

**Olefin Metathesis over Supported MoO_x Catalysts: Influence of the Oxide Support**

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ARTICLE

Olefin Metathesis over Supported MoO_x Catalysts: Influence of the Oxide Support

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A series of supported MoO_x catalysts on different oxide supports (Al₂O₃, TiO₂, ZrO₂, SiO₂) were synthesized and investigated for propylene metathesis, characterized with *in situ* spectroscopies (DRIFTS, Raman, UV-Vis) and chemically probed with propylene-TPSR-MS, propylene-TPSR-IR, and ethylene/2-butene titration. Under dehydrated conditions at monolayer coverage or maximum surface dispersion, the surface MoO_x sites are present as a mixture of isolated di-oxo (O=)₂Mo(-O-Al)₂ and oligomeric mono-oxo O=Mo(-O-Al)_{4/5} sites on Al₂O₃, primarily oligomeric mono-oxo O=Mo(-O-Ti)_{4/5} on TiO₂, isolated di-oxo (O=)₂Mo(-O-Zr)₂ and oligomeric mono-oxo O=Mo(-O-Zr)_{4/5} on ZrO₂, and isolated di-oxo (O=)₂Mo(-O-Si)₂ on SiO₂. The bridged (S₂-OH) and tri-coordinated (S₃-OH) anchoring surface hydroxyls of the oxide supports with strong support cation electronegativity control the activation and number of active surface MoO_x sites at low temperatures (<100 °C). The isolated anchoring surface hydroxyls (S-OH) of the oxide supports with strong support cation electronegativity control the activation and number of active surface MoO_x sites at high temperatures (>350 °C). Olefin metathesis by the more redox active supported MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts is retarded by the formation of stable surface acetone and acetate species that block olefin adsorption. The oxide supports are potent ligands that tune the activation and surface chemistry of the surface MoO_x sites for olefin metathesis. This is the first time that the influence of oxide supports on the activation and surface chemistry of supported MoO_x sites has been systematically examined.

Keywords: metathesis, propylene, molybdate, supported, Raman, DRIFTS, UV-vis

I. Introduction

Due to the feedstock shift in steam cracking and oil refineries, there is a growing gap between global propylene supply and demand. The olefin metathesis reaction is an on-purpose method to react ethylene and 2-butene to produce two propylene molecules.¹⁻³ The supported transition metal oxide (Re, Mo, W) catalysts dispersed on high surface area oxide supports (Al₂O₃ or SiO₂) are highly effective catalysts for the olefin metathesis reaction. The Shell Higher Olefin Process (SHOP) was developed to produce linear higher olefins with supported MoO_x/Al₂O₃ catalysts.³ The activation of surface MoO_x sites for olefin metathesis is reported to strongly depend on the specific oxide support. It's generally concluded that the supported MoO_x/Al₂O₃ catalyst is ~10x more active than the supported MoO_x/SiO₂ catalyst, while supported MoO_x/ZrO₂ and MoO_x/TiO₂ catalysts are inactive for olefin metathesis.⁴⁻⁸ Reductive pre-treatment of surface MoO_x sites with H₂ is claimed to activate surface MoO_x sites on non-Al₂O₃ and non-SiO₂ supports. Tanaka *et al.* showed that the H₂ treated supported MoO_x/TiO₂ catalyst exhibits propylene metathesis activity at 25°C and proposed that Mo(+4) and Mo(+5) are

active sites with *ex situ* XPS.⁶ Indovina *et al.* studied the H₂ reduced supported MoO_x/ZrO₂ catalyst with *ex situ* ESR and XPS and claimed that only H₂ reduced Mo(+5) sites are active for propylene metathesis at 25°C.⁷

The molecular and electronic structure of surface MoO_x sites on different oxide supports under oxidatively dehydrated conditions have been studied with *in situ* Raman,⁹⁻¹³ IR,¹⁴⁻¹⁵ UV-vis,^{10, 12-13} XAS,¹⁶⁻¹⁸ etc. It was found that the structure of the surface MoO_x sites depends on the surface MoO_x coverage and specific oxide support. For the Al₂O₃-, ZrO₂- and TiO₂-supported MoO_x catalysts, the isolated surface MoO₄ sites predominate at low surface coverage on the supports, and both isolated surface MoO₄ and oligomeric surface MoO_{5/6} co-exist at high surface coverage. The surface MoO_x sites, however, are only present as isolated MoO₄ sites on SiO₂ supports.^{9, 10, 11-12, 16-17} The nature of the surface MoO_x sites on the Al₂O₃ and SiO₂ supports during propylene metathesis reaction conditions have been recently reported,^{10, 13, 15, 19-20} but the nature of the surface MoO_x sites on the ZrO₂ and TiO₂ supports during propylene metathesis reaction conditions have still not been reported.

Over the years, there have been studies trying to correlate the olefin metathesis catalytic activity to the nature of the surface MoO_x sites,^{8-11, 21-22} but correlations between the catalyst acidic or redox properties and olefin metathesis are still being debated. The reducibility of supported MoO_x catalysts was determined from H₂-TPR and followed the trend MoO_x/TiO₂ > MoO_x/ZrO₂ > MoO_x/SiO₂ > MoO_x/Al₂O₃.²¹ This reducibility trend

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suggests that MoO_x sites on ZrO₂ and TiO₂ supports may be over-reduced under propylene metathesis reaction conditions.²³ Kim *et al.* reported a different reducibility trend from H₂-TPR: MoO_x/TiO₂ > MoO_x/ZrO₂ > MoO_x/Al₂O₃ > MoO_x/SiO₂.¹¹ More recently, Otroshchenko *et al.* compared the metathesis activity of the surface MoO_x sites on different oxides supports with the redox and Lewis/Brønsted acid properties of the surface MoO_x sites, but could not reach any general structure-activity relationships.⁸ The simple correlations made between H₂-TPR reducibility and propylene metathesis activity of surface MoO_x sites²³ has the following issues: (i) the reducibility determined from H₂-TPR is not representative of the reducibility by olefins, and (ii) the nature of the surface MoO_x sites during the propylene metathesis reaction conditions are still unknown.

The objective of this study is to determine the influence of the oxide support on the molecular structure and activity of the surface MoO_x sites on multiple oxide supports (Al₂O₃, SiO₂, TiO₂ and ZrO₂) under oxidatively dehydrated and propylene metathesis reaction conditions. The supported MoO_x catalysts were physically characterized with *in situ* spectroscopy (DRIFTS, Raman, and UV-Vis) and chemically probed with C₃⁼-TPSR-MS, C₃⁼-TPSR-IR, ethylene/2-butene titration, and steady state propylene self-metathesis. Comparison of these physical and chemical properties will allow building fundamental structure-activity relationships for propylene metathesis by the supported MoO_x catalysts on different oxide supports.

II. Experimental Details

Catalyst Synthesis.

The supported MoO_x catalysts were prepared by incipient-wetness impregnation (IWI) of aqueous ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, Matheson, Coleman & Bell, 99.9%) onto different oxide supports (Al₂O₃ (Puralox, SCCa 5/200, 197 m²/g), ZrO₂ (Degussa, 60 m²/g), TiO₂ (Evonik P25, 51 m²/g), SiO₂ (Cabot, Cab-O-Sil, EH-5, 350 m²/g). Before impregnation, the Al₂O₃ support was calcined at 500 °C for 2 hours under flowing air. The SiO₂ support was treated with DI water and calcined at 500°C for 4h to condense the fluffy powders. The impregnated MoO_x catalysts were dried at room temperature overnight, then dried at 120°C for 2h in flowing air (100 mL/min), and finally calcined by ramping the temperature at 1 °C/min in flowing air (100 mL/min) to 500°C and hold 500°C for 4h. The loading (surface coverage) of Mo for Al₂O₃, TiO₂, ZrO₂ and SiO₂ support MoO_x catalysts is 18% (4.6 Mo/nm²), 5.8% (4.6 Mo/nm²), 5.8% (4.3 Mo/nm²), 7.5% (0.9 Mo/nm²) that are close to monolayer surface coverage, with the exception of SiO₂ that is not able to form complete surface metal oxide monolayers because of the poor reactivity of the surface silanols.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).

The *in situ* DRIFTS spectra of the supported MoO_x catalysts were collected by a Thermo Scientific Nicolet 8700 FT-IR spectrometer equipped with a Harrick Praying Mantis attachment (DRA-2 with CaF₂ window). A Mercury-Cadmium-

Telluride (MCT) detector was used to collect the spectra with a resolution of 4 cm⁻¹ and an accumulation of 96 scans/min. For each experiment, ~20mg of catalysts powders were loaded into an *in situ* cell (Harrick, HVC-DR2 with a CaF₂ window). The gas flow rates were controlled by Brooks 5850E mass flow controller. The procedure for collecting dehydrated *in situ* DRIFTS spectra was as follows: the catalyst was heated at 10°C/min from room temperature to 500°C under flowing 10% O₂/Ar (Praxair, UHP, 30 mL/min) and held for 1 h. Then the temperature was cooled at 10°C/min to 120°C under flowing 10% O₂/Ar. The procedure for collecting *in situ* Propylene-TPSR-IR was the same as the procedure below in TPSR with MS.

In situ Raman Spectroscopy.

The *in situ* Raman spectra of supported MoO_x catalysts were collected by a Horiba Labram HR Evolution spectrometer (532nm). The laser was focused on the catalysts through a confocal microscope equipped with a X50 objective lens (Olympus BX-30). A 900 grooves/nm grating was selected to optimize the spectral resolution (~1 cm⁻¹). The calibration of Raman spectrometer was performed with a silicon standard possessing a reference peak of 520.7 cm⁻¹. The gas flow rates were monitored with the same mass flow controllers as indicated above. Approximately 20mg of catalysts powders were loaded into an *in situ* cell (Harrick Scientific HVC-MRA-5). The spectra were collected with an accumulation of 3 scans (20s/scan) by a CCD camera detector (Horiba-Jobin Yvon CCD-3000 V). The dehydration procedure is the same as the DRIFTS above.

In situ UV-Vis Diffuse Reflectance Spectroscopy (DRS).

The *in situ* UV-Vis spectra of the supported MoO_x catalysts were obtained with an Agilent Cary 5000 UV-vis-NIR spectrophotometer. Approximately 20 mg of catalyst powders were loaded into an *in situ* cell described above. The UV-Vis spectrum was collected in the 200-800 nm range. A MgO (Sigma-Aldrich, 99.999%) white standard was used as the standard for spectra baseline. The gas flow rates were monitored with the same mass flow controllers as indicated above. The edge energy (E_g) values were calculated from the intercept of the straight line for the low-energy rise of a plot of [F(R)hv]² versus the incident photon energy (hv).¹² The dehydration procedure is the same as the DRIFTS above.

Propylene-Temperature Programmed Surface Reaction (TPSR) with MS.

The C₃H₆-TPSR spectroscopy was performed with an Altamira Instruments AMI-200. The catalysts powders (~0.1 g) were loaded into a U-tube quartz reactor. The dehydration procedure was similar as indicated above in DRIFTS experiments. After dehydration, the reactor was flushed with Ar (Air Gas, UHP, 30 mL/min) for 30 minutes at 30°C, then 5% C₃H₆/Ar (Praxair, Purity 99%, 30 mL/min) was flowed and held at 30°C for several minutes to stabilize the MS signal. The reactor was heated at 10°C/min to 600 °C. An online quadrupole Mass Spectrometer (Dycor ProLine Process) was equipped with AMI-200 to analyze the outgoing gases. The monitoring mass/charge channels were

$m/z=18$ (H_2O), $m/z=28$ (CO), $m/z=42$ (C_3H_6), $m/z=44$ (CO_2)
 $m/z=56$ (C_4H_8) and $m/z=58$ (acetone).

Ethylene/2-Butene Titration.

The C_2H_4/C_4H_8 -Titration experiments were performed with the same Altamira Instruments AMI-200. The dehydration procedure was the same as the above DRIFTS experiments. After flushing with Ar at 30°C for 30 min, 1% C_4H_8/Ar (Praxair, Purity 99%, 30 mL/min) was flowing at 30°C for 30 min to chemisorb 2-butene. The gas flow was then immediately switched to 1% C_2H_4/Ar (Praxair, Purity 99%, 30 mL/min) for 30 min to titrate the surface intermediates achieved from 2-butene flowing. The same m/z channels were monitored as for the above C_3H_6 -TPSR experiments. It was assumed that only one surface $Mo=CHCH_3$ intermediate was present on the surface. The number of activated surface MoO_x sites was calculated by the amount of C_3H_6 produced during $C_2H_4-C_4H_8$ titration accordingly.

Steady State Propylene Metathesis.

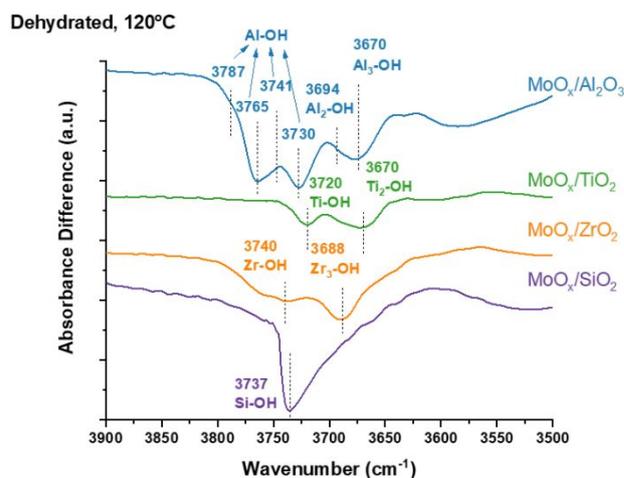
The steady-state propylene self-metathesis activities were collected in a fix-bed reactor under differential conditions (propylene conversion < 15%). The gas tubes were heated to 130°C to avoid propylene reactant and products condensation. Approximately 0.1 g of catalyst was loaded in a tube reactor. A clam shell furnace was equipped around the reactor to control the reactor temperature. The dehydration procedure was similar as indicated above in DRIFTS experiments. After dehydration, the reactor was cooled to 100°C with 10% O_2/Ar and flushed with Ar (Air Gas, UHP, 30 mL/min). 1% C_3H_6/Ar (Praxair, Purity 99%, 50 mL/min) was flowing at 100°C. The steady-state propylene self-metathesis conversion was collected after 60min reaction. An online Agilent 6890 gas chromatograph (GC) equipped with a GS-Alumina (Agilent 1153552) column and an Agilent G1531 flame ionization detector (FID) was used to analyze the outgoing gases from the reactor. The catalytic activities (mmol/g/h) were obtained by normalizing the conversion of propylene by the flow rate and catalyst weight. The turnover frequency (TOF) values were obtained by normalizing the steady-state activity by the number of activated MoO_x sites derived from C_2H_4/C_4H_8 titration.

III. Results

In situ DRIFTS of Surface Hydroxyl Anchoring Sites.

The *in situ* DRIFTS difference spectra and original spectra reveal the surface hydroxyls of oxide supports are involved in anchoring MoO_x species and are presented in Figures 1 and S1. The bare oxide supports have multiple surface hydroxyls (isolated S-OH, bridged S_2 -OH and tri-coordinated S_3 -OH, with S representing the support cation) that depend on the specific oxide support. The bare SiO_2 support has isolated Si-OH (3737 cm^{-1}) and unique geminal Si(-OH)₂ (broad peak ~3727-3755 cm^{-1}) surface hydroxyls and the MoO_x species primarily anchor at the isolated Si-OH surface hydroxyls. The slight perturbation of the vibrations of the geminal Si(-OH)₂ surface hydroxyls occur because of band broadening from hydrogen bonding between the geminal surface hydroxyls and adjacent surface MoO_x sites

at maximum surface MoO_x coverage. The bare TiO_2 support contains isolated Ti-OH (3720 cm^{-1}) and bridged Ti-(OH)-Ti (3670 cm^{-1}) and the MoO_x species anchors at both surface hydroxyls at monolayer coverage. The bare ZrO_2 support exhibits isolated Zr-OH (3740 cm^{-1}) and tri-coordinated Zr_3 -OH (3688 cm^{-1}) and the MoO_x species anchor at both surface hydroxyls at monolayer surface MoO_x coverage. The bare Al_2O_3 support has multiple surface hydroxyls (isolated Al-OH ($HO-\mu_1-Al_{IV}$ at 3787 cm^{-1} , $HO-\mu_1-Al_{VI}$ at 3765 cm^{-1} , $HO-\mu_1-Al_V$ at 3741 and 3730 cm^{-1}), bridged Al_2 -OH ($HO-\mu_2-Al_V$ at 3694 cm^{-1}) and tri-coordinated Al_3 -OH ($HO-\mu_3-Al_{VI}$ at 3674 cm^{-1})) and the MoO_x species anchor at all five surface hydroxyls at monolayer surface MoO_x coverage.



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Figure 1. *In situ* DRIFTS difference spectra of the surface hydroxyl region of the supported MoO_x catalysts under dehydrated conditions. The spectrum of the dehydrated oxide support was subtracted from the spectrum of each supported MoO_x catalyst.

In situ Raman under dehydrated conditions.

The *in situ* Raman spectra of the supported MoO_x catalysts under dehydrated conditions are presented in Figure 2(A). The Al_2O_3 , TiO_2 and ZrO_2 supports don't give rise to Raman bands in the 900-1200 cm^{-1} region. The TiO_2 support has a very weak Raman band ~ 800 cm^{-1} from anatase phase of TiO_2 . The SiO_2 support has a weak band ~970 cm^{-1} from Si-OH that is overshadowed by the stronger Mo=O band of the surface MoO_x sites.³¹⁻³² Crystalline MoO_3 nanoparticles (NPs) are not present on the Al_2O_3 -, TiO_2 -, ZrO_2 -, and SiO_2 -supported MoO_x catalysts because of the absence of sharp and strong Raman bands of crystalline MoO_3 ~820 and ~997 cm^{-1} . The surface MoO_x sites on SiO_2 give rise to both a strong $\nu_5(Mo=O)$ band at ~986 cm^{-1} and a weaker $\nu_{as}(Mo=O)$ band at ~965 cm^{-1} from dioxo ($O=$)₂ MoO_4 sites.³³ Only the surface MoO_x sites on Al_2O_3 and ZrO_2 give rise to a broad band ~ 862-865 cm^{-1} from the bridging Mo-O-Al and Mo-O-Zr vibrations. The bridging Mo-O-Ti and Mo-O-Si Raman bands are too weak to be observed. The Raman bands from the surface MoO_x sites on the other supports give rise to broader bands in the ~997-1006 cm^{-1} region associated with the

$\nu_s(\text{Mo}=\text{O})$ vibration of the surface mono-oxo $\text{O}=\text{MoO}_4$ sites.^{10, 12} The Raman bands for the surface MoO_x sites are broader on the non- SiO_2 supports because of the presence of multiple anchoring surface hydroxyl sites and surface MoO_x structures.

In situ UV-Vis spectroscopy under dehydrated conditions.

The *in situ* UV-Vis spectra of the supported MoO_x catalysts under oxidatively dehydrated conditions are presented in Figure 2 (B). The dehydrated supported $\text{MoO}_x/\text{SiO}_2$ catalyst exhibits two LMCT bands at 240 and 285 nm ($E_g \sim 4.0$ eV) corresponding to isolated surface MoO_x sites. The TiO_2 support possesses strong absorbance in the region below 350 nm and, thus, the bands of the surface MoO_x sites are overshadowed by the much stronger TiO_2 support bands and are not reported. The dehydrated supported $\text{MoO}_x/\text{ZrO}_2$ catalyst has one modest band at 235 nm from the ZrO_2 support and one broad LMCT band at 250-350 nm corresponding to both isolated and oligomeric MoO_x sites ($E_g \sim 3.6$ eV), respectively. The dehydrated supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst exhibits two LMCT bands at ~ 240 and 320 nm ($E_g \sim 3.6$ eV) corresponding to isolated MoO_x and oligomeric MoO_x sites, respectively.^{10, 12, 31} The UV-Vis LMCT bands at 240-320 nm and absence of UV-Vis d-d bands at 350-800 nm indicate that the dehydrated surface MoO_x sites on the Al_2O_3 , ZrO_2 and SiO_2 supports are fully oxidized as $\text{Mo}(+6)$. Although the LMCT bands for the dehydrated $\text{MoO}_x/\text{TiO}_2$ could not be determined because of the strong absorbance of the TiO_2 support, the nature of the surface MoO_x sites were determined from *in situ* XANES^{12, 16} and found to primarily consist of oligomeric $\text{Mo}(+6)\text{O}_x$ sites. The XANES study¹⁶ also revealed that MoO_x sites on Al_2O_3 and ZrO_2 supports are similar, and consist of both isolated $\text{Mo}(+6)\text{O}_x$ and oligomeric $\text{Mo}(+6)\text{O}_x$ sites. The surface MoO_x sites on SiO_2 support appear to possess only isolated $\text{Mo}(+6)\text{O}_x$ sites.

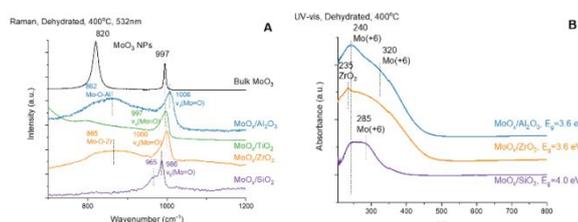


Figure 2. (A) *In situ* Raman spectra of the supported MoO_x catalysts under dehydrated conditions at 400°C. (B) *In situ* UV-Vis DRS spectra of the supported MoO_x catalysts under dehydrated conditions at 400°C

Propylene-TPSR-MS (C_3^- -TPSR-MS).

The surface chemistry of the supported MoO_x catalysts were chemically probed with C_3^- -TPSR-MS. The C_3^- -TPSR-MS spectra of dehydrated supported MoO_x catalysts and Mo-Free oxide supports are presented in Figures 3 and S2. The Mo-free oxide supports don't produce any olefin or acetone reaction products between 30-600 °C. Only CO , CO_2 and H_2O formation from the combustion of propylene was observed above 500°C. The supported $\text{MoO}_x/\text{TiO}_2$ and $\text{MoO}_x/\text{ZrO}_2$ catalysts essentially don't produce any 2-butenes over the 30-600°C temperature range. The supported $\text{MoO}_x/\text{SiO}_2$ catalyst only produces 2-butenes at the high temperatures of ~ 350 -600°C (Peak Temperature - $T_p=520^\circ\text{C}$). The dehydrated supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst

produces 2-butenes in two temperature ranges: ~ 30 -200°C ($T_p=62^\circ\text{C}$) and ~ 400 -600°C ($T_p=530^\circ\text{C}$). Oxygenated combustion products (CO , CO_2 , H_2O) are also observed on all the supported MoO_x catalysts during C_3^- -TPSR-MS, which reflects the partial reduction of the surface MoO_x sites upon exposure to propylene at very high temperatures. Acetone is produced during the activation of the surface MoO_x sites and the acetone desorption temperature varies slightly with the specific support: $\text{MoO}_x/\text{Al}_2\text{O}_3$ ($T_p=221^\circ\text{C}$), $\text{MoO}_x/\text{TiO}_2$ ($T_p=273^\circ\text{C}$), $\text{MoO}_x/\text{ZrO}_2$ ($T_p=250^\circ\text{C}$), and $\text{MoO}_x/\text{SiO}_2$ ($T_p=190, 520^\circ\text{C}$). Comparison of the C_3^- signals during C_3^- -TPSR-MS in Figure S3 indicates that propylene is only consumed and selectively converted to 2-butene by the supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst at low temperatures and both the supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ and $\text{MoO}_x/\text{SiO}_2$ catalysts at elevated temperatures. Consumption of propylene is very limited by the supported $\text{MoO}_x/\text{TiO}_2$ and $\text{MoO}_x/\text{ZrO}_2$ catalysts and CO_2 is the dominant reaction product at elevated temperatures with essentially no 2-butene production.

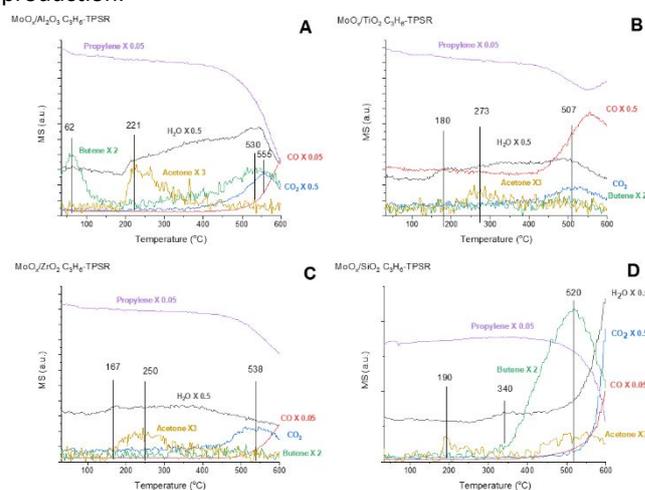


Figure 3. Propylene-TPSR (30-600°C) with online MS for the supported MoO_x catalysts: (A) $\text{MoO}_x/\text{Al}_2\text{O}_3$, (B) $\text{MoO}_x/\text{TiO}_2$, (C) $\text{MoO}_x/\text{ZrO}_2$, (D) $\text{MoO}_x/\text{SiO}_2$.

In situ Propylene-TPSR-IR (C_3^- -TPSR-IR).

The *in situ* C_3^- -TPSR-IR spectra from the dehydrated supported MoO_x catalysts are presented in Figure 4. The gas phase propylene molecule gives rise to IR bands ~ 1376 , 1392, 1444, 1455, 1636, and 1664 cm^{-1} .^{14, 34} At 30°C, the IR spectra are dominated by the vibrations of gas phase propylene as presented in Figure S4. Only the supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ shows the presence of a $\nu(\text{C}=\text{O})$ vibration at ~ 1686 cm^{-1} from surface acetone species.¹⁴ The gas phase propylene bands diminish above 120°C from the supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst that reflect consumption of propylene. Strong bands from $\nu(\text{C}=\text{C})$ ~ 1664 cm^{-1} of adsorbed propylene on MoO_x sites and $\nu(\text{C}-\text{C})$ ~ 1250 cm^{-1} , $\delta_s(\text{CH}_3)$ ~ 1375 cm^{-1} and $\nu(\text{C}=\text{O})$ ~ 1686 cm^{-1} of adsorbed acetone predominate between 120-220°C. The surface acetone further reacts from 220-600°C to form surface acetate intermediates with $\nu_s(\text{COO}^-)$ at ~ 1441 cm^{-1} and $\nu_{\text{as}}(\text{COO}^-)$ at ~ 1570 cm^{-1} vibrations.¹⁴ The supported $\text{MoO}_x/\text{TiO}_2$ and $\text{MoO}_x/\text{ZrO}_2$ catalysts behave similarly during C_3^- -TPSR-IR with

the gas phase propylene bands diminishing above 120°C and the IR bands from $\nu(\text{C-C})$ at $\sim 1250\text{ cm}^{-1}$, $\delta_s(\text{CH}_3)$ at $\sim 1375\text{ cm}^{-1}$ and a much stronger $\nu(\text{C=O})$ band at $\sim 1680\text{--}1665\text{ cm}^{-1}$ from vibration of adsorbed surface acetone predominates between 120–420°C. The IR band from the $\nu(\text{C=C})$ $\sim 1664\text{ cm}^{-1}$ vibration of adsorbed propylene on the surface MoO_x sites are relatively weak and overshadowed by the very strong IR $\nu(\text{C=O})$ vibration at $\sim 1680\text{--}1665\text{ cm}^{-1}$. However, the strong IR bands for the surface acetate intermediates ($\nu_s(\text{COO}^-)$ at $\sim 1441\text{ cm}^{-1}$ and $\nu_{as}(\text{COO}^-)$ at $\sim 1570\text{ cm}^{-1}$ vibrations) reveals that the surface acetate intermediates dominate between 220–600°C. The gas phase propylene bands only diminish above 320°C for the supported $\text{MoO}_x/\text{SiO}_2$ catalyst reflecting the lower activity of this catalyst among the catalysts. Additionally, surface intermediates could not be detected during C_3H_6 -TPSR-IR, most probably due to the extremely low population of surface intermediates. The broad IR bands at ~ 1279 and 1570 cm^{-1} from $\text{MoO}_x/\text{SiO}_2$ are induced by a thermal effect on the spectral baseline, and not from surface intermediates, as indicated in Figure S5. The C_3H_6 -TPSR-IR spectra reveal that while the surface of the supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst is dominated by adsorbed acetone species at 120–420°C, the surfaces of the supported $\text{MoO}_x/\text{TiO}_2$ and

supported catalysts barely contain any activated surface MoO_x sites when exposed to 2-butene at 30°C.

The steady state propylene self-metathesis activity of the supported MoO_x catalysts at 100°C are also shown in Table 1. The supported $\text{MoO}_x/\text{TiO}_2$, $\text{MoO}_x/\text{ZrO}_2$ and $\text{MoO}_x/\text{SiO}_2$ do not show any steady state activity for propylene metathesis at 100°C. Only the supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst is active for propylene metathesis at 100°C. The turnover frequency (TOF) values were calculated by normalizing the steady state activity values by the number of activated surface MoO_x sites determined from the ethylene/2-butene titration at 30°C. Given that the supported $\text{MoO}_x/\text{TiO}_2$, $\text{MoO}_x/\text{ZrO}_2$ and $\text{MoO}_x/\text{SiO}_2$ catalysts do not produce butene, their TOF values are zero within our detection limits. Therefore, the TOF can only be determined for the supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst. In contrast, the conversion and turnover frequency (TOF) value for the supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst could be determined and found to be 8.1% and $3.8 \times 10^{-4}\text{ s}^{-1}$.

	$\text{MoO}_x/\text{Al}_2\text{O}_3$	$\text{MoO}_x/\text{TiO}_2$	$\text{MoO}_x/\text{ZrO}_2$	$\text{MoO}_x/\text{SiO}_2$
Fraction of Activated MoO_x Sites	17%	0.3%	0.2%	0.2%
Steady State Activity (100°C, mmol/g/h)	0.29	0	0	0
TOF (s^{-1})	3.8×10^{-4}	0	0	0

Table 1. Fraction of activated surface MoO_x sites calculated from Ethylene/2-Butene titration, steady-state activity at 100°C and propylene metathesis turnover frequency (TOF).

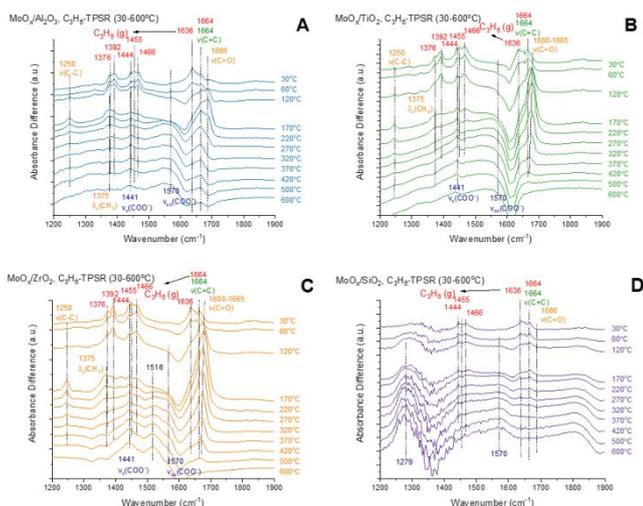


Figure 4. Propylene-TPSR (30–600°C) with *in situ* DRIFTS difference spectra of supported MoO_x catalysts. The spectra of dehydrated MoO_x catalysts at 30°C were subtracted from the spectra of MoO_x catalysts during TPSR with propylene: (A) $\text{MoO}_x/\text{Al}_2\text{O}_3$, (B) $\text{MoO}_x/\text{TiO}_2$, (C) $\text{MoO}_x/\text{ZrO}_2$, (D) $\text{MoO}_x/\text{SiO}_2$.

$\text{MoO}_x/\text{ZrO}_2$ catalysts are dominated by adsorbed surface acetate intermediates in the 220–420°C

Ethylene/2-Butene Titration and Steady State Propylene Metathesis.

Ethylene/2-butene titration measurements were undertaken to determine the number of activated sites for the supported MoO_x catalysts and the values are presented in Table 1. Although the number of activated sites was relatively high for the supported $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst, the ZrO_2 , TiO_2 and SiO_2 -

IV. Discussion

Anchoring Surface Hydroxyls for MoO_x Species.

Anchoring the maximum amount of surface MoO_x sites on the oxide supports titrates all the accessible S-OH , $\text{S}_2\text{-OH}$ and $\text{S}_3\text{-OH}$ surface hydroxyls. Only the geminal $\text{Si}(\text{OH})_2$ surface hydroxyls on the SiO_2 support are unreactive or minimally reactive towards anchoring of the MoO_x species (see Figure 1).^{35–36} Besides the nature of the surface hydroxyl anchoring sites (isolated, bridged or tri-coordinated), the chemical properties of the surface hydroxyls may also be influenced by the local surface coordination (AlO_{5-6} , TiO_6 , ZrO_7 , SiO_4)^{24–25, 37–39} and cation electronegativity ($\text{Si} > \text{Al} > \text{Ti} > \text{Zr}$)⁴⁰ of the oxide support.

Molecular and Electronic Structure of Dehydrated Surface MoO_x sites.

The dehydrated surface MoO_x sites for all the supported MoO_x catalysts are fully oxidized as $\text{Mo}(+6)$ (only LMCT bands and absence of d-d bands from reduced surface MoO_x sites). The supported $\text{MoO}_x/\text{SiO}_2$ catalyst only stabilizes the isolated dioxo surface ($\text{O=})_2\text{MoO}_2$ sites since only the Si-OH surface hydroxyl is available for anchoring.^{16, 33, 41–42} The supported $\text{MoO}_x/\text{TiO}_2$ catalyst mostly contains oligomeric mono-oxo surface $\text{MoO}_{5/6}$ sites at monolayer surface coverage.^{16, 41, 43–45} The supported

MoO_x/ZrO₂ catalyst consists of isolated dioxo surface MoO₄ and oligomeric mono-oxo surface MoO_{5/6} sites at monolayer surface coverage.^{16, 41, 46-47} The supported MoO_x/Al₂O₃ catalyst also contains a mixture of isolated dioxo surface MoO₄ and oligomeric mono-oxo surface MoO_{5/6} sites at monolayer surface coverage.^{10, 12, 16, 41} The presence of oligomeric surface MoO_{5/6} sites on the Al₂O₃, TiO₂ and ZrO₂ supports is related to the more acidic S₂-OH and S₃-OH surface hydroxyls available as anchoring sites on these oxide supports at high surface MoO_x coverage. This is consistent with the observation that at low surface MoO_x coverage, the MoO_x species are preferentially anchored at the more basic S-OH sites that only stabilizes isolated surface MoO_x sites.^{10, 48-49}

Surface Chemistry of the Supported MoO_x Catalysts.

The surface chemistry of the supported MoO_x catalysts was monitored with *in situ* IR spectroscopy. Only the supported MoO_x/Al₂O₃ catalyst formed C=O bonds from propylene adsorption at 30°C (Figure S4) that is attributed to surface isopropoxide species formed by protonation of the surface propylene species. The surface isopropoxide species further form adsorbed acetone bonded to the surface MoO_x sites.¹⁴ The supported MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts are completely inactivated at 30°C. At higher temperatures of 120-220°C, the surface MoO_x sites on Al₂O₃, TiO₂ and ZrO₂ produce surface acetone that desorbs from the surface above 220°C or further oxidize to stable surface acetate intermediates (Figure 4). Above 220°C, the surface MoO_x sites on TiO₂ and ZrO₂ produce more surface acetone (stronger ν(C=O) IR bands) than the surface MoO_x sites on Al₂O₃. While the surface acetone intermediates persist until 420°C on MoO_x/TiO₂ and MoO_x/ZrO₂, the surface acetone intermediates only persist up to 270°C on MoO_x/Al₂O₃ (Figure 4). At the higher temperatures, the adsorbed acetone species further oxidize to stable surface acetate intermediates. The greater amount of surface acetate intermediates for the supported MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts is related to the greater redox activity of these two catalysts probed by H₂-TPR (MoO_x/TiO₂ > MoO_x/ZrO₂ > MoO_x/Al₂O₃ > MoO_x/SiO₂).^{11, 21} The greater population of more stable surface acetate species on the supported MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts indicates that very few sites will be available for propylene adsorption and metathesis (site blocking).¹⁴ The supported MoO_x/SiO₂ catalyst might only have trace amounts of surface intermediates at both low and high temperatures because of the absence of IR peaks from surface intermediates. The formation of surface oxygenates are only related to surface MoO_x sites, not related to the reduction of the oxide supports, even for the more reducible TiO₂ and ZrO₂ supports (see Figure S2).

Comparison of the TOF values of surface MoO_x sites.

The steady-state reaction was performed under differential reaction conditions with highly diluted (1%) propylene to avoid heat and mass transfer issues during the propylene metathesis reaction. The supported MoO_x catalysts were extensively studied in the literature and the activities were measured with various oxide supports and reaction conditions: MoO_x/SiO₂ at

20 °C,¹³ MoO_x/Al₂O₃-SiO₂ at 150 °C,^{50, 51} MoO_x/SBA-15 at 50 °C,¹⁵ MoO_x/Al₂O₃, MoO_x/SiO₂, and MoO_x/Al₂O₃-SiO₂ at 30 °C,⁵² MoO_x/SBA-1,⁵³ MoO_x/Si-SBA-1 and MoO_x/Al-SBA-1⁵⁴ at 50 °C. To make a quantitative comparison between TOF values reported in the literature, the TOF values need to be corrected for the following factors: (i) correction based on the number of activated sites N_s, which depends on the oxide support and surface MoO_x coverage, (ii) correction based on the reaction temperatures and (iii) correction based on partial pressure of reactants (1st order reaction). The TOF values of our MoO_x/Al₂O₃ catalyst and the TOF values reported in the literature can't be quantitatively compared since the number of activated sites N_s are not determined and reported in the literature. Earlier studies only reported olefin metathesis activities of H₂ reduced MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts. Non H₂-reduced supported MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts have been found to be inactive for olefin metathesis as reported in the present study.^{6,7} It is well established that maximum olefin metathesis activity corresponds to monolayer surface coverage,^{10, 17} the loading of supported MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts were carefully controlled to maximize the coverage of surface MoO_x sites without generating crystalline MoO₃ nanoparticles, thus, the surface coverage of supported MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts in this study are properly selected to determine the activity of the catalysts. It's also well accepted that supported MoO_x/SiO₂ catalyst requires high temperature pre-activation under reducing environment for propylene metathesis.^{13, 52-55} The activity of high temperature pre-activated MoO_x/SiO₂ catalysts, however, will be addressed in a forthcoming paper since the current study only focuses on the low temperature activity of supported MoO_x catalysts without high temperature pre-activation.

Influence of oxide support on the activation and activity of surface MoO_x sites.

The activation of the surface MoO_x sites on the different oxide supports by propylene is reflected by the appearance of the propylene metathesis C₄= products during C₃=-TPSR-MS (Figure 3). Only the surface MoO_x sites on Al₂O₃ become activated below 100 °C and surface MoO_x sites on Al₂O₃ and SiO₂ also become activated above 500 °C, but the supported MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts do not become activated for propylene metathesis. The facile formation of acetone and propylene metathesis products from the supported MoO_x/Al₂O₃ catalysts below 100 °C indicates the ease of activation of the surface MoO_x sites on Al₂O₃. The surface MoO_x sites anchored at the isolated hydroxyls could only be activated at high temperatures, while the surface MoO_x sites anchored at the bridged or tri-coordinated hydroxyls permit activation at low temperatures.^{10,56} Besides isolated surface hydroxyls, the Al₂O₃, TiO₂ and ZrO₂ contain either bridged (Al₂O₃, TiO₂) or tri-coordinated surface hydroxyls (Al₂O₃, ZrO₂) serving as the anchoring sites for MoO_x. What is different between them is the different support cations with Al₂O₃ having a higher electronegativity than the TiO₂ and ZrO₂ cations.^{38,40} The SiO₂ support, however, has a higher electronegativity than Al₂O₃ and SiO₂ is not able to activate the surface MoO_x sites at low

temperatures. The difficulty of activating the surface MoO_x sites on SiO₂ at low temperature is related to the absence of S₂-OH or S₃-OH anchoring hydroxyls for surface MoO_x sites. At high temperature, the surface MoO_x sites anchored at the isolated Si-OH exhibit a better activation than the MoO_x sites anchored at isolated Al-OH (Figure S6) due to the stronger electronegativity of SiO₂. The stronger electronegative support cation will influence the electron deficiency of the anchoring surface hydroxyls, thus, making the anchored surface MoO_x sites more electron deficient for interaction with electron rich olefins. Oxide supports with more electronegative cations will more readily activate the surface MoO_x sites for olefin metathesis. It is concluded that surface MoO_x sites anchored at isolated surface hydroxyls with strong support electronegativity (Al-OH, Si-OH) enables the activation of the surface MoO_x sites at high temperatures, while surface MoO_x sites anchored at bridged/tri-coordinated surface hydroxyls with strong support electronegativity (Al₂-OH, Al₃-OH) enables the activation of MoO_x sites below 100 °C. Furthermore, the presence of stable surface acetone and acetate surface intermediates further retards olefin metathesis for the more redox MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts. The Influence of surface Lewis/Brønsted acidity on propylene metathesis has recently been reviewed in detail⁵⁶ and a general conclusion about the influence of surface Lewis/Brønsted acidity on olefin metathesis could not be reached from the literature findings.

V. Conclusions

The oxide support tunes the anchoring, molecular structure, activation and surface chemistry of the surface MoO_x sites. Anchoring of molybdena species at the bridged and tri-coordinated surface hydroxyls (S₂-OH and S₃-OH) with higher support cation electronegativity (Al > Ti > Zr) permits the activation of surface MoO_x sites at low temperatures (<100 °C). The isolated surface hydroxyls (S-OH) with strong support cation electronegativity (Si > Al > Ti > Zr) are responsible for the activation of surface MoO_x sites at high temperatures (>350 °C). Oligomeric surface MoO_x sites on Al₂O₃ activate at low temperatures and isolated surface MoO_x sites on Al₂O₃ and SiO₂ also activate at high temperatures. The significant accumulation of surface acetone and acetate species on the more redox active supported MoO_x/TiO₂ and MoO_x/ZrO₂ catalysts retards olefin metathesis. The above trends are responsible for the resulting propylene metathesis activity for supported MoO_x catalysts: MoO_x/Al₂O₃ > MoO_x/SiO₂ > MoO_x/TiO₂ ~ MoO_x/ZrO₂.

Conflicts of interest

There are no conflicts to declare.

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