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ARTICLE

Comparison of SiO_2-Supported Molybdena, Tungsta and Rhenia Catalysts for Olefin Metathesis

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The characteristics of supported MO_x/SiO_2 catalysts (M = Re, Mo, W) for olefin metathesis were compared side-by-side to understand the differences among these catalyst systems. The series of SiO_2-supported metal oxide (ReO_x, MoO_x, WO_x) catalysts, with maximum achievable dispersion of surface MO_x sites, was synthesized by incipient-wetness impregnation of the corresponding aqueous precursors, molecularly characterized (*in situ* Raman and DRIFTS), chemically probed with transient studies (C_3H_6-TPSR-MS, C_3H_6-TPSR-IR, and C_2H_4/2-C_4H_8 titration with C_2H_4-TPSR-MS) and steady state activity for C_3H_6 metathesis. Under dehydrated conditions, the initial SiO_2-supported surface metal oxide sites are fully dispersed as isolated sites on SiO_2 and present as isolated tri-oxo $(O=)_3ReO$ sites, isolated di-oxo $(O=)_2MoO_2$ sites and a mixture of isolated di-oxo $(O=)_2WO_2$ and mono-oxo $(O=)WO_4$ sites (dioxo >> mono-oxo) anchored at the isolated Si-OH surface hydroxyls of SiO_2 support. High temperature propylene pre-treatments were required to activate the SiO_2-supported MO_x catalysts, but also resulted in MO_x volatilization (ReO_x > MoO_x >> WO_x). The number of activated surface MO_x sites and TOF values varied with the specific MO_x site, activation temperatures and reaction temperatures, which are related to the stability of the surface M=O oxo and M=Carbene bonds. The higher thermal stability, activity and TOF of the surface WO_x sites on SiO_2 at elevated temperatures relative to the supported ReO_x/SiO_2 and MoO_x/SiO_2 catalysts account for adoption of the supported WO_x/SiO_2 catalyst as the industrial olefin metathesis catalyst among these supported MO_x/SiO_2 catalysts.

Keywords: metathesis, propylene, silica, molybdena, rhenia, tungsta, Raman, DRIFTS, TPSR, activation

I. Introduction

There is a growing gap between the global supply and demand of propylene attributed to a feedstock shift from steam cracking of natural gas and oil refinery operation. The olefin metathesis reaction is considered a promising approach to address the global shortage of propylene by cleaving and rearranging the C=C bonds in ethylene and 2-butene. Among olefin metathesis catalysts employed in industry, high surface area oxide supported-MO_x (M = Re, Mo, W) catalysts have attracted substantial research attention due to their high activity and selectivity.[1] Among these catalysts, only the SiO_2-supported WO_x catalyst is the preferred propylene metathesis catalysts of small olefins in industrial practice (Philips Triolefin Process and Lummus Olefin Conversion Technology)[2-3], while SiO_2-supported ReO_x and MoO_x catalysts are essentially not industrially employed.[4-5] Previous studies found that the supported ReO_x/Al_2O_3 catalyst is highly active for propylene metathesis at ambient temperature, while the supported ReO_x/SiO_2 catalyst is difficult to activate.[6-7] The supported MoO_x/SiO_2 catalyst is also reported to require high temperatures (>400 °C) for activation with propylene[8-9] and is about an order of magnitude less active than the supported MoO_x/Al_2O_3 catalyst used for Shell Higher Olefin Process.[1,10] The supported WO_x/SiO_2 catalyst is a major industrial propylene metathesis catalyst that operates at 400-600℃ and also requires high temperature pre-activation with propylene.[11] Although the supported WO_x/SiO_2 catalyst exhibits a longer lifetime than the corresponding supported ReO_x and MoO_x catalysts,[11] a direct comparison of the catalytic surface active sites (molecular structure, anchoring sites, activation, number of activated sites, thermal stability, activity and TOF values for propylene self-metathesis) of SiO_2 supported transition metal oxide catalysts is still lacking and needed to better understand the superior properties of the supported WO_x/SiO_2 catalyst system.

The objective of this study is to investigate the behavior of the surface ReO_x, MoO_x and WO_x sites on SiO_2 during activation with propylene and during propylene metathesis. Although the oxide support was found to have a pronounced effect on the activation and catalytic activities of supported MO_x catalysts,[6,13] the present study only focuses on supported MO_x/SiO_2 catalysts in order to obtain fundamental insights into the behavior of the commercial-type supported WO_x/SiO_2 catalyst compared to the corresponding supported ReO_x/SiO_2 and MoO_x/SiO_2 catalysts by their side-by-side comparison. The SiO_2-supported catalysts were characterized with *in situ*

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Raman and DRIFTS and chemically probed with transient (double C_3H_6-TPSR-MS, double *in situ* C_3H_6-TPSR-IR, C_2H_4/2-C_4H_8 titration followed with C_2H_4-TPSR-MS) and steady state self-metathesis of propylene. This is the first time the similarities and differences of the supported ReO_x, MoO_x and WO_x sites on the same metal oxide support (SiO_2) have been compared for propylene metathesis. The side-by-side comparison of these SiO_2-supported transition metal oxide catalysts will examine the molecular structure, anchoring sites, activation, number of activated sites, thermal stability, activity and TOF values for propylene self-metathesis. The present investigation will provide insights about the reasons for the relative behavior of the SiO_2-supported ReO_x, MoO_x and WO_x catalysts during propylene activation and self-metathesis of propylene. The reversibility of the propylene metathesis reaction (2 $C_3H_6 \rightleftharpoons C_2H_4$ + 2-C_4H_8) assures that the reaction pathway proceeds similarly in the forward and reverse directions (microscopic reversibility), with also the same number of sites titratable in both directions.[32-33]

II. Experimental Details

Catalyst Synthesis.

The supported ReO_x, MoO_x and WoO_x catalysts were prepared by incipient-wetness impregnation (IWI) of aqueous perrhenic acid (HReO4, Alfa Aesar, 75-80%), aqueous ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, Alfa Aesar, 99%) and aqueous ammonium metatungstate hydrate ($((NH_4))_6H_2W_{12}O_{40}{\cdot}xH_2O$, Pfaltz and Bauer, 99.5%) into the SiO_2 (Cabot, Cab-O-Sil, EH-5, 350 m^2/g) support. Prior to IWI, the SiO_2 support was treated with H_2O to increase the number of surface hydroxyls and calcined in air at 500°C for 4h. After impregnation of the aqueous precursors, the supported catalysts were dried at room temperature overnight, then at 120°C for 2h in air before finally being calcined by ramping the temperature at 1°C/min in flowing air (100 mL/min) to 500°C and held at this temperature for 4h. Due to the poor reactivity of the SiO_2 surface silanols, the maximum achieved loading (surface coverage) of ReO_x, MoO_x and WO_x on the SiO_2 support was 5.5% ReO_x ($2.3x10^{-4}$ mol Re atoms/g; 0.4 Re/nm^2), 7.5% MoO_x ($3.1x10^{-4}$ mol Mo atoms/g; 0.9 Mo/nm^2), and 6.0% WO_x ($2.5x10^{-4}$ mol W atoms/g; 0.5 W/nm^2).

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

The *in situ* DRIFTS spectra of SiO_2-supported metal oxide catalysts were collected with a Thermo Scientific Nicolet 8700 FT-IR spectrometer equipped with a Harrick Praying Mantis attachment (DRA-2 with CaF_2 window). The collected spectra employed a Mercury-Cadmium-Telluride (MCT) detector having a resolution of 4 cm^{-1} with an accumulation of 96 scans/min. About 20mg of catalyst powder was loaded into the *in situ* reaction cell (Harrick, HVC-DR2 with a CaF2 window) for DRIFTS spectral collection. A Brooks 5850E mass flow controller controlled the gas flow rate through the *in situ* cell. The procedure for collecting *in situ* DRIFTS spectra of dehydrated catalysts was as follows: the catalyst was heated at 10°C/min from room temperature to 500°C under flowing 10% O_2/Ar (Praxair, UHP, 30 mL/min) and held for 1 h, the temperature was subsequently cooled at 10°C/min to 120°C under flowing 10% O_2/Ar. The procedure for collecting *in situ* C_3H_6-TPSR-DRIFTS spectra is the same as described below for the C_3H_6-TPSR-MS studies.

***In situ* Raman Spectroscopy.**

The *in situ* Raman spectra of SiO_2-supported metal oxide catalysts were collected by a Horiba Labram HR Evolution spectrometer (442nm). The laser was focused on the catalysts with a confocal microscope equipped with an Olympus BX-30 X50 objective lens. A 900 grooves/nm grating was selected to optimize the spectral resolution to approximately 1 cm^{-1}. Daily calibration of the Raman spectrometer employed a silicon standard having a reference peak of 520.7 cm^{-1}. The same mass flow controllers as indicated above were used to monitor the gas flow rates. Approximately 20mg of catalysts powders were loaded into an *in situ* reaction cell (Harrick Scientific HVC-MRA-5) that was controlled by a pre-calibrated temperature controller (ATK-024-4). The thermocouple of the controller is in direct contact with the catalyst bed to obtain accurate temperature reading. The Raman spectra were collected with an accumulation of 3 scans (20s/scan) with a Horiba-Jobin Yvon CCD-3000 V CCD camera detector. The following procedure was employed for collecting the *in situ* Raman spectra: (1) the reaction cell was heated at 10°C/min in flowing 10% O_2/Ar (Praxair, UHP, 30 mL/min) to the dehydration/reaction temperatures (450°C (ReO_x/SiO_2), 550°C (MoO_x/SiO_2), 650°C (WO_x/SiO_2))and held for 60min at the final indicated temperatures, (2) the flowing gas was switched to 5% C_3H_6/Ar (Praxair, Purity 99%, 30 mL/min) for 90min at the reaction temperature, and (3) the catalysts were re-oxidized with 10% O_2/Ar (Praxair, UHP, 30 mL/min) at the dehydration temperature for 60 min. The internal standard for normalization of the Raman spectra was the Raman band of the SiO_2 support at ~ 607 cm^{-1}. The dehydration, activation and re-oxidation temperatures were determined from the 1st C_3H_6-TPSR-MS findings given below.

C_3H_6-Temperature Programmed Surface Reaction (TPSR)-MS.

The C_3H_6-TPSR-MS measurements were performed on the Altamira Instruments system (AMI-200). Approximately 0.1g of catalyst powder was loaded into a U-tube quartz reactor and placed in the AMI-200 system. The dehydration procedure was the same as indicated above for the Raman experiments. Following catalyst dehydration, Ar (Air Gas, UHP, 30 mL/min) was first flown through the reactor at 30°C for 30 minutes and followed by two C_3H_6-TPSR cycles: (1) in the 1st cycle, 5% C_3H_6/Ar (Praxair, Purity 99%, 30 mL/min) was initially flown and held at 30°C for several minutes to stabilize the MS signal and the reactor was subsequently heated at 10°C/min to 600°C (ReO_x/SiO_2, MoO_x/SiO_2) and 800°C (WO_x/SiO_2); and (2) in the 2nd cycle, the reactor was cooled to room temperature with flowing Ar (Air Gas, UHP, 30 mL/min), switched to 5% C_3H_6/Ar (Praxair, Purity 99%, 30 mL/min) and heated again at 10°C/min to 600°C (ReO_x/SiO_2, MoO_x/SiO_2) and 800°C (WO_x/SiO_2). The

higher reaction temperature for WO_x/SiO_2 was employed because olefin metathesis with this catalyst required higher activation and reaction temperatures. The outlet of the reactor was connected to an online quadrupole mass spectrometer (MS, Dycor ProLine Process) to measure the exiting gases. The following mass/charge ratio channels were used for analysis of propylene and the reaction products: 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). The MS signals were calibrated for each channel and corrected for cracking contributions from different components.

Ethylene/2-Butene Titration and Ethylene-TPSR-MS.

The C_2H_4/2-C_4H_8-Titration and subsequent C_2H_4-TPSR-MS experiments were also performed with the Altamira Instruments AMI-200. The dehydration procedure was the same as given above for the Raman studies. After dehydration, the catalysts were activated with 1% 2-C_4H_8/Ar (Praxair, Purity 99%, 30 mL/min) at activation temperatures of 450℃ (ReO_x/SiO_2), 550℃ (MoO_x/SiO_2), and 650℃ (WO_x/SiO_2)) for 30 min. Different activation temperatures were employed because the catalysts activated at different temperatures. The reactor was then cooled to 100℃ in flowing 1% 2-C_4H_8/Ar (Praxair, Purity 99%, 30 mL/min), and the temperature was then held at 100℃ for 30min in flowing 1% C_2H_4/Ar (Praxair, Purity 99%, 30 mL/min). Subsequently, the temperature was ramped at 10℃/min to 600℃ for ReO_x/MoO_x and 800℃ for WO_x catalysts to titrate the surface intermediates generated from 2-butene chemisorption after the high temperature activation. Only one surface $Re{=}CHCH_3/Mo{=}CHCH_3/W{=}CHCH_3$ intermediates was assumed to be present on the SiO_2-supported $ReO_x/MoO_x/WO_x$ catalysts, respectively, after saturation of the surface with 2-butene at 100℃. The number of activated surface sites was assumed to be equal to the number of C_3H_6 molecules produced during subsequent C_2H_4-C_4H_8 titration with the C_2H_4-TPSR-MS experiment. The same m/z channels were monitored as for the above 2nd C_3H_6-TPSR-MS experiments.

Steady State Propylene Metathesis.

The steady state propylene self-metathesis activities were also measured in the Altamira Instruments AMI-200. The dehydration procedure was the same as indicated above for the Raman experiments. After dehydration, the catalysts were activated with 5% C_3H_6/Ar (Praxair, Purity 99%, 30 mL/min) at the activation temperatures of 450℃ (ReO_x/SiO_2), 550℃ (MoO_x/SiO_2), and 650℃ (WO_x/SiO_2)) for 30 min. The reactor temperature was then changed to various steady state reaction temperatures from 100℃ up to 550℃in flowing Ar (Air Gas, UHP, 30 mL/min). Note that each catalyst required a different activation and reaction temperature because of the different stability or reducibility of the surface MO_x sites on SiO_2. The steady state reaction was performed by flowing 5% C_3H_6/Ar (Praxair, Purity 99%, 30 mL/min) at the reaction temperatures for 60min. 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 surface sites determined from the C_2H_4/C_4H_8 titration.

III. Results

***In situ* DRIFTS of Surface Hydroxyl Anchoring Sites.**

The *in situ* DRIFTS difference spectra of the SiO_2–supported metal oxide catalysts under dehydrated conditions are presented in Figure 1. The bare SiO_2 support contains both isolated Si–OH (3737 cm^{-1}) and geminal $Si(–OH)_2$ (broad peak ~3727–3755 cm^{-1}) surface hydroxyls. The difference spectra between the supported MO_x/SiO_2 catalysts and the SiO_2 support reveal that the supported ReO_x, MoO_x and WO_x sites mainly anchored at the isolated Si-OH surface hydroxyls.[6, 12-13]

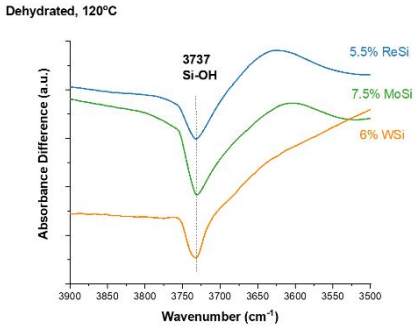

Figure 1. *In situ* DRIFTS difference spectra of the surface hydroxyl region of the SiO_2-supported catalysts metal oxide under dehydrated conditions (120℃). The spectrum of the dehydrated SiO_2 support was subtracted from the spectrum of each SiO_2-supported metal oxide catalyst.

***In situ* Raman under dehydrated, activated and re-oxidized conditions.**

Dehydrated Conditions. The *in situ* Raman spectra of the SiO_2-supported metal oxide catalysts under dehydrated, activated and re-oxidized conditions are presented in Figure 2 with the assignments of the vibrational bands. The SiO_2 support gives rise to Raman bands ~500, 607, 800 cm^{-1}, along with a weak band ~970 cm^{-1} from the surface Si-OH vibration that is overshadowed by the strong Mo=O and W=O bands of the surface metal oxides.[12,14] The absence of strong Raman bands from crystalline Re_2O_7 (798, 820, 993 cm^{-1}), MoO_3 (820, 997 cm^{-1}) and WO_3 (715, 806 cm^{-1}) indicate that the surface coverage of ReO_x, MoO_x and WO_x sites are maximized without formation of crystalline Re_2O_7, MoO_3 and WO_3 nanoparticles on the SiO_2 support.[12] Furthermore, the absence of bridging Re-O-Re, Mo-O-Mo and W-O-W Raman bands at ~200-300 cm^{-1} indicates that these surface metal oxides are present as isolated sites, which is also confirmed with UV-vis.[6,12-13,15] The surface ReO_x sites have a strong ν_s(Re=O) band at 1012 cm^{-1} and a relatively weak ν_{as}(Re=O) band at 987 cm^{-1} from tri-oxo $(O{=})_3$Re-O-Si sites.[6,15] The surface MoO_x sites exhibit a strong ν_s(Mo=O) band at 986 cm^{-1} and a relatively weak ν_{as}(Mo=O) band at 964 cm^{-1} from surface dioxo $(O{=})_2Mo(\text{-}O\text{-}Si)_2$ sites.[13,15] The surface WO_x sites possess a strong ν_s(W=O) band at 980

cm^{-1} from di-oxo $(O=)_2W-O_2$ sites and a relatively weak v_s(W=O) band at 1008 cm^{-1} from a minor amount of mono-oxo $O=W(-O-Si)_4$ sites.[12,15]

Activation and Re-oxidation Conditions. The prior dehydration, activation and re-oxidation temperatures were determined from the 1st C_3H_6-TPSR-MS findings given below. The *in situ* Raman spectra of SiO_2 supported metal oxide catalysts under activation and re-oxidization conditions are shown in Figure 2 and S1. After 90 min of C_3H_6 activation at high temperatures, the intensity of the Raman bands of all the SiO_2-supported metal oxide catalysts significantly diminished primarily due to the accumulation of coke on the surface, blocking the detection of surface metal oxide sites. After re-oxidation with O_2 for 60min, the surface coke was burned off and the activated surface ReO_x, MoO_x and WO_x sites that only represent a smaller portion of total surface metal oxide sites were successfully re-oxidized back to their dehydrated state. The Raman bands of v_s(Re=O) and v_{as}(Re=O) from the surface ReO_x sites and v_s(Mo=O) and v_{as}(Mo=O) bands from the surface MoO_x sites exhibit notably lower Raman band intensities compared to the band intensities after the initial dehydration. The approximate decrease in the area of the Raman bands relative to the SiO_2 support band at ~607 cm^{-1} follows the trend: ReO_x (~49%) > MoO_x (~38%) >> WO_x (~4%). The reduction in intensity of the Raman bands indicates the significant loss of surface ReO_x[16] and MoO_x[17] sites from these catalysts due to their volatility at high temperatures. The intensity of the Raman band of the v_s(W=O) of surface WO_x sites, however, was almost fully recovered to that of the initial band intensity after the initial dehydration treatment, reflecting minimal volatilization of WO_x at elevated temperatures.

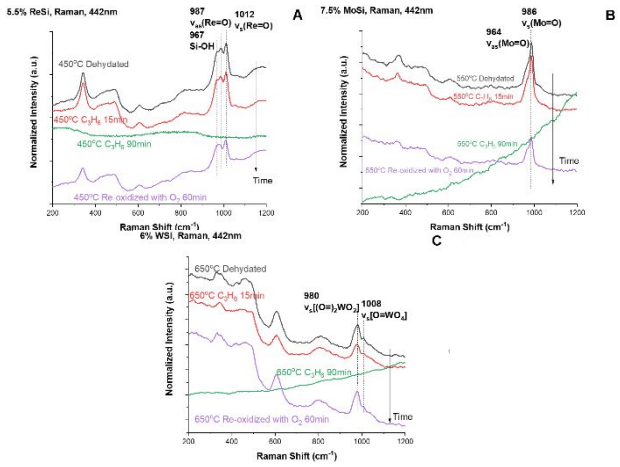

Figure 2. *In situ* Raman spectra (200-1200 cm^{-1}) of the SiO_2-supported metal oxide catalysts after dehydration, propylene activation and re-oxidization conditions: (A) ReO_x/SiO_2 at 450 °C , (B) MoO_x/SiO_2 at 550 °C and (C) WO_x/SiO_2 at 650 °C.

C_3H_6-TPSR-MS.

1st C_3H_6-TPSR-MS cycle. The 1st C_3H_6-TPSR-MS spectra of the dehydrated SiO_2 supported metal oxide catalysts are presented in Figure 3. The dehydrated supported ReO_x/SiO_2 catalyst only produces C_4H_8 at the high temperatures of ~ 420-550°C (Tp=450°C). Similarly, the dehydrated supported MoO_x/SiO_2 catalyst only produces C_4H_8 at somewhat higher temperatures of ~ 350-600°C (Tp=520°C). The dehydrated supported WO_x/SiO_2 catalyst only produces C_4H_8 at even higher temperatures of ~ 550-785°C (Tp=718°C). All the SiO_2-supported metal oxide catalysts also produce oxygenated products (CO, CO_2, and H_2O) at high temperatures from partial reduction of surface metal oxide sites by propylene during the catalyst activation stage. While the combustion products precede the formation of butene for the supported ReO_x/SiO_2 catalyst, the combustion products primarily form after the start of butene formation for the supported MoO_x/SiO_2 and WO_x/SiO_2 catalysts. The supported WO_x/SiO_2 catalyst has relatively higher CO/CO_2 production ratio than the supported ReO_x/SiO_2 and MoO_x/SiO_2 catalysts. The propylene metathesis activation product acetone is only observed from the supported ReO_x/SiO_2 (Tp=133, 412°C) and MoO_x/SiO_2 (Tp=190, 520 °C) catalysts. It is possible that acetone decomposed at the much higher temperatures required for activation of the surface WO_x sites on SiO_2 or that a different activation path is followed by the supported WO_x/SiO_2 catalyst.

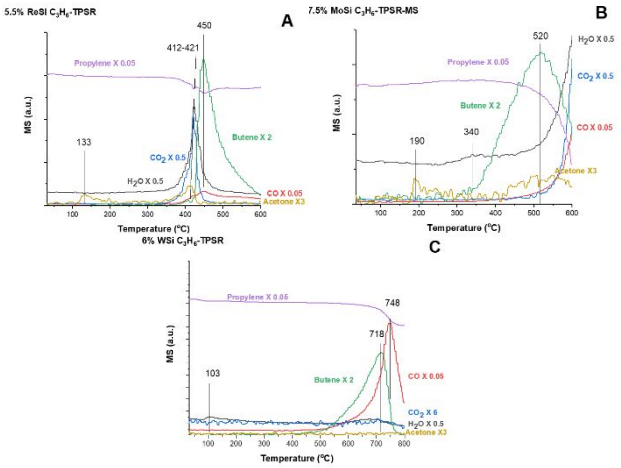

Figure 3. The 1st C_3H_6-TPSR-MS cycle spectra (30-600/800°C) of the SiO_2-supported metal oxide catalysts: (A) ReO_x/SiO_2, (B) MoO_x/SiO_2, and (C) WO_x/SiO_2.

2nd C_3H_6-TPSR-MS cycle. The 2nd C_3H_6-TPSR-MS spectra of SiO_2-supported metal oxide catalysts that have been activated by the 1st C_3H_6-TPSR cycle are presented in Figure 4, and allows chemically probing the properties of the activated sites in the 1st C_3H_6-TPSR cycle. The activated supported ReO_x/SiO_2 catalyst produces C_4H_8 at intermediate temperatures ~ 250-400°C (Tp=300 °C) and high temperatures ~ 420-550°C (Tp=470°C), but the amount of C_4H_8 produced is drastically decreased compared to the 1st cycle. The activated supported MoO_x/SiO_2 catalyst produces C_4H_8 at both low ~ 30-250°C (Tp=107°C) and high temperatures ~ 250-600°C (Tp=470°C) with a much larger

amount of C_4H_8 produced compared to the 1st cycle. The activated supported WO_x/SiO_2 catalyst produces C_4H_8 at both low ~ 30-170℃ (Tp=87°C) and high temperatures ~ 350-800°C (Tp=576°C) with a much larger amount of C_4H_8 produced compared to the 1st cycle. The C_4H_8 production during the 2nd C_3H_6-TPSR cycle follows the trend (i) at low temperatures: MoO_x > WO_x >> ReO_x, and (ii) at high temperatures WO_x > MoO_x >> ReO_x. The consumption of C_3H_6 during the 2nd C_3H_6-TPSR cycle is compared in Figure S2. The activated supported MoO_x/SiO_2 and WO_x/SiO_2 catalysts consume propylene for C_3H_6 self-metathesis at low temperature and consume propylene for both C_3H_6 self-metathesis and C_3H_6 combustion at high temperature. The activated supported ReO_x/SiO_2 catalyst exhibits only minor C_3H_6 consumption at both low and high temperatures.

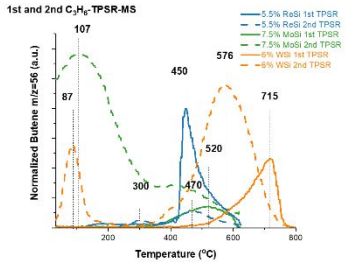

Figure 4. The C_4H_8 production of 1st and 2nd C_3H_6-TPSR -MS (30-600/800 °C) cycles with online MS for the SiO_2 supported metal oxide catalysts. The MS signals of C_4H_8 were normalized by the MS signals of the Ar carrier gas.

C_3H_6-TPSR-IR.

The *in situ* C_3H_6-TPSR-IR spectra of the dehydrated SiO_2 supported metal oxide catalysts are presented in Figure S3. There is no notable difference between the 1st and 2nd cycle *in situ* C_3H_6-TPSR-IR spectra. For all the SiO_2 supported metal oxide catalysts, the *in situ* IR spectra at 30°C are primarily composed of gas phase propylene (The *in situ* IR bands at ~ 1444, 1455, 1472, 1638, and 1664 cm^{-1} correspond to gas phase propylene[18]). No detectable *ν*(C=O) vibration at 1686 cm^{-1} of surface acetone is observed on the SiO_2-supported metal oxide catalysts. Above 320°C, there are no IR bands of gas phase propylene and surface intermediates, reflecting thermal broadening of the gas phase bands and an extremely low density of surface intermediates, respectively. The broad *in situ* IR bands at ~1279 and ~1570 cm^{-1} for SiO_2-supported metal oxide catalysts result from a thermal effect on the spectral baseline, and not from surface intermediates.[13]

Ethylene/2-Butene Titration.

The C_2H_4/2-C_4H_8 titration measurements were performed by activating the catalyst with 2-C_4H_8 at elevated temperatures, titrating the resulting surface M=$CHCH_3$ intermediates with flowing C_2H_4-TPSR and quantifying the number of C_3H_6 molecules produced with the online MS as shown in Figure S4. The initial C_2H_4/2-C_4H_8 titration studies at 100°C (Figure S4 A), reveal that much more surface MoO_x sites were activated than surface ReO_x and WO_x sites at 100°C. The C_2H_4-TPSR-MS spectra for the supported MO_x/SiO_2 catalysts are presented in Figure S4 B and the corresponding number of activated sites are given in Table 1. The 2-butene activated supported ReO_x/SiO_2 catalyst has only one C_3H_6-TPSR peak at 505°C, which represents activation of 17.1% of the total surface ReO_x sites. The 2-butene activated supported MoO_x/SiO_2 catalyst exhibits two C_3H_6-TPSR peaks at 100 °C and 540°C that represent 20.0% (100 °C) and 1.1% (540°C) of activated surface MoO_x sites, respectively. Since a portion of the surface ReO_x and MoO_x sites volatize during the high temperature C_3H_6 activation, the actual fraction of activated surface ReO_x and MoO_x sites will be higher than the fractions indicated in Table 1. The 2-butene activated supported WO_x/SiO_2 catalyst shows only one C_3H_6-TPSR peak at 705°C that represents 2.1% of activated surface WO_x sites. Although the supported ReO_x/SiO_2 and MoO_x/SiO_2 catalysts have a higher number of activated sites (~ 20% of the initial oxidized sites), the supported WO_x/SiO_2 catalyst has an order of magnitude lower number of activated sites (~ 2% of the initial oxidized sites). Furthermore, since only surface MoO_x sites exhibit a C_3H_6-TPSR peak at low temperatures (~100°C), this indicates that the surface Mo=$CHCH_3$ intermediates are much more reactive at low temperatures than the surface Re=$CHCH_3$ and W=$CHCH_3$ intermediates towards ethylene titration.

Catalyst (wt.%)	Total Number of Initial Surface MO_x Sites (mol)	Number of C_3H_6 Produced (mol)	Fraction of Activated surface Sites
5.5%ReSi	$2.3x10^{-5}$	$3.9x10^{-6}$ (505°C)	17% (505°C)
7.5%MoSi	$3.1x10^{-5}$	$6.2x10^{-6}$ (100°C) $3.5x10^{-7}$ (540°C)	20% (100°C) 1.1% (540°C)
6%WSi	$2.5x10^{-5}$	$5.3x10^{-7}$ (703°C)	2.1% (703°C)

Table 1. Number of activated surface MO_x sites calculated from activation by 2-C_4H_8 and subsequent titration with C_2H_4-TPSR-MS. Fraction of activated sites referenced against total number of initial oxidized sites.

Steady State Propylene Metathesis of catalysts activated with C_3H_6.

The steady state propylene self-metathesis activity (mmol/g/h) and TOF (s^{-1}) values of the activated SiO_2-supported metal oxide catalysts are presented in Table 2 as a function of reaction temperature and activation temperatures. At the reaction temperature of 100°C, the supported MoO_x/SiO_2 catalyst is the most active catalyst while the supported ReO_x/SiO_2 and WO_x/SiO_2 catalysts are two-orders of magnitude less active. Increasing the reaction temperature decreases the activity of the supported MoO_x/SiO_2 catalyst and increases the activity of the supported ReO_x/SiO_2 and WO_x/SiO_2 catalysts. Surprisingly, the activity of the supported MoO_x/SiO_2 catalyst increases somewhat at a reaction temperature of 550°C. At the highest reaction temperature of

450-550℃, the supported WO_x/SiO_2 catalyst is about an order of magnitude more active than the supported MoO_x/SiO_2 and ReO_x/SiO_2 catalysts. The corresponding TOF values follow the same trends as the activity values and reveal low specific reaction rates for olefin metathesis over this set of catalysts. At 100℃, the supported MoO_x/SiO_2 has the highest TOF that is one to two orders of magnitude greater than the supported ReO_x/SiO_2 and WO_x/SiO_2 catalysts. At 550℃, the supported WO_x/SiO_2 catalyst exhibits the highest TOF value that is about two orders of magnitude greater than that of the supported MoO_x/SiO_2 and ReO_x/SiO_2 catalysts. These olefin metathesis SiO_2-supported metal oxide catalysts exhibit a wide range of activity and TOF values that reveal different dependence on the reaction temperature with the supported MoO_x/SiO_2 catalyst most active at lower temperatures and supported WO_x/SiO_2 catalyst most active at high temperatures.

Catalyst (Activation Temperature)	Steady State Activity (mmol/g/h) (TOF (s^{-1}))* *TOF normalized by number of sites determined with C_2H_4/C_4H_8 titration				
	100°C	200°C	300°C	400°C	450°C or 550°C
5.5%ReSi (450℃)	0.03 ($0.22x10^{-3}$)	0.03 ($0.22x10^{-3}$)	0.10 ($0.73x10^{-3}$)	0.38 ($2.80x10^{-3}$)	0.51 (450°C) ($3.70x10^{-3}$)
7.5%MoSi (550℃)	4.0 ($1.7x10^{-2}$)	2.0 ($0.85x10^{-2}$)	0.03 ($0.13x10^{-3}$)	0.01 ($0.43x10^{-4}$)	0.48 (550°C) ($0.20x10^{-2}$)
6%WSi (650 ℃)	0.02 ($0.11x10^{-2}$)	0.03 ($0.16x10^{-2}$)	0.03 ($0.16x10^{-2}$)	0.23 ($0.12x10^{-1}$)	3.6 (550°C) ($1.9x10^{-1}$)

Table 2. Steady state activity (mmol/g/h) and TOF values of C_3H_6 pre-activated catalysts (catalyst activation temperatures are indicated in Table 2).

IV. Discussion

Anchoring of MO_x Species on SiO_2 Surface Hydroxyls

The metal oxides preferentially anchor at the isolated Si-OH surface hydroxyls. The geminal $Si(-OH)_2$ surface hydroxyls are either unreactive or minimally reactive towards anchoring of the aqueous ReO_x, MoO_x and WO_x species (Figure 1). Consequently, all three metal oxides primarily anchor at the same isolated silanol Si-OH surface hydroxyls.[19-20]

Molecular and Electronic Structure of Surface ReOx, MoO_x, WO_x sites on SiO_2 under oxidative dehydration and olefin activation conditions.

The initial dehydrated surface MO_x sites on SiO_2 are completely dispersed as isolated sites on the SiO_2 support. The presence of only isolated surface metal oxide sites on SiO_2 supports is related to the low density of reactive surface hydroxyl anchoring sites associated with the isolated Si-OH surface hydroxyls. Crystalline Re_2O_7, MoO_3, and WO_3 nanoparticles are not present and are only present when the surface coverage is well above the maximum dispersion limit on SiO_2 or monolayer coverage.[12] The dehydrated surface ReO_x sites are present as fully oxidized Re(+7) cations with an isolated tri-oxo $(O=)_3ReO$ structure.[6,15] The dehydrated surface MoO_x sites are present as fully oxidized Mo(+6) cations as isolated di-oxo $(O=)_2MoO_2$ sites.[13,15] The surface dehydrated WO_x sites are present as fully oxidized W(+6) with a mixture of isolated di-oxo $(O=)_2WO_2$ and a small amount of mono-oxo $(O=)WO_4$ sites.[15,21] These surface isolated MO_x structures are in agreement with the structures reported in the literature for dehydrated supported MO_x/SiO_2 catalysts from multiple *in situ* characterization studies (Raman,[12, 15, 22-24] UV-vis,[22-23] IR,[22] and XAS[22,24]) and DFT calculations[25-27]. The nature of the activated surface MO_x sites on SiO_2, however, still require direct spectroscopic characterization because the activated surface MO_x sites possess the same oxidation state as the unactivated sites, which complicates the spectroscopic deconvolution of the unactivated and activated sites. The presence of carbon deposits (coke) on the catalysts also adds additional complexity to the analysis. The initial formation of surface metal=carbene proceeds via a mechanism where the fully oxidized surface metal-oxo sites ($Re(=O)_3$, O=Mo=O, O=W=O, W=O) initially reduce to a lower oxidation state by the olefins as the oxo-oxygen is removed and then re-oxidized back to the highest oxidation state via formation of surface $M=CH_2$ and $M=CHCH_3$ species.[25] The $C_2H_4/2\text{-}C_4H_8$ titration studies clearly demonstrate that surface $M=CHCH_3$ and $M=CH_2$ intermediates are indeed present on the activated catalysts.

Volatilization of surface MO_x sites from the SiO_2 support during activation

Volatilization of the active component in heterogeneous catalysts is a serious concern since it leads to loss of expensive catalyst components as well as catalyst deactivation (fewer catalytic active sites). The current study demonstrated that an appreciable fraction of surface ReO_x (~49%) and MoO_x (~38%) sites on SiO_2 volatilizes during the high temperature C_3H_6 activation, which is a required step for activation of active olefin metathesis catalysts.[2, 8] In contrast, only a negligible fraction of surface WO_x sites (~4%) on SiO_2 volatizes (Figure 2). Additional surface ReO_x and MoO_x sites probably volatize under olefin metathesis reaction conditions at high temperatures and catalyst regeneration under oxidizing conditions that are required to remove catalyst coke, especially at elevated temperatures. Volatilization of surface MO_x sites on SiO_2 takes place by hydrolysis of bridging M-O-Si bonds that forms M-OH and HO-Si, which weakens the metal oxide-silica interaction.[28, 29] The extent of volatilization is related to the lower sublimation temperatures of Re_2O_7 (~250°C)[16] and MoO_3 (~525°C)[17] compared to WO_3 (800°C)[30]. Thus, the supported WO_x/SiO_2 catalyst is more robust in comparison to the supported ReO_x/SiO_2 and MoO_x/SiO_2 catalysts for olefin metathesis, especially under harsh elevated temperatures. It is important to note that the initial number of surface MO_x sites on the SiO_2 support is not a critical parameter since the number of stable surface MO_x sites is

controlled by metal oxide volatilization during catalyst activation and the olefin metathesis reaction.

Number of Activated Surface MO_x Sites on SiO_2

Although both surface MoO_x and WO_x on SiO_2 predominantly possess the same initial dioxo surface $(O=)_2M(-O)_2$ sites, they have very different responses towards activation by the ethylene/2-butene titration. A higher fraction (~20%) of the surface $Mo=CHCH_3$ intermediates undergo metathesis with C_2H_4 at low temperatures to yield C_3H_6. In contrast, only a minor fraction of the surface $W=CHCH_3$ intermediates undergo metathesis with C_2H_4 and require high temperatures to yield C_3H_6. This difference in fraction of activated sites between MoO_x/SiO_2 and WO_x/SiO_2 catalysts is related to the more facile reduction by propylene of surface MoO_4 sites on SiO_2 than the surface WO_4 sites on SiO_2 (Mo (Tp = 520℃) and W (Tp=715℃). The fraction of activated sites in MoO_x/SiO_2 and WO_x/SiO_2 catalysts are limited by the suitable geometry and neighborhood of surface sites that can be effectively activated by alkenes.[26] The trioxo surface $(O=)_3Re(-O)$ sites possess a different structure than the surface MoO_4 and WO_4 sites, but responds similarly to the surface MoO_4 sites with ~17% of the surface ReO_4 sites becoming activated by exposure to propylene (Tp = 450℃). The facile reduction by propylene of the surface ReO_4 sites is related to rhenia's intrinsic ease of reduction.[7]

Activation of SiO_2-supported MO_x catalysts by C_3H_6

The lower activation temperature of the supported MoO_x/SiO_2 catalyst than the supported WO_x/SiO_2 catalyst is agreement with the DFT calculation that reveals lower predicted overall activation Gibbs energies for the MoO_x/SiO_2 than the WO_x/SiO_2 catalyst.[31] The 1st C_3H_6-TPSR indicates the temperatures where each of the surface MO_x sites on SiO_2 become activated, while the 2nd $C_3^=$-TPSR reveals the reactivity of the activated surface MO_x sites. Both supported MoO_x/SiO_2 and WO_x/SiO_2 catalysts reveal the presence of highly active surface MO_x sites on SiO_2 at ~100℃℃ after high temperature activation (>400℃℃). For supported MoO_x/SiO_2, however, most of the activated sites perform olefin metathesis at ~100℃ while most of the activated sites for supported WO_x/SiO_2 perform olefin metathesis at ~600℃. This difference in activity is reflected in the olefin metathesis reaction rates of these two supported MO_x/SiO_2 catalysts, which will be elaborated upon below. The activated surface ReO_x sites on SiO_2 don't possess low temperature activated sites and only exhibit modest olefin metathesis activity at intermediate reaction temperatures (~470℃).

Activity and TOF of SiO_2-supported MO_x catalysts for propylene metathesis.

The steady state activity (mmol/g/h) of the catalysts, which doesn't take into account the number of volatized MoO_x sites, indicates that the supported MoO_x/SiO_2 and WO_x/SiO_2 catalysts are the most active for propylene metathesis. However, the supported MoO_x/SiO_2 is most active at low temperatures (100℃) while supported WO_x/SiO_2 is most active at high temperatures (550℃). It appears that the steady state olefin metathesis activity is dominated by the abundant number of low temperature active surface MoO_x sites for MoO_x/SiO_2 while the steady state olefin metathesis activity is dominated by the abundant number of high temperature activated surface WO_x sites for WO_x/SiO_2. This difference in low temperature metathesis activity is a direct consequence of the reactivity of the surface $M=CHCH_3$ and $M=CH_2$ intermediates (Mo >> W). This is further reflected in the specific reactivity (TOF) values where supported MoO_x/SiO_2 exhibits a TOF values of 1.7 x 10^{-2}/s at 100℃ and 0.20 x 10^{-2}/s at 550℃. The decreasing performance of the supported MoO_x/SiO_2 catalyst with increasing temperatures may be related to additional volatilization of MoO_x during olefin metathesis or possibly coking of the catalyst since catalytic kinetics should increase with reaction temperature. The corresponding supported WO_x/SiO_2 exhibits TOF values of 0.11 x 10^{-2}/s at 100℃ and 1.9 x 10^{-1}/s at 550℃. In contrast to the activated supported MoO_x/SiO_2 and WO_x/SiO_2 catalysts, the supported ReO_x/SiO_2 possesses I don't much lower TOF values of 0.22 x 10^{-3}/s at 100℃ and 3.7 x 10^{-3}/s at 450℃. Since the surface MO_x sites are isolated on the SiO_2 support and almost exclusively anchored at the same surface silanol, the TOF values will be independent of surface MO_x coverage. Note that these TOF values are true TOF values that are only based on the remaining active sites titrated after activation and volatilization. At high temperatures, the surface WO_x sites possess the most active sites (highest TOF) compared to the surface MoO_x sites (TOF is ~10x less active) and surface ReO_x sites (TOF is ~100x less active). The differing activation temperatures and reaction temperatures for the supported MO_x/SiO_2 catalysts are related to the stability of the surface M=O oxo and M=Carbene bonds, respectively.

V. Conclusions

The side-by-side comparison of the SiO_2-supported ReO_x, MoO_x and WO_x catalysts provides fundamental insights about the different characteristics of these supported MO_x/SiO_2 catalysts for olefin metathesis. All three metal oxides selectively anchor at the isolated surface Si-OH silanols and are present as isolated sites. The surface MoO_x and WO_x on SiO_2 essentially possess the same molecular structures (dioxo $(O=)_2MoO_2$ and $(O=)_2WO_2$) while the surface ReO_x on SiO_2 is present as trioxo ($(O=)_3ReO$). The different molecular structures are related to the greater number of bonding electrons in the surface $Re^{7+}O_x$ site than the surface $Mo^{6+}O_x$ and $W^{6+}O_x$ sites. These surface MO_x sites on SiO_2 require activation by olefins at elevated temperatures to become active for olefin metathesis. The activation process removes the initial M=O oxo bonds forming coordinative unsaturated sites that allow for olefin chemisorption as surface $M=CHCH_3$ and $M=CH_2$ intermediate species, which are confirmed by the titration studies. The high temperature activation process, however, also leads to volatilization of the surface MO_x sites from the SiO_2 support (ReO_x (~49%) > MoO_x (~38%) >> WO_x (~4%)).

In spite of the MO_x volatilization, about 20% of the surface MO_x sites become activated for olefin metathesis by the supported

MoO_x/SiO_2 and ReO_x/SiO_2 catalysts at lower temperatures. In contrast, only about 2% of the surface WO_x sites become activated for olefin metathesis by the supported WO_x/SiO_2 catalysts at high temperatures. The number of activated sites is related to the ease of reduction of the initial surface MO_x sites on SiO_2. The reactivity of the surface M=carbenes ($M=CHCH_3/M=CH_2$) for olefin metathesis also follows the same trend: Mo=carbene > Re=carbene > W=carbene. As a result, during the steady state metathesis the surface MoO_x sites are active at lower temperatures (~100℃), the surface WO_x sites are active at high temperatures (~600℃) and the surface ReO_x sites are active at intermediate temperatures (~470℃). Consequently, the surface MoO_x sites are the most active at lower temperatures (TOF= 1.7 x 10^{-2}/s at 100℃), the surface ReO_x sites are the least active at intermediate temperatures (TOF=3.7 x 10^{-3}/s at 450℃) and the surface WO_x sites are the most active at high temperatures (TOF=1.9 x 10^{-1}/s at 550℃).

The superior performance of the commercial supported WO_x/SiO_2 catalysts compared to the supported MoO_x/SiO_2 and ReO_x/SiO_2 catalysts is a consequence of its more robust properties: (*i*) much lower volatility, (*ii*) higher steady state activity at elevated temperatures, and (*iii*) higher TOF at elevated temperatures. In spite of the superior olefin metathesis performance by the supported WO_x/SiO_2 catalyst, the supported WO_x/SiO_2 catalyst suffers from (*i*) being more difficult to activate that requires much higher activation temperatures, and (*ii*) only forming a low number of activated sites. Nevertheless, the positive features significantly outweigh the negative features making the supported WO_x/SiO_2 catalyst the superior catalyst for olefin metathesis of small olefins.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. The experimental data generated and analyzed during this study are included in this published article and its supplementary information files.

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The data that support the findings of this study are available from the corresponding author upon reasonable request. The following datasets are included:

- **Experimental Data**: Raw spectroscopy data (.csv files and .xlsx files). These files are available upon request.
- **Supporting Information**: Additional data, including detailed experimental procedures, supplementary figures, and tables (.pdf files). These files are available upon request.