

Electronic Supplementary Information

Effect of AlSiO_x support modification by alkali or alkaline earth metals on propene formation in the metathesis of C_2H_4 and 2- C_4H_8 over MoO_x -based catalysts

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Experimental part

Catalyst synthesis

Before the usage as support for catalyst preparation, commercial Siral 70 (70wt% SiO₂ and 30wt% Al₂O₃, Sasol) was calcined in air flow at 500°C for 8h. The calcined support was impregnated through an incipient impregnation method using an aqueous solution of nitrate of Li, Na, K, Rb, Cs, Mg, Ca, Sr, or Ba. The impregnated materials were dried at 110°C overnight and finally calcined at 500°C in flowing air for 4 h. An apparent surface density of each support additive was set to 0.075 nm⁻². In the case of Li-containing supports, an apparent surface metal density was additionally varied from 0.015 to 1.5 nm⁻². All supports were then impregnated (incipient wetness impregnation) with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (99%, Alfa Aesar), followed by drying at 110°C overnight and calcination at 500°C in flowing air for 8 h. A nominal surface Mo density was set to 1.5 nm⁻², which corresponds to 7.5 wt% of Mo. The amounts of additives, Mo precursors, and water required for support/catalyst synthesis were calculated by considering the specific surface area of Siral 70 (312 m²·g⁻¹) and its absorptive capacity. The catalysts were abbreviated as Mo/M/Siral 70, with “M” standing for the support additive (Li, Na, K, Rb, Cs, Mg, Ca, Sr, or Ba). For the Mo/Li/Siral 70 catalyst series, the following abbreviation was used: Mo/xLi/Siral 70, where “x” stands for the apparent surface density of Li.

Catalyst characterization

UV-vis measurements of all catalysts were carried out using an Avantes spectrometer (AvaSpec-2048-USB2-RM) equipped with a high-temperature reflection UV-vis probe, an Ava-Light-DH-S-BAL deuterium-halogen light source and a CCD array detector. The probe consisting of six radiating optical fibers and one reading fiber was threaded through the furnace to face the wall of the quartz tube reactor at the position where the catalyst (200mg) was located. Before recording the UV-vis spectra, each sample was calcined in flowing air at 500°C for 1 h

and cooled down to room temperature. The UV-vis spectra were recorded at room temperature in the range from 200-800 nm. Barium sulfate (99.998%, Aldrich) was used as a white standard.

Raman spectra of selected catalysts were collected on a Horiba Jobin Yvon LabRam micro-spectrometer iHR 550 using a 473 nm laser. A diffraction grating of 1800 mm⁻¹ and an entrance slit in the spectrometer of 100 μm was used. The spectra were acquired using a laser power on the samples of ≈0.1 mW to ≈10 mW with a power density of 2.8 x 10⁵ W·cm⁻². Data analysis was performed by LabSpec 6, Jobin Yvon Horiba, built-in software.

Specific surface area (BET) of the catalysts was measured at 77 K using a Belsorp mini II setup (Bel Japan). Desorption isotherms were evaluated according to the BET method.

X-ray diffraction (XRD) analysis of the samples was performed on a Panalytical X'Pert diffractometer equipped with a Xcelerator detector, automatic divergence slits and Cu tube (kα₁/α₂ radiation, 40 kV, 40 mA, λ = 0.015406 nm, 0.0154443 nm). Cu beta-radiation was excluded by using nickel filter foil. The crystallite size was calculated by the Scherrer equation (Eq. (1))

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (1)$$

where the K parameter was set to 1.0747, β is the integrated breadth of (111) reflection peak, θ is the diffraction angle.

ICP analysis of the samples was performed on a Varian 715-ES ICP-Emission-Spectrometer. Approximately 10 mg of the sample were mixed with 8 ml of aqua regia and 2 ml of hydrofluoric acid. The digestion was performed in a microwave-assisted sample preparation system "Multiwave PRO" from Anton Paar at ~ 220°C and ~ 50 bar pressure. The digested solution was filled up to 100 ml with deionized water and measured with ICP-OES. The data analysis was performed on the Varian 715-ES software "ICP Expert".

Temperature-programmed reduction tests with H₂ (H₂-TPR) were carried out in an in-house developed setup containing eight individually heated continuous-flow fixed-bed quartz reactors. This set-up was also used for temperature-programmed desorption tests with NH₃ (NH₃-TPD), 2-C₄H₈ (C₄H₈-TPD) or C₂H₄ (C₂H₄-TPD) as well as for temperature-programmed surface reaction (TPSR) measurements with C₂H₄ or C₄H₈.

For H₂-TPR tests, 100 mg of each sample were heated in flowing air to 500°C for 1 h, cooled down to room temperature and purged with Ar for 15 min. Hereafter, the catalysts were heated in a flow of 5 vol% H₂ in Ar (10 mL·min⁻¹) up to 900°C with a heating rate of 10 K·min⁻¹. An on-line mass spectrometer (Pfeiffer Vacuum OmniStar GSD 320) was used to record signals at *m/z* of 2 (H₂) and 40 (Ar), with the latter signal being a reference standard.

Before NH₃-TPD tests, each sample (50 mg) was calcined in flowing air at 500°C for 1 h, cooled down to 120°C, and purged with Ar for 15 min. Hereafter, the treated materials were exposed to a flow of 1 vol% NH₃ in Ar (10 mL·min⁻¹) at 120°C for 1 h, flushed with Ar for 5 h to remove weakly bound NH₃, and cooled down to 80°C in the same flow. Then, they were heated in Ar flow up to 900 °C with a heating rate of 10 K·min⁻¹. Desorbed ammonia was registered mass spectrometrically. The signals at *m/z* of 15 (NH) and 40 (Ar) were recorded.

Each sample (100 mg) was calcined in flowing air at 500°C for 1 h and cooled down to 150°C in Ar flow before starting C₄H₈-TPD or C₂H₄-TPD. Hereafter, the treated materials were exposed to a flow of 2-C₄H₈ (5 vol% 2-C₄H₈ in Ar, 10 mL·min⁻¹) or C₂H₄ (5 vol% C₂H₄ in Ar, 10 mL·min⁻¹) at 150°C for 1 h. The oxygenates formed during the adsorption of 2-C₄H₈ were analyzed by an on-line mass spectrometer. The signals at *m/z* of 43 (CH₂COH) and 40 (Ar) were recorded. After adsorption stage, all catalysts were flushed with Ar at 150 °C for 7 h to remove weakly bound 2-C₄H₈ or C₂H₄. Then, they were heated in Ar flow up to 700 °C with a heating rate of 10 K·min⁻¹. Desorbed 2-C₄H₈ and C₂H₄ were recorded using an on-line mass

spectrometer at m/z of 56 (C_4H_8) and 27 (C_2H_4) respectively. Ar (40) was used as an internal standard.

Before starting TPSR tests with C_2H_4 and C_4H_8 , all catalysts (20 mg for each sample) were *in situ* calcined at 500 °C in flowing air for 1 h and then cooled down to 30 °C. Hereafter, the catalysts were flushed with Ar for 30 min and exposed to a flow of $C_2H_4/trans\text{-}2\text{-}C_4H_8/Ar=1/1/98$ (10 mL·min⁻¹). The temperature of all catalysts was kept at 30°C for 5 min to stabilize the MS signal. Then, the catalysts were heated up to 500 °C with a heating rate of 10 K·min⁻¹. The signals at m/z of 42 (C_3H_6), 56 (C_4H_8), 27 (C_2H_4), 18 (H_2O), 44 (CO_2), and 40 (Ar) were collected mass spectrometrically.

Ex situ XPS (X-ray photoelectron spectroscopy) measurements were performed on an ESCALAB 220iXL (Thermo Fisher Scientific) with monochromatic Al K α radiation ($E=1486.6$ eV). The samples were prepared on a stainless-steel holder with conductive double-sided adhesive carbon tape. The electron binding energies were obtained with charge compensation using a flood electron source and referenced to the C 1s core level of adventitious carbon at 284.8 eV (C–C and C–H bonds).

Electron paramagnetic resonance (EPR) measurements were carried out at 105 K on a Bruker EMX CW-micro X-band EPR spectrometer equipped with an ER4119HS high-sensitivity resonator, with a microwave power of Ca 6.9 mW, modulation frequency of 100 kHz, and amplitude of 5 G. The EPR spectrometer was equipped with a temperature controller and liquid N₂ cryostat for low temperature measurements. For each measurement, close catalyst amounts were used, and the corresponding EPR signal intensities were normalized to 1 mg.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements were performed using a Thermo Scientific Nicolet iS10 spectrometer equipped with a Harrick Praying Mantis and high-temperature reaction chamber. Prior to collecting the

spectra, each sample was heated in N₂ flow (10 mL·min⁻¹, heating rate 10 K·min⁻¹) from room temperature to 450°C, then calcined in air flow (12 mL min⁻¹) at 450°C for 1 h and cooled down in N₂ flow to 150°C. The spectra were collected with a resolution of 4 cm⁻¹ and an accumulation of 64 scans in the range of 400–4000 cm⁻¹ under flowing N₂ (10 mL·min⁻¹) or trans-2-C₄H₈ in N₂ (trans-2-C₄H₈/N₂ molar ratio = 5/6, total flow 22 mL·min⁻¹).

Catalytic tests

Catalytic tests were performed at 1.25 bar (abs.) in an in-house developed set-up equipped with 14 continuous-flow fixed-bed quartz reactors. The catalysts (20 mg, sieve fraction of 315–710 μm) were heated in flowing N₂ up to 500°C and calcined in air flow at 500°C for 3 h. Hereafter, they were cooled down in N₂ flow to 150°C and exposed to a flow (22 mL·min⁻¹ per reactor) of C₂H₄/trans-2-C₄H₈/N₂=5/5/1. All gases were purified over molecular sieve 3 Å filters (Roth). Nitrogen was further purified with an additional AIO-750-2 filter (Pure Gas Products).

The feed components and the reaction products were analysed by an on-line gas chromatograph (Agilent 6890) equipped with AL/S capillary column (for hydrocarbons), connected to a flame ionization detector and a PLOT/Q (for CO₂) / Molsieve 5 (for H₂, O₂, N₂, and CO) capillary column combination connected to a thermal conductivity detector. To calculate the initial rate of propene formation ($r(C_3H_6)$) equation 2 was used. The relative rate of propene formation was calculated according to equation 3. The rate was determined after 420 s on stream at a degree of ethylene conversion below 15%.

$$r(C_3H_6) = \frac{F_{feed} \times \frac{x_{N_2}^{in}}{x_{N_2}^{out}} \times x^{out}(C_3H_6)}{V_m \times m_{cat}} \quad (2)$$

$$r(C_3H_6)_{Rel} = \frac{r(C_3H_6)_M}{r(C_3H_6)_{None}} \quad (3)$$

Here, F_{feed} is the volumetric flow rate of the feed gas ($\text{mL} \cdot \text{min}^{-1}$) under reference conditions (0°C , 1 atm), x_i with superscripts “in” or “out” stand for molar fractions of gas-phase components at the reactor inlet or outlet. V_m is the molar volume ($22414 \text{ mL} \cdot \text{mol}^{-1}$). m_{cat} is the catalyst amount (g). $r(C_3H_6)_M$ and $r(C_3H_6)_{None}$ are the initial rates of propene formation over an modified catalyst (Mo/M/Siral 70) and the unmodified reference catalyst (Mo/Siral 70), respectively.

The deactivation rate constant (k_d) was calculated according to the equation (4)

$$k_d = \frac{\ln \frac{1-X_{final}}{X_{final}} - \ln \frac{1-X_{initial}}{X_{initial}}}{t} \quad (4)$$

Here, X_{final} and $X_{initial}$ stand for the ethene conversion after 28 min and 0 min, respectively, t is reaction time.

Tables

Table S1 The specific surface area (S_{BET}) of selected support materials measured by nitrogen physisorption experiments.

Sample	$S_{\text{BET}} / \text{m}^2 \cdot \text{g}^{-1}$
Siral 70	312
Li/Siral 70	307
Na/Siral 70	312
K/Siral 70	314
Cs/Siral 70	310
Mg/Siral 70	308
Ca/Siral 70	313

Table S2 Actual content of Mo and additives in Mo/M/Siral 70 catalysts determined by ICP; specific surface area (S_{BET}) and pore size of the samples measured by nitrogen physisorption experiments; crystallite size of MoO_3 calculated from XRD diffractograms.

Sample	$S_{\text{BET}} / \text{m}^2 \cdot \text{g}^{-1}$ ^a	Pore size / nm ^a	Mo / wt% ^b	Additives / wt% ^b	MoO_3 / nm ^c
Mo/Siral 70	242	17.6	5.9	-	19.1
Mo/Li/Siral 70	239	18.7	5.7	-	16.6
Mo/Na/Siral 70	246	18.4	5.9	0.081	18.8
Mo/K/Siral 70	238	19.1	5.5	-	18.3
Mo/Rb/Siral 70	263	18.4	5.7	0.19	18.6
Mo/Cs/Siral 70	255	19.4	6.1	0.46	17.5
Mo/Mg/Siral 70	261	18.8	5.6	0.057	16.5
Mo/Ca/Siral 70	236	19.3	5.8	0.063	17.9
Mo/Sr/Siral 70	236	18.9	6.1	0.13	16.8
Mo/Ba/Siral 70	256	19.2	5.8	0.22	17.0

a: Determined from N_2 adsorption-desorption isotherms

b: Determined by ICP

c: Calculated from XRD diffractograms

Table S3 The relative concentration of dioxo $(\text{O}=\text{O})_2\text{MoO}_2$ (I_{995}/I_{817}) and mono-oxo $(\text{O}=\text{MoO}_{4/5})_n$ (I_{1005}/I_{817}) species as well as their ratio (I_{995} / I_{1005}) determined from Raman spectra (Fig. S3).

Sample	I_{995} / I_{817}	I_{1005} / I_{817}	I_{995} / I_{1005}
Mo/Siral 70	0.53	0.05	10.60
Mo/Li/Siral 70	0.38	0.28	1.36
Mo/Na/Siral 70	0.59	0.11	5.36
Mo/K/Siral 70	0.58	0.10	5.80
Mo/Rb/Siral 70	0.53	0.09	5.89
Mo/Cs/Siral 70	0.63	0.26	2.42
Mo/Mg/Siral 70	1.53	2.03	0.75
Mo/Ca/Siral 70	0.69	0.44	1.57
Mo/Sr/Siral 70	0.54	0.08	6.75
Mo/Ba/Siral 70	0.54	0.07	7.71

Table S4 Actual Mo and Li content determined by ICP for Mo/Li/Siral 70 samples.

Samples	Mo / wt% ^a	Li / wt% ^a
Mo/0.015Li/Siral 70	5.6	-
Mo/0.045Li/Siral 70	6.1	-
Mo/0.075Li/Siral 70	5.7	-
Mo/0.15Li/Siral 70	6.0	0.042
Mo/0.375Li/Siral 70	5.8	0.095
Mo/0.75Li/Siral 70	5.8	0.20
Mo/1.5Li/Siral 70	5.6	0.38

a: Determined by ICP

Table S5 Temperature of the maximal rate of H₂ consumption over the catalysts determined from H₂-TPR experiment (T_{max}-H₂); number of acidic sites related to 1 g of each catalyst (N(a.s.)) or support (numbers in brackets), and temperature of the maximal rate of NH₃ desorption from the catalysts (T_{max}-NH₃) determined from NH₃-TPD experiment.

Sample	T _{max} -H ₂ , °C	N(a.s.)·10 ²⁰ , g ⁻¹	T _{max1} -NH ₃ , °C	T _{max2} -NH ₃ , °C
Mo/Siral 70	614	2.09 (0.76)	361	686
Mo/Li/Siral 70	650	1.98 (0.77)	362	701
Mo/Na/Siral 70	643	2.01 (0.74)	347	716
Mo/K/Siral 70	639	2.12 (0.77)	347	694
Mo/Rb/Siral 70	604	1.93(0.73)	328	674
Mo/Cs/Siral 70	587	1.61 (0.63)	383	686
Mo/Mg/Siral 70	632	1.59 (0.62)	406	716
Mo/Ca/Siral 70	640	2.13 (0.72)	347	709
Mo/Sr/Siral 70	671	1.81 (0.65)	383	710
Mo/Ba/Siral 70	645	1.85 (0.76)	359	692

Figures

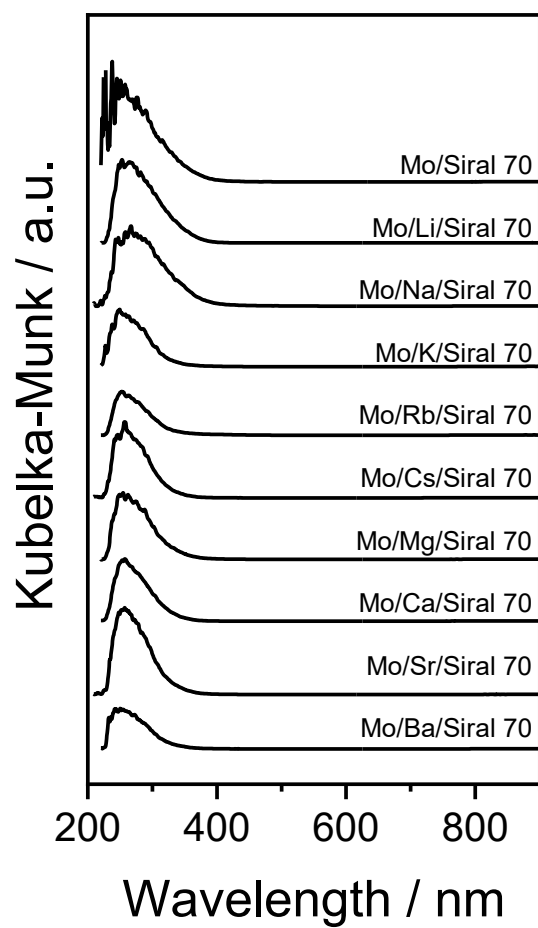


Fig. S1 UV-vis spectra of MoO_x-based catalysts.

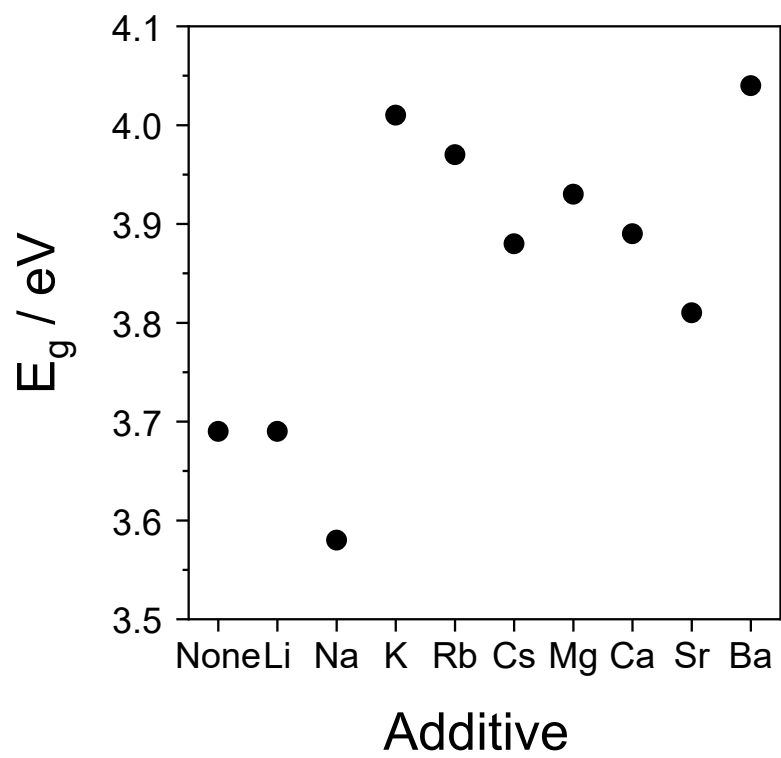


Fig. S2 UV-vis E_g values of supported MoO_x species.

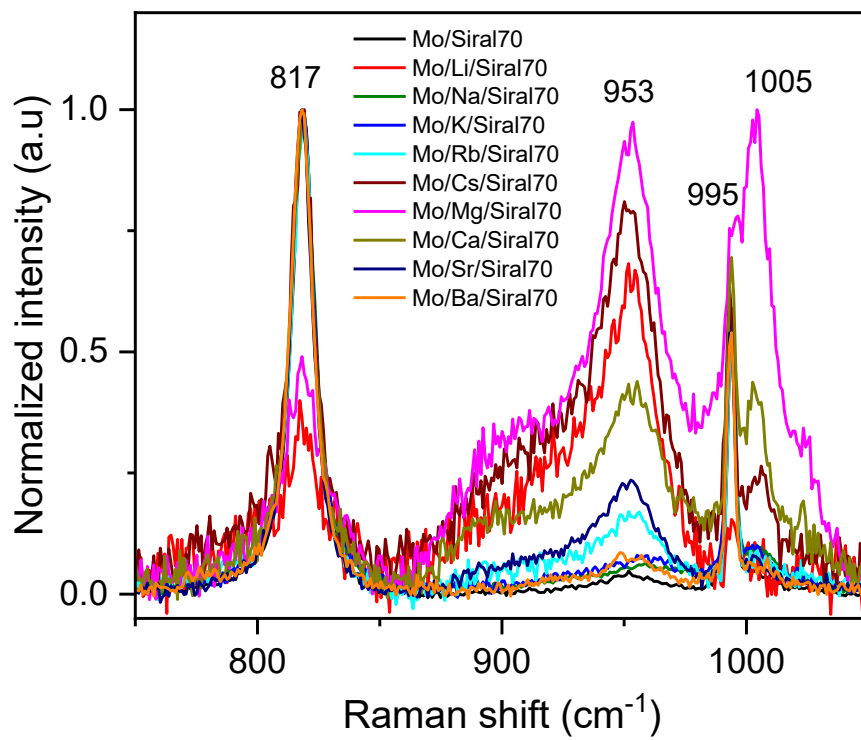


Fig. S3 Raman spectra of MoO_x-based catalysts.

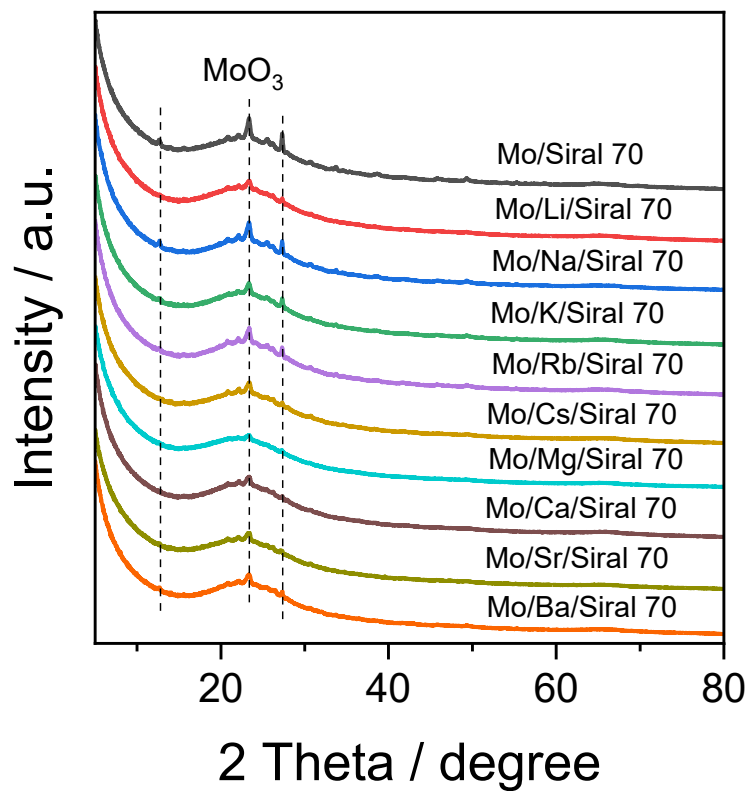


Fig. S4 XRD diffractograms of MoO_x-based catalysts.

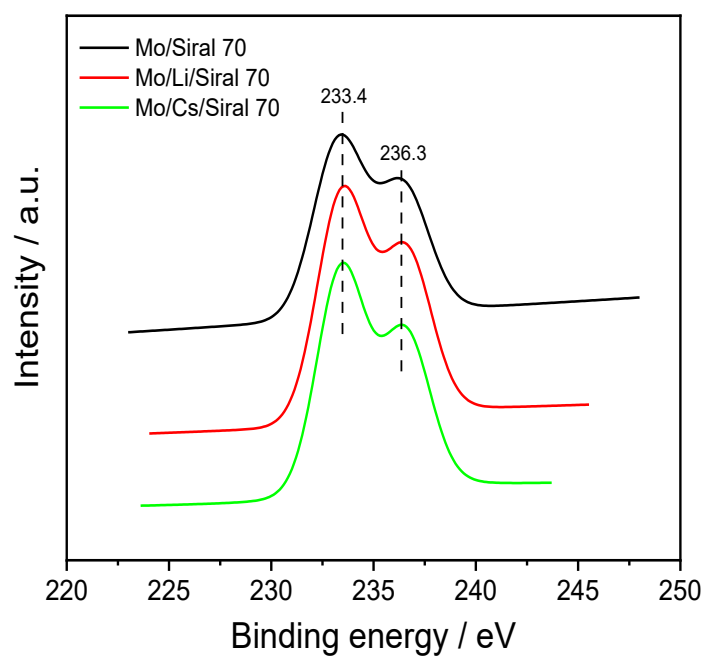


Fig. S5 XP spectra of the $\text{Mo}^{6+} 3d_{5/2}$ (233.4 eV) and $\text{Mo}^{6+} 3d_{3/2}$ (236.3 eV) of Mo/Siral 70, Mo/Li/Siral 70 and Mo/Cs/Siral 70.

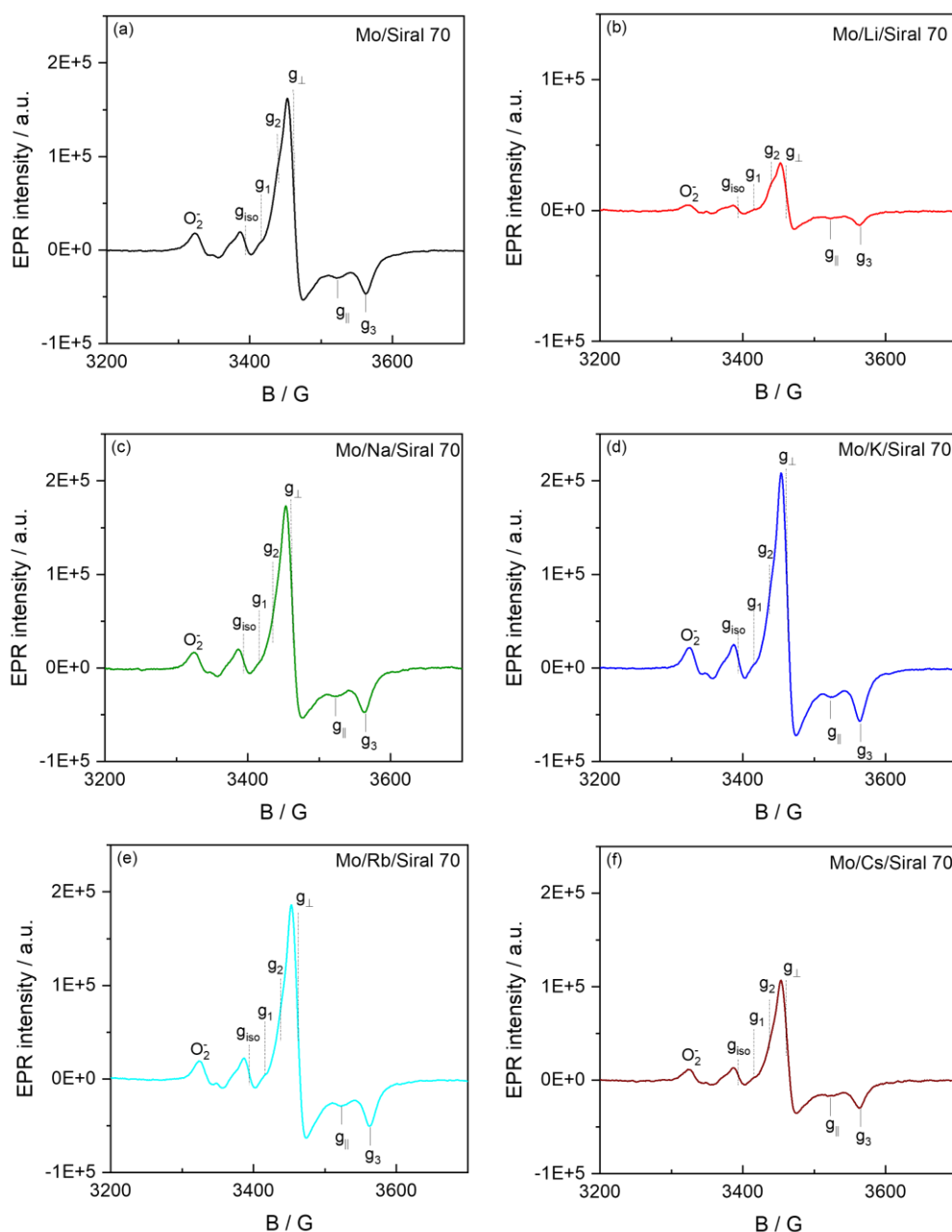


Fig. S6 EPR spectra of (a) Mo/Siral 70, (b) Mo/Li/Siral 70, (c) Mo/Na/Siral 70, (d) Mo/K/Siral 70, (e) Mo/Rb/Siral 70, and (f) Mo/Cs/Siral 70 recorded at 105K and normalized to 1 mg.

The spectra showed different Mo^{5+} signals with different intensity; a rhombic at $g_1 = 1.957$, $g_2 = 1.944$, $g_3 = 1.876$ assigned to Mo^{5+} in an octahedral field with rhombic distortion, an axial signal at $g_{\perp} = 1.927$, $g_{\parallel} = 1.895$ assigned to hexa-coordinate Mo^{5+} in axially distorted octahedron and less anisotropic signal at $g_{\text{iso}} = 1.969$ interpreted as tetra-coordinate Mo^{5+} species in $\text{MoO}_3/\text{SiO}_2^1$. Additionally, there is a rhombic signal at $g = 2.002, 2.006, \text{ and } 2.002$ related to the formation of O_2^{2-} . The sample Mo/Li/Siral 70 shows the lowest intensity of Mo^{5+} signals, indicating a decrease in the reducibility of Mo/Siral 70 in the presence of Li as evident from H_2 -TPR investigations.

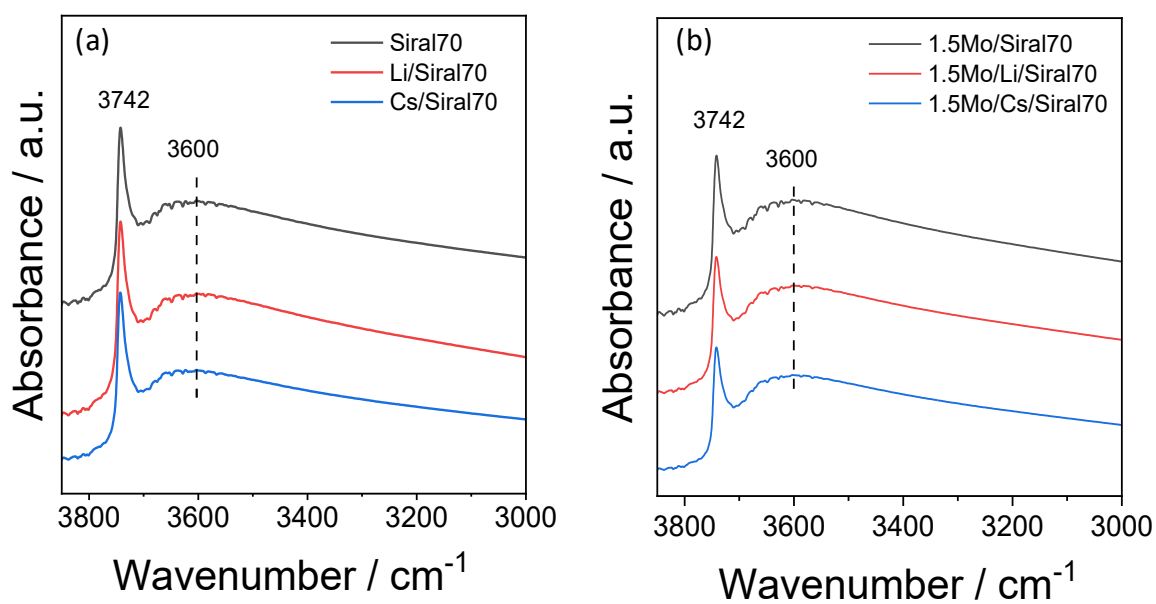


Fig. S7 In situ DRIFT spectra of (a) selected support materials and (b) the corresponding Mo-based catalysts. The spectra were recorded at 150°C after catalyst pretreatment in air at 450°C for 1h.

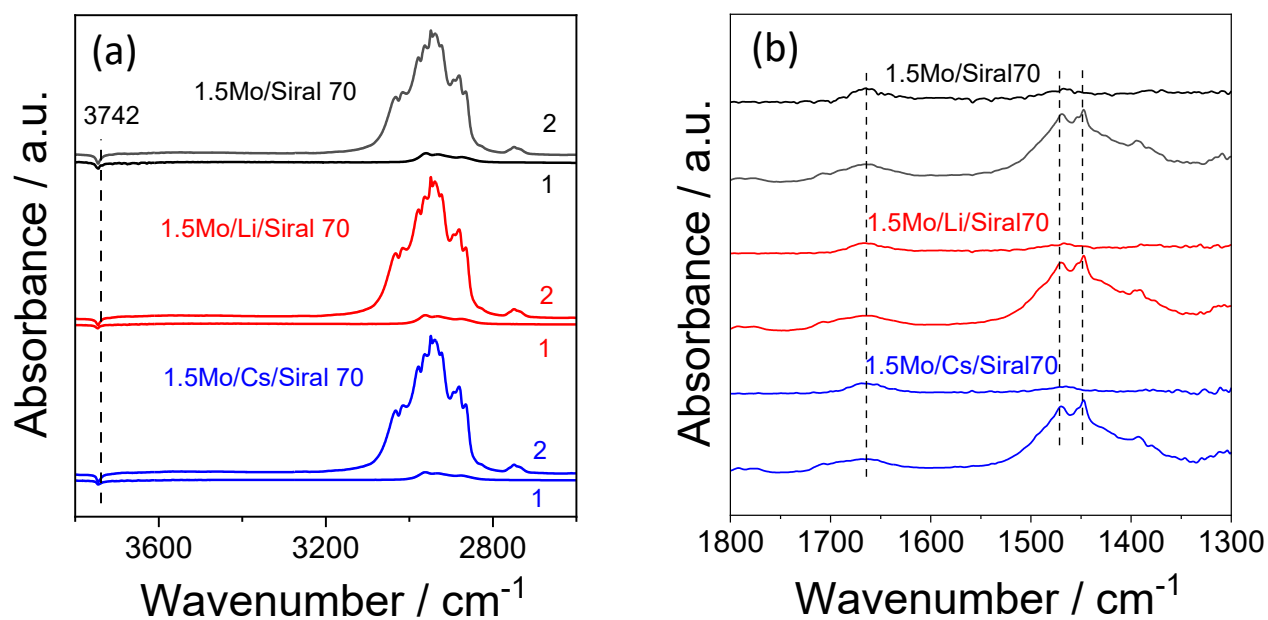


Fig. S8 Difference DRIFT spectra of selected Mo-based catalysts in the wavenumber range of (a) 2600-3800 cm^{-1} and (b) 1300-1800 cm^{-1} . The spectra were obtained by subtracting the spectra of fresh samples from those obtained after (1) exposing the samples to $\text{C}_4\text{H}_8\text{-N}_2$ at 150°C, or (2) treating the samples with $\text{C}_4\text{H}_8\text{-N}_2$ at 150°C for 15 min followed by flushing in N_2 for 15 min.

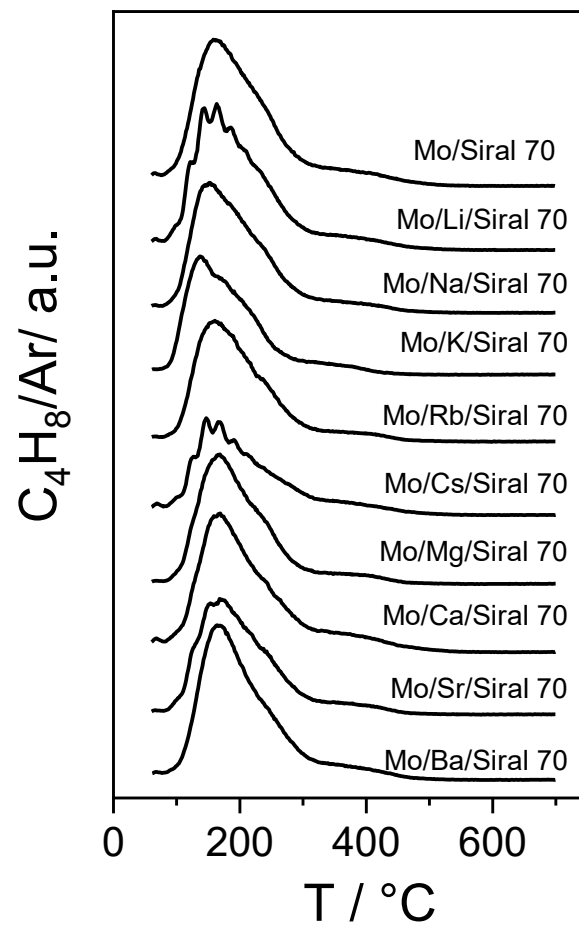


Fig. S9 2- C_4H_8 -TPD spectra of Mo/M/Siral 70: normalized MS signals of C_4H_8 ($m/z = 56$).

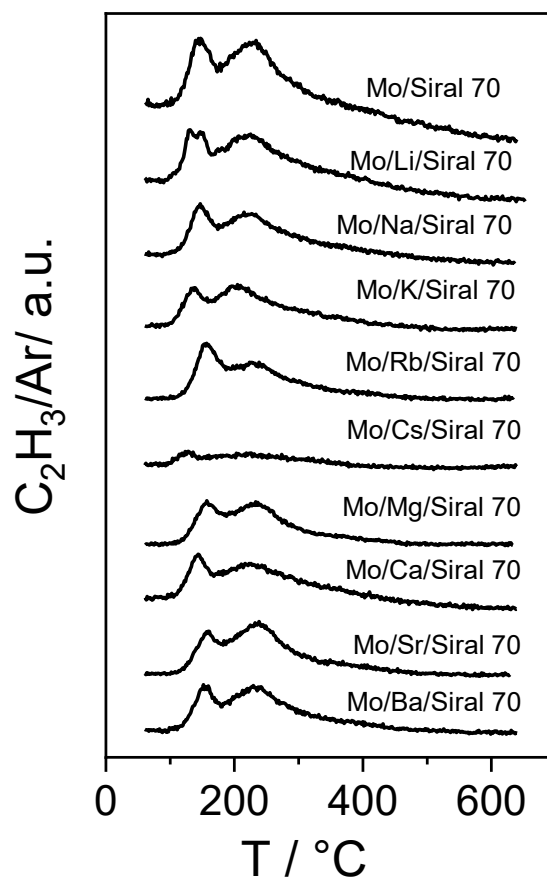


Fig. S10 C_2H_4 -TPD spectra of Mo/M/Siral 70: normalized MS signals of C_2H_3 fragment ($m/z = 27$).

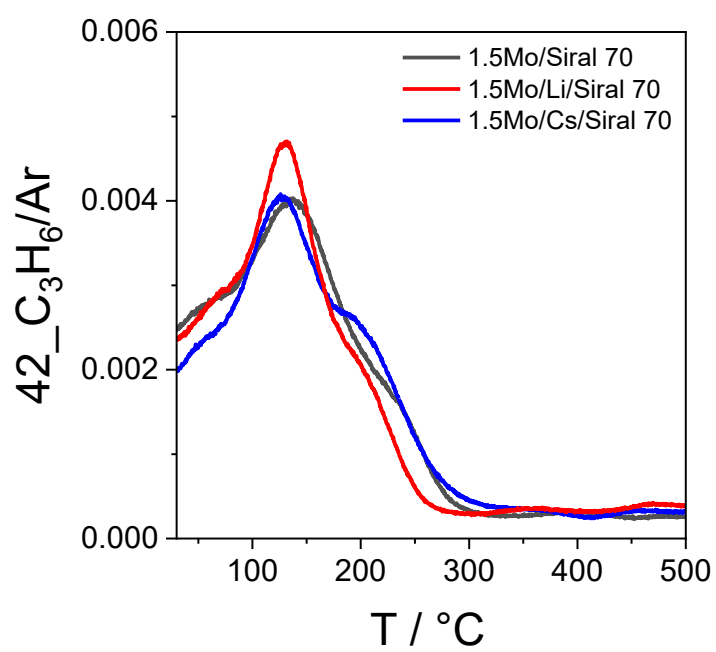


Fig. S11 $C_2^=/C_4^=$ -TPSR spectra collected from 30 to 500 °C for Mo/Siral 70, Mo/Li/Siral 70, Mo/Cs/Siral 70: normalized MS signals of C_3H_6 ($m/z = 42$).

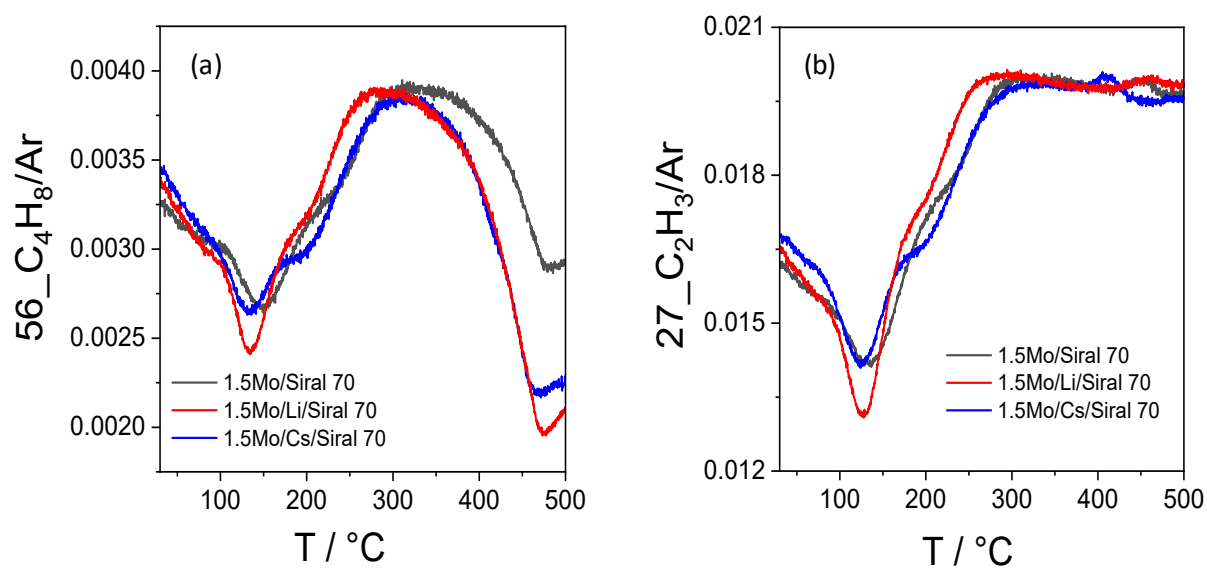


Fig. S12 C₂=/C₄=-TPSR spectra collected from 30 to 500°C for Mo/Siral 70, Mo/Li/Siral 70, Mo/Cs/Siral 70: normalized MS signals of (a) C₄H₈ (*m/z* = 56) and (b) C₂H₃ fragment (*m/z* = 27).

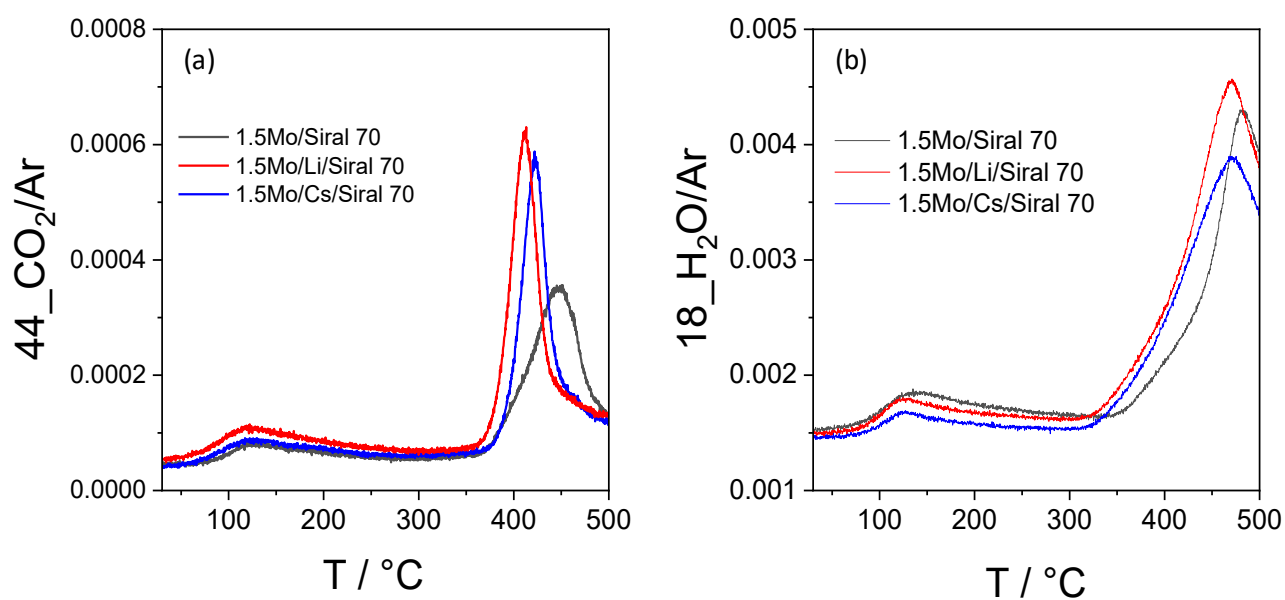


Fig. S13 C_2^-/C_4^- -TPSR spectra collected from 30 to 500°C for Mo/Siral 70, Mo/Li/Siral 70, Mo/Cs/Siral 70: normalized MS signals of (a) CO₂ ($m/z = 44$) and (b) H₂O ($m/z = 18$).

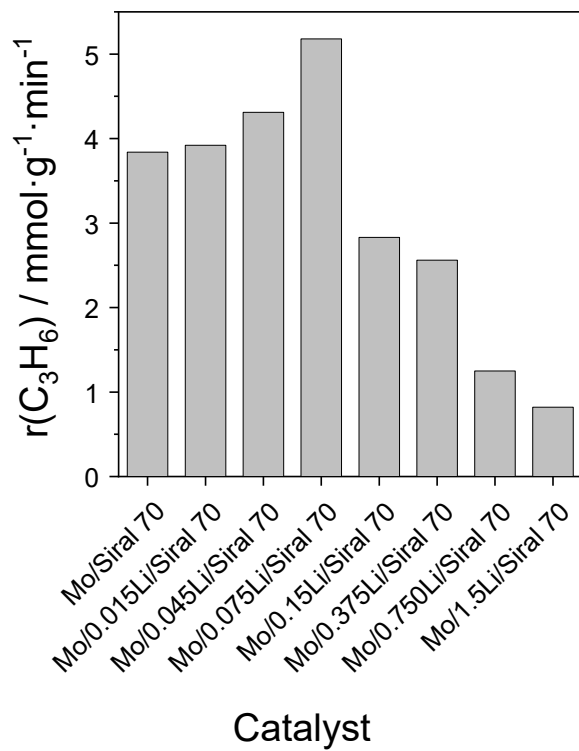


Fig. S14 The rate of propene formation over Mo/xLi/Siral series of catalysts with different Li surface density determined at 150°C.

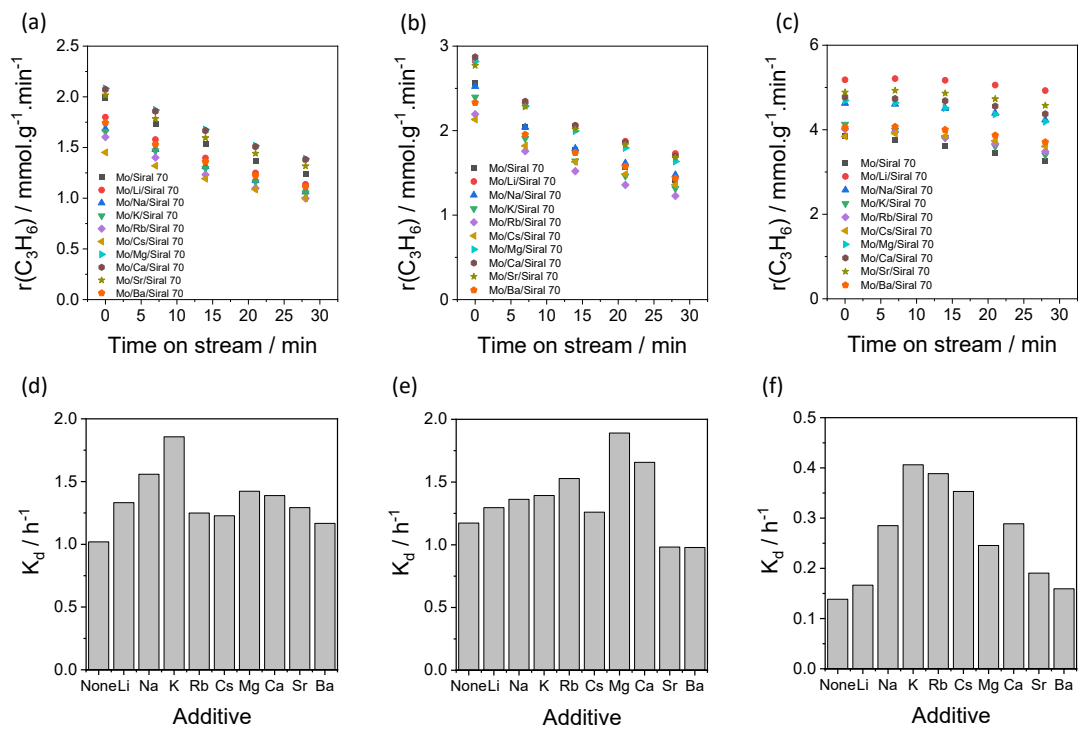


Fig. S15 Time on stream changes of the rate of propene formation at (a) 50°C (b) 100°C and (c) 150°C. Deactivation rate constants determined for different catalysts at (d) 50°C (e) 100°C and (f) 150°C.

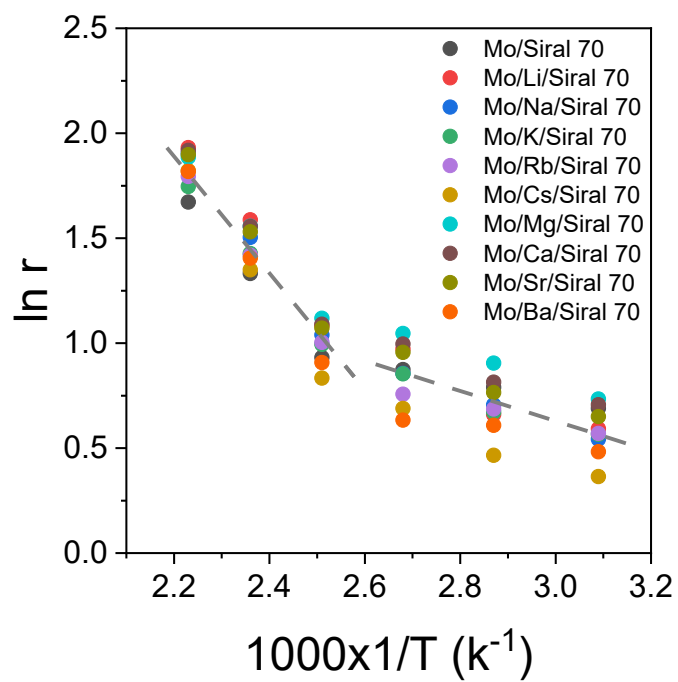


Fig. S16 Arrhenius plots for metathesis of ethylene with 2-butene over Mo-containing catalysts. Reaction conditions: $T=50-175^{\circ}\text{C}$, feed composition: $\text{C}_2\text{H}_4/\text{trans-2-C}_4\text{H}_8/\text{N}_2=5/5/1$.

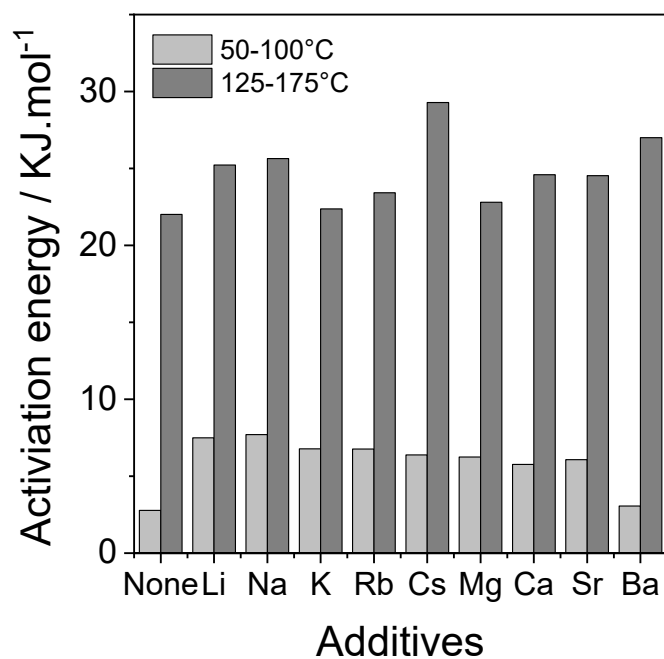


Fig. S17 Apparent activation energies of metathesis of ethylene with 2-butene over Mo-containing catalysts. Reaction conditions: T=50-100°C and 125-175°C, feed composition: C₂H₄/trans-2-C₄H₈/N₂=5/5/1.

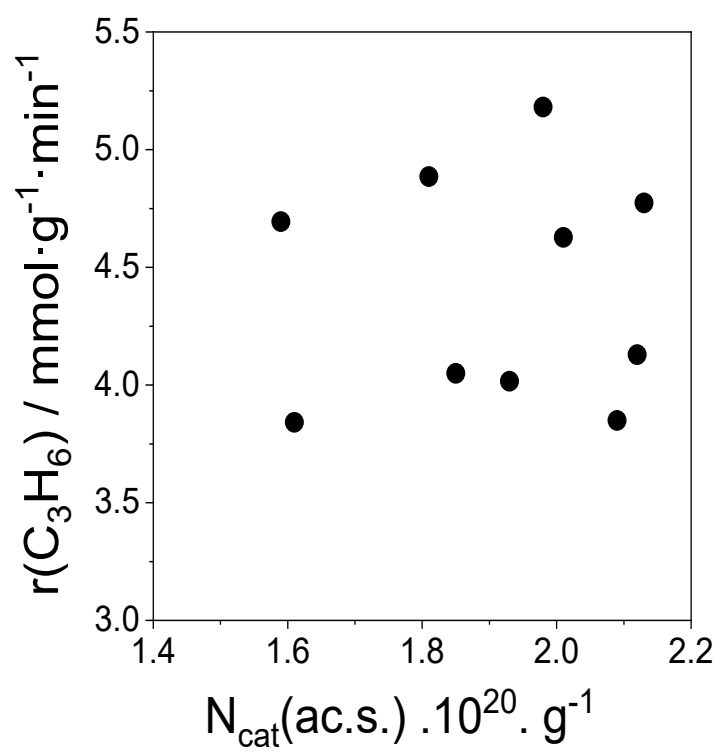


Fig. S18 Dependence of the rate of propene formation determined at 150°C over Mo/M/Siral 70 on the number of acid sites in the catalysts related to 1 g.

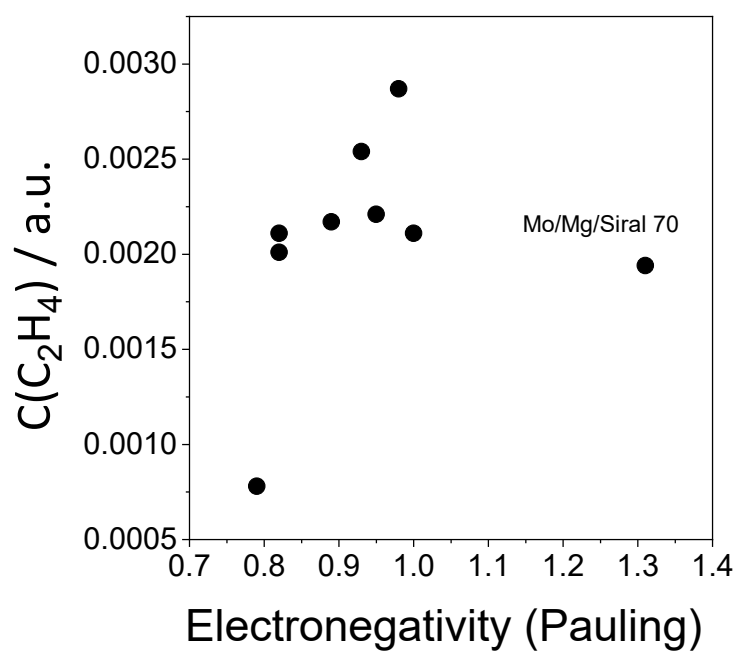


Fig. S19 Influence of the electronegativity of additive on $C(C_2H_4)$ value representing total amount of ethylene desorbed during C_2H_4 -TPD experiment.

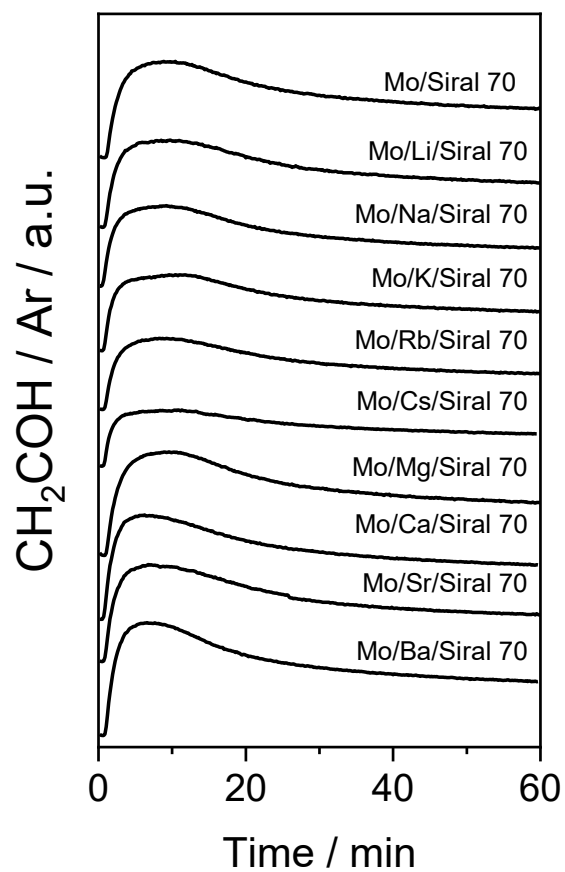


Fig. S20 Normalized MS signal of CH_2COH ($m/z = 43$) collected during the adsorption of 2- C_4H_8 on Mo/M/Siral 70 at 150°C .

References

- (1) Louis, C.; Che, M., EPR investigation of the coordination sphere of Mo⁵⁺ ions on thermally reduced silica-supported molybdenum catalysts prepared by the grafting method. *J. Phys. Chem.* **1987**, 91, 2875-2883.
- (2) Huang, M.; Johns, J. R.; Howe, R. F., EPR study of the superoxide ion in molybdenum zeolites. *J. Phys. Chem.* **1988**, 92, 1291-1295.