Determination of Number of Activated Sites Present during Olefin Metathesis by Supported ReO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} Catalysts

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1. INTRODUCTION

The number of activated surface rhenia sites present during olefin metathesis by supported rhenia/Al\textsubscript{2}O\textsubscript{3} catalysts has been under debate in the catalysis literature for many years.\textsuperscript{1–8} Some studies reported the number of activated rhenia sites to only be \(\sim 1\text{−}2\%\) of the total supported Re atoms after activation with olefins at room temperature and evacuation for 1−6 h.\textsuperscript{1,2,8} In contrast, \(\sim 35\%\) of the total supported rhenia sites have concluded to be activated by olefins at room temperature after 2 h of evacuation on supported rhenia/Al\textsubscript{2}O\textsubscript{3} catalysts prepared in a hydrochloric acid medium.\textsuperscript{3} Adsorption of \(^{13}\text{C}_3\text{=}\) on supported (CH\textsubscript{3})\textsubscript{3}ReO\textsubscript{3}/alumina followed by evacuation and titration at room temperature with C\textsubscript{2}\text{=} gave \(\sim 15\%\) activated rhenia sites.\textsuperscript{7} Other studies estimated the number of activated rhenia sites using kinetic models and concluded that less than 1% of the sites become activated at 25−95 °C.\textsuperscript{4,5} The complexity and assumptions of these kinetic models allows for fitting of the data and the active Re site density, but the results greatly depend on assumptions made to derive the mathematical models. An earlier study employed NO poisoning of activated supported rhenia/Al\textsubscript{2}O\textsubscript{3} catalysts to determine the number of activated rhenia sites, by measuring the consumption of NO, and found that less than 0.3% rhenia sites were activated.\textsuperscript{6} This approach, however, ignores the fact that the activated supported rhenia/Al\textsubscript{2}O\textsubscript{3} catalyst contains surface intermediates coordinated to the activated rhenia sites that would block chemisorption of NO. The lack of consensus in the literature about the number of activated surface rhenia sites on alumina for olefin metathesis is most likely associated with the different catalyst syntheses, site counting methodologies, surface rhenia coverage, and experimental conditions (e.g., temperature, pressure, evacuation time, etc.).

The objective of this study is to resolve this debate by determining the number of activated surface rhenia sites on alumina in the presence of olefins under different experimental conditions. Quantification of the number of surface reaction intermediates present during activation by olefins was achieved by olefin titration as a function of experimental variables (surface rhenia coverage, temperature, pressure, and evacuation time). To quantify the number and reactivity of the surface intermediates present on the catalyst after olefin adsorption, 2-butene was initially adsorbed and then titrated with ethylene to yield propylene. An advantage of this protocol is that physically adsorbed 2-butene on the catalyst would not participate in the metathesis reaction to form propylene. The titration studies revealed that there are two types of surface reaction intermediates, weakly bound and strongly bound. The weakly bound surface intermediates are both easily desorbed and titrated with olefins at room temperature. The strongly bound surface intermediates can only be titrated and reacted/desorbed at elevated temperatures (>100 °C).

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis. The supported ReO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} and ReO\textsubscript{x}/TaO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts were prepared by impregnation of 65−70 wt % aqueous solution of perrhenic acid, HReO\textsubscript{4}.
(Sigma-Aldrich) and toluene solution of tantalum ethoxide (Ta-(OC₂H₅)₅, Alfa Aesar, 99.999%) onto the Al₂O₃ support (Engelhard batch no. H5433C), respectively. The rhenia loading is expressed as wt % ReO₄ on Al₂O₃, and the notation 15.6 ReAl corresponds to 15.6 wt % ReO₄/Al₂O₃. The notation Re/Ta/Al refers to the Ta-promoted ReAl catalyst. The full procedure of incipient-wetness impregnation, drying and calcination can be found in a previous publication.⁹

2.2. Titration and Temperature-Programmed Surface Reaction (TPSR) Spectroscopy. The titration and temperature-programmed surface reaction experiments were performed using an Altamira Instruments (AMI-200) system. The outlet gases were connected to an online Dymaxicon Dycor mass spectrometer (DME200MS) and a TCD detector for analysis. Typically, ~100–300 mg of catalyst was loaded into the U-tube reactor. Blank tests with known concentrations of olefins were run for the mass spectrometer (MS) calibration before the experiments. The signals for the mass spectra were also normalized with catalyst weight for comparison. The MS m/z (mass to charge) values used for detection of various reactants were as follows: propylene (m/z = 42), ethylene (m/z = 28), 2-butene (m/z = 56), acetaldehyde (m/z = 43), formaldehyde (m/z = 30), carbon dioxide (m/z = 44), acetone (m/z = 58), oxygen (m/z = 32), and water (m/z = 18). The MS cracking patterns were carefully determined with blank runs using calibration gases and used to correct for the background MS signals. The catalysts were initially dehydrated in 10 vol % O₂/Ar (Air Gas, UHP certified gas mixture) at 500 °C (30 mL/min) for 30 min and cooled in flowing Ar (30 mL/min) (Air Gas, UHP certified gas mixture) to the experimental conditions of interest. Catalyst activation was performed by flowing 1 vol % C₂H₄ (trans-2-butene)/Ar (30 mL/min) (Praxair, Purity 99.9%), and titration of the surface intermediates were performed with flowing 1 vol % C₂H₂ ethylene)/Ar (Praxair, Purity 99.9 vol %) to yield C₂H₂. After the constant temperature titration, the remaining surface intermediates were reacted during TPSR (10 °C/min) in flowing 1 vol % C₂H₂/Ar up to 500 °C. The specific experimental protocol for each experiment is given in SI 1.1–1.3.

3. RESULTS

3.1. Effect of Evacuation/Flush Time between Activation by C₂H₂ and Titration with C₂H₂. Titration of the surface intermediate(s) formed by 2-C₄H₈ activation of the supported 15.6% ReO₄/Al₂O₃ catalyst with C₂H₂ produces propylene at two temperature ranges, 30 °C and ~50–150 °C, as shown in Figure 1. The two temperature ranges suggest that two distinct types of surface intermediates are present on the catalyst after 2-butene adsorption, weakly and strongly bound surface intermediates. Increasing the time between C₂H₂ adsorption and C₂H₂ titration with an Ar purge (from 0 to 240 min) dramatically decreased the number of weakly bound surface intermediates (Figure 1a) but does not affect the number of strongly bound surface intermediates (Figure 1b). Without an Ar purge between C₂H₂ adsorption and C₂H₂ titration (0 min), the ratio of propylene produced at low temperature to high temperature was ~7.5 (corresponding to a total C₂H₂/Re ratio of 0.087). After 240 min of an Ar purge between C₂H₂ adsorption and C₂H₂ titration, the ratio of propylene produced at low temperature to high temperature was only ~0.7 (corresponding to a C₂H₂/Re ratio of 0.008). This demonstrates that the weakly adsorbed intermediates at 30 °C are in equilibrium with the gas-phase 2-butene and that removal of C₂H₂ from the gas phase by an Ar purge produces additional gas-phase 2-butene from the surface intermediates on the catalyst.

In addition to the production of propylene during ethylene titration of the surface intermediates resulting from 2-butene activation, desorption of C₄H₂ also takes place. Upon switching from a C₂H₂/Ar flow to an Ar flow, C₂H₂ desorption continues for several minutes reflecting the equilibrium between the surface intermediates and gas-phase C₂H₂ (see Figure S1). A minor amount of C₄H₂ desorbs again from the catalyst upon switching to a flow of C₂H₂/Ar (see Figure S1). This is especially evident when C₂H₂ is introduced after flowing inert Ar, and the amount of desorbed C₂H₂ increases (see 30, 60, and 240 min experiments of Figure S1). Additional modest amounts of C₄H₂ also appear at higher temperatures during TPSR (indicated by an * in Figure S1) and may be related to adsorption of C₄H₂ product during the titration (self-metathesis of propylene forms C₂H₂ and C₂H₂). Desorption of C₄H₂ upon exposure to C₂H₂ was not observed for the Refree Al₂O₃ support, and thus, the desorbed C₄H₂ is associated with the surface ReO₄ sites.

These new findings indicate that the accepted titration method significantly undercounts the number of surface reaction intermediates formed by olefin activation and metathesis of supported ReO₄/Al₂O₃ catalysts.

3.2. Contribution of Propylene Formed by Cross-Metathesis of C₂H₂ and C₄H₂. The simultaneous presence of 2-butene and ethylene in the gas phase in the absence of an Ar
purge at 30 °C necessitated determining the catalytic activity between these two gas-phase reactants by the supported 15.6% ReO4/Al2O3 catalyst. The simultaneous introduction of 2-butene (1 vol % C4H6/Ar) and ethylene (1 vol % C2H4/Ar) in the reactor only accounted for a maximum of ~14% of the propylene formed during the C2H4/C4H6 titration experiment without an Ar purge. The actual contribution is actually much lower since the gas-phase concentrations of C2H4 and C4H6 are much lower when both gases are present during the titration measurement. This shows that the propylene formed by C2H4 titration of the surface intermediates from C4H6 adsorption dominates the titration results even when both gases are present.

### 3.3. Effect of C2H4 Partial Pressure on Number of Surface Reaction Intermediates.

The influence of the titrant C2H4 partial pressure on production of C4H6 by reaction with the surface intermediates formed from initial C4H6 adsorption is shown in Figure S2. The number of propylene molecules produced from the weakly adsorbed intermediates at 30 °C monotonically increases with the gas-phase concentration of C2H4 (0, 0.33, and 0.67 vol %) and saturating at ~1 vol % C2H4. Quantitative analysis indicates that the number of C4H6 molecules formed varies as ~ first-order in C2H4 partial pressure for the 0 to 0.67 vol % C2H4 concentration range (Figure S3). The number of C4H6 molecules produced from the strongly bound surface intermediates between 50 and 150 °C, however, is relatively constant and independent of the C2H4 partial pressure. The different responses of the surface intermediates to ethylene partial pressures at low and high temperatures again reflects the presence of two distinct types of surface reaction intermediates that are weakly and strongly adsorbed. The reported titration studies employed C2H4 titrant partial pressures sufficiently high where the number of titrated surface intermediates is independent of C2H4 partial pressure.

The amount of C4H6 desorbing during the titration is also dependent on C2H4 partial pressure (see Figure S4). This trend suggests that the desorbing C4H6 is mostly related to desorption of weakly bound surface reaction intermediates as increasing C2H4 partial pressure consumes more of these intermediates. The faster C4H6 elution times with increasing C2H4 partial pressure reflects displacement of weakly bound surface intermediates in the presence of gas-phase C2H4 and supports the conclusion that this 2-butene probe results from reaction/desorption of surface reaction intermediates from the catalyst.

### 3.4. Effect of Activation Temperature on Number of Surface Reaction Intermediates.

The influence of C4H6 activation temperature on the number of C4H6 molecules produced during C2H4 titration is presented in Figure S5. The number of C4H6 molecules formed at 30 °C decreases as the C4H6 activation temperature is raised, especially above 70 °C (Figure S5a). This reflects the facile reaction among the surface intermediates to yield C4H6 and the resulting lower coverages of the surface intermediates at elevated temperatures during the catalyst activation stage. The number of C4H6 molecules formed during C2H4 titration from the strongly bound surface intermediates at higher temperatures (~50–250 °C) was also a strong function of the initial activation temperature (Figure S5b). The number of surface reaction intermediates titrated with ethylene to produce propylene at low and high temperatures as a function of C4H6 activation temperature is plotted in Figure S6. The number of C4H6 molecules formed from the strongly bound intermediates initially increased with the activation temperature of 70 °C and then sharply diminished to almost zero after the 300 °C activation. The higher temperatures required for the formation of C4H6 indicate that even more strongly bound surface intermediates are created from higher C4H6 pretreatment temperatures. For the most part, the reported titration studies in the literature were performed between 30 and 70 °C, which means that the titration numbers were only minimally affected by the different activation temperatures1–3,8

### 3.5. Effect of ReO4 Loadings on Number of Surface Reaction Intermediates.

The time-dependent evolution of C4H6 molecules produced from C2H4 titration of weakly bound surface intermediates formed from C4H6 activation at 30 °C are shown in Figure 2 as a function of ReO4 loading on alumina.

Figure 2. Evolution of C4H6 during C2H4 titration of surface intermediates resulting from C4H6 adsorption (60 min at 30 °C) as a function of ReO4 loading and time at 30 °C (x-axis represents the time of C2H4 flow).

For most of the catalysts, almost all of the surface intermediates created by C4H6 activation react within 10 min of C2H4 titration at 30 °C. The strongly bound surface intermediates require elevated temperatures for their reaction as shown in Figures 1(b), S2(b) and S5(b).

The total number of C4H6 molecules produced by C2H4 titration at 30 °C monotonically increases with rhena loading on alumina (Figure 3-right axis). The percentage ratio of C4H6 molecules produced to surface ReO4 sites, however, strongly depends on surface rhena coverage (Figure 3-left axis). For low rhena loadings (<7% ReO4), the C4H6/Re percentage ratio monotonically increases with surface rhena coverage on alumina. At high rhena loadings (>7% ReO4), the C4H6/Re percentage ratio becomes relatively independent of surface rhena coverage on alumina. The C4H6/Re percentage ratio is further increased by a factor of 1.4 (7.4% for 9.4ReAl vs. 10% for 9.4ReTaAl) by introduction of the surface TaO2 promoter that blocks formation of inactive surface ReO4–I sites (elaborated upon below).9

### 4. DISCUSSION

#### 4.1. Number of Activated Surface Rhena Sites on Alumina. Titration Methods.

The new findings demonstrate that the number of reactive surface intermediates on supported ReO4/Al2O3 catalysts measured by initial activation with C4H6 and subsequent titration with C2H4 is not a constant value and is strongly dependent on experimental variables. The sensitivity to experimental conditions is related to the presence of both weakly and strongly adsorbed surface intermediates with the surface coverage of the former strongly dependent on the
Experimental variables. Evaporation or flushing decreases the number of surface reaction intermediates by ∼90% because of the equilibrium that exists between the surface intermediates and gas-phase olefins. This occurs because evaporation or flushing removes the gas-phase molecules, which forces the surface intermediates to establish equilibrium with the gas phase by reacting and desorbing into the gas-phase olefins. This accounts for the extremely low number of titrated surface intermediates reported by the studies employing the evaporation or flushing step\(^1\) and the order of magnitude higher number of titrated surface intermediates in studies not evaporating or flushing the catalyst after adsorption of the first olefin.\(^2,3\)

Furthermore, not all surface intermediates are titrated at low temperatures because of their recombination/desorption into the gas phase during titration and the presence of strongly bound surface intermediates that are sluggishly titrated at low temperatures. Titration is an indirect method that is an ensemble averaging method that assumes (i) each activated surface rhenium site on alumina contains one surface intermediate, (ii) only one type of surface intermediate is present, (iii) all surface intermediates can be titrated at low temperature, and (iv) does not take into consideration possible lateral interactions between the surface intermediates that would decrease the intermediate/Re ratio. Consequently, the accepted titration method of the surface intermediates with olefins at room temperature as a reflection of the activated surface rhenium sites is an indirect counting method that is flawed by many unanticipated issues that significantly cloud the resulting quantitative numbers.

### 4.2. Number of Activated Surface Rhenium Sites on Alumina. Spectroscopic Method.

Direct monitoring with in situ Raman spectroscopy reveals that there are two surface rhenium sites anchored at basic (ReO\(_4\)--I) and acidic (ReO\(_4\)--II) surface hydroxyls of the Al\(_2\)O\(_3\) support.\(^9\) Operando Raman spectroscopy studies, however, demonstrate that propylene selectively interacts with the surface ReO\(_4\)--I sites and does not interact with the surface ReO\(_4\)--II sites.\(^7\) Consequently, a small fraction of surface rhenium sites is activated during olefin metathesis below ∼7% ReO\(_4\)/Al\(_2\)O\(_3\) (0.98 Re/nm\(^2\)), where the noninteracting surface ReO\(_4\)--I sites dominate, whereas the majority of surface rhenium sites is activated above ∼5% ReO\(_4\)/Al\(_2\)O\(_3\) (0.74 Re/nm\(^2\)), where the interacting surface ReO\(_4\)--II sites dominate. When formation of surface ReO\(_4\)--I sites is blocked by the surface TaO\(_x\) promoter, only surface ReO\(_4\)--II sites are present on the alumina support and 100% of the surface rhenium sites become activated because they are bonding to the adsorbed hydrocarbons.\(^3\)

By definition, the number of sites (Ns) is represented by the number of exposed surface sites.\(^10\) This suggests that the correct Ns value to use for calculating the reaction TOF (turnover frequency: reactant molecules converted per activated Re site per second) is not the number of titrated surface intermediates, but the number of all surface ReO\(_4\) sites initially present on the Al\(_2\)O\(_3\) support. Given that operando Raman spectroscopy revealed that only the surface ReO\(_4\)--II sites interact with olefins during metathesis,\(^9\) a more appropriate value for Ns would be the number of surface ReO\(_4\)--II sites. A fraction of the surface ReO\(_4\)--II sites, however, may only contain surface intermediates that react at low temperatures such as 30 °C, as shown by Figure 1. Furthermore, examination of the reported titration studies in the literature reveals that most of the publications employed supported rhenium/alumina catalysts with surface rhenium coverages containing high concentrations of the noninteracting surface ReO\(_4\)--I sites.\(^9\) The high fraction of surface ReO\(_4\)--I sites in many of these studies further contributed to determination of low C\(_4^+\)/Re values.

### 5. CONCLUSIONS

In conclusion, the number of surface rhenium sites on alumina participating in olefin metathesis is dependent on the surface rhenium coverage on alumina. At low surface rhenium loadings (<0.98 Re/nm\(^2\)), noninteracting surface ReO\(_4\)--I sites dominate. At high surface rhenium loading (>0.74 Re/nm\(^2\)), interacting surface ReO\(_4\)--II dominate. Consequently, the proper value for the number of surface rhenium sites (Ns) participating in olefin metathesis is the total number of surface ReO\(_4\)--II sites. The accepted olefin titration method underestimates the number of surface reaction intermediates by factors of 10\(^{-2}\)--10\(^{-3}\) because of many invalid assumptions. These new fundamental insights finally resolve the long-standing debate about the number of surface rhenium sites on alumina participating in the catalytic olefin metathesis reaction.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01597.

Listings of experimental details and figures S1–S6 (PDF)

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### Notes

The authors declare no competing financial interest.

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