Supplementary Information - Relevance of the Mo-precursor State in H-ZSM-5 for the Methane Dehydroaromatization

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Na exchange (ICP)

ICP was performed on HZ-M after Na-exchange to confirm the complete exchange of protons with Na. Table S2 shows that the Na/Al ratio is between 0.8 and 0.86 From Pyridine IR it is known that about 20 % of Al is present as EFAl, which means that all BAS are associated with Na after the Na-exchange method applied here.

Table S1: Molar ratio Na/Al after sodium exchange as determined by ICP.

	Na/Al
NaHZ-M	0.80
NaHZ-M duplicate	0.86

Morphology

X-ray powder diffraction (XRD) data was collected on a Bruker D8 Advance diffractometer, operating in Bragg-Brentano geometry using Co *Kα* radiation (λ = 0.179 nm) and a Lynxeye position sensitive detector to collect data in the range of 2ϑ from 5° to 50° with a scan-speed of 0.2°s^{-1} and a sample rotation of 30 rpm.

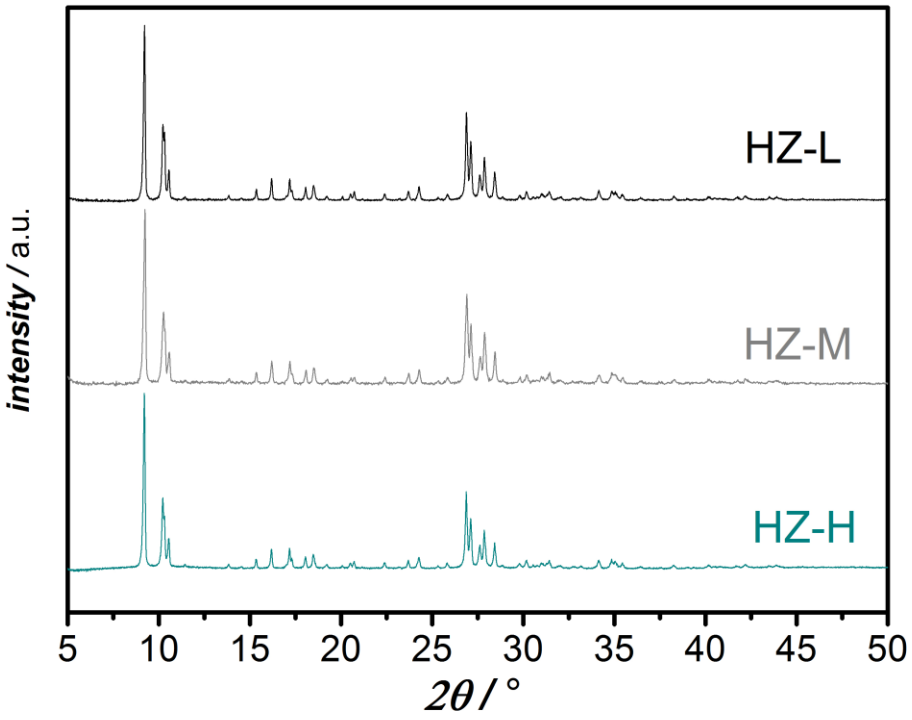

Figure S1: Normalized XRD patterns of all samples with the typical diffraction peaks for MFI zeolite.

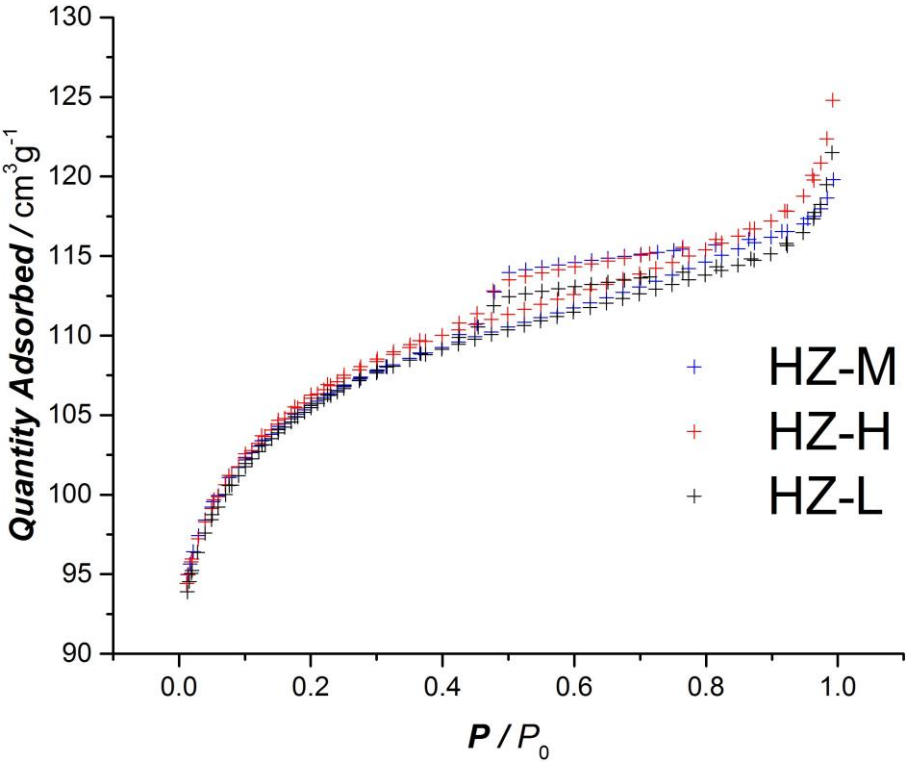

Figure S2: N_2 Adsorption Isotherms at 77 K for the three different H-ZSM-5 zeolites.

^{27}Al NMR

^{27}Al solid-state NMR (ssNMR) measurements were recorded on a wide-bore Bruker Avance III 500 MHz spectrometer equipped with 3.2 mm magic angle spinning (MAS) probe. The temperature was set to 298 K and the MAS frequency was 18 kHz, resulting in an effective temperature of approximately 303 K. ^{27}Al spectra were referenced externally to the ^{27}Al signal at 0 ppm of a non-spinning $Al(NO_3)_3$ solution. The spectra were recorded using a 0.78 us pi/12 excitation pulse and an acquisition time of 6.6 ms. 1024 Scans were accumulated with a recycle delay of 0.8 s. Spectra were processed using a 20 Hz line-broadening window.

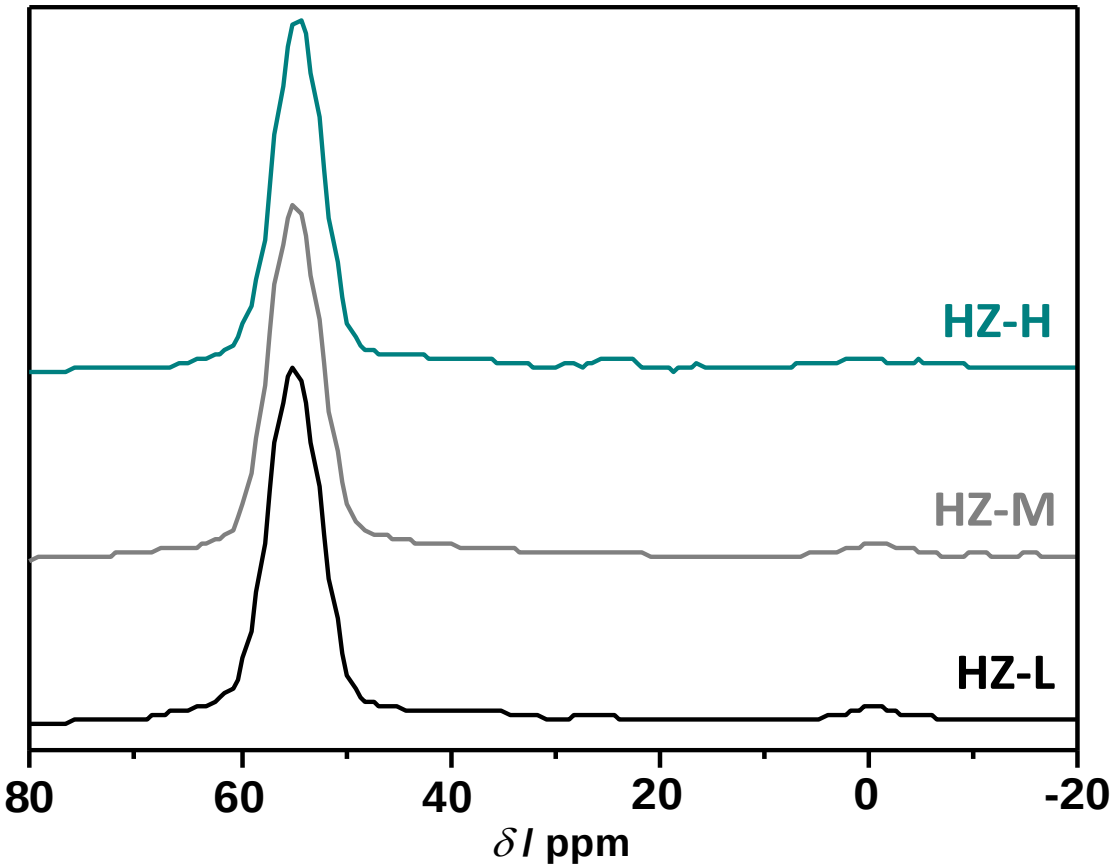

Figure S3: ^{27}Al NMR for the three different zeolites.

Acidity

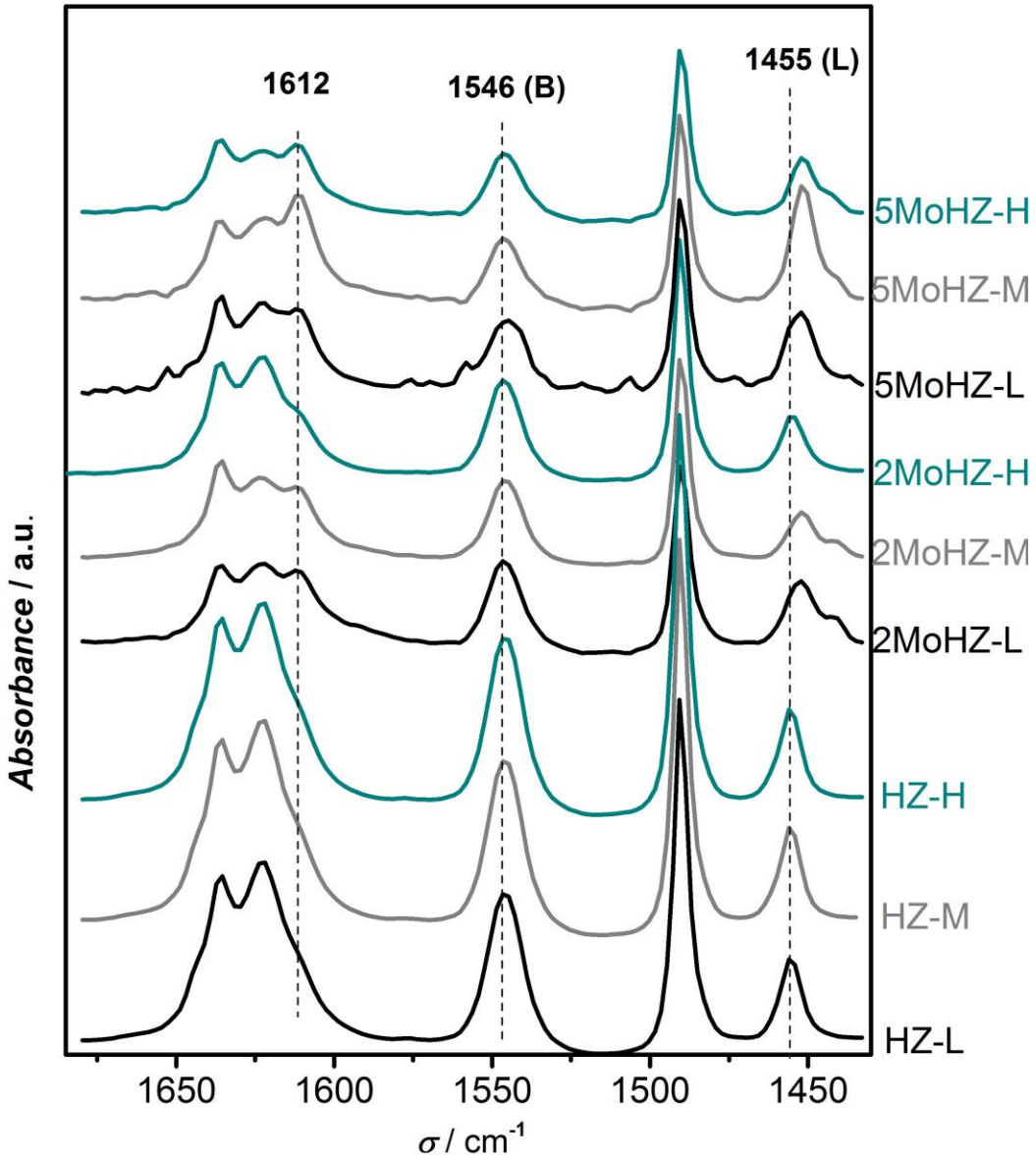

Figure S4: Transmission pyridine FTIR spectra of (from bottom to top) increasing amounts of Mo incorporated into the samples

FTIR with the probe molecule pyridine was performed to characterize both Lewis (LAS) as well as Brønsted acidity (BAS). 50 mg of zeolite sample was pressed into round wafers with a diameter 80 mm using 4 TON pressure. Quantification was achieved by assuming an acid concentration of 0.6 mmol/g for the bare zeolite as this is the value corresponding to the Al content of a zeolite with Si/Al = 25. It was assumed that all Al contributes to the acidity only 4-5% of Al was present as extra-framework Al (EFAl) as shown by ^{27}Al NMR. All other samples where quantified in relation to this value. The error of the measurements can be estimated comparing the values obtained for the three pristine zeolites. Since we know from the TMPO study as well as ^{27}Al NMR that the three pristine zeolites have very similar acidity, differences seen with Py IR can be estimated to represent the error. This amounts to 0.052 mmol/g. FIGURE S3 shows the spectra of the samples before incorporation of Mo and with 2 wt.% as well as with 5 wt.% Mo. The fresh samples before

Mo incorporation show a band for BAS at 1546 cm^{-1} as well as one for Lewis acidity at 1455 cm^{-1}, probably arising from EFAL.[1] The bands at 1621 cm^{-1} and 1635 cm^{-1} also correspond to LAS and BAS, respectively. Comparing spectra before and after incorporation of Mo, a new band appears (1612 cm^{-1}) corresponding to Lewis acidity arising from Mo oxide species anchored to the zeolite. Upon incorporation of more Mo, the LAS band at 1455 cm^{-1} shifts to 1452 cm^{-1} while a new band appears at 1440 cm^{-1} for 2 wt.% loading and disappears again at 5 wt.% Mo loading. To confirm the adequacy of the degassing pre-treatment at 400 °C, one sample, 2MoHZ-M was subjected to 10 min of re-calcination at 550 °C, followed by degassing for 1 h at the same temperature. For this a custom-made quartz cell that could withstand such high temperatures was developed. A pellet with a diameter of 10 mm was prepared from 50 mg and pressed at 4 tonne. After the re-calcination treatment, the sample was subjected to pyridine treatment, then left under excess of pyridine for 1 h at 160 °C after which is was evacuated for 5 h. For comparison, the same sample degassed under the same conditions as the samples shown in FIGURE S3, but in the custom-made quartz cell and then subjected to pyridine as described above. FIGURE 4 shows the spectra for both treatments. It can be seen that the re-calcination leads to an increase in acidity accompanied by changes in the LAS bands. This is likely due to clustering happening during the re-calcination treatment. It is clear that a re-calcination treatment does lead to the unwanted redistribution of Mo, which is hard to control at such high temperatures. We conclude that degassing the sample at 400 °C is a more suitable pre-treatment for Py IR, if one wants to compare different Mo/HZSM-5 catalysts.

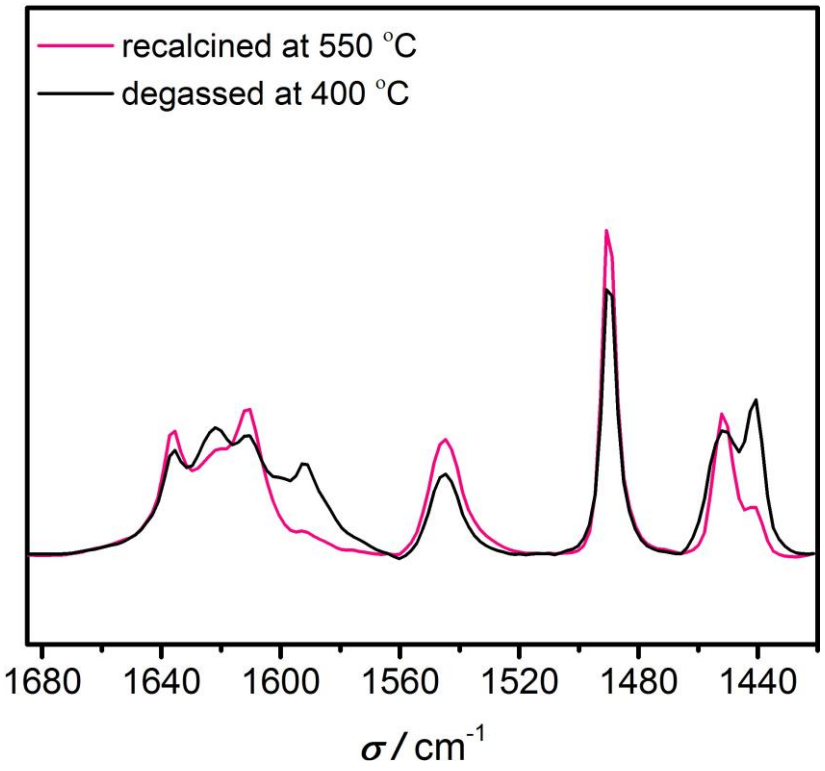

Figure S5: Transmission pyridine FTIR spectra of **2MoHZ-M** re-calcined at 550 °C compared to the same sample degassed in the same manner as the samples shown in **Figure S3**.

^{31}P NMR of adsorbed TMPO

To confirm that not only concentration of LAS and BAS are similar for the three parent zeolites, we performed additional characterization by solid-state NMR spectrometry using trimethylphosphine oxide (TMPO) as a probe molecule (FIGURE S6). For solid-state NMR measurements using trimethoxyphosphine oxide (TMPO) as a probe molecule, the preparation procedure was adapted from Wiper et al.[2] TMPO (17 mg) was dissolved in anhydrous CH_2Cl_2 (5 mL) in an Ar glove box. A 5 mL volume of this solution was added to 150 mg of the zeolite, dehydrated at 400 °C for 16 h, and left under stirring for 1 h. Subsequently, materials were evacuated under cooling to -10 °C and subsequently heated at 150 °C for 1 h under vacuum to allow homogeneous distribution of TMPO. Finally, cooled down samples were transferred into a zirconia MAS rotor (3.2 mm). ^{31}P solid-state NMR (ssNMR) measurements were recorded on a wide-bore Bruker Avance III 500 MHz spectrometer equipped with 3.2 mm magic angle spinning (MAS) probe. The temperature was set to 298K and the MAS frequency was set to 19 kHz. ^{31}P spectra were acquired using a ^{1}H-^{31}P cross-polarization transfer by using a 46kHz field on ^{31}P and a ramped (70 to 100%) 94 kHz field on ^{1}H with a contact time of 4.2 ms. During acquisition 83 kHz ^{1}H decoupling was employed using SPINAL64. The ^{31}P spectra were referenced externally to the ^{31}P signal at 0 ppm of a non-spinning H_3PO_4 solution. Each experiment was acquired with 256 scans and a recycle delay of 4 s.[3]

The ^{31}P resonance peaks at 75, 70, 64, 50, 38 and 30 ppm are observed for all three zeolites. The resonance peak at 30 ppm is ascribed to "mobile" TMPO, and peaks at 50 and 38 ppm are characteristic for physisorbed TMPO.[4, 5] Peaks in the range between 60 and 90 ppm are arising from $TMPOH^+$ complexes on Brønsted acid sites.[6] The location of the peaks as well as the intensities are very similar for the three parent zeolite, confirming that not only acid site concentration, but also acid strength is very similar for the three parent zeolites.

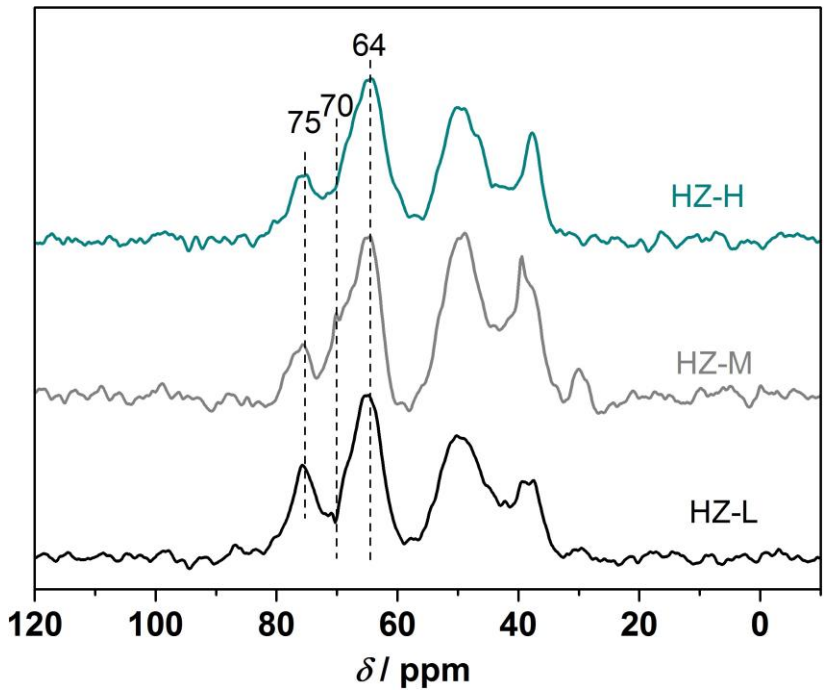

Figure S6: ^{1}H-^{31}P CP MAS NMR spectra for TMPO adsorbed on **HZ-*x***.

Mo content (ICP)

Table S2: Molar ratio Mo/Al as determined by ICP.

	Mo/Al
2MoHZ-L	0.35
2MoHZ-M	0.34
2MoHZ-H	0.29
5MoHZ-L	0.86
5MoHZ-M	0.76
5MoHZ-H	0.70

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analysis was performed in order to identify any agglomeration of Mo on the zeolite surface. A Thermo Scientific K-alpha spectrometer equipped with a monochromatic Al *Kα* X-ray source and a 180° double-focusing hemispherical analyzer with a 128-2 channel detector was used.
Since XPS is a surface sensitive technique and only propagates a few nm into the material,[7] comparing the Mo loading obtained from XPS with ICP results, which is a bulk technique can give information about agglomeration and clustering on the zeolite surface. In FIGURE S5 the ratio Mo/(Al+Si) obtained from XPS is compared to the one measured with ICP. For 2wt.% Mo loadings, the two techniques lead to approximately the same value, while XPS reveals far higher loadings of Mo on the surface for 5 wt.% and 7.5 wt.% loading of Mo.

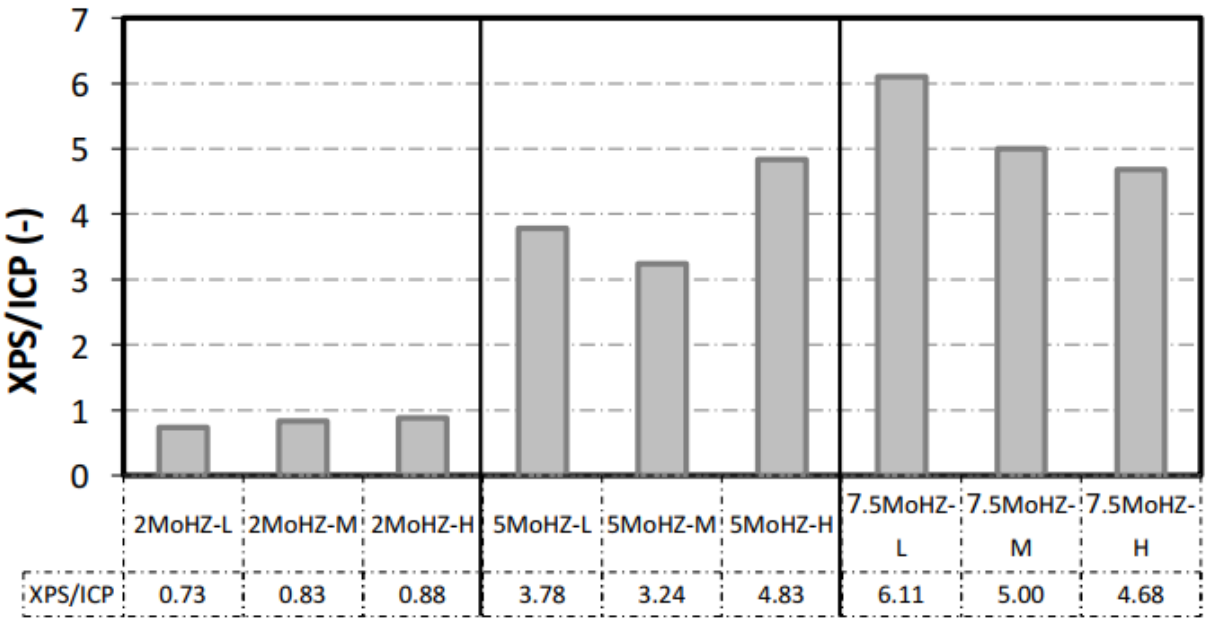

Figure S7: The molar ratio Mo/(Al+Si) obtained from ICP compared to the same ratio obtained by XPS. Values are compared by again taking another ratio of the two ratios obtained from the different techniques.

UV-Vis

UV-Vis spectra of the Mo reference compounds were collected using the undiluted compound measured against $BaSO_4$ as a white standard. The edge energy (E_g) was determined by fitting a straight line to $(F(R_\infty)h\nu)^2$ plotted against the incident photon energy $h\nu$ in the low energy rise region.[8]

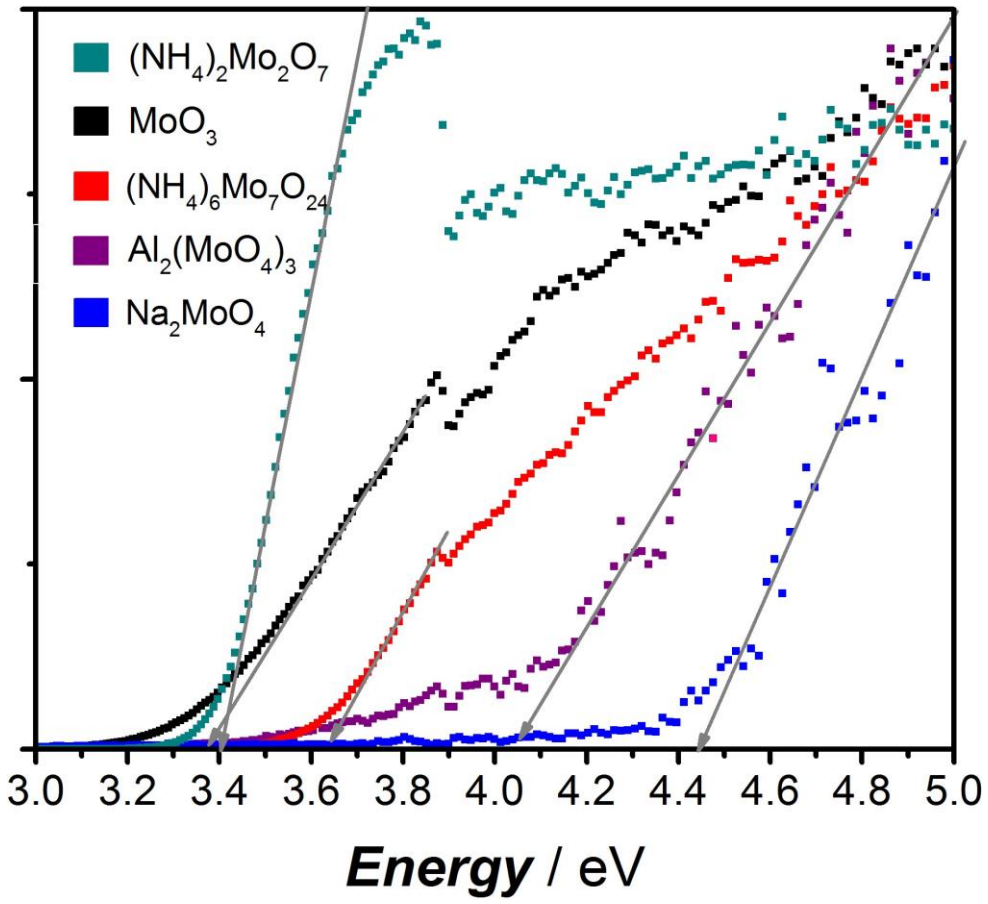

Figure S8: Tauc plots for determination of the edge energy E_g for references.

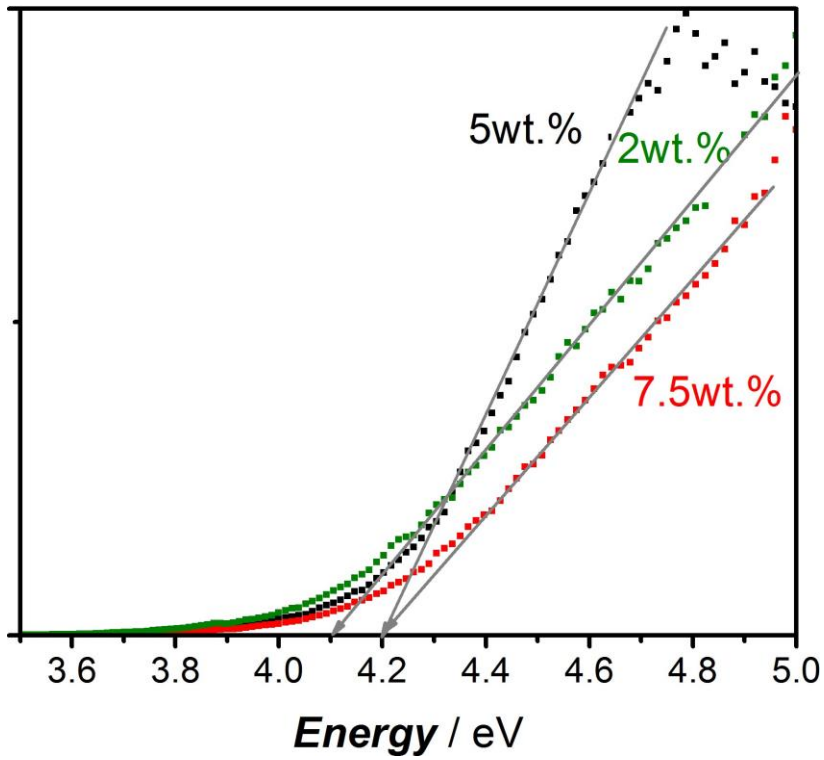

Figure S9: Determination of the edge energy E_g for **HZ-L** with 2, 5, 7.5 wt.% loading of Mo.

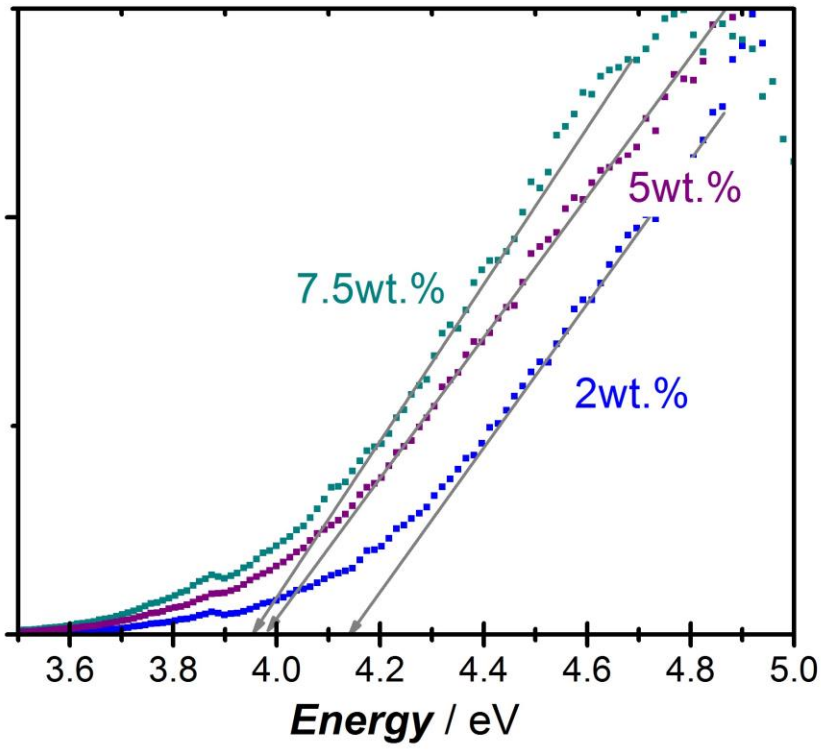

Figure S10: Tauc plots for determination of the edge energy E_g for **HZ-M** with 2, 5, 7.5 wt.% loading of Mo.

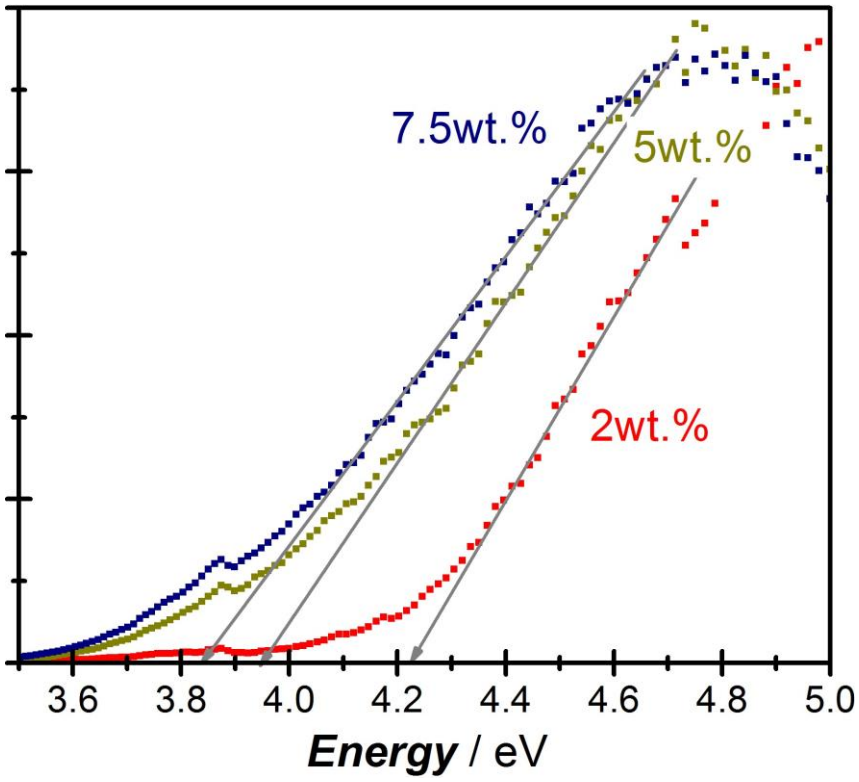

Figure S11: Tauc plots for determination of the edge energy E_g for **HZ-H** with 2, 5, 7.5 wt.% loading of Mo.

Catalytic performance at 760 ^{o}C

To investigate, the influence of reaction temperature on the performance of the catalysts, all three 5MoHZ-x samples were also tested at 760 ^{o}C. The methane conversion reaches 20% in the initial period of the reaction, but decreases to about 4.5% during the initial 2 h on stream (**Figure S12**). Benzene is formed with the highest yield, followed by naphthalene. Only negligible amounts of toluene, ethane and ethylene are formed. Within experimental accuracy the catalytic performance (activity, selectivity and deactivation) of all three zeolites is the same. While conversion is increased by a factor of 2.7, the deactivation rate is increased simultaneously. This can be seen in **Figure S13**, where the benzene yield normalized by its maximum value is compared for both temperatures. The benzene yield at 760 ºC decreased to 11% of its maximum value after 238 min, while it only decreased to 33% of its initial value for 650 ºC.

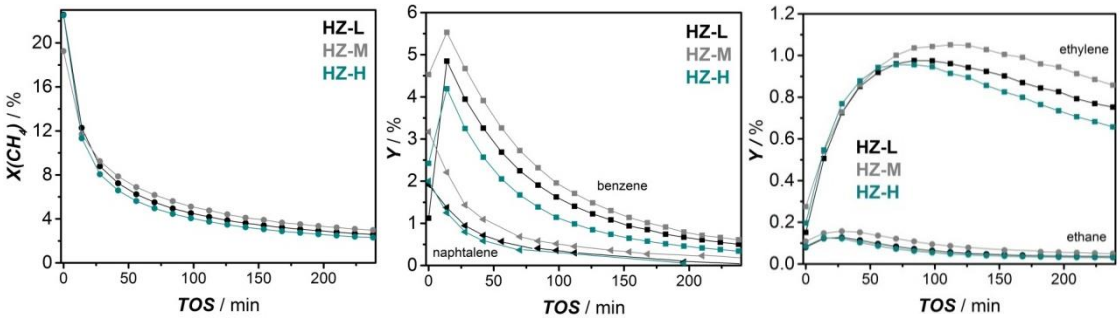

Figure S12: CH_4 conversion (a), naphthalene and benzene yield (b), ethylene and ethane yield (c), for **5MoHZ-*x*** at 760 °C with *WHSV* = 1.21 h^{-1} and 500 mg catalyst.

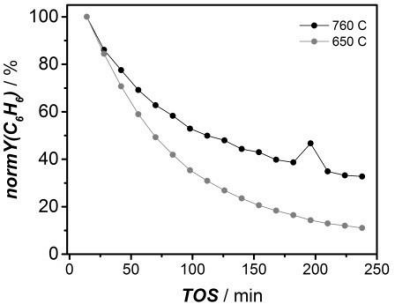

Figure S13: Benzene yield normalized by its maximum value with time on stream for **5HZ-M** tested at 650 ^{o}C and 760 ^{o}C with *WHSV* = 1.21 h^{-1} and 500 mg catalyst.

Diffusion limitations

In addition, diffusion limitations of benzene were explored at 700 ºC on a commercial zeolite (Südchemie) with Si/Al=13 and 2 wt.% Mo loading. The breakthrough curve was recorded on a mass spectrometer with 300 mg of catalyst and a flow 1.8 kPa of benzene in 30 ml/min of Ar. The profile of the benzene breakthrough curve shown in **Figure S14** is very steep, demonstrating that there is insignificant adsorption of benzene in the catalyst bed. The time lapse between benzene added to the feed and the appearance of benzene is correlated to the volume of the system (lines plus reactor, ca. 35-40 ml), so there is no significant uptake by the zeolite catalyst.

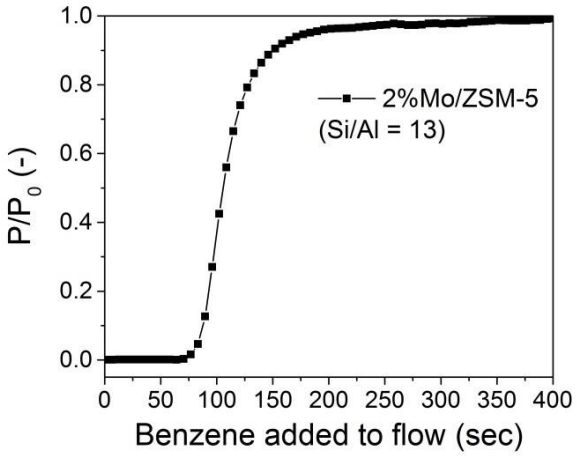

Figure S14: Breakthrough of benzene through a catalyst bed of 300 mg of 2 wt.%Mo on HZSM-5 (Si/Al-13) with a flow of 1.8 kPa benzene in 30 ml/min of Ar.

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