ACS Catalysis
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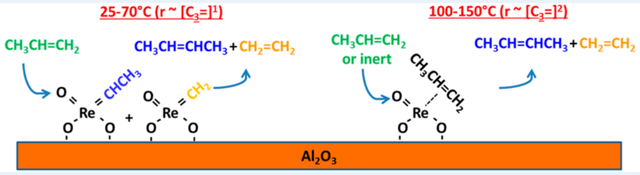
Reaction Mechanism and Kinetics of Olefin Metathesis by Supported ReO_x/Al_2O_3 Catalysts

Soe Lwin and Israel E. Wachs*

Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, United States

Ⓢ *Supporting Information*



ABSTRACT: The self-metathesis of propylene by heterogeneous supported ReO_x/Al_2O_3 catalysts was investigated with in situ Raman spectroscopy, isotopic switch ($D{-}C_3^= \rightarrow H{-}C_3^=$), temperature-programmed surface reaction (TPSR) spectroscopy, and steady-state kinetic studies. The in situ Raman studies showed that two distinct surface ReO_4 sites are present on alumina and that the olefins preferentially interact with surface ReO_4 sites anchored at acidic surface sites of alumina (olefin adsorption: $C_4^= > C_3^= > C_2^=$). The isotopic switch experiments demonstrate that surface $Re^*{=}CH_3$ and $Re^*{=}CHCH_3$ are present during propylene metathesis, with Re^* representing activated surface rhenia sites. At low temperatures (<100 °C), the rate-determining step is adsorption of propylene on two adjacent surface sites (rate $\approx [C_3^=][Re^*]^2$. At high temperatures (>100 °C), the rate-determining step is the recombination of two surface propylene molecules (rate $\approx [C_3^=]^2[Re^*]$). To a lesser extent, the recombination of surface $Re^*{=}CH_3$ and $Re^*{=}CHCH_3$ intermediates also contributes to self-metathesis of propylene at elevated reaction temperatures.

KEYWORDS: *catalyst, supported, rhenia, Al_2O_3, metathesis, olefins, mechanism, kinetics*

1. INTRODUCTION

Olefin metathesis has been a sustainable reaction to produce important chemicals for the past 50 years.[1] Supported ReO_x/Al_2O_3 catalysts for olefin metathesis were originally discovered by British Petroleum (BP) in 1964.[2] The high reactivity and selectivity of supported ReO_x/Al_2O_3 catalysts under ambient conditions allows performing metathesis of functionalized olefins, which is assisted by promoters.[3] The high price and volatility of rhenium oxides limit the use of ReO_x catalysts only to production of fine chemicals,[3] but recent patent activity indicates a resurgence of interest in this catalytic system due to a shortage of both linear and functionalized olefins.[4]

Although olefin metathesis by supported ReO_x/Al_2O_3 catalysts has been investigated over the years, conflicting reports still exist about the reaction mechanism and kinetics of this catalytic reaction. Supported ReO_x/Al_2O_3 catalysts can be activated upon exposure to propylene and 2-butene at room temperature, but activation by ethylene is a slow process or is even not possible.[5−7] Aldag et al., however, concluded from self-metathesis of C_2H_3D, yielding both C_2H_4 and $C_2H_2D_2$, that ethylene can initiate metathesis by supported ReO_x/Al_2O_3 catalysts at slightly higher temperatures (95 °C).[8] By combining steady-state kinetic studies with simultaneous thermal gravimetric analysis (TGA) to determine the quantity of adsorbed ethylene during the reaction, the metathesis reaction rate was found to vary with the square of the adsorbed ethylene.[8] It was proposed that the ethylene metathesis reaction involves two mobile adsorbates, resulting in second-order kinetics with respect to the adsorbate concentration.[8,9] This suggests that ethylene self-metathesis proceeds via a four-membered reaction intermediate. During steady-state ethylene self-metathesis, Aldag et al. found that the reaction rate had a 1.4 reaction order with respect to the ethylene partial pressure, consistent with more than one ethylene molecule participating in the rate-determining step (rds) at elevated temperatures.[9] Spinicci et al. concluded that desorption of propylene from supported ReO_x/Al_2O_3 catalysts follows second-order kinetics with temperature-programmed desorption (TPD) studies.[10] Some kinetic studies suggested that olefin metathesis proceeds via the Langmuir−Hinshelwood kinetic model,[8,11,12] but Kapteijn et al. considered the L-H model inadequate and developed a first-order kinetic model based on intermediate carbene species ($Re{=}CH_2$ and $Re{=}CHCH_3$) with product desorption being the rate-determining step.[13] This mechanism is more in line with Chauvin's metallacyclobutane mechanism that was proposed for homogeneous and supported organometallic catalysts.[14]

The lack of agreement among researchers about the reaction mechanism and kinetics of olefin metathesis by supported ReO_x/Al_2O_3 catalysts is due to the use of different catalysts (variable BET surface areas and rhenia loadings) and reaction conditions (different olefins, olefin partial pressures, and reaction temperatures). The motivation of this study is to resolve these issues by systematically applying in situ Raman spectroscopy, temperature-programmed surface reaction (TPSR) spectroscopy, and steady-state propylene self-meta-

Received: October 5, 2015
Revised: November 3, 2015

DOI: 10.1021/acscatal.5b02233
ACS Catal. 2016, 6, 272−278

thesis kinetic studies under various conditions to develop a comprehensive model of olefin metathesis by supported ReO_x/Al_2O_3 catalysts.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. The supported ReO_x/Al_2O_3 and $ReO_x/TaO_x/Al_2O_3$ were prepared by impregnation of a 65−70 wt % aqueous solution of perrhenic acid, $HReO_4$ (Sigma-Aldrich) and a toluene solution of tantalum ethoxide ($Ta\text{-}(OC_2H_5)_5$, Alfa Aesar, 99.999%) onto the Al_2O_3 support (Engelhard batch no. H5433C). The 9.4% ReO_x/Al_2O_3 (Harshaw) catalyst was used for the in situ Raman studies because lower fluorescence from this alumina support gave rise to higher quality in situ Raman spectra at lower temperatures. The reaction studies were performed with the 15.6% ReO_x/Al_2O_3 (Engelhard) catalyst, since only a limited amount of the discontinued Harshaw alumina was available. The percentage of Re above 6% would not change in situ studies, since all of these catalysts would contain the same two species and their interactions with olefins will not be different. The full procedure of incipient-wetness impregnation, drying, and calcination can be found in another paper.[15]

2.2. In Situ Raman Spectroscopy. The Raman spectra of the supported ReO_x/Al_2O_3 catalysts were obtained with a Horiba-Jobin Ybon LabRam HR instrument equipped with three laser excitations (532, 442, and 325 nm) and a liquid N_2 cooled CCD detector (Horiba-Jobin Yvon CCD-3000 V). The 442 nm laser was chosen, since it minimized sample fluorescence. Spectral resolution was approximately 1 cm^{-1}, and the wavenumber calibration was checked using the silica standard line at 520.7 cm^{-1}. The lasers were focused on the samples with a confocal microscope using a 50× objective (Olympus BX-30-LWD). Typically, the spectra were collected at 30 s/scan and 5 scans with a 200 μm hole. Approximately 5−25 mg of each catalyst in powder form was loaded into an environmental cell (Harrick, HVC-DR2) with a SiO_2 window and O-ring seals which was kept cool by flowing water. The catalysts were initially dehydrated at a heating rate of 10 °C/min up to 500 °C and held for an hour under a 30 mL/min flow of 10% O_2/Ar (Airgas, certified, 9.989% O_2/Ar balance). After cooling in Ar to 30 °C, a spectrum was taken before 1% $C_2^=$ (ethylene), 1% $C_3^=$ (propylene), or 1% $C_4^=$ (*trans*-2-butene) in argon or helium (balance) was introduced (three separate experiments). After 60 min of each olefin flow at 30 °C, another spectrum was taken.

2.3. Steady-State Kinetics Studies. The catalytic activity measurements were performed in a fixed-bed catalytic reactor under differential conditions (propylene conversion <15%). A separate molecular sieve moisture trap was installed in the inlet propylene gas line to purify the reactants. Both inlet and outlet gas lines were heated using external electric heaters to ~200 °C to prevent condensation of the reactants and products. The catalysts were pretreated in 10% O_2/Ar at 500 °C for 30 min before cooling in Ar to either 70 or 150 °C. Then a gas mixture of 1−10% C_3H_6/Ar was introduced at the rate of ~100 mL/min. The desired concentration was achieved by diluting the 10% C_3H_6/Ar gas with Ar. The products were analyzed using an online gas chromatograph (Agilent GC 6890) equipped with flame ionization (Agilent Serial No. USC250823H) and thermal conductivity (Restek Product No. PC3533) detectors. Conversion was normalized with propylene flow rate and catalyst weight to obtain reactivity, reported in mmol/(g h).

2.4. Temperature-Programmed Surface Reaction (TPSR) Spectroscopy. The temperature-programmed surface reaction experiments were performed using an Altamira Instruments system (AMI-200). The outlet gases were connected to an online Dymaxicon Dycor mass spectrometer (DME200MS) for analysis. Typically ~100−200 mg of catalyst was loaded into the U-tube reactor. The cracking patterns were carefully adjusted with blank gas runs. The supported 15.6% ReO_x/Al_2O_3 (15.6ReAl) catalyst was used for the following experiments. As in other experiments, the catalyst was always initially pretreated with 10% O_2/Ar at 500 °C for 30 min and then cooled in Ar to the conditions of interest. Details of the specific experimental protocols are given in the Supporting Information.

3. RESULTS

3.1. In Situ Raman Spectroscopy. The in situ Raman spectra of the supported 9.4% ReO_x/Al_2O_3 catalyst exposed to flowing Ar, $C_2^=$/Ar, $C_3^=$/Ar, and 2-$C_4^=$/Ar at 30 °C are shown in Figure 1. The dehydrated catalyst in flowing Ar exhibits two bands from surface dioxo ReO_4-I (~1003 cm^{-1}) and ReO_4-II (~1013 cm^{-1}) sites anchored at basic and acidic surface hydroxyls of alumina, respectively.[15] The interaction of the olefins with the surface rhenia sites increases with olefin size ($C_2^= < C_3^= < C_4^=$), as reflected by the decreasing intensity of the Raman Re═O oxo bands. The decrease in intensity of the Raman Re═O oxo bands is from both bonding of the olefins to the surface rhenia sites and the corresponding darkening of the sample, with the latter dependent on the amount of coordinated olefins. In all cases, olefins preferentially coordinate to the surface ReO_4-II sites, which show a greater decrease in intensity upon olefin adsorption in comparison to the surface RO_4-I sites. Previously, it was shown that the surface ReO_4-II sites are the catalytically active sites and that catalysts with 100% of surface ReO_4-II sites can be synthesized by promotion with surface TaO_x sites that block formation of inactive surface ReO_4-I sites (ReTaAl catalysts).[15]

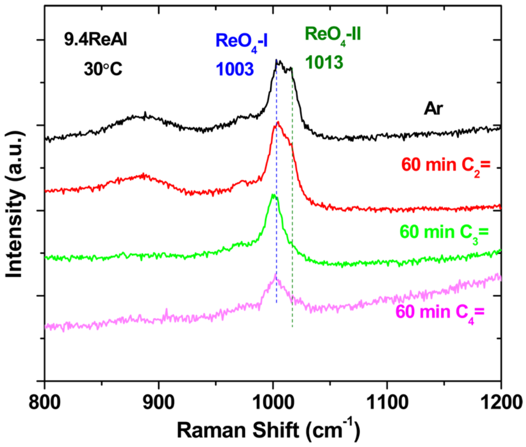


Figure 1. In situ Raman spectra of the supported 9.4% ReO_4/Al_2O_3 catalyst after 60 min exposure to olefins at 30 °C.

3.2. Steady-State Kinetics for Self-Metathesis of C_3H_6. *3.2.1. Reaction Order.* The steady-state kinetics for self-metathesis of C_3H_6 to C_2H_4 and C_4H_8 by the supported 15.6% ReO_x/Al_2O_3 catalyst was examined as a function of $C_3^=$ partial pressure and reaction temperature and are presented in Figure 2. The conversions of propylene were maintained below 15% to maintain differential reaction conditions and emphasize the forward metathesis reaction. The self-metathesis of propylene reaction order in $C_3^=$ partial pressure is a strong function of temperature with ~0.9 at 70 °C and increases to ~1.8 at 150 °C. The propylene self-metathesis reaction products of $C_2^=$ and $C_4^=$ were formed in equimolar amounts and also follow the same reaction orders (see Figure S1 in the Supporting Information).

3.2.2. Apparent Activation Energy. The apparent activation energy for the steady-state self-metathesis of propylene was found from an Arrhenius plot (see Figure S2 in the Supporting Information). The apparent activation energy values below and above 100 °C, corresponding to the different reaction order regions, were found to be ~7 and ~21 kJ/mol, respectively.

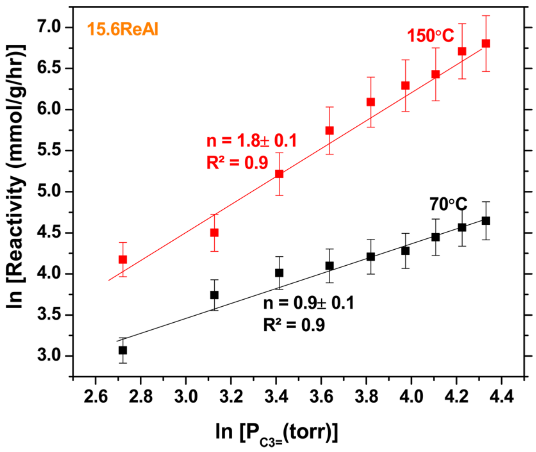


Figure 2. Self-metathesis of propylene as a function of C_3H_6 partial pressure and temperature. The reactivity was determined from propylene molecules converted.

3.2.3. Number of Surface ReO_x Sites Involved in the Rate-Determining Step (rds). The number of surface rhenia sites (n) involved in the rds of the self-metathesis of C_3H_6 to C_2H_4 and C_4H_8 can also be determined from the slope of the ln(reactivity/(g h)) vs ln(ReO_4-II) loading because the surface ReO_4-II catalytically active sites are completely dispersed on the alumina support, giving the general relationship of rate ≈ $[ReO_x]^n$. Note that TaO_x promotion blocks formation of the inactive surface ReO_4-I sites, allowing for a direct comparison of the reaction rate and the number of active surface ReO_4-II sites.[15] The ln(rate)−ln($[ReO_x]$) plot presented in Figure 3 for propylene self-metathesis yields a slope of ∼2.1, suggesting that $n = 2$ and implying that two surface ReO_x-II sites are involved in the rds of the self-metathesis of C_3H_6 reaction.

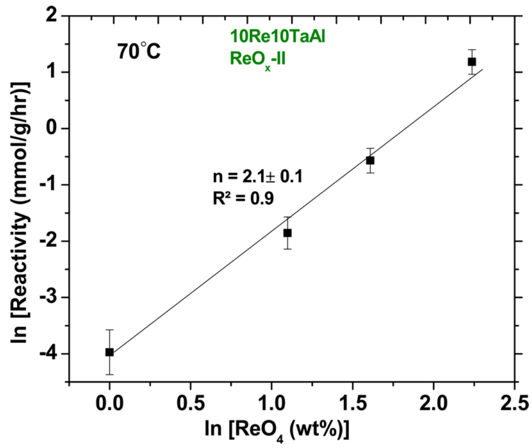


Figure 3. ln−ln plot of reactivity (mmol/(g h) for $C_3^=$ consumption) vs ReO_4-II loading for the ReTaAl catalyst that only contains the active surface ReO_4-II sites.[15]

3.3. Self-Metathesis of C_3H_6/C_3D_6. *3.3.1. Steady-State Isotope Switch C_3D_6 → C_3H_6.* The self-metathesis of propylene was investigated by first equilibrating the catalyst with D−$C_3^=$ for 30 min and then switching to a flow of H−$C_3^=$, as shown in Figure 4. This steady-state isotope switch experiment provides many key mechanistic and kinetic insights into the propylene self-metathesis reaction. Before the isotope switch, D−$C_2^=$ and D−$C_4^=$ were produced in a 1:1 ratio from D−$C_3^=$ self-metathesis. Shutting off the flow of D−$C_3^=$ causes an instantaneous drop in the formation of D−$C_2^=$ and D−$C_4^=$, indicating that the self-metathesis reaction is first order in D−$C_3^=$ partial pressure at 30 °C. Furthermore, the rate-determining-step (rds) is the adsorption of D−$C_3^=$, since if decomposition of a surface intermediate were the rds, then the formation of D−$C_2^=$ and D−$C_4^=$ would lag the removal of the D−$C_3^=$ feed from the gas phase, which does not seem to occur. Replacement of D−$C_3^=$ with H−$C_3^=$ initially causes a perturbation in the flow that leads to a small increase in the formation of $D_2C{=}CH_2$ > $CH_2{=}CH_2$ > $CD_3CD{=}CH_2$. As the H−$C_3^=$ partial pressure increases, the transient $D_2C{=}CH_2$, $CH_3CH{=}CD_2$, and $CD_3CD{=}CH_2$ isotopomers are formed with the exact same time-resolved pattern, suggesting the same kinetic pattern (see Figure S3 in the Supporting Information). The formation of $CD_3CD{=}CHCH_3$ and $CD_3CD{=}CDCD_3$, however, was not observed. MS signals at m/z 29 and 31 were also observed and are primarily from cracking of $CH_3CH{=}CH_2$ in the MS. The MS m/z 29 and 31 signals could also be from $CH_2{=}CHD$ and $CHD{=}CD_2$ reaction products, but the time-dependent behavior of these signals followed that of $CH_3CH{=}CH_2$ and not of the labeled $D_2C{=}CH_2$. Thus, there is no evidence that significant $CH_2{=}CHD$ and $CHD{=}CD_2$ ethylene products were formed. The ratio of products containing $=CD_2$/$=CDCD_3$ during titration with H−$C_3^=$ is surprisingly ∼7, as indicated in Table 1. This suggests that the concentration of surface $=CD_2$ intermediates is significantly greater than that of surface $=CDCD_3$ intermediates during self-metathesis of D−$C_3^=$ at 30 °C.

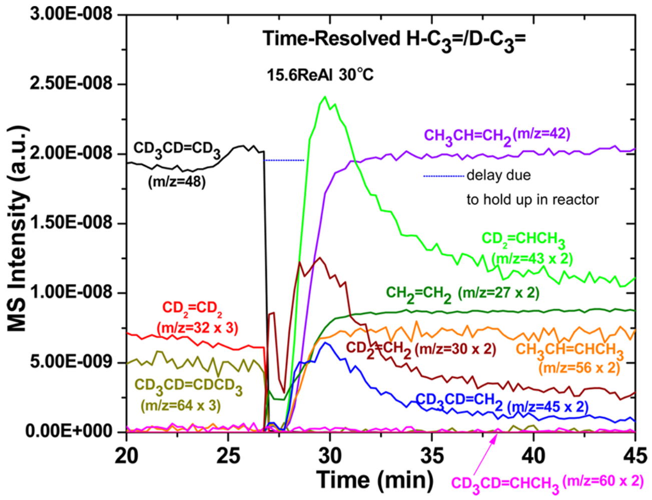


Figure 4. Reaction products from steady-state transient isotope kinetic analysis (SSITKA): catalyst equilibration with D−$C_3^=$ for 30 min followed by switch to H−$C_3^=$.

Subsequent H−$C_3^=$-TPSR studies from 30 to 200 °C titrates the strongly bound surface intermediates, yielding the isotopomers $CH_3CH{=}CD_2$ > $CD_2{=}CH_2$ > $CD_3CD{=}CH_2$, which are presented in Figure 5. The $=CD_2$/$=CDCD_3$ containing product ratio of ∼22 during TPSR (see Table 1) further indicates that surface $=CDCD_3$ intermediates are a minority surface intermediate. These findings suggest that surface $=CD_2$ species are the most abundant reaction intermediates during D−$C_3^=$ self-metathesis. The pronounced reaction between H−$C_3^=$ and strongly bound surface $=CD_2$ above 200 °C indicates that this is a preferred reaction pathway in this temperature range and is also reflected by the

DOI: 10.1021/acscatal.5b02233
ACS Catal. 2016, 6, 272−278

Table 1. Number of Surface Intermediates Determined for Titration Studies with the Supported 15.6% ReO_x/Al_2O_3 Catalyst[a]

adsorbate	titrant	reaction product monitored	30 °C[b]	TPSR[b]
$D-C_3^=$	$H-C_3^=$	$CD_3CD{=}CH_2$	0.2	0.4
		$CD_2{=}CH_2$	0.4	2.1
		$CD_2{=}CHCH_2$	1.0	7.3
		$CD_3CD{=}CHCH_3$	0.0	0.0

[a] Titration initially performed at 30 °C and continued with increasing temperature during TPSR. [b] Percentage of Re sites producing each product.

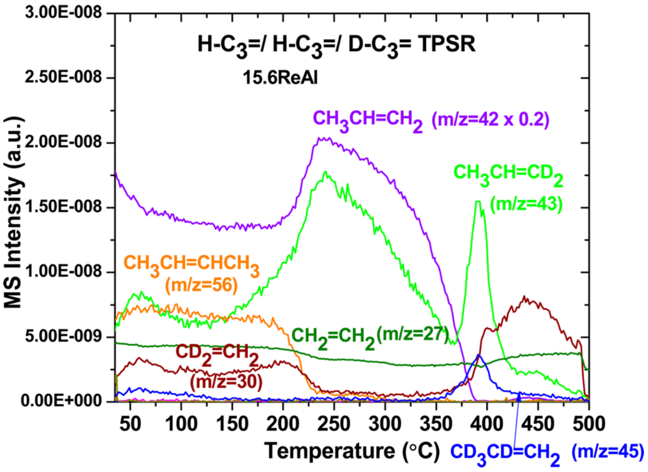


Figure 5. Reaction products from $H-C_3^=$-TPSR after 30 min exposure to $D-C_3^=$ at 30 °C followed by 30 min exposure to $H-C_3^=$ at 30 °C.

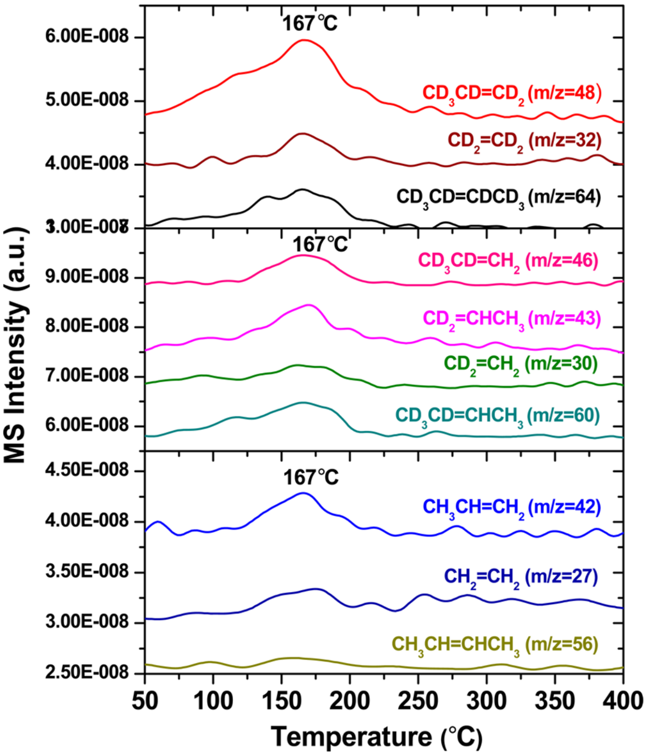


Figure 6. Isotope-labeled reaction products from Ar/C_3D_6(30 °C)/C_3H_6(100 °C)-TPSR.

simultaneous significant increase in formation of $H-C_3^=$. The titration results in Table 1 also demonstrate that more D-containing surface intermediates were titrated above room temperature than at room temperature (factor of ∼6 (84%/16%)). Between 30 and 200 °C, the formation rates of $H-C_2^=$ and $H-C_4^=$ are ∼1:1. Furthermore, the self-metathesis reaction rate shows a kinetic isotope effect (KIE) of $H-C_3^=/D-C_3^= \approx 1.96$. Although H−C/D−C bonds are not directly involved in the self-metathesis reaction, surprisingly, they appear to have an influence on the olefin metathesis transition state. Grubbs et al. also observed such an H−C/D−C isotope effect in the early stages of decadiene metathesis by the supported $CoO\text{-}MoO_3/Al_2O_3$ catalyst and attributed the isotope effect to formation of a surface π-allyl intermediate during the initiation stage, which is the precursor to the active system.[16]

3.3.2. Self-Metathesis of Surface Intermediates ($H-C_3^=$ + $D-C_3^=$). The self-metathesis of surface intermediates formed during propylene metathesis was also examined in the absence of gas-phase $C_3^=$. Self-metathesis of $H_3CCH{=}CH_2$ was initially conducted at 100 °C to equilibrate the catalyst with stable surface intermediates, then the catalyst was cooled to room temperature in flowing Ar, and finally $CD_3CD{=}CD_2$ was adsorbed at room temperature. Performing the TPSR experiment in flowing Ar assured that gas-phase propylene would minimally influence the surface reactions. Almost all isotopomer metathesis products were formed at high temperature, as shown in Figure 6. The D-containing products dominated because $D-C_3^=$ was adsorbed at 30 °C, which gave a higher surface concentration of intermediates than initial adsorption of $H-C_3^=$ at 100 °C. The major ethylene isotopomer products were $CD_2{=}CD_2$ and $CH_2{=}CD_2$, with only a minor amount of $CH_2{=}CH_2$ formed. For propylene, the major isotopomer products were $CD_3CD{=}CD_2$, $CD_3CD{=}CH_2$, and $CH_3CH{=}CD_2$ with only minor amounts of $CH_3CH{=}CH_2$. For 2-butene, the major isotopomer products were $CD_3CD{=}CDCD_3$, $CD_3CD{=}CHCH_3$, and $CH_3CH{=}CHCH_3$. All of the olefin products appear at the same reaction temperature (T_p = 167 °C), reflecting that breaking of C−H/C−D bonds does not take place during this olefin metathesis surface reaction at elevated temperatures, since such a rds would exhibit a kinetic isotope effect. This experiment nicely demonstrates that the surface $=CD_2/=CH_2$ and $=CDCD_3/=CHCH_3$ intermediates can readily undergo bimolecular reactions to form the olefin isotopomer products in the absence of gas-phase propylene.

The bimolecular surface kinetics for propylene self-metathesis in the absence of gas-phase propylene was confirmed with TPSR studies that varied the coverage of the surface intermediates. After adsorption of $C_3^=$ at 30 °C, the catalyst was briefly preheated to 50, 75, 100, or 125 °C to desorb a portion of the surface intermediates to vary their surface coverage. The resulting TPSR spectra are shown in Figure 7 and reveal a strong dependence of propylene formation kinetics upon the surface coverage. The decreasing T_p value with increasing surface coverage indicates second-order surface reaction kinetics (see section S5 in the Supporting Information for a detailed discussion and data analyses). The same exact trend was also found for production of ethylene and 2-butene, with all olefins appearing at the same T_p for a given coverage (see Figure S5 in the Supporting Information). This TPSR experiment reveals that surface $=CH_2$ and $=CHCH_3$ intermediates are also able to recombine by bimolecular reactions to form $C_2^=$, $C_3^=$, and $C_4^=$ metathesis reaction products in the absence of gas-phase propylene.

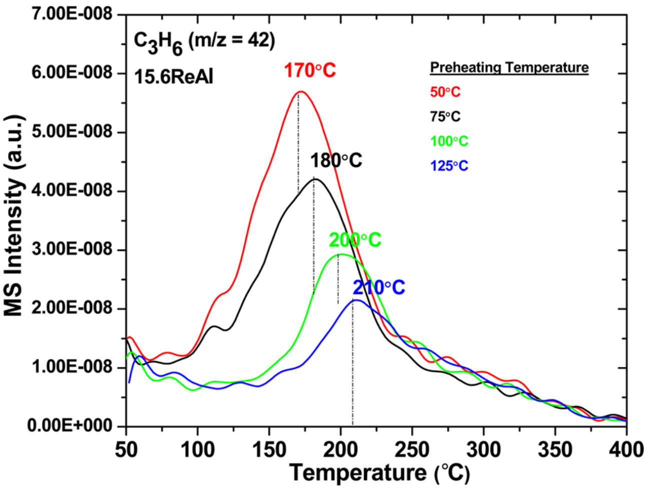


Figure 7. Self-metathesis of C_3H_6 in flowing Ar after C_3H_6 adsorption at 30 °C as a function of preheating temperature (50, 75, 100, and 125 °C) to control coverage of surface intermediates. The full experimental procedure can be found in section S1 in the Supporting Information. The C_2H_4 and C_4H_8 signals follow the same T_p values as C_3H_6 (see Figure S5 in the Supporting Information).

4. DISCUSSION

4.1. Nature of Catalytic Active Sites. In situ Raman spectroscopy reveals that two distinct isolated dioxo surface ReO_4 sites (ReO_4-I 1003 cm^{-1} and ReO_4-II ~1013 cm^{-1} in Figure 1) are present on the Al_2O_3 support[15] and that all olefins preferentially coordinate to the initial surface ReO_4-II sites. The extent of interaction increases with olefin size ($C_4^= > C_3^= > C_2^=$). This suggests that only the initial surface ReO_4-II sites anchored to the acidic surface hydroxyls of the alumina support become activated upon exposure to olefins and are the catalytically active sites for olefin metathesis.[15] The nature of the activated surface rhenia sites is elaborated upon below.

4.2. Surface Reaction Intermediates. The in situ IR spectra were previously presented and revealed that adsorbed $C_3^=$ π complexes are also present on the supported ReO_x/Al_2O_3 catalyst. The in situ IR spectra could not provide any insights about surface reaction intermediates because of the strong contributions to the IR signal from a surface propylene π complex and propylene adsorbed on the Al_2O_3 support.[17] The IR spectra, however, did demonstrate that the surface intermediates react and/or desorb by ~150 °C in the absence of gas-phase propylene.

The isotopic $D{-}C_3^= \rightarrow H{-}C_3^=$ switch experiment clearly indicates that both surface ${=}CD_2$ and $=CDCD_3$ intermediates are present on the catalyst during self-metathesis of $D{-}C_3^=$ (Figure 4). Similarly, surface $=CH_2$ and $=CHCH_3$ intermediates are present on the catalyst from adsorption of both $H{-}C_3^=$ and $D{-}C_3^=$ (Figure 6). The appearance of the isotopomer olefin products at several different temperatures during the isotopic switch-TPSR experiment suggests that multiple surface $=CD_2/=CH_2$ and $=CDCD_3/=CHCH_3$ intermediates are present that differ in their bonding strength to the catalytically active sites. The origin of the weakly and strongly bound surface intermediates is currently not fully understood: it is related to different surface rhenia oxidation states or surface intermediates with different bonding strengths. Surprisingly, the surface concentrations of the $=CD_2/=CH_2$ intermediates are significantly greater than those of the surface $=CDCD_3/=CHCH_3$ intermediates during self-metathesis of propylene. This indicates that surface $=CD_2/=CH_2$ intermediates are the most abundant reactive intermediates during propylene self-metathesis by supported ReO_x/Al_2O_3 catalysts. The greater surface concentration of $Re^*{=}CD_2$ in comparison to $Re^*{=}CDCD_3$ suggests that the reaction between surface $Re^*{=}CDCD_3$ and $Re^*{=}CDCD_3$ intermediates is just barely faster that the reaction between surface $Re^*{=}CD_2$ + $Re^*{=}CD_2$ intermediates, as previously reported for olefins with different lengths.[18,19]

4.3. Reaction Mechanism(s) and Kinetics. *4.3.1. First-Order Kinetics at Low Temperatures.* At low temperatures (30−70 °C), the catalyst surface has a high concentration of surface intermediates with the coverage of surface $=CH_2$ being greater than that of surface $=CHCH_3$. The first-order steady-state kinetics with regard to propylene partial pressure is a consequence of propylene adsorption being the rds. This conclusion is supported by the isotopic $D{-}C_3^= \rightarrow H{-}C_3^=$ switch, showing the direct dependence of $D{-}C_2^=$ and $D{-}C_4^=$ formation on the $D{-}C_3^=$ partial pressure (Figure 4) and the direct dependence of $CD_2{=}CH_2$, $CH_3CH{=}CD_2$, and $CD_3CD{=}CH_2$ on the $H{-}C_3^=$ partial pressure. In addition, the reaction rate dependence on the surface rhenia sites varies as $\sim[Re^*]^2$ (Figure 3), where Re* represents an activated, coordinatively unsaturated surface rhenia site. This suggests that the adsorption site consists of a dual site (requiring two adjacent surface Re* sites). These insights support the following forward reaction mechanism for the low-temperature self-metathesis of propylene, which dominates at low propylene conversions.

At steady-state and low temperatures, the surface is saturated with surface $CH_2{=}Re^*$ and $CH_3CH{=}Re^*$ intermediates resulting in

$$CH_3{-}CH{=}CH_2 + CH_2{=}Re^* + CH_3CH{=}Re^* \\ \rightarrow CH_2{=}Re^*{=}CH_2 + CH_3CH{=}Re^*{=}CHCH_3 \quad (1)$$

$$CH_2{=}Re^*{=}CH_2 \rightarrow Re^* + CH_2{=}CH_2 \quad (2)$$

$$CH_3CH{=}Re^*{=}CHCH_3 \rightarrow Re^* + CH_3CH{=}CHCH_3 \quad (3)$$

The molecular details of the surface intermediates in eqs 2 and 3, as well as the other reaction pathways, are not kinetically significant since the rds is the adsorption step (eq 1). Consequently, the reaction rate kinetic expression is given by

$$\text{rate} = k_{rds}[C_3^=][CH_2{=}Re^*][CH_3CH{=}Re^*] \quad (4)$$

Assuming that the surface concentrations of the surface $[CH_2{=}Re^*{=}CH_2]$ and $[CH_3CH{=}Re^*{=}CHCH_3]$ intermediates are small with the dominant surface intermediates being the activated sites, then

$$[Re^*]_0 = [CH_2{=}Re^*] + [CH_3CH{=}Re^*] \quad (5)$$

Assuming that the ratio of surface intermediates is constant since propylene always reacts with each of the two surface intermediates during the metathesis reaction according to eq 1

$$[CH_2{=}Re^*]/[CH_3CH{=}Re^*] = n \ (n > 1) \quad (6)$$

which leads to

$$\text{rate} = (k_{rds}/n)[C_3^=][Re^*]_0^{\,2} = k'_{rds}[C_3^=][Re^*]_0^{\,2} \quad (7)$$

The absence of first-order dependence on the number of activate surface sites, rate ≈ $[Re^*]_0$, indicates that the decomposition of the surface intermediates (eqs 2 and 3) is not the rate-determining step at low temperatures.

4.3.2. Second-Order Kinetics at High Temperatures. The steady-state kinetic studies reveal that the high-temperature reaction pathway proceeds via a bimolecular mechanism involving reaction between two surface species. The apparent reaction order of 1.8 rather than 2 in propylene partial pressure at elevated temperatures may be reflecting the minor contribution of the first-order reaction kinetics at the higher reaction temperature (see more below on this additional pathway). The steady-state second-order reaction kinetics, however, can only be derived by reaction between two adsorbed $C_3^=$ molecules, since a bimolecular reaction between surface Re*═CH$_2$ and surface Re*═CHCH$_3$ does not give rise to second-order kinetics (see below). This suggests that the surface intermediates present on the catalyst at high temperature are adsorbed $C_3^=$ π complexes and that the high-temperature reaction pathway proceeds via a four-centered intermediate proposed in some of the early metathesis studies.[8,9,11,12] According to this bimolecular reaction mechanism, the olefins can exchange their individual half-components to yield the metathesis products. The kinetics for the second-order self-metathesis of propylene are derived by assuming reaction between two surface $C_3^=$ π complexes:

$$C_3^= + Re^* \rightleftharpoons Re^*{-}C_3^= \quad K_{ads} \tag{8}$$

$$\begin{aligned}Re^*{-}C_3^= + Re^*{-}C_3^= &\rightarrow 2Re^* + CH_2{=}CH_2\\ &+ CH_3CH{=}CHCH_3 \quad k_{rds}\end{aligned} \tag{9}$$

with the bimolecular reaction step eq 9 being the rds, which gives the rate expression

$$\text{rate} = k_{rds}[Re^*{=}C_3^=]^2 \tag{10}$$

From the equilibrium step eq 8

$$[Re^*{=}C_3^=] = K_{ads}[Re^*][C_3^=] \tag{11}$$

From the surface site balance

$$[Re^*]_0 = [Re^*] + [Re^*{=}C_3^=] \tag{12}$$

with $[Re^*]_0$ representing all the activated surface sites, $[Re^*]$ representing vacant sites, and $[Re^*{=}C_3^=]$ representing the sites occupied by adsorbed $C_3^=$. At elevated temperatures, the surface coverage of the surface intermediates is low, as previously shown by in situ IR spectroscopy.[17] Consequently

$$[Re^*]_0 = [Re^*] \tag{13}$$

which gives

$$\text{rate} = k_{rds}\{K_{ads}[C_3^=][Re^*]_0\}^2 \tag{14}$$

The second-order kinetics suggests that at high temperatures the reaction involves two adsorbed $C_3^=$ π complexes and proceeds via a four-centered intermediate. Aldag et al. previously proposed that the ethylene self-metathesis reaction at elevated temperatures involves two mobile adsorbates that form four C-membered surface intermediates, resulting in second-order kinetics with respect to the adsorbate concentration.[8]

4.3.3. Self-Metathesis of Surface Intermediates at High Temperatures. The TPSR studies in flowing Ar reveal that the surface CH$_2$═Re* and CH$_3$CH═Re* intermediates from propylene adsorption also recombine above ∼100 °C to form all three olefin products:

$$CH_2{=}Re^* + CH_2{=}Re^* \rightleftharpoons CH_2{=}CH_2 + 2Re^* \tag{15}$$

$$\begin{aligned}&CH_3CH{=}Re^* + CH_3CH{=}Re^*\\ &\quad\rightleftharpoons CH_3CH{=}CHCH_3 + 2Re^*\end{aligned} \tag{16}$$

$$CH_2{=}Re^* + CH_3CH{=}Re^* \rightleftharpoons CH_3CH{=}CH_2 + 2Re^* \tag{17}$$

These surface bimolecular recombination pathways also occur above 100 °C and probably are also contributing to the overall reaction kinetics during steady-state propylene self-metathesis at elevated temperatures. In the presence of gas-phase $C_3^=$

$$C_3H_6 + 2Re^* \rightleftharpoons CH_2{=}Re^* + CH_3CH{=}Re^* \tag{18}$$

$$K_{ads} = [CH_3CH{=}Re^*][CH_2{=}Re^*]/[C_3H_6][Re^*]^2 \tag{19}$$

$$\begin{aligned}&\text{surface site balance } [^*]_0\\ &\quad= [Re^*] + [CH_2{=}Re^*] + [CH_3CH{=}Re^*]\end{aligned} \tag{20}$$

At high temperatures, surface intermediate coverage is low and

$$[Re^*]_0 \approx [Re^*] \tag{21}$$

From adsorption equilibrium (eq 19)

$$[CH_2{=}Re^*][CH_3CH{=}Re^*] = K_{ads}[C_3H_6][Re^*]^2 \tag{22}$$

$$\begin{aligned}\text{rate} &= k_{rds}[CH_2{=}Re^*][CH_3CHRe^*]\\ &= k_{rds}K_{ads}[C_3H_6][Re^*]_0{}^2\end{aligned} \tag{23}$$

This bimolecular reaction involving recombination of surface intermediates was earlier proposed by Spinicci et al. from TPD studies of propylene desorption.[10] The bimolecular recombination of surface intermediates cannot be dominant at elevated temperatures, since it would give a reaction order of 1 with respect to propylene partial pressure, which is much lower than the measured reaction order of ∼1.8. The steady-state apparent reaction order of slightly less than 2, ∼1.8, may reflect the partial contribution of this surface bimolecular reaction pathway at elevated temperatures.

The bimolecular recombination of surface intermediates for olefin metathesis has been previously proposed for both supported metal oxide heterogeneous and homogeneous systems.[8−12,20] The current kinetic study demonstrates that, although this bimolecular reaction pathway does take place at elevated temperatures for supported metal oxide catalysts, this reaction pathway is not the dominant reaction pathway at elevated temperatures.

5. CONCLUSIONS

The olefins preferentially interact with the surface ReO$_4$-II sites on acidic sites of the alumina support. The surface Re*═CH$_2$ and Re*═CHCH$_3$ intermediates are present on activated supported ReO$_x$/Al$_2$O$_3$ catalysts, with the Re*═CH$_2$ intermediate being dominant. The propylene metathesis reaction by supported ReO$_x$/Al$_2$O$_3$ catalysts occurs via multiple reaction pathways that depend on reaction temperature. At low temperatures (<100 °C), the catalyst is saturated with surface

Re*═CH_2 and Re*═$CHCH_3$ intermediates and the rds involves adsorption/reaction of gas-phase propylene with the surface intermediates (rate ≈ $[C_3^=]$). At elevated temperatures (>100 °C), the catalyst exhibits low coverage of surface intermediates and the rds proceeds via recombination of two molecularly adsorbed $C_3^=$ π complexes (rate ≈ $[C_3^=]^2$). To a lesser extent, bimolecular recombination of surface Re*═CH_2 and Re*═$CHCH_3$ intermediates also contributes to propylene self-metathesis at elevated temperatures (rate ≈ $[C_3^=]^1$). The presence of multiple reaction mechanisms at different temperatures accounts for the variation of the reaction orders in propylene partial pressure with reaction temperature.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b02233.

> Additional steady state and TPSR graphs (Figures S1−S5) with detailed analysis (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for I.E.W.: iew0@lehigh.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.L. and I.E.W. acknowledge financial support from U.S. DOE Basic Energy Sciences (Grant No. FG02-93ER14350).

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