Electronic Supplementary Information (ESI)

Time-, space- and energy-resolved *in situ* characterization of catalysts by X-ray absorption spectroscopy

Stefan Peters,[a] Benny Kunkel,[a] Cafer Tufan Cakir,[b] Anke Kabelitz,[b] Steffen Witte,[b] Thomas Bernstein,[b] Stephan Bartling,[a] Martin Radtke,[b] Franziska Emmerling,[b] Ali Mohamed Abdel-Mageed,[a] Sebastian Wohlrab[a]* and Ana Guilherme Buzanich[b]*

[a] Leibniz Institute for Catalysis (LIKAT Rostock), Albert-Einstein-Str. 29a, 18059 Rostock, Germany

[b] Federal Institute for Materials Research and Testing (BAM), Richard-Willstaetter-Str. 11, 12489 Berlin, Germany

Experimental Section

MDA Catalyst Synthesis:

MDA catalysts were prepared by wet impregnation of commercially available NH_4ZSM-5 (CBV3024E, Zeolyst International, Si/Al = 15). In a typical synthesis for a Mo loading of 6 wt.%, 5.057 g of the zeolite material (5 g accounting for NH_3 loss) were suspended in 50 mL of deionized water containing of 612.7 mg of $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$ precursor under continuous stirring for 24 h at 25 °C. The water was then slowly evaporated using a rotary evaporator and the resulting solid was dried under vacuum. Afterwards the sample was heated up to 550 °C with a temperature ramp of 10 °C min^{-1} in static air and calcined at this temperature for 6 h to convert the support material to its acidic form and the metal precursor to its respective oxide. The ICP-OES analysis results revealed a Mo loading of 6.3 wt.%. The calcined catalyst was subsequently pressed with a hydraulic press at a pressure of 1.4 t cm^{-2}, crushed and sieved to obtain particle sizes of 400-600 µm. The catalyst is denoted as 6Mo/HZSM-5.

MDA Reaction Procedure:

Spent MDA catalyst has been obtained by treatment in methane. Specifically, 300 mg of the catalyst sample was positioned inside a quartz reactor ($ø_i$ = 7 mm) between quartz wool plugs. The reactor was then fixed inside an electrical 3-zone furnace equipped with PID controllers. The sample was subsequently heated up in a continuous nitrogen flow (Linde, purity 5.0, 16 SCCM) to 600 °C at a rate of 33.75 °C min^{-1}. After reaching a stable temperature, the gas flow was changed to 16 SCCM of a mixture consisting of 90 % CH_4 (purity 4.5) and 10 % N_2 (purity 5.0), pre-mixed and supplied by Linde. Catalysts were held under these conditions for 360 min. Reactants and products were analyzed via a custom multicolumn Agilent GC 7890D equipped with three detectors (TCD, FID and MSD 5977B), whereas the MSD was exclusively used for aromatic products. Transfer lines were kept at 200 °C to avoid product condensation. After the reaction the furnace was turned off and allowed to cool down over night under continuous flow of N_2. Results for methane conversion and categorical product yields are shown in Figure S3.

Ex situ and *operando* near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS):

The *ex situ* analyses for the fresh (after calcination) and spent (exposed to MDA reaction for 360 min) 6Mo/HZSM-5 catalysts were performed on an ESCALAB 220iXL (Thermo Fisher Scientific) with monochromated Al Kα X-rays (E = 1486.6 eV). Samples were prepared on a stainless-steel holder with conductive double-sided adhesive carbon tape. Charge compensation was achieved using a flood electron system combining low energy electrons and Ar^+ ions ($p_{Ar} = 1\times10^{-7}$ mbar). Spectra are shown in Figure 2, results for the sample surface composition are displayed in Table S2.

Operando measurements were performed on a laboratory NAP-XPS instrument (SPECS Surface Nano Analysis GmbH, Germany). The device includes a differentially pumped Phoibos 150 electron energy analyzer with a nozzle of 500 µm diameter, a monochromated Al Kα X-ray source (E = 1486.6 eV), and a laser system for sample heating during pretreatment and reaction. Gas flow into the analysis chamber was established with mass flow controllers (Brooks, GF40) at a total pressure of 2 mbar. A quadrupole mass spectrometer (QMS, MKS e-vision 2) attached to the lens system of the spectrometer allowed online analysis of reactants and products. The catalyst samples were prepared by crushing and pressing into small discs (5 mm diameter) on a stainless-steel sample plate using a laboratory press and a load of about 1 t. Temperature was controlled / monitored by a thermocouple attached to a sample plate pressed onto the sample surface. Surface analysis results for different times and temperatures are found in Table S3. These experiments will be discussed in more detail in a submitted publication.

For both methods the electron binding energies were referenced to the Si 2p core level of ubiquitous SiO_2 species in HZSM-5 at an energy of 103.3 eV. For quantitative analysis, the peaks were deconvoluted with Gaussian Lorentzian curves using the software Unifit 2021 and assigned to different oxidation states according to literature.[1] The peak areas were normalized by the transmission function of the spectrometer and the element specific sensitivity factor of Scofield.

In situ spatially resolved dispersive X-ray absorption spectroscopy (XAS):

XAS measurements were performed at the synchrotron BESSY II in Berlin, Germany. The setup for time-, space- and energy-resolved XAS was installed at the BAM*line*.[2] A more detailed view of the geometrical arrangement of this setup is displayed in Figure 1B. This beamline is quite versatile owed to a 7 T wavelength shifter (WLS) that produces an energy spectrum up to 100 keV. The setup covers a range of elements which absorption lines fall between 5-40 keV. The setup is fairly straightforward. For each element the geometry follows the equation displayed in Figure 1A. The parameters used for this set of experiments are listed in Table S1. For Mo K-edge (20000 eV) we used a Pd mirror together with a 60 µm thick Al-filter that produces the spectral flux distribution displayed in Figure 1B. This polychromatic beam traverses the sample cell. The beam transmitted through the sample is subsequently dispersed by a convexly bent Si(111) crystal under the angle θ. The small portion in light purple that is displayed in Figure S1 corresponds to the diffracted beam by the Si(111), which is collected by a CCD detector under 2θ (Figure 1).

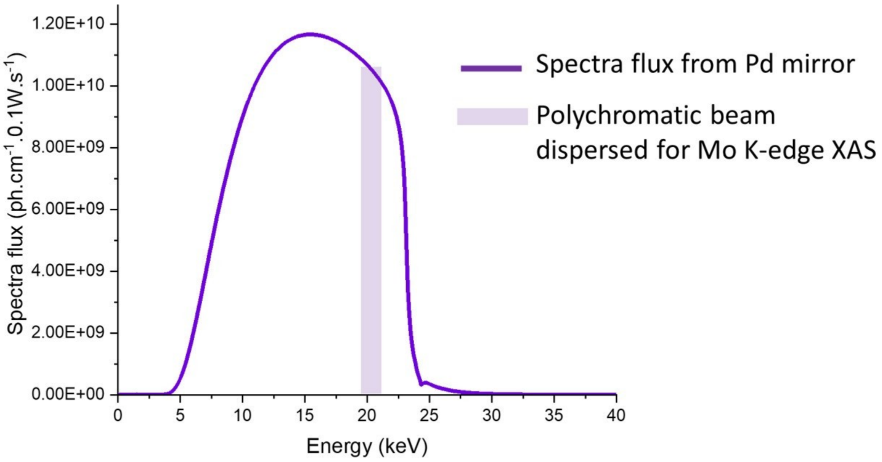

Fig. S1 Visualization of the energy-dependent photon flux of the incident X-ray beam as well as the energy range of the CCD detector achieved by dispersion on an Si(111) crystal (light purple).

The *in situ* experiments were performed by first filling the sample cavity of the measurement cell with powdered 6Mo/HZSM-5 and flushing the cell with a mixture of 20 % CH_4 in N_2 (total flow 50 SCCM) at ambient temperature. Gas concentrations have been chosen to facilitate time resolution, to minimize the production of condensable products (C_{6+}) and due to mass flow controller limitations. After 30 min a heating ramp to 600 °C (10 °C min^{-1}) was applied and the continuous dispersive XAS measurement was started. One data point was recorded every 5 s. The temperature was kept constant at 600 °C for an additional 60 min.

Table S1 Summary of the experimental and geometric arrangements for the dispersive XAS measurements at the Mo K-edge (20000 eV).

<table>
<tr><th colspan="8">Mo (20000 eV)</th></tr>
<tr><td>E_{min}</td><td>19850 eV</td><td>E_{max}</td><td>20300 eV</td><td>θ_{max}</td><td>5.7161°</td><td>θ_{min}</td><td>5.4021°</td></tr>
<tr><td colspan="4">E_{avg} = 20075 eV</td><td colspan="4">θ_{avg} = 5.5591°</td></tr>
<tr><td>BW</td><td>4 mm</td><td>bending</td><td>0.15 mm</td><td>Crystal-CCD</td><td>745 mm</td><td>A_{CCD}</td><td>8 mm</td></tr>
</table>

Results Section

Table S2 Surface elemental compositions of fresh and spent 6Mo/HZSM-5 determined by XPS. Values are given in at.%.

Catalyst	**C**	**Al**	**Si**	**O**	**Mo^{6+}**	**Mo^{5+}**	**Mo^{4+}**	**Mo^{2+}**
fresh	9.63	1.38	27.57	58.06	2.29	0.46	0	0
spent	20.45	1.57	26.65	49.37	0.92	0.46	0.15	0.41

Table S3 Surface elemental compositions of 6Mo/HZSM-5 determined by *operando* NAP-XPS in an atmosphere of 90 % CH_4 / 10 % N_2 (total pressure 2 mbar). Times are measured after reaching 627 °C. Values are given in at.%; Al was not considered in the quantification. The absolute surface concentration of Mo increased significantly over the course of the experiment. This phenomenon was not observed in our *ex situ* sample (see Table S2) and is likely related to the reduced pressure employed during NAP XPS.

Conditions	**C**	**Si**	**O**	**Mo^{6+}**	**Mo^{5+}**	**Mo^{4+}**	**Mo^{2+}**
127 °C	8.1	29.8	59.4	2.3	0.4	0	0
627 °C, 0.5 h	6.6	27.0	59.6	2.3	1.1	3.4	0
627 °C, 2.8 h	5.6	22.2	59.8	2.3	2.2	7.9	0
627 °C, 5.7 h	7.8	19.2	57.7	1.8	2.3	10.0	1.2

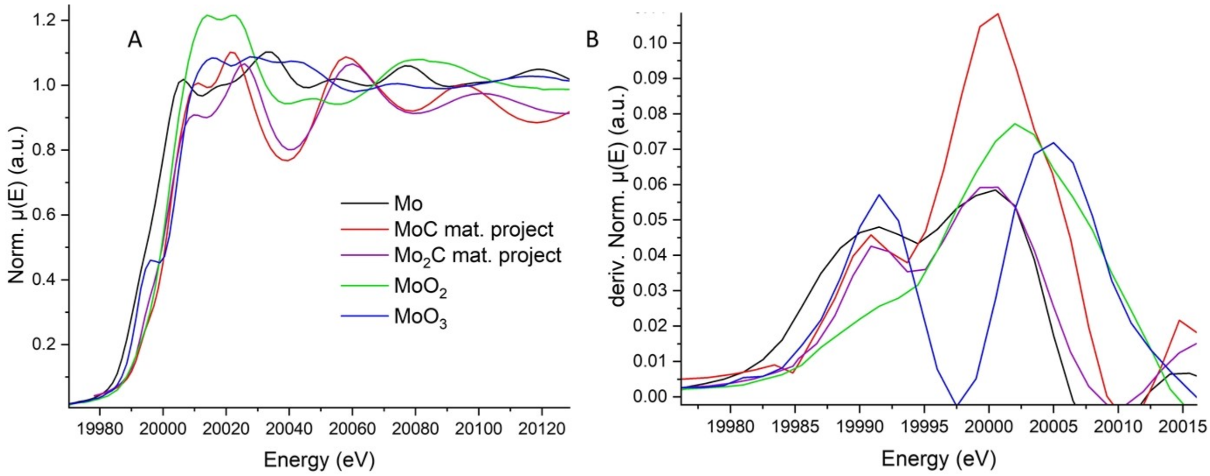

Fig. S2 XANES curves for reference Mo compounds (A) and first derivatives of the recorded XANES (B). Mo foil, MoO_2 and MoO_3 were measured experimentally. MoC and Mo_2C were retrieved the materials project repository.[3]

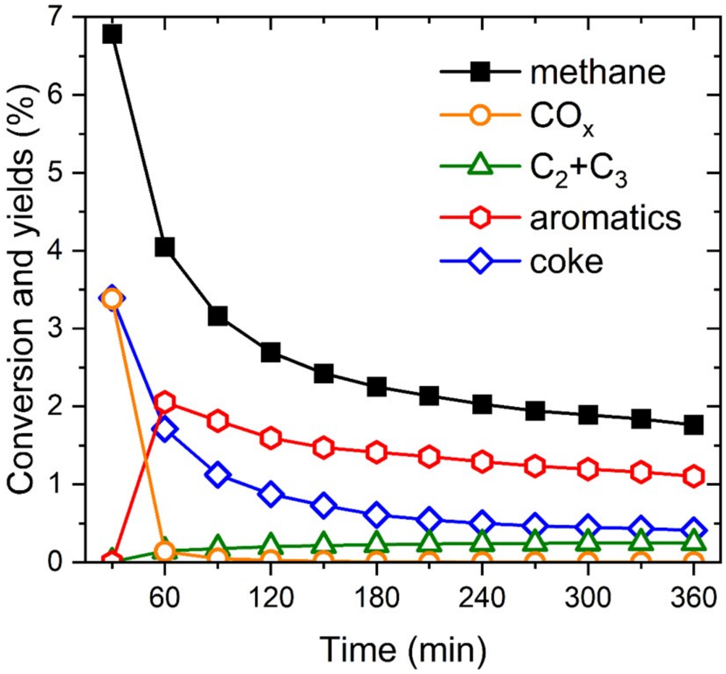

Fig. S3 Methane conversion and categorical product yields for the MDA reaction on 6Mo/HZSM-5 (300 mg catalyst, 600 °C, 16 SCCM 90 % CH_4 / 10 % N_2).

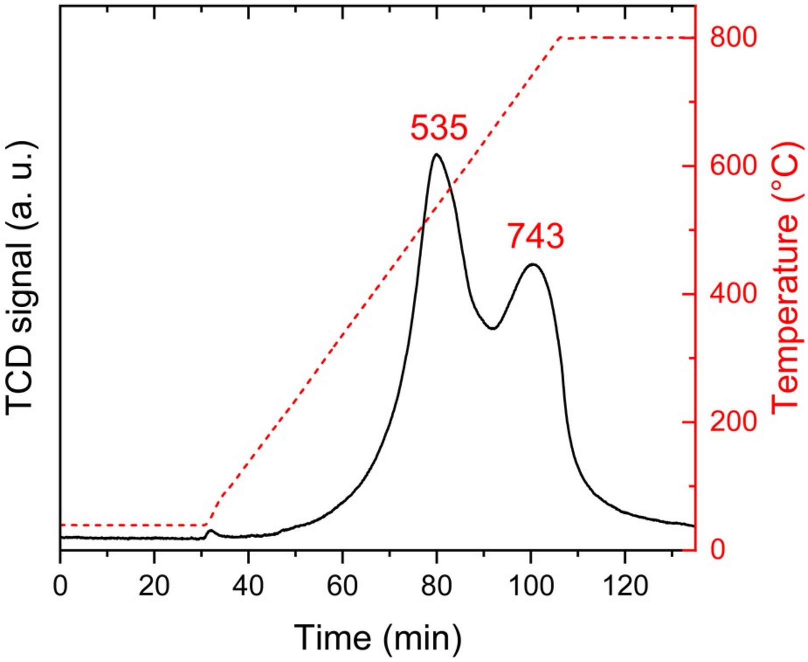

Fig. S4 Temperature-programmed reduction profile of 6Mo/HZSM-5 in 5 % H_2 / 95 % N_2. The applied temperature ramp was 10 °C min^{-1} (dashed red line).

References

1 K. Murugappan, E. M. Anderson, D. Teschner, T. E. Jones, K. Skorupska and Y. Román-Leshkov, *Nat. Catal.*, 2018, **1**, 960-967.

2 A. Guilherme Buzanich, M. Radtke, K. V. Yusenko, T. M. Stawski, A. Kulow, C. T. Cakir, B. Röder, C. Naese, R. Britzke, M. Sintschuk and F. Emmerling, *J. Chem. Phys.*, 2023, **158**, 244202.

3 K. Mathew, C. Zheng, D. Winston, C. Chen, A. Dozier, J. J. Rehr, S. P. Ong and K. A. Persson, *Sci. Data*, 2018, **5**, 180151.