Room-Temperature Metathesis of Ethylene with 2-Butene to Propene Over MoO_x -Based Catalysts: Mixed Oxides as Perspective Support Materials

Tatiana Otroshchenko¹ · Qiyang Zhang¹ · Evgenii V. Kondratenko¹

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Abstract

We investigated the effect of supports based on ZrO_2 , TiO_2 , Al_2O_3 , and SiO_2 on the rate of propene formation in the metathesis of ethylene with 2-butene at 50 °C over Mo-containing catalysts possessing highly dispersed MoO_x . Large improvements in this rate were achieved when using supports composed of mixed oxides ($\text{ZrO}_2\text{--SiO}_2$, $\text{ZrO}_2\text{--PO}_4$, $\text{TiO}_2\text{--SiO}_2$; $\text{Al}_2\text{O}_3\text{--SiO}_2$) rather than of individual oxides (ZrO_2 , TiO_2 , Al_2O_3 , SiO_2). Although previous literature studies dealing with the metathesis reaction over Al_2O_3 - or SiO_2 -supported catalysts at higher temperatures suggest the importance of redox or acidic properties of supported MoO_x species for catalyst activity, we were not able to establish any general direct correlation in this regard. Contrarily, the rate of propene formation can be significantly enhanced when promoting supports with an oxide promoter. We suggest that the created support lattice defects may facilitate the transformation of MoO_x to Mo carbenes under reaction conditions or improve the intrinsic activity of the latter.

Graphic Abstract

Keywords Metathesis · Ethylene · Butene · Propene · Molybdenum oxide

1 Introduction

Metathesis of ethylene with 2-butene is one of the industrial processes for on-purpose production of propene [1]. Typical heterogeneous catalysts include oxides of Re, W,

✉ Tatiana Otroshchenko
 tatiana.otroshchenko@catalysis.de

¹ Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a,
 18059 Rostock, Germany

or Mo supported on SiO₂, Al₂O₃, or SiO₂-Al₂O₃ [2]. WO_x/SiO₂ applied on the large scale is characterized by low price, long lifetime, and resistance to poisoning [3–5]. WO_x-based catalysts are, however, active at relatively high temperatures (~350–450 °C), while MoO_x- or ReO_x-based catalysts demonstrate high activity at lower temperatures (25–200 °C) [2, 6].

The activity of MoO_x-containing catalysts depends on polymerization degree of MoO_x species, surface acidity, pretreatment conditions or presence of co-catalyst [7–9]. Isolated di-oxo or oligomeric mono-oxo supported MoO_x show high activity for propene production, while crystalline MoO₃ is not active [10, 11]. The influence of surface acidity on the activity of Mo-based catalysts was investigated in several independent works [9, 12–14]. Apparently, Brønsted acidic sites in close vicinity to MoO_x species are relevant for high propene production at temperatures above 100 °C. The activity can also be enhanced after thermal catalyst pretreatment in inert gas [15], propene, ethylene, methane [16], methanol [13] or after photoreductive treatment in CO or H₂. [17] The influence of co-catalysts such as CaO, Al₂O₃ or SiO₂-Al₂O₃ on the metathesis of ethylene and 2-butene to propene over MoO_x/Al_xSi_yO_z was investigated by Goelden et al. [8]. Although these co-catalysts are inactive in this reaction, the activity of Mo-based catalysts is improved when one of them is used as an upstream-located pre-bed for the main catalyst.

To the best of our knowledge, most of previous studies of the metathesis of ethylene with 2-butene to propene were carried out with catalysts based on SiO₂, Al₂O₃, or SiO₂-Al₂O₃ supports. Thus, we decided to check the potential application of catalysts based on TiO₂- or ZrO₂-containing supports. From a fundamental viewpoint, it was important to check if the general activity-governing relationships established for the often-tested catalysts are also relevant for the above-mentioned alternatives and particularly at 50 °C. To this end, we prepared a series of Mo-containing catalysts possessing highly dispersed MoO_x species on the surface of TiO₂- or ZrO₂-based supports as well as of SiO₂, Al₂O₃ and SiO₂-Al₂O₃. They were tested for their activity in the metathesis of ethylene with 2-butene and characterized by complementary state-of-the-art techniques.

2 Experimental Part

2.1 Catalyst Synthesis

Several in-house prepared (SiO₂, see Supporting Information (SI)) and commercial (Al₂O₃ (Chempur neutral), ZrO₂-SiO₂ (~5 wt% SiO₂, Saint Gobain NorPro), ZrO₂-PO₄ (8 wt% PO₄, Daiichi Kigenso Kagaku-Kogyo Co), TiO₂-SiO₂ (Ti/Si ratio = 9/1, Sachtleben), ZrO₂ (Daiichi Kigenso

Kagaku-Kogyo Co), and TiO₂ (P25, Degussa)) supports were used for catalyst preparation. The commercial supports were calcined at 500 °C for 8 h. The catalysts were prepared by an incipient wetness impregnation method. Each support was impregnated with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (Riedel de Haen) to obtain the nominal metal surface density of 1.5 nm⁻². Hereafter, the catalyst precursors were dried at 110 °C overnight and calcined at 500 °C for 8 h (at 575 °C for SiO₂-supported catalysts for 16 h). The obtained catalysts are abbreviated as 1.5Mo/X, with “X” standing for support. The amounts of metal precursor and water required for catalyst synthesis were calculated by considering specific surface areas of supports and their absorptive capacity (Table S1 in SI). 1.5Mo/Siral 10 (10 wt% SiO₂ in Al₂O₃), 1.5Mo/Siral 40 (40 wt% SiO₂ in Al₂O₃), and 1.5Mo/Siral 70 (70 wt% SiO₂ in Al₂O₃) are from our previous study [18].

2.2 Catalyst Characterization

Specific surface area (S_{BET}) of the calcined supports was determined by nitrogen physisorption experiments at –196 °C using a Belsorp mini II setup (Bel Japan). Adsorption isotherms were evaluated according to the BET method using the adsorption data in the relative pressure (p/p⁰) range of 0.05–0.3.

UV–vis measurements 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. Each sample was in situ calcined in flowing air at 500 °C for 1 h and cooled down to 50 °C in the same flow. The UV–vis spectra were recorded at 50 °C in the range of 200–800 nm. BaSO₄ was used as a white standard for calculating the Kubelka–Munk function.

TEM analysis was conducted on a FEI Tecnai G 2 20 S-TWIN instrument operating at 200 kV. Each sample was ground into a fine powder and dispersed in ethanol using an ultrasonic bath. Hereafter, it was transferred onto copper grids coated with a 2 nm carbon layer and dried at 60 °C for 5 min. Additionally, a second copper grid coated with 2 nm carbon layer was placed on top.

Temperature-programmed desorption of ammonia (NH₃-TPD) was carried out in an in-house developed setup containing eight individually heated continuous-flow fixed-bed quartz reactors. 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

by an on-line mass spectrometer (Pfeiffer Vacuum OmniStar GSD 320). The signals at m/z of 15 (NH) and 40 (Ar) were recorded, with the latter being a reference standard.

For distinguishing between Brønsted and Lewis acidic sites, we performed IR measurements of adsorbed pyridine on a Tensor 27 spectrometer (Bruker). Prior to the measurement, each catalyst was pressed into a self-supporting wafer with a diameter of 20 mm. Prior to pyridine adsorption, the wafer was calcined in air flow at 400 °C in the IR cell for 10 min and cooled down in N₂ flow to room temperature. Pyridine was adsorbed at 25 °C until saturation. Then the reaction cell was evacuated for removing physisorbed pyridine. After heating the sample in vacuum up to 150 °C, the IR spectrum of adsorbed pyridine was recorded.

Temperature-programmed reduction with H₂ (H₂-TPR) was carried out in the same set-up used for NH₃-TPD. 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. MS signals at m/z of 2 (H₂) and 40 (Ar) were recorded.

Temperature-programmed surface reaction with trans-2-C₄H₈ (C₄H₈-TPSR) was carried out in the same set-up used for NH₃-TPD and H₂-TPR. 100 mg of each sample were heated in flowing air up to 500 °C for 1 h and then cooled down in Ar flow to room temperature. Hereafter, the catalysts were heated in a flow of 5 vol% C₄H₈ in Ar (10 mL·min⁻¹) up to 700 °C with a heating rate of 10 K·min⁻¹. The signals at m/z of 56 (C₄H₈), 43(CH₃CO), 42 (C₃H₆), 44 (CO₂), 18 (H₂O), and 40 (Ar) were recorded.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements were collected 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 of 10 K·min⁻¹) from room temperature to 450 °C, then treated in air flow (12 mL min⁻¹) at 450 °C for 1 h and cooled down in N₂ flow (10 mL min⁻¹) 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).

2.3 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 for 1.5Mo/Siral 10, 1.5Mo/Siral 40, and 1.5Mo/Siral 70 or 100 mg for the remaining catalysts, 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 50 °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 (propene, cis-2-butene and traces of C₅-olefins) 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 related to one Mo atom, i.e. turnover frequency of propene formation (TOF_{Mo}) Eq. 1 was used. The rate was determined after 420 s on stream at a degree of ethylene conversion below 15%. No catalyst activation but continuous deactivation was observed during 35 min on stream.

$$TOF_{Mo} = \frac{F_{feed} \times \frac{\dot{x}_{N_2}^{in}}{\dot{x}_{N_2}^{out}} \times x^{out}(C_3H_6) \times N_A}{V_m \times m_{cat} \times 60 \times 1.5 \times 10^{18} \times S_{BET}} \quad (1)$$

Here, F_{feed} is the volumetric flow rate of the feed gas (mL·min⁻¹) under reference conditions (0 °C, 1 atm), x_{N_2} with superscripts “in” or “out” stand for the molar flow (mol·mL⁻¹) of N₂ at the reactor inlet or outlet, $x^{out}(C_3H_6)$ is the molar fraction of propene at the reactor outlet, N_A is the Avogadro's number (6.02×10^{23} mol⁻¹), V_m is the molar volume (22,414 mL·mol⁻¹), and m_{cat} is catalyst weight (g), 1.5×10^{18} stands for the apparent surface density of Mo (1.5×10^{18} m⁻²), S_{BET} is the specific surface area (m² g⁻¹).

3 Results and Discussion

3.1 Supported MoO_x Species and Their Formation

The catalysts were treated at 500 °C in air before recording the UV-vis spectra at 50 °C in N₂ atmosphere. The UV-vis spectra of the catalysts (Fig. 1) are characterized by strong absorption bands at 250 nm and 295 nm, related to highly dispersed and small linear-chained tetrahedral MoO_x species. A band at ~330 nm can be assigned to octahedral polymerized MoO_x species [9]. As no absorption band at 400 nm ascribed to small MoO₃ crystallites [19] could be identified, all the catalysts should possess highly dispersed MoO_x as a result of low surface density of Mo (1.5 nm⁻²). Strong absorption background in the range 200–400 nm for the TiO₂-containing samples is due to the intrinsic bandgap of TiO₂ (~3.16 eV) [20].

To prove additionally high dispersion of MoO_x species, selected catalysts (1.5Mo/ZrO₂, 1.5Mo/ZrO₂-PO₄, 1.5Mo/Siral 40) were characterized by transmission

Fig. 1 UV-vis spectra of MoO_x-based catalysts. Barium sulfate (99.998%, Aldrich) was used as a white standard

electron microscopy (TEM). Some representative TEM images of the catalysts are shown in Figure S1. Since no evidence of the existence of MoO_x nanoparticles can be observed, MoO_x species seem to be highly dispersed in agreement with the results of our UV-vis analysis (Fig. 1).

We also applied in situ DRIFTS to analyze if and how surface hydroxyl sites of support materials participate in the formation of supported MoO_x species. The DRIFT spectra of dehydrated supports and the corresponding catalysts in the hydroxyl vibration region are shown in Figure S2. ZrO₂ support possesses terminal Zr-OH (~ 3763 cm⁻¹), bi-bridged Zr₂-OH (~ 3729 cm⁻¹), and tribridged Zr₃-OH (~ 3678 cm⁻¹ and ~ 3669 cm⁻¹) species [21]. Mixed ZrO₂-SiO₂ is characterized by the presence of terminal Zr-OH (~ 3764 cm⁻¹), terminal Si-OH (~ 3738 cm⁻¹) as well as multi-coordinated hydroxyls absorbing at similar wavenumbers as those observed for ZrO₂ (~ 3725 cm⁻¹, ~ 3678 cm⁻¹, and ~ 3665 cm⁻¹). Terminal Zr-OH (~ 3762 cm⁻¹) and at least two types of multi-coordinated hydroxyls (~ 3671 cm⁻¹, ~ 3640 cm⁻¹) exist on the surface of ZrO₂-PO₄. TiO₂ (P25) possesses several types of surface sites classified by Deiana et al. [22] as linear OH ($\nu(\text{OH}) > 3680$ cm⁻¹) and bridged ($\nu(\text{OH}) < 3680$ cm⁻¹). Each type of hydroxyl species has more than one local structure since several vibrations were observed (3717 cm⁻¹, 3686 cm⁻¹, 3668 cm⁻¹, 3640 cm⁻¹). Mixed TiO₂-SiO₂ possesses terminal Si-OH (~ 3737 cm⁻¹), terminal Ti-OH (~ 3720 cm⁻¹, ~ 3700 cm⁻¹) and at least three types of

multi-coordinated hydroxyls (~ 3677 cm⁻¹, ~ 3662 cm⁻¹, ~ 3639 cm⁻¹). The DRIFT spectrum of Al₂O₃ support has at least 5 different bands related to hydroxyl species differing in the coordination number of both OH groups and Al cations. Acid strength of OH groups increases with decreasing the corresponding wavenumber of the absorption band [23]. The observed bands can be related to the terminal Al-OH (AlO₃-OH at 3788 cm⁻¹ and AlO₅-OH at 3748 cm⁻¹), bridged Al-OH-Al (AlO₅-OH-AlO₅ at 3723 cm⁻¹ and AlO₅-OH-AlO₃ at 3698 cm⁻¹), and tricoordinated (AlO₅)₃-OH at 3679 cm⁻¹. [24] The DRIFT spectrum of SiO₂ is characterized by an absorption band at around 3743 cm⁻¹ related to isolated Si-OH (silanols) [25]. The DRIFT spectra of mixed Al₂O₃-SiO₂ oxides (Siral 10, Siral 40, Siral 70) are characterized by the presence of bands at wavenumbers similar to those for SiO₂ (~ 3736 - 3740 cm⁻¹) and Al₂O₃ (3788 cm⁻¹, 3723 cm⁻¹, 3698 cm⁻¹, 3679 cm⁻¹) implying the existence of several types of hydroxyls including terminal Si-OH and Al-OH as well as multi-coordinated ones. It is however worth mentioning that the highly intensive band related to Si-OH sites overlaps with those related to OH sites bonded to Al cations. Moreover, increasing SiO₂ content in mixed Al₂O₃-SiO₂ samples leads to the appearance of geminal Si-OH**Si-OH hydroxyls characterized by a poorly resolved broad band at around 3600 cm⁻¹ that complicates observation of other possible bands in this region.

Deposition of MoO_x species on support material resulted in consumption (partial or complete) of some hydroxyls, which are, therefore, can be considered as anchoring sites. For example, terminal Zr-OH present on the surface of ZrO₂ (band at 3763 cm⁻¹) and ZrO₂-SiO₂ (band at 3764 cm⁻¹) should actively participate in the formation of MoO_x species. Similarly, terminal Ti-OH groups in TiO₂ are also involved in this process. For other catalysts, no preferential consumption of certain OH groups for binding MoO_x could be established.

3.2 Acidic and Redox Properties

In order to distinguish between Brønsted and Lewis acidic sites on the surface of catalysts, we performed IR measurements of adsorbed pyridine on all catalysts with the exception of those based on SiO₂-Al₂O₃ supports (acidic properties of these catalysts were fully investigated in Ref. [9]). The obtained IR spectra are shown in Figure S3 in ESI. Noticeably, the spectra of all catalysts are characterized by the presence of bands typical for pyridine adsorbed on Lewis acidic sites (1600 and 1450 cm⁻¹). The only catalyst also possessing Brønsted acidic sites (band at 1540 cm⁻¹ in IR spectrum) is 1.5Mo/SiO₂. Comparing the integral intensity of bands characteristic for different kind of acidic sites, it can be assumed that the number of Brønsted acidic sites in 1.5Mo/SiO₂ is much lower than that of Lewis acidic sites.

As the catalysts mainly contain Lewis acidic sites, it is possible to use NH_3 -TPD for deeper analysis of their acidic properties.

Figure 2a shows the NH_3 -TPD profiles of the catalysts and the corresponding support materials, while the temperature of the maximal rate of NH_3 desorption and the number of acidic sites related to 1 nm^2 of support are listed in Table S2. Among the support materials, TiO_2 is characterized by the highest density of acidic sites ($N_{\text{sup(a.s.)}}$), while SiO_2 does not possess acidic sites. Noticeably, the bare supports composed of a single oxide (except SiO_2) have stronger acidic sites (high $T_{\text{max-NH}_3\text{-sup}}$) than their promoted/mixed counterparts. The maximum of NH_3 desorption peak shifts to higher temperatures for most of the Mo-containing samples. Deposition of MoO_x on ZrO_2 , Siral 10, Siral 40, Siral 70 and SiO_2 leads to an increase in the total amount of acidic sites, while the presence of MoO_x on $\text{ZrO}_2\text{-SiO}_2$, $\text{ZrO}_2\text{-PO}_4$, TiO_2 , $\text{TiO}_2\text{-SiO}_2$, and Al_2O_3 results in a decrease in the total number of acidic sites. Noticeably, for $\text{ZrO}_2\text{-SiO}_2$, $\text{ZrO}_2\text{-PO}_4$, $\text{TiO}_2\text{-SiO}_2$, and Al_2O_3 , weak acidic sites are preferentially consumed upon deposition of MoO_x species, while for other supports no preference can be observed.

Redox properties of the catalysts were analyzed by H_2 -TPR to check if and how the kind of support affects reducibility of supported MoO_x species. For most catalysts,

the H_2 -TPR profiles are characterized by several minima in the outlet H_2 flow (Fig. 2b). They are due to H_2 consumption through reaction with differently reducible MoO_x species and/or bare support (at temperatures higher than 600°C). The values of the temperature ($T_{\text{max-H}_2}$) of the first hydrogen consumption peak are shown in Table S2. With respect to $T_{\text{max-H}_2}$, MoO_x supported on individual oxides can be ordered as follows: $1.5\text{Mo}/\text{TiO}_2 < 1.5\text{Mo}/\text{ZrO}_2 < 1.5\text{Mo}/\text{Al}_2\text{O}_3 < 1.5\text{Mo}/\text{SiO}_2$. In most cases, when the support is a promoted/mixed oxide, $T_{\text{max-H}_2}$ shifts to higher temperatures, i.e. reducibility of MoO_x is worsened.

To study reducibility of MoO_x species on different supports by trans-2-butene, temperature-programmed surface reaction (TPSR) tests with this olefin were also carried out. Oxygenates CH_3COR , C_3H_6 , CO_2 and H_2O were observed as reaction products. Among all catalysts, only $1.5\text{Mo}/\text{ZrO}_2\text{-PO}_4$, $1.5\text{Mo}/\text{TiO}_2\text{-SiO}_2$, $1.5\text{Mo}/\text{Siral 10}$, $1.5\text{Mo}/\text{Siral 40}$, and $1.5\text{Mo}/\text{Siral 70}$ consumed C_4H_8 at relatively low temperature (Figure S4a). Such consumption was accompanied by formation of oxygenates and propene (Figure S4 (b) and (c) respectively). It is generally assumed that oxygenates are formed upon transformation of MoO_x to carbenes through reaction with fed olefins [7, 10]. Accordingly, the formation of oxygenates in the present C_4H_8 -TPSR tests can be considered as a proof of reductive activation of MoO_x species. Propene formation can be explained through

Fig. 2 **a** NH_3 -TPD profiles of the bare supports (dashed lines) and the corresponding catalysts (solid lines); **b** H_2 -TPR profiles of the catalysts

1-and 2-butene metathesis. Thus, it can be concluded that activation of MoO_x species supported on binary oxides (ZrO₂-PO₄, TiO₂-SiO₂, Al₂O₃-SiO₂) proceeds easier than that of those supported on individual oxides (ZrO₂, TiO₂, Al₂O₃, SiO₂) since no oxygenates and propene were formed at low temperature in the C₄H₈-TPSR tests with the latter materials. High-temperature C₄H₈ consumption ($T > 400$ °C) was observed for all catalysts and is related to oxidation of this olefin by MoO_x to CO₂ (Figure S4 (d)) and H₂O (Figure S4 (e)).

3.3 Catalyst Activity in Metathesis of Ethylene with 2-Butene

The rate of propene formation in the metathesis of ethylene with 2-butene was determined at 50 °C and related to one Mo atom to obtain an apparent turnover frequency (TOF_{Mo}). The calculated values are shown in Fig. 3. The catalysts based on individual metal oxides can be ordered in this regard as follows: 1.5Mo/Al₂O₃ > 1.5Mo/SiO₂ > 1.5Mo/TiO₂ > 1.5Mo/ZrO₂. Importantly, the activity strongly increases when MoO_x species are located on the surface of promoted/mixed oxides. Thus, the TOF_{Mo} values for 1.5Mo/ZrO₂-PO₄ and 1.5Mo/TiO₂-SiO₂ are more than 350 and 100 times higher than those for 1.5Mo/ZrO₂ and 1.5Mo/TiO₂, respectively. It should be noted that MoO_x species supported on promoted ZrO₂ or TiO₂ reveal higher activity than those supported on bare Al₂O₃ or SiO₂. Our catalysts are, however, less active than the most active state-of-the-art Mo-based

catalysts based on SiO₂-Al₂O₃ supports (Table S3) [13, 18, 26, 27].

According to the results shown in Fig. 3, there is an obvious impact of the kind of support on catalyst activity. Considering the UV-vis spectra (Fig. 1), TEM (Figure S1), H₂-TPR (Fig. 2b) results, and the Mo content well below a monolayer coverage, we are quite sure that our catalysts do not possess inactive MoO₃, which would negatively affect the TOF values. However, we cannot exclude that Mo-carbenes formed from differently structured highly dispersed and small linear-chained tetrahedral MoO_x species may differ in their intrinsic metathesis activity.

3.4 Factors Affecting Metathesis Activity of MoO_x Species

Due to technical limitations for identification/quantification of Mo carbenes, we decided to follow a common approach used for metathesis catalysts tested at high temperatures to reveal possible origin(s) of different activity [9]. To this end we tried to correlate redox and acidic catalyst properties with catalyst activity. Redox properties of MoO_x might play a crucial role due to the following reason. It is generally accepted that Mo=CHR carbenes are active sites for olefin metathesis [7, 13, 28, 29]. Such sites are assumed to be created through in situ activation of Mo⁶⁺O_x by olefin molecule into Mo⁴⁺O_{x-1} followed by oxidative addition of another olefin molecule (Fig. 4).

Fig. 3 The Mo-related rate of propene formation (TOF_{Mo}) determined at 50 °C over catalysts based on different supports. Ethylene conversion was below 1% over 1.5Mo/ZrO₂, 1.5Mo/TiO₂, 1.5Mo/Al₂O₃, and 1.5Mo/SiO₂, about 2% over 1.5Mo/ZrO₂-SiO₂, 1.5Mo/ZrO₂-PO₄, and 1.5Mo/TiO₂-SiO₂, about 4% over 1.5/Siral 10 and 1.5/Siral 70 and about 11% over 1.5Mo/Siral 40

Fig. 4 Possible reaction pathways of in situ creation of active carbene species from MoO_x

Since the proposed pathway includes the reduction stage, it can be suggested that high reducibility of Mo^{6+}O_x might be favorable for high activity. To check this idea, we tried to correlate the TOF_{Mo} values with the $T_{\text{max}}\text{-H}_2$ values given in Table S2 as well as with the temperature of C_3H_6 release peak observed in C_4H_8 -TPSR profiles in Figure S4 (c). As no obvious relationships could be established (Fig. 5a and Figure S5), this catalyst property does not seem to be decisive.

The role of catalyst acidity in olefin metathesis is documented in several works [9, 12, 30]. Density functional

theory calculations of the metathesis of ethylene with 2-butene over Mo/HBeta suggest that the presence of acidic sites could increase propene productivity due to decreasing the activation barrier for MoO_x conversion into Mo-carbenes [12]. Based on the results of IR analysis of adsorbed pyridine, Hahn et al. [9] established a correlation between the concentration of Brønsted acidic sites in $\text{MoO}_x/\text{Siral}$ s and TOF_{Mo} determined at 150 °C, i.e. 100 °C higher than in the present study. Moreover, those authors considered the total amount of Brønsted acidic sites and did not pay attention to

Fig. 5 Dependence of TOF_{Mo} determined at 50 °C on the temperature of **a** the first hydrogen consumption peak in H_2 -TPR profiles or **b** NH_3 desorption peak in NH_3 -TPD profiles as well as on the number of acidic sites in **c** the catalysts or **d** the support materials related to 1 nm^2

their strength. It can be however expected that the stronger the acidic sites, the higher the contribution of side reactions is as suggested in Ref. [12] To check if the strength of acidic sites and/or their concentration in the catalysts or support materials are important for propene formation at 50 °C over the present catalysts, we plotted the activity and the acidity data in Fig. 5b–d. Noticeably, most of the catalysts desorbing NH₃ at lower temperatures are more active than those desorbing NH₃ at higher temperatures (Fig. 5b). Accordingly, it can be assumed that weak acidic sites are preferable for metathesis reaction. Nevertheless, no general direct correlation between the activity and the strength of acidic sites could be established. Regarding the influence of concentration of acidic sites in the catalysts (Fig. 5c) or in the support materials (Fig. 5d) on the TOF_{Mo} values, no obvious dependence could also be found.

Accordingly, the direct influence of redox and acidic properties of the catalysts on the intrinsic activity of supported MoO_x species in propene formation at 50 °C was not confirmed. It can be assumed that besides redox and acidic properties, the kind of support also influences the molecular structure of highly dispersed and small linear-chained tetrahedral MoO_x species and therefore their ability to form carbenes and/or the intrinsic activity of the latter. Therefore, considering the molecular level complexity of the mechanism of carbene formation and the metathesis reaction itself, it is unlikely to establish general factors determining activity of MoO_x species supported on different materials. Thus, further studies are required to check if there are universal fundamentals relevant for this reaction. In particular, the role of support defects created upon promoting of supports with an oxide promoter seems to deserve a special attention.

4 Conclusions

For the first time, we have demonstrated that Mo-containing catalysts based on doped ZrO₂ or TiO₂ supports are attractive candidates for the metathesis of ethylene with 2-butenes to propene at only 50 °C and outperform their often-investigated counterparts based on individual SiO₂ or Al₂O₃ supports. Their higher activity might be related to the presence of lattice defects created in support materials after promotion with an oxidic promoter. This knowledge opens a possibility for purposeful preparation of supports and, accordingly, catalysts on their basis for low-temperature propene formation from ethylene and 2-butenes.

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Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

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