

Active Sites in Olefin Metathesis over Supported Molybdena Catalysts

Kazuhiko Amakawa,^[a] Jutta Kröhnert,^[a] Sabine Wrabetz,^[a] Benjamin Frank,^[a]
Felix Hemmann,^[b,c] Christian Jäger,^[c] Robert Schlögl,^[a] and Annette Trunschke*^[a]

Abstract: Metathesis of propene to ethene and 2-butenes was studied over a series of MoO_x/SBA-15 catalysts (molybdenum oxide supported on mesoporous silica SBA-15; Mo loading 2.1~13.3 wt%, apparent Mo surface density 0.2~2.5 nm⁻²). The catalysts have been prepared by an ion exchange technique. Nitrogen adsorption, ¹H-MAS-NMR, Raman, and FTIR spectroscopies were applied to characterize the catalysts. Adsorption of the reactant propene and the probe molecule NH₃ was studied by in situ FTIR, microcalorimetry and temperature-programmed desorption. Irrespective of the loading, only ca. 1% of the Mo atoms in the MoO_x/SiO₂ catalysts transform into active carbene (Mo=CHR) sites catalyzing propene metathesis. Isolated, distorted molybdenum di-oxo species in close vicinity to two silanol groups have been shown to be the precursor of the active site. Targeted active site creation by pretreatment with methanol resulted in an increase in initial catalytic activity by a factor of 800.

Introduction

The current yearly production of C2-C4 olefins exceeds 200 million tons. Propene production by cross-metathesis of ethene and 2-butenes is an economic strategy to satisfy the increasing propene demand,^[1] where silica-supported tungsten oxide catalysts are currently employed at high temperature (>573 K).^[2] It has been considered to substitute the W-based catalysts by more active molybdenum oxides catalysts operating at mild conditions.^[3] Supported molybdenum oxide catalysts exhibit the additional advantage that regeneration is possible. Recent studies suggest that Mo oxides supported on acidic materials (e.g., silica-alumina) are the most promising candidates.^[4] Metal-carbene species (M=CHR) are the active sites in olefin metathesis^[5] and they are generated in situ through surface

reactions between the supported metal oxide and the olefin itself. Apparently, only a small fraction of metal atoms (ca. 1% in silica-supported molybdena catalysts) are involved in active site formation.^[6] Recently, we proposed a mechanism of the formation of Mo=CHR sites in silica-supported molybdena, wherein Mo(VI) exclusively present in the freshly pretreated catalyst is reduced by propene to Mo(IV), which is followed by oxidative addition of another propene molecule to yield a surface Mo(VI)=CHR species (as exemplified in Scheme 1a).^[6b] The mechanism postulates Brønsted acidity and oxidation ability of the catalyst. Though the general route of carbene generation was clarified, the structural identification of the relevant surface molybdenum oxide precursor species remains an elusive challenge, as it demands discrimination of a small minority (ca. 1%) from the majority of spectator species. As for alumina-supported molybdenum oxide catalysts the nature of the precursor structure has been controversially discussed, favoring both monomeric^[7] as well as oligomeric^[8] surface MoO_x species. Here, we study correlations between surface density of molybdenum oxide species, acid-base properties and catalytic properties taking a series of silica-supported molybdenum oxide catalysts with different Mo loading as basis. Combined application of spectroscopic and functional analyses allows us to further elucidate the nature of the active site precursor in olefin metathesis over supported molybdenum oxide catalysts.

Results and Discussion

Propene self-metathesis at 323 K over monolayer-type molybdena supported on meso-porous silica SBA-15 (MoO_x/SBA-15) was studied as a model for the desired reverse reaction (*i.e.*, propene production). The surface Mo density was varied changing the Mo content (Table 1) with the aim to identify the relevant pre-catalyst species that give active carbenes (Mo=CHR). A detailed structural characterization of the catalyst series by nitrogen adsorption, XRF, XRD, SEM-EDX, IR, Raman, UV-vis, O K-edge NEXAFS, Mo K-edge XANES/EXAFS and DFT calculations has been reported elsewhere.^[9]

Textural properties of the MoO_x/SBA-15 catalysts are summarized in Table 1. The introduction of surface molybdenum oxide species at the expense of silanol groups results in a decrease of the specific surface area A_s while preserving the large mesopores (ca. 7 nm) of SBA-15. The decrease in the micropore surface area A_{μ} suggests a preferential anchorage of surface molybdena in the micropores.

The surface Mo density shows a great impact on the propene metathesis activity (Figures 1 (top)) The time trend of the fresh and regenerated catalysts that exhibits an increase in the

[a] Dr. K. Amakawa, J. Kröhnert, Dr. S. Wrabetz, Dr. B. Frank, Prof. Dr. R. Schlögl, Dr. A. Trunschke
Department of Inorganic Chemistry
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, 14195 Berlin (Germany)
E-mail: trunschke@fhi-berlin.mpg.de

[b] Dr. F. Hemmann, Prof. Dr. C. Jäger
BAM Federal Institute for Materials Research and Testing
Richard-Willstätter-Strasse 11, 12489 Berlin (Germany)

[c] Dr. F. Hemmann
Department of Chemistry
Humboldt-Universität zu Berlin
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)

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propene metathesis with time on stream (constant activity after 15–21 h) is presented in the supporting Information (Figure S1)

Table 1. Properties of MoO₃/SBA-15 catalysts.

Mo loading ^[a]	Surface density	A _s	A _μ ^[e]	V _p ^[g]	d _p ^[h]		
(wt%)	Mo ^[b] (nm ⁻²)	Isolated SiOH ^[c,d] (nm ⁻²)	(m ² /g)	(m ² /g)	(%) ^[f]	(ml/g)	(nm)
0	0	1.6 ^[c]	859	261	36	1	7.5
2.1	0.21	1.1 ^[d]	637	164	31	0.79	7.1
5.1	0.58	0.88 ^[d]	554	127	28	0.71	7.1
6.6	0.85	0.68 ^[d]	490	135	28	0.61	7.1
9.7	1.09	0.39 ^[d]	556	96	21	0.78	7.2
13.3	2.51	0.07 ^[d]	332	36	13	0.55	7.4

[a] by XRF. [b] Mo loading (at%) divided by A_s. [c] by TG. [d] by IR at the dehydrated state using relative heights of the silanol peak at 3745 cm⁻¹. [e] micropore (< ~0.9 nm of width) surface estimated by *t*-plot method. [f] A_μ divided by A_s. [g] at P/P₀ = 0.95. [h] at the dehydrated state. [i] estimated by NLDFT approach.

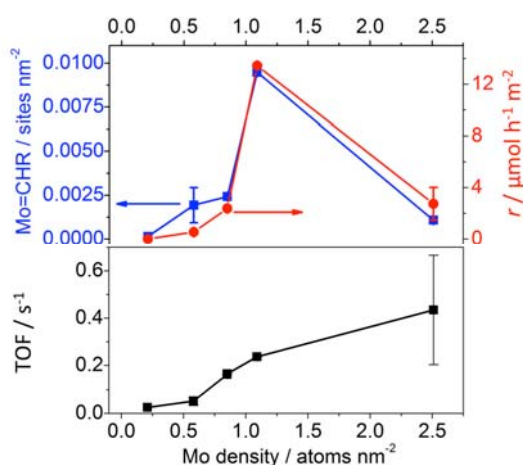


Figure 1. Propene metathesis performance of MoO₃/SBA-15 at 323 K measured after 15–21 h time on stream. (top) Metathesis rate and surface concentration of active carbene sites (Mo=CHR). (bottom) Turnover frequency (TOF). Error bars are estimated by two repeated measurements using fresh and regenerated catalysts. The catalysts were pretreated or regenerated in 20% O₂ at 823 K for 0.5 h.

The surface concentration of active carbene species (Figure 1 (top), blue line) determined by post-reaction titration by ethene-d₄ metathesis^[6b] is at most 1% of all surface Mo atoms and coarsely follows the trend of the activity (Figure 1 (top), red line),

indicating that the number of active sites is the dominant factor for activity. Dividing the rate by the active site density yields the turnover frequency (TOF; Figure 1 (bottom)), which shows a significant increase with increasing Mo density. The Mo density evidently affects both the probability of active site formation and the intrinsic metathesis activity (*i.e.*, TOF) of the Mo=CHR species (Figure 1). Propene adsorption studies were performed to explain this pattern. The carbene generation process was traced upon propene adsorption by in situ FTIR spectroscopy and microcalorimetry (Figure 2). Bands due to C-H vibrations (stretching : 2983, 2939, 2880 cm⁻¹; deformation: 1465, 1455, 1389, 1375 cm⁻¹) and ν(C=O) at 1668 cm⁻¹ in the infrared spectra (Figure 2a) are assigned to isopropoxide and acetone, respectively.^[6b] Formation of these intermediates indicates the protonation of propene to isopropoxide and its subsequent oxidation to acetone, where Brønsted acidity and oxidation ability of surface molybdena are involved (Scheme 1a; 1 to 4). This finding agrees with our previous study that included only a single catalyst with Mo density of 1.1 Mo nm⁻².^[6b] The intensity of the observed bands does not follow the Mo surface density.

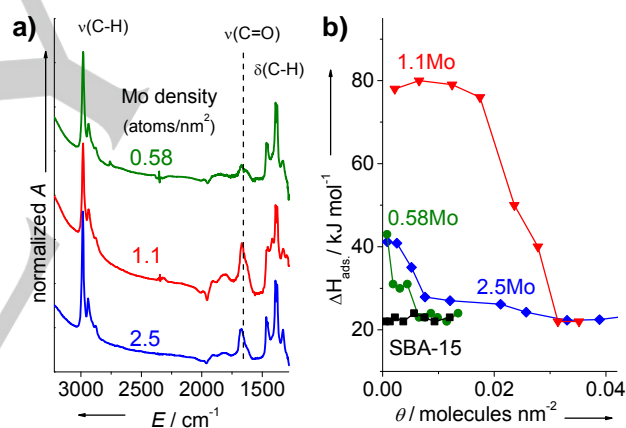


Figure 2. Adsorption of propene on MoO₃/SBA-15 with different Mo loadings at 323 K. (a) FTIR spectra collected after propene dosing at 3 hPa for 18 h and subsequent evacuation. (b) Differential heat of propene adsorption as a function of coverage determined by microcalorimetry. Surface Mo density (Mo atoms nm⁻²) is indicated close to the data.

The quantity and strength of the propene adsorption sites were evaluated by microcalorimetry (Figure 2b). Heat of adsorption as well as amount of adsorbed propene do also not follow the trend in surface Mo density but increase in the order 0.58Mo ≈ 2.5Mo < 1.1Mo. A similar tendency is observed in the overall rate and the number of surface carbene species (Figure 1(top)). Such a positive correlation between the surface concentration of Mo=CHR species in catalysis and the number as well as the strength (*i.e.*, heat of adsorption) of propene adsorption sites is also shown in the supporting (Figure S2). The observation suggests the involvement of the corresponding propene

adsorption sites in the generation of active species. The surface concentration of Mo=CHR is significantly lower than the overall number of propene adsorption sites (Figure S2b), confirming that only a fraction of the adsorbed propene yields the active sites

Bi-functionality of the catalyst in terms of acidity (protonation of propene to isopropoxide) and redox activity (oxidation of isopropoxide to acetone) is considered to be indispensable for the carbene generation.^[6b] To identify the nature of the Brønsted acid sites, hydrogen species were characterized by ¹H-NMR (Figure 3). While bare SBA-15 possesses virtually isolated silanol groups only (Figure 3a, 1.75 ppm),^[10] the loading of surface molybdenum oxide species leads to an occurrence of hydrogen-bonded silanol groups (Figure 3a, broad band at 2-5 ppm),^[10] and a perturbation of isolated silanol (*i.e.*, shift to 1.93 ppm). The results are consistent with the structural analysis by Raman, IR, UV-Vis, Mo K-edge XANES/EXFAS, O K-edge NEXAFS, and DFT calculations,^[9] which show the formation of two-fold anchored tetrahedral di-oxo (Si—O—)₂Mo(=O)₂ structures as the predominant surface molybdenum oxide species at the expense of surface silanol groups at all loadings. A fraction of the residual silanol groups is in hydrogen bonding with these molybdenum oxide species. The fraction of OH groups adjacent to molybdenum oxide species becomes smaller with increasing Mo surface density.

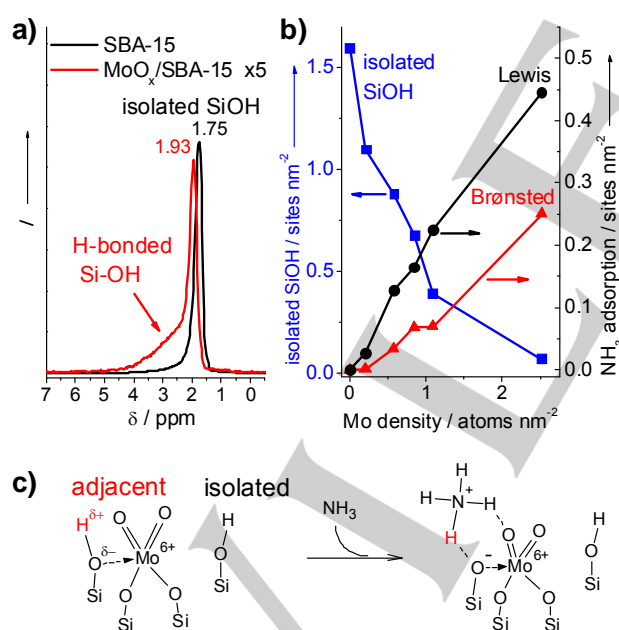


Figure 3. Study on acidity and hydroxyl groups in MoO_x/SBA-15. (a): ¹H-MAS-NMR spectra of SBA-15 and MoO_x/SBA-15 (1.27 Mo atoms nm⁻²). The spectrum of MoO_x/SBA-15 is magnified by factor of 5. (b): Density of isolated silanol groups and ammonia adsorption sites estimated by IR. (c): Schematic illustration of the suggested model for Brønsted acid sites. The original IR spectra are presented in the Supporting Information (Figure S3). The catalysts were pretreated in pure O₂ at 823 for 0.5 h.

Probing the acid sites by ammonia adsorption monitored by IR reveals a monotonous increase of the surface concentration of both Brønsted and Lewis acid sites (coordinatively unsaturated Mo centers) with increasing Mo density, where at most 10% of total Mo atoms serve as Brønsted acid sites (Figures 3b, and S3). Note that extinction coefficients used for calculating the surface concentration of Brønsted and Lewis acid sites have been taken from literature.^[11] Consequently, the analysis represents just a rough estimation.

Provided no indication for the presence of molybdenol groups by ¹H-NMR (Figure 3a; Mo—OH likely occurs below 1 ppm^[12]) and by other spectroscopic characterization,^[9] silanol sites in the vicinity of surface molybdena species are the most likely and actually the only possible source of Brønsted acidity. Analogously to Brønsted acid sites in silica-alumina materials,^[13] the conjugated Brønsted base ammonia appears to be protonated in a bonding configuration that is illustrated in Figure 3c. The hydrogen atom of the silanol group in close vicinity to a surface molybdena species interacts with the nitrogen atom of ammonia, because it bears a partial positive charge due to the interaction of the oxygen atom in the OH species with the adjacent Lewis acidic Mo site. At the same time, the ammonia molecule undergoes hydrogen-bonding to a terminal oxygen atom of the surface molybdenum oxide species. Such a configuration may have an unknown impact on the extinction coefficient of the ammonium species, and, consequently, on the quantification of Brønsted acid sites by ammonia adsorption. The uncertainty is reflected by the observation that the overall acid strength (*i.e.*, including the Lewis sites) estimated by temperature-programmed desorption of ammonia (Figure S4) appears to be similar for all catalysts, *i.e.*, the trends in ammonia adsorption seem to be dominated by weak adsorption of NH₃ on Lewis acid sites.

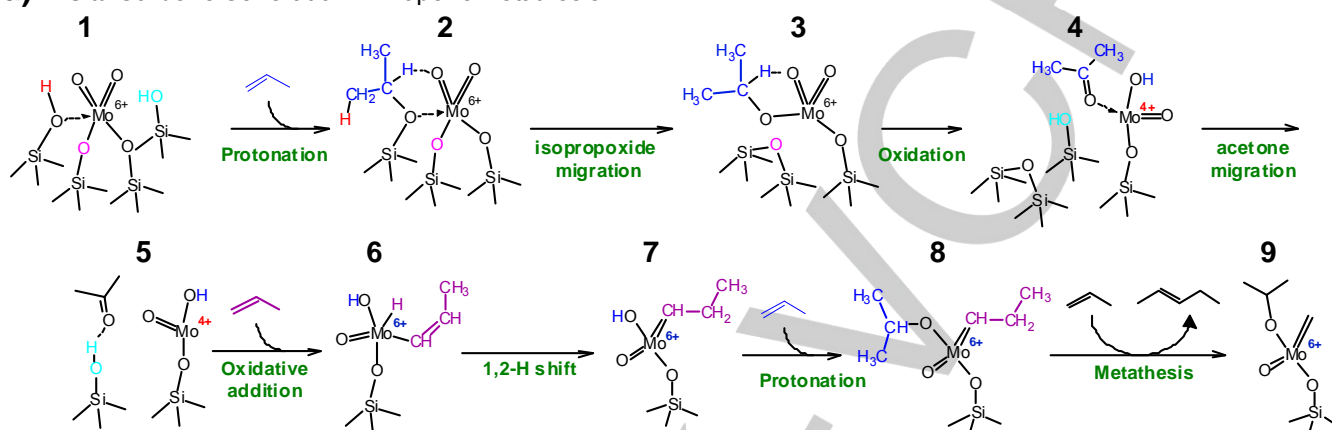
In summary, ¹H-NMR and FTIR indicate that Brønsted acidity in silica-supported MoO_x arises from silanol groups that are located in close proximity to surface molybdenum oxide species. Propene adsorption allows the semi-quantitative estimation of relevant acidity when taking into account that propene adsorption sites exhibit a heat of adsorption higher than 30 kJ mol⁻¹. The propene uptake represents at most 3% of total Mo atoms and shows a non-linear dependence to the Mo density (Figures S2, and 2b; ~0.03 C₃H₆ molecules nm⁻² for 1.1 Mo atoms nm⁻²), in which the maximum has been found at a Mo density of 1.1 atoms per nm², which corresponds to the most active catalyst.

To transform propene to acetone (Scheme 1a; 3 to 4), the isopropoxide species formed at a Brønsted acidic silanol site needs to migrate to a Mo(VI) center that exhibits oxidation ability. Such migration of surface alkoxide species across silanol sites and molybdenum oxide sites was observed by in situ IR using isotope labeling.^[14] However, the underlying mechanism remains unclear. The IR data show an increased acetone formation at high Mo density (Figure 2a; ν(C=O) at 1668 cm⁻¹), suggesting a higher probability of the migration, which is in line with the increased reactivity of the surface molybdenum oxide species due to the increased strain at the anchoring Mo—O—Si bonds that has been observed by O K-edge NEXAFS in combination

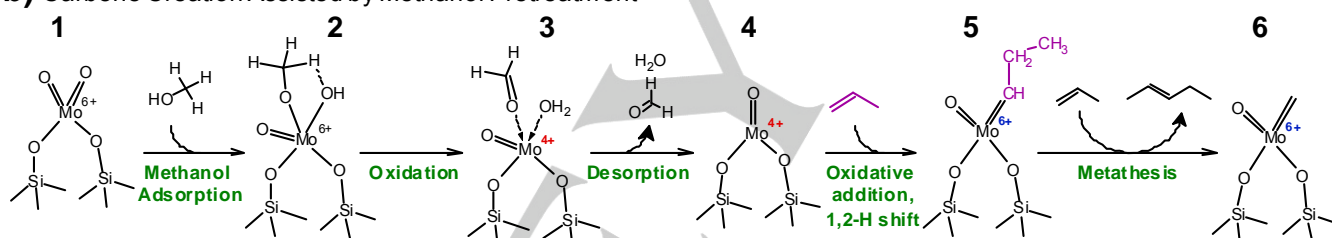
with DFT calculations.^[9] Based on the IR observation and the structural characterization, we propose that the migration involves a breaking of a Mo—O—Si bond and concurrent formation of a Si—O—Si bond (Scheme 1a, 2 to 3), wherein a

high strain at Mo—O—Si emerging at high Mo density is expected to be a key driving force of the rearrangement event.

a) In Situ Carbene Generation in Propene Metathesis



b) Carbene Creation Assisted by Methanol Pretreatment



Scheme 1. Suggested mechanisms for the generation of a Mo(IV)—carbene site in propene metathesis **(a)** without pretreatment and **(b)** with methanol pretreatment.

The formed acetone needs to desorb to allow access of another propene molecule to the Mo(IV) center that leads to the formation of active Mo(VI)=CHR sites (Scheme 1a, 4 to 5). These processes are expected to occur simultaneously, as it was shown recently for the exchange of pyridine at acid sites.^[15] The desorption of acetone upon heating after catalysis (Figure S5) suggests a reversible capture of acetone by hydrogen-bonding at silanol groups^[16] in the vicinity to the molybdena sites.^[6b] The low activity at the highest Mo density (Figure 1a) may be, therefore, related to the low silanol density due to the extensive coverage of the support by molybdenum oxide species (Figure 3b).

Summarizing the structural assignments for the required functions for carbene generation on silica-supported molybdenum oxide catalysts, a model for the catalyst precursor is envisaged. This model (Scheme 1a, 1) is characterized by a (Si—O—)₂Mo(=O)₂ structure exhibiting high strain at the Mo—O—Si bonds^[9] surrounded by at least two adjacent silanol groups that equip Brønsted acidity and a trapping function for the by-product acetone. Following the sequential reactions discussed above, a mono-anchored tetrahedral Mo(VI)—

propylidene is expected to occur (Scheme 1a, 7), which may further undergo the alkoxide formation (Scheme 1a, 8) and transformation to Mo(VI)—methylidene by propene metathesis (Scheme 1a, 9). The strained molybdena species occur at relatively high Mo density,^[9] while it still needs adjacent silanol sites to form the active sites. This accounts for the presence of an optimum Mo density at sub-monolayer coverage (Figure 1a). The low intrinsic activity at low Mo density (Figure 1b) may be due to increased steric hindrances by abundant silanol groups surrounding the carbene center and blocking the access of propene^[17] and/or subtle variations in the geometric configuration (e.g., bond lengths and angles),^[16,17] as suggested by theoretical studies.^[18]

The population balance of surface molybdenum oxide species and surrounding silanol groups is reflected in the $\nu(\text{Mo}=\text{O})$ stretching frequency in vibrational analysis. The original spectra^[9] are presented in the Supporting Information (Figure S6). With increasing molybdenum loading, the $\nu_s(\text{Mo}=\text{O})$ Raman band at 980—997 cm^{-1} becomes sharper and is blue-shifted (Figure S6a), which is also observed in the corresponding infrared spectra (Figure S6b). The $\nu(\text{Mo}—\text{O}—\text{Si})$ band at 926—

943 cm^{-1} , visible in the infrared spectra (Figure S6b), is also blue-shifted. The blue shift of the bands with increasing Mo loading indicates the decrease of hydrogen bonding due to surrounding silanol groups since fewer silanol groups are available with increasing molybdenum oxide loading. A clear structure—activity relationship exhibiting a volcano-type profile (Figure 4) suggests the presence of an optimum degree of hydrogen bonding of surface molybdena species, supporting the hypothesis that molybdena—silanol ensembles are precursors of the active sites.

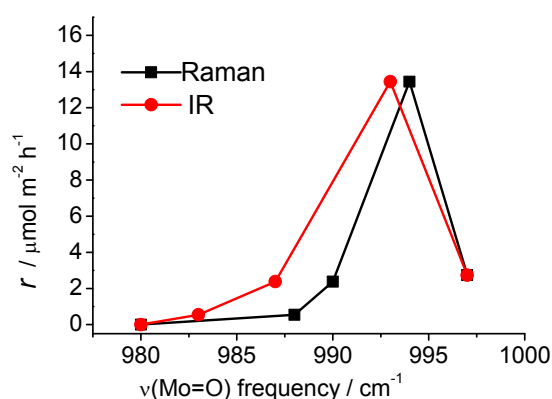


Figure 4. Correlation between the $\nu(\text{Mo}=\text{O})$ frequency detected in Raman/IR analysis and propene metathesis activity of $\text{MoO}_x/\text{SBA-15}$ at 323 K and at 15–21 h time on stream. The catalysts were pretreated or regenerated in 20% O_2 at 823 K for 0.5 h. The vibrational spectra are presented in the Supporting Information (Figure S6).

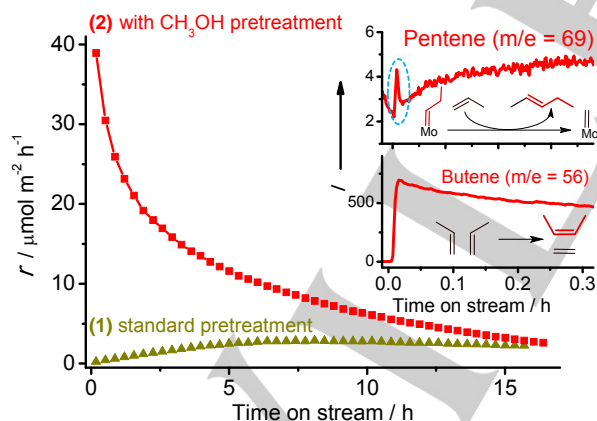


Figure 5. Propene metathesis activity of a $\text{MoO}_x/\text{SBA-15}$ catalyst ($0.85 \text{ Mo atoms nm}^{-2}$) after different pretreatment procedures. (1) Standard pretreatment (20% O_2 , 823 K, 0.5 h). (2) Methanol pretreatment (4% $\text{CH}_3\text{OH}/\text{Ar}$, 523 K, 0.5 h) and subsequent desorption (Ar , 823 K, 0.5 h) after the standard pretreatment. The inset shows signal of mass spectrometer for $m/e=69$ (pentene) and $m/e=56$ (butenes) at the initial period of the reaction after methanol pretreatment.

Having understood the mechanism of carbene generation, controlled active site creation is feasible. To enhance the formation of coordinatively unsaturated Mo(IV) sites, the catalyst was first treated with methanol at 523 K followed by a heat treatment in Ar at 823 K. The reduction of the abundant di-oxo $(\text{Si}-\text{O}-)_{2}\text{Mo}(\text{=O})_{2}$ species by methanol does not require Brønsted acidity,^[19] leaving coordinatively unsaturated Mo(IV) sites after the desorption of by-products in the post-treatment in Ar (Scheme 1b, 1 to 4). This procedure increases the initial catalytic activity by a factor of 800 (Figure 5). The high initial activity allows detection of the temporal formation of pentene at the initial period of the reaction (Figure 5, inset), which indicates the occurrence of Mo(VI) —propylidene species (Scheme 1b, 5) that corroborates the suggested mechanism of carbene formation. A continuous deactivation was observed in the case of the methanol pretreatment, implying that the anticipated two-fold anchored Mo(VI) —carbene (Scheme 1b, 6) is less stable than the mono-hapto structure (Scheme 1a, 9). Indeed, the gradual deactivation of the two-fold anchored tetrahedral Mo(VI) —carbene was reported previously,^[20] whereas mono-anchored Schrock-type Mo(VI) —alkylidene on dehydroxylated silica, which is similar to the anticipated structure in the case of the standard pretreatment (Scheme 1a, 9), exhibits a stable activity.^[21]

Conclusions

In summary, we specified the structures of the active sites for propene metathesis in $\text{MoO}_x/\text{SBA-15}$ by integrating the inputs from quantification of active sites, probe molecule adsorption and structural characterization. We propose that ensembles of strained, two-fold anchored tetrahedral di-oxo $(\text{Si}-\text{O}-)_{2}\text{Mo}(\text{=O})_{2}$ structures and adjacent silanol groups represent the precursor of the active carbene species. The suggested prominent role of adjacent silanol groups may help to understand the beneficial effect of using acidic supports.^[4] The obtained insights pave the way for evolution of metathesis catalysts by rational approaches, as has been exemplified in Figure 5.

Experimental Section

Preparation of the $\text{MoO}_x/\text{SBA-15}$ catalysts

The $\text{MoO}_x/\text{SBA-15}$ catalysts (molybdena supported on mesoporous silica SBA-15; Mo loading 2.1–13.3 wt%) were prepared by an ion exchange protocol.^[22] The details of the preparation were described elsewhere.^[9] In brief, freshly synthesized metal-free SBA-15 (internal sample ID 8233) was functionalized with propylammonium chloride using (3-aminopropyl)trimethoxysilane followed by treatment with hydrochloric acid. Then, the functionalized SBA-15 powder was stirred in an aqueous solution containing the desired amount of ammonium heptamolybdate to perform an anion exchange. After washing with water and filtration, the material was dried and calcined at 823 K in air, yielding supported $\text{MoO}_x/\text{SBA-15}$ with the actual Mo loadings of 2.1, 5.1, 6.6, 9.7 and 13.3 % (internal sample ID 8442, 8440, 11054, 8438, 8441, respectively).

The properties of the catalysts are summarized in Table 1. Additionally, a SBA-15 (BET surface area = 833 m²/g, internal ID 8261) and a MoO_x/SBA-15 (BET surface area = 532 m²/g, 10.8 Mo%, 1.27 Mo/nm², internal ID 13578) were prepared using the same procedure but in different batches for the ¹H-NMR study.

Characterization of the MoO_x/SBA-15 catalysts

Nitrogen adsorption Nitrogen adsorption was carried out at 77 K on a Quantachrome Autosorb-6B analyzer. Prior to the measurement, the samples were outgassed in vacuum at 393 K for 16 h. The data were processed on Autosorb software (Quantachrome). The specific surface area A_s was calculated according to the multipoint Brunauer-Emmett-Teller method (BET) in the pressure range $p/p_0 = 0.05-0.15$ assuming a N₂ cross sectional area of 16.2 Å². The micropore surface area A_{μ} and micropore volume V_{μ} were estimated using the t -plot method in the statistical thickness $t = 4.5-6.5$ Å range. The total pore volume V_p was estimated by using the amount of physisorbed nitrogen at a relative pressure $p/p_0 = 0.95$. The pore size distribution was determined by NLDFT method using a model based on equilibrated adsorption of N₂ on silica assuming cylindrical pores at 77 K.

¹H-NMR Solid-state magic angle spinning (MAS) NMR experiments were performed on a Bruker DMX 400 spectrometer (400.1 MHz, 9.4 T) at room temperature. Measurements were run with single pulse excitation using a MAS frequency of 12.5 kHz. The ¹H background signal of the probe was corrected by subtracting the ¹H MAS NMR spectrum of an empty rotor. ¹H chemical shifts were referenced versus adamantane. The pretreated samples were transferred into an air-tight rotor in a glove box to avoid exposure to air. Approximately the same amount of sample was charged into the rotor for every experiment.

FTIR Diffuse reflectance FT infrared (IR) spectra were collected at room temperature on a Bruker IFS66 spectrometer equipped with a liquid nitrogen-cooled MCT detector at a spectral resolution of 4 cm⁻¹ and accumulation of 1024 scans. An in situ cell (Harrick Praying Mantis™ diffuse reflectance attachment DRP-P72 in combination with a HVC-VUV reaction chamber) was used. KBr was used as reference material. The spectra were normalized using the silica band at 1865 cm⁻¹.

Raman. Confocal Raman spectra were collected at room temperature using a Horiba-Jobin Yvon LabRam instrument equipped with a red laser excitation (633 nm / 1.96 eV, 1.5 mW at the sample position). Spectral resolutions were better than 2 cm⁻¹. An in situ cell (a home-made quartz cell) was used to measure the dehydrated state.

Prior to spectroscopic measurements, the samples were pretreated in dry oxygen (20 kPa, neat or diluted with a dry inert gas) at 823 K (heating rate 10 K·min⁻¹) for 0.5 h, then cooled to room temperatures in the presence of oxygen in order to achieve the fully oxidized and dehydrated state of the catalyst.

Propene Metathesis and Post-reaction Active Site Counting

Propene metathesis The catalytic activity for the self metathesis of propene to ethene and 2-butenes was measured using a fixed-bed tube flow reactor at atmospheric pressure. All the gases were thoroughly dehydrated and deoxygenated (except oxygen) using trapping filters. The catalysts were pressed under ~135 MPa, crushed and sieved to a particle size of 250-355 μm. Then, 100 mg of the catalyst was loaded into a U-shaped quartz reactor with an inner diameter of 4 mm. Guard beds consisting of silica gel (BET surface area = 428 m² g⁻¹) were placed both immediately above (100 mg) and below (50 mg) the catalyst bed in

order to protect the catalyst bed from possible contamination by water. The use of the silica guard beds is essential to obtain a good catalytic performance. A blank test using bare SBA-15 with silica beds confirmed inertness of the apparatus and the guard beds. The catalyst was activated at 823 K (heating rate 10 K·min⁻¹) for 0.5 h, cooled to 323 K in a 20 % O₂ in Ar (20 ml min⁻¹), and then flushed with a flow of Ar (20 ml min⁻¹) before reaction. A neat propene flow of 8 ml min⁻¹ was fed to start the reaction. Inlet and outlet gases were analyzed by on-line gas chromatography using an Agilent Technologies 6890A GC system equipped with a flame ionization detector. The conversion of propene was kept below 5 % to stay in a differential regime. The selectivity to the metathesis products (ethane, cis- and trans-butene) was above 99.5 %, while trace amounts of 1-butene and higher hydrocarbons were detected. The activity is presented as formation rate of the metathesis products (*i.e.* sum of ethane, cis- and trans-butene) normalized by the BET surface area of the catalyst. The catalytic test was repeated after a regeneration procedure. The regeneration procedure is the same as the initial activation (823 K (heating rate 10 K·min⁻¹) for 0.5 h and cooled to 323 K in a dehydrated 20 % O₂ in Ar, then flushed with Ar before starting the reaction). Error bars are estimated by two repeated measurements using fresh and regenerated catalysts.

Active Site Counting by Post-reaction Ethene-*d*₄ Metathesis

After the metathesis reaction, the reactor was flushed with flowing Ar (20 ml min⁻¹ for 10 min, then 5 ml min⁻¹ for 20 min), then the feed gas was switched to 5 ml min⁻¹ of 1% C₂D₄ in Ar. The formation of propene-1,1-*d*₂ was monitored and quantified with a quadrupole mass spectrometer (QMS200, Balzer) using the signal of $m/z = 43$. The formation of propene-1,1-*d*₂ was also confirmed by the simultaneous detection of the molecular ion ($m/z = 44$). The two-fold amount of the liberated amount of propene-1,1-*d*₂ normalized by the BET surface area of the catalyst was assumed as the active site density.

Post-reaction temperature programmed desorption After the active counting procedure, the reactor was flushed with flowing Ar (20 ml min⁻¹ for 30 min) followed by a temperature ramp at rate of 10 K min⁻¹. Evolved species are monitored by a mass spectrometer (QMS200, Balzer). Signal of Ar ($m/e = 40$) was used as internal standard.

Adsorption of Probe Molecules

Prior to the adsorption, the samples were pretreated in dry oxygen (20 kPa, neat or diluted with a dry inert gas) at 823 K (heating rate 10 K·min⁻¹) for 0.5 h, then cooled to room temperatures in the presence of oxygen in order to achieve the fully oxidized and dehydrated state of the catalyst.

Microcalorimetry of Propene Adsorption Differential heats of propene adsorption were determined at 323 K using a MS70 Calvet Calorimeter (SETRAM). The calorimeter was combined with a custom-designed high vacuum and gas dosing apparatus. Propene was stepwise introduced into the initially evacuated cell ($p < 3 \cdot 10^{-6}$ Pa), and the pressure evolution and the heat signal were recorded for each dosing step. Though the propene was dosed at the reaction temperature for propene metathesis, possible thermal and volumetric contribution of the metathesis reaction can be neglected owing to the thermo- and stoichiometric-neutral nature of the reaction.^[6b]

In situ IR for Adsorption of Propene and Ammonia

Adsorption of propene and ammonia was studied by in situ FTIR spectroscopy. The IR experiments were carried out in transmission mode using a Perkin Elmer 100 FTIR spectrometer equipped with a DTGS detector at a spectral resolution of 4 cm⁻¹ and accumulation of 64 scans. The samples were pressed (125 MPa) into self-supporting wafers, which

were placed in an in situ IR cell. The IR cell was directly connected to a vacuum system (residual pressure of 3×10^{-6} Pa) equipped with a gas dosing line. Propene was dosed at 323 K at the pressure up to 3 hPa. Ammonia was dosed at 353 K at the pressure up to 7 hPa. In each experiment, the spectrum taken before probe dosing was used as background. Contribution of gas phase species was corrected by subtracting the spectrum without sample wafer. The spectra shown were normalized by the areal weight density of the wafer. The concentration of ammonia adsorption sites were estimated using the band at 1614 and $\sim 1430 \text{ cm}^{-1}$ for Lewis acid sites and Brønsted acid sites, respectively. Extinction coefficients of $16 \text{ cm} \mu\text{mol}^{-1}$ (Brønsted acid sites) and $1.46 \text{ cm} \mu\text{mol}^{-1}$ (Lewis acid sites) were used.^[11] Since the extinction coefficients have been taken from literature, the quantitative analysis of Lewis and Brønsted acid sites, respectively, represents a rough estimation.

Temperature-Programmed Desorption of Ammonia (NH₃-TPD)

Temperature-programmed desorption of ammonia (NH₃-TPD) was performed using a fixed bed reactor. About 30 mg of catalyst was used. Adsorption of NH₃ was done at 353 K by feeding 1% NH₃ in Ar (40 ml/min) for 0.5 h. After flushing the reactor with He at 353 K for 0.5 h, the bed temperature was raised with a heating rate of 10 K/min in He flow (40 ml/min). The desorption of NH₃ was monitored by a quadrupole mass spectrometer (OmniStar GSD301, Pfeiffer) using the signal of $m/e = 16$. The helium signal ($m/e = 4$) was used as internal standard.

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- [1] J. Ding, W. Hua, *Chemical Engineering & Technology* **2013**, 36, 83-90.
 [2] J. C. Mol, *Journal of Molecular Catalysis A: Chemical* **2004**, 213, 39-45.
 [3] S. Lwin, I. E. Wachs, *ACS Catalysis* **2014**, 4, 2505-2520.
 [4] ^aX. Zhu, X. Li, S. Xie, S. Liu, G. Xu, W. Xin, S. Huang, L. Xu, *Catal Surv Asia* **2009**, 13, 1-8; ^bD. P. Debecker, M. Stoyanova, F. Colbeau-Justin,

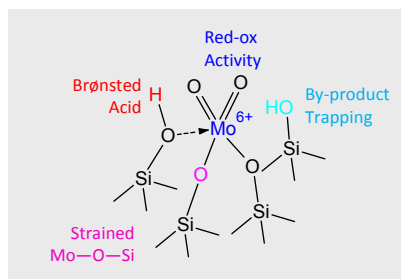
- U. Rodemerck, C. Boissière, E. M. Gaigneaux, C. Sanchez, *Angewandte Chemie International Edition* **2012**, 51, 2129-2131.
 [5] Y. Chauvin, *Angewandte Chemie International Edition* **2006**, 45, 3740-3747.
 [6] ^aJ. Handzlik, J. Ogonowski, *Catalysis Letters* **2003**, 88, 119-122; ^bK. Amakawa, S. Wrabetz, J. Kröhnert, G. Tzolova-Müller, R. Schlögl, A. Trunschke, *Journal of the American Chemical Society* **2012**, 134, 11462-11473.
 [7] D. P. Debecker, B. Schimmoeller, M. Stoyanova, C. Poleunis, P. Bertrand, U. Rodemerck, E. M. Gaigneaux, *Journal of Catalysis* **2011**, 277, 154-163.
 [8] T. Hahn, U. Bentrup, M. Armbrüster, E. V. Kondratenko, D. Linke, *ChemCatChem* **2014**, 6, 1664-1672.
 [9] K. Amakawa, L. Sun, C. Guo, M. Hävecker, P. Kube, I. E. Wachs, S. Lwin, A. I. Frenkel, A. Patlolla, K. Hermann, R. Schlögl, A. Trunschke, *Angewandte Chemie International Edition* **2013**, 52, 13553-13557.
 [10] J. Trébosc, J. W. Wiench, S. Huh, V. S. Y. Lin, M. Pruski, *Journal of the American Chemical Society* **2005**, 127, 3057-3068.
 [11] V. A. Matyshak, O. V. Krylov, *Kinetics and Catalysis* **2002**, 43, 391-407.
 [12] J. Herrera, J. Kwak, J. Hu, Y. Wang, C. Peden, *Topics in Catalysis* **2006**, 39, 245-255.
 [13] F. Leydier, C. Chizallet, A. Chaumonnot, M. Digne, E. Soyer, A.-A. Quoineaud, D. Costa, P. Raybaud, *Journal of Catalysis* **2011**, 284, 215-229.
 [14] M. Seman, J. N. Kondo, K. Domen, S. T. Oyama, *Chemistry Letters* **2002**, 31, 1082-1083.
 [15] F. Hemmann, I. Agirrezabal-Telleria, E. Kemnitz, C. Jäger, *The Journal of Physical Chemistry C* **2013**, 117, 14710-14716.
 [16] V. Crocellà, G. Cerrato, G. Magnacca, C. Morterra, *The Journal of Physical Chemistry C* **2009**, 113, 16517-16529.
 [17] X. Cao, R. Cheng, Z. Liu, L. Wang, Q. Dong, X. He, B. Liu, *Journal of Molecular Catalysis A: Chemical* **2010**, 321, 50-60.
 [18] ^aJ. Handzlik, *The Journal of Physical Chemistry B* **2005**, 109, 20794-20804; ^bJ. Handzlik, *The Journal of Physical Chemistry C* **2007**, 111, 9337-9348.
 [19] L. J. Gregoriades, J. Döbler, J. Sauer, *The Journal of Physical Chemistry C* **2010**, 114, 2967-2979.
 [20] K. A. Vikulov, B. N. Shelimov, V. B. Kazansky, J. C. Mol, *Journal of Molecular Catalysis* **1994**, 90, 61-67.
 [21] F. Blanc, N. Rendon, R. Berthoud, J.-M. Basset, C. Coperet, Z. J. Tonzetich, R. R. Schrock, *Dalton Transactions* **2008**, 3156-3158.
 [22] J. P. Thielemann, G. Weinberg, C. Hess, *ChemCatChem* **2011**, 3, 1814-1821.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Only ca. 1% of isolated distorted Mo di-oxo species that are in close vicinity to two silanol groups have been shown to be the precursor of the active carbene (Mo=CHR) sites on MoO_x/SiO₂ catalysts for propene metathesis. Targeted active site creation resulted in an increase in initial catalytic activity by a factor of 800.



*Dr. Kazuhiko Amakawa, Jutta Kröhnert,
Dr. Sabine Wrabetz, Dr. Benjamin Frank
Dr. Felix Hemmann,
Prof. Dr. Christian Jäger,
Prof. Dr. Robert Schlögl,
and Dr. Annette Trunschke**

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**Active Sites in Olefin Metathesis over
Supported Molybdena Catalysts**