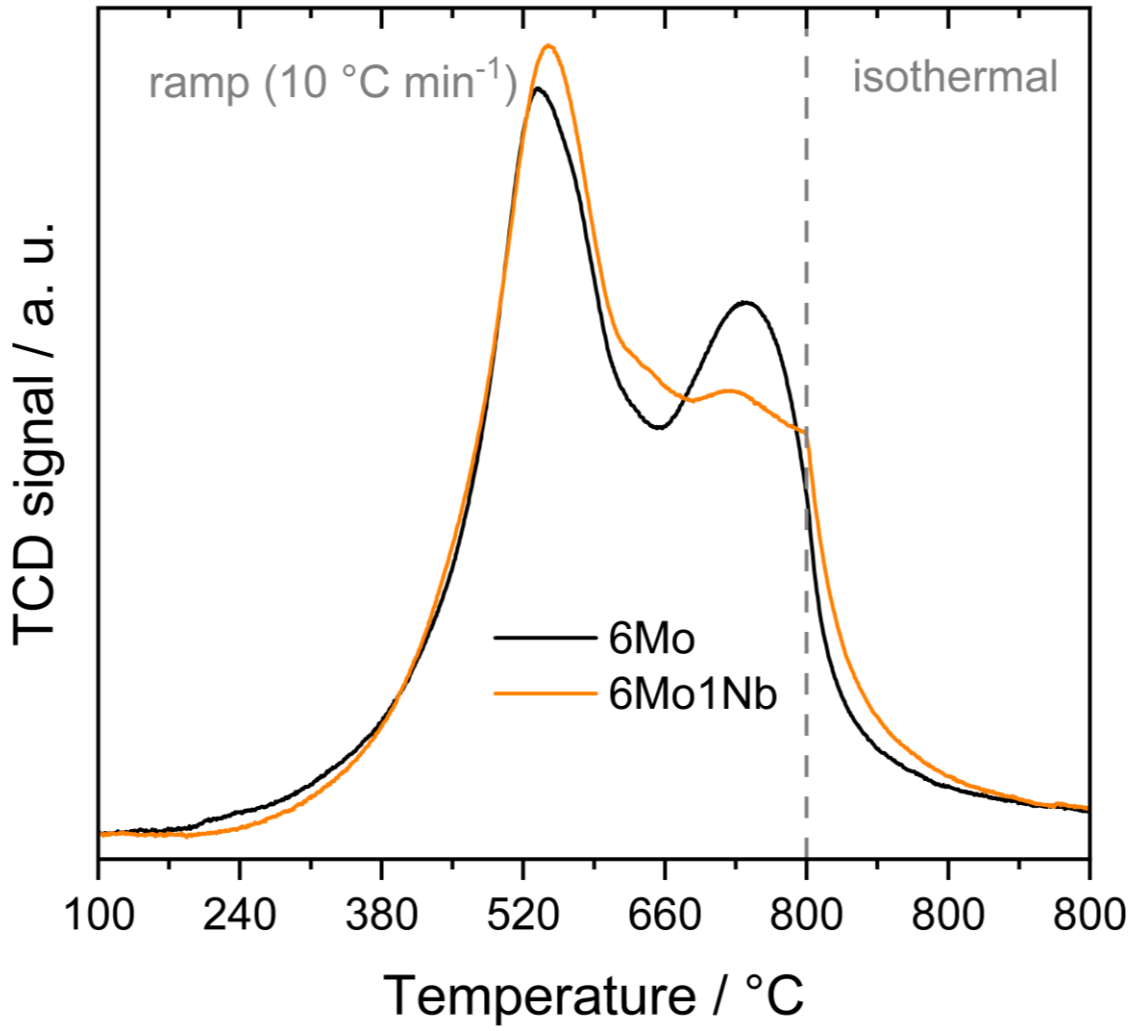

Figure S23: Recorded temperature-programmed reduction (TPR) curves in 5 % H_2/N_2 for fresh 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 catalysts.

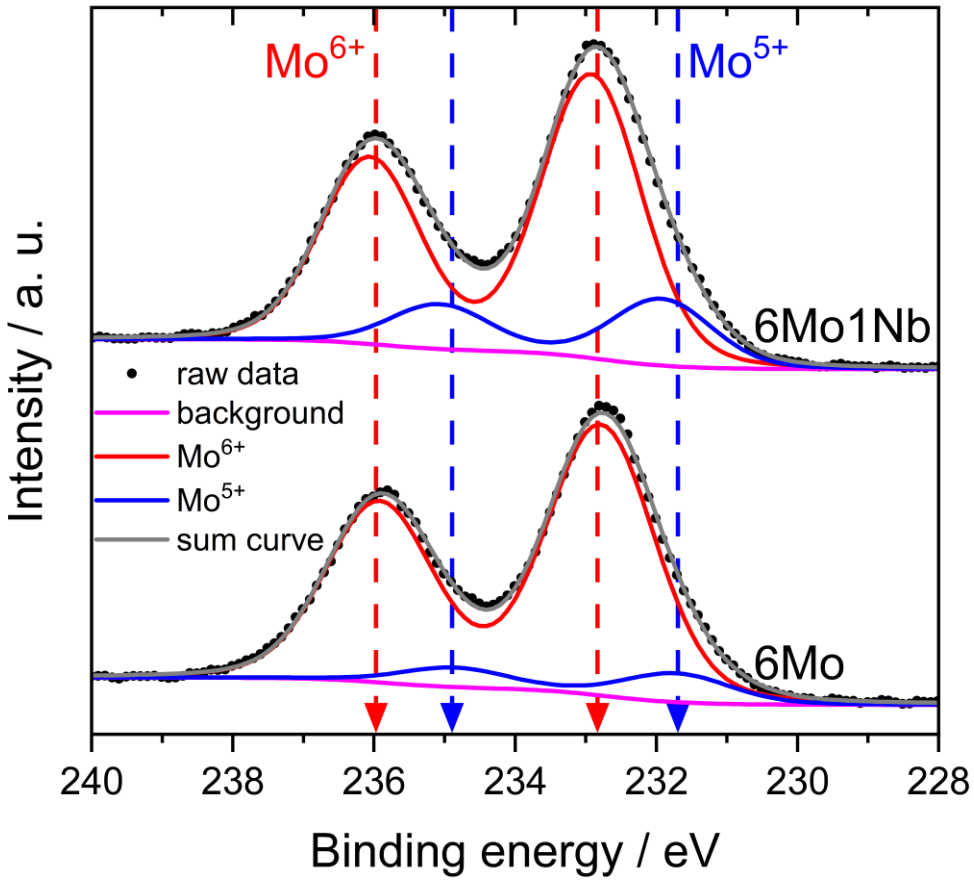

Figure S24: Normalized X-ray photoelectron spectra (XPS) for the Mo 3d level of 6Mo/HZSM-5 and 6Mo1Nb/HZSM-5 catalysts after four reaction / regeneration cycles. Reaction conditions: 700°C, 300 mg catalyst, 90 % CH_4 + 10 % N_2, 3200 SCC g_{cat}^{-1} h^{-1}, 6 h; Regeneration conditions: 450°C, air, 1100 SCC g_{cat}^{-1} h^{-1}, 45 min.

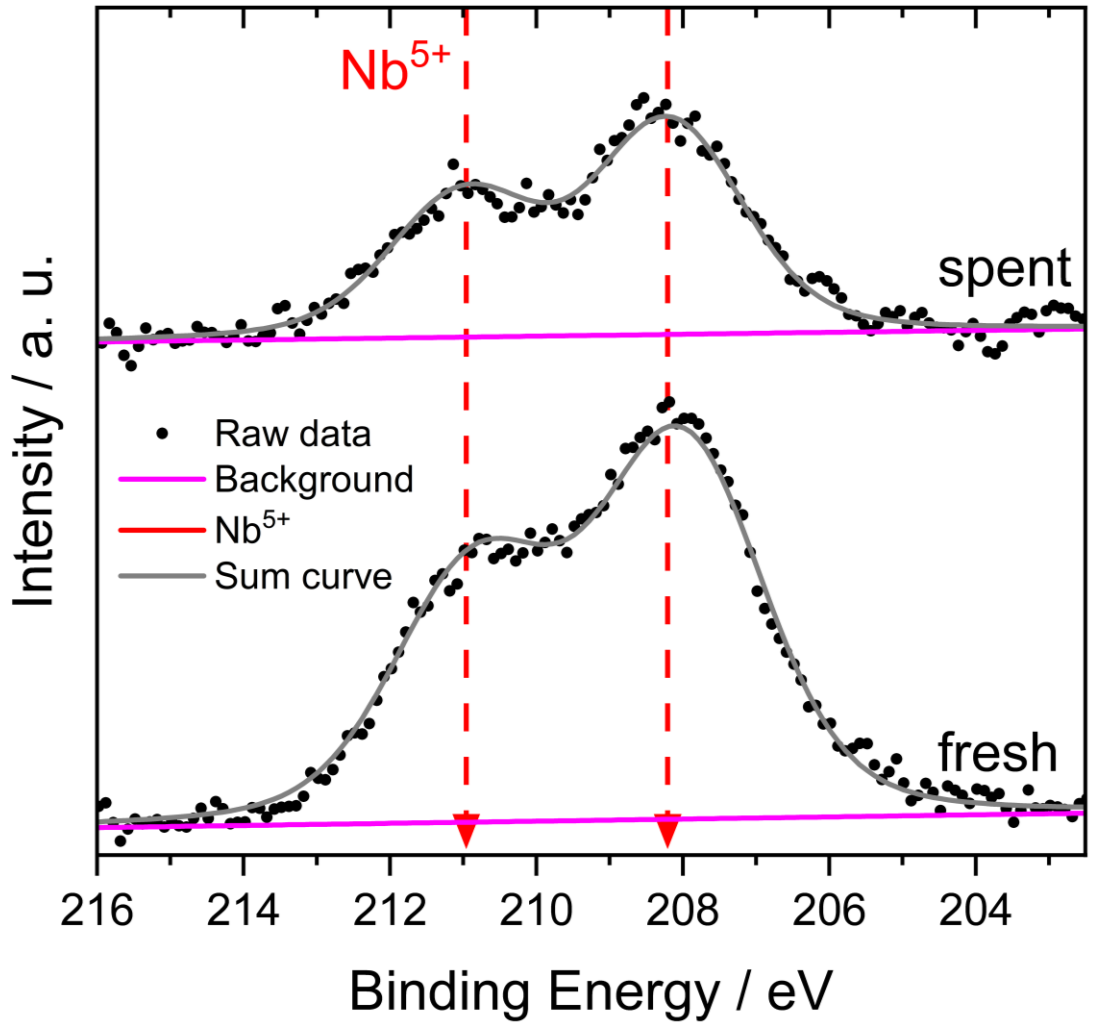

Figure S25: XPS for the Nb 3d level of 1Nb/HZSM-5 before and after reaction with methane. Reaction conditions: 700 °C, 300 mg catalyst, 90 % CH_4 + 10 % N_2, 3200 SCC g_{cat}^{-1} h^{-1}, 6 h. Intensities were not normalized. Dashed arrows were added as a visual guide.

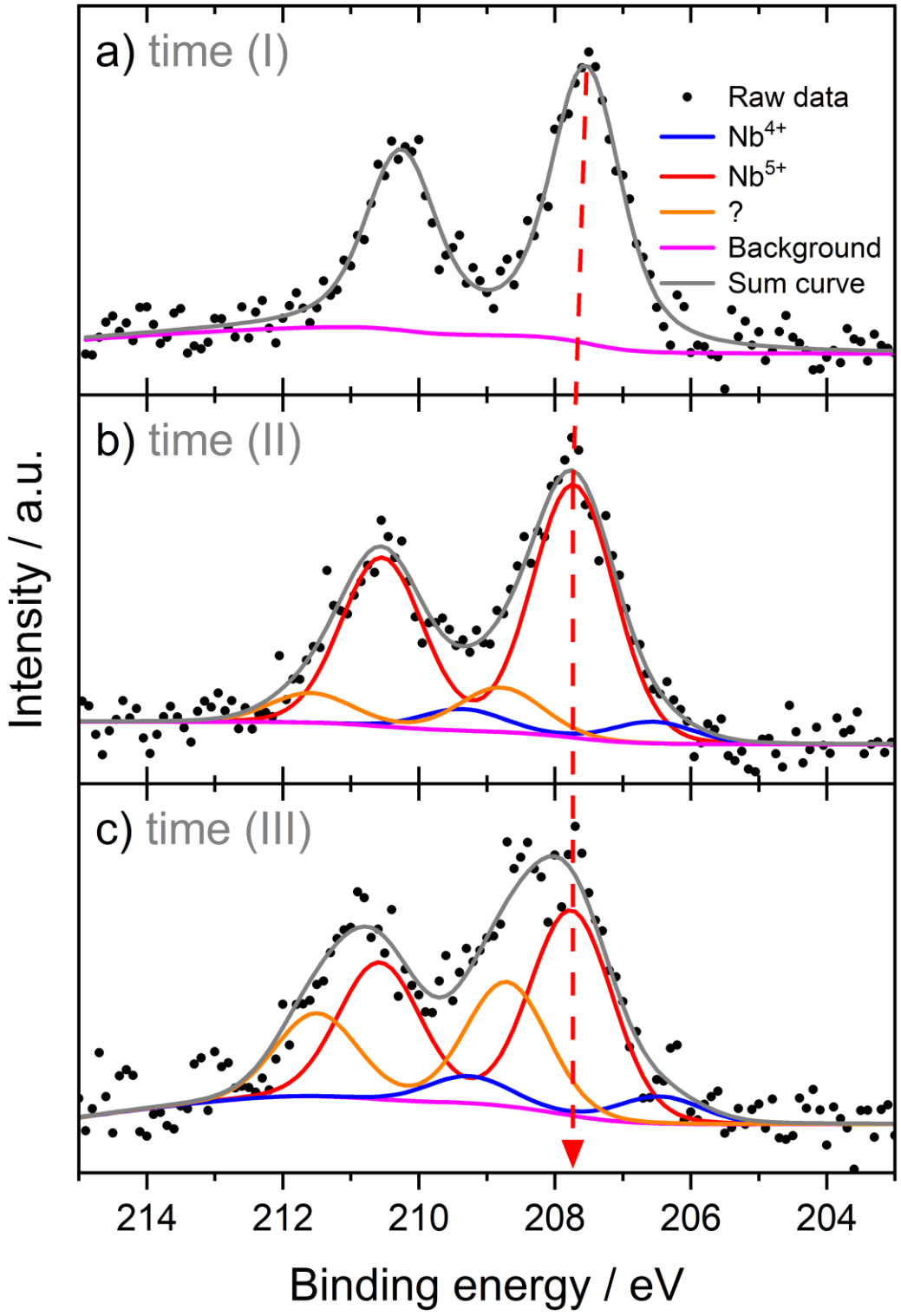

Figure S26: *In situ* collected Nb 3d spectra at different times (a: time (I) - 55 min @ 127 °C; b: time (II) - 2.0 h @ 627 °C; c: time (III) - 7.2 h @ 627 °C) during the NAP-XPS study of 6Mo1Nb/HZSM-5 at a total pressure of 2 mbar in the reaction atmosphere 90 % CH_4 / 10 % N_2. Times are given in relative time (see Figure 8e in the main manuscript).

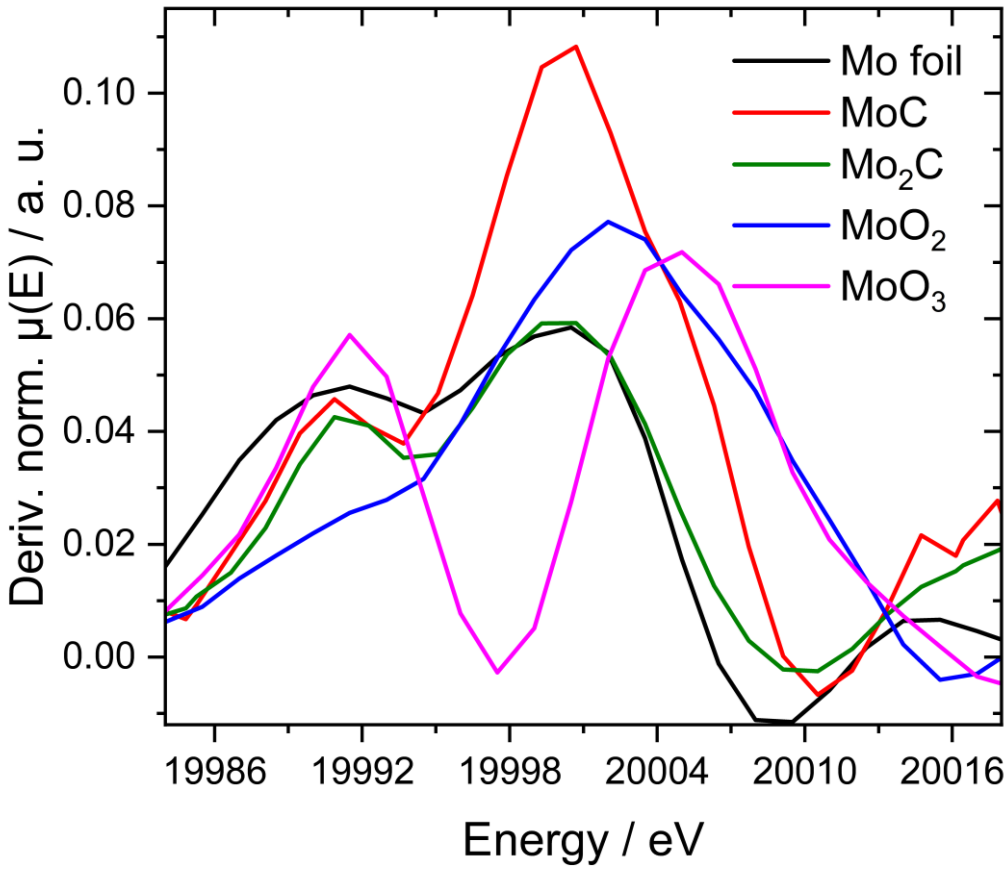

Figure S27: derivative XANES spectra of selected Mo reference materials (see further information on evaluation of the spectra in Ref. [2].

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1. S. Peters, C. Rieg, S. Bartling, M. Parlinska-Wojtan, M. Dyballa, S. Wohlrab and A. M. Abdel-Mageed, *ACS Catal.*, 2023, DOI: 10.1021/acscatal.3c02385, 13056-13070.
2. S. Peters, B. Kunkel, C. T. Cakir, A. Kabelitz, S. Witte, T. Bernstein, S. Bartling, M. Radtke, F. Emmerling and A. M. Abdel-Mageed, *Chem. Commun.*, 2023, **59**, 12120-12123.
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4. C. Bornes, J. A. Amelse, M. Peacock, C. L. Marshall, M. M. Schwartz, C. F. G. C. Geraldes, J. Rocha and L. Mafra, *Eur. J. Inorg. Chem.*, 2020, **2020**, 1860-1866.