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Determination of Number of Activated Sites Present during Olefin Metathesis by Supported ReO_x/Al_2O_3 Catalysts

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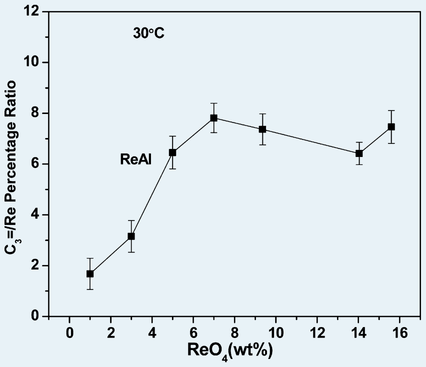
Supporting Information

ABSTRACT: The number of surface rhenia sites on alumina participating in olefin metathesis, usually counted by chemical titration of surface reaction intermediates with olefins, has been debated for several decades. The current olefin titration measurements, however, demonstrate that the number of reactive surface intermediates on supported rhenia/alumina catalysts is strongly dependent on the experimental variables. The new findings reveal that the accepted titration procedures significantly undercount the number of activated surface rhenia sites upon exposure to olefins by ~10^1−10^2 because of invalid assumptions.



KEYWORDS: *rhenia, alumina, sites, olefin metathesis, titration, Raman*

1. INTRODUCTION

The number of activated surface rhenia sites present during olefin metathesis by supported rhenia/Al_2O_3 catalysts has been under debate in the catalysis literature for many years.[1−8] Some studies reported the number of activated rhenia sites to only be ~1−2% of the total supported Re atoms after activation with olefins at room temperature and evacuation for 1−6 h.[1,2,8] In contrast, ~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_2O_3 catalysts prepared in a hydrochloric acid medium.[3] Adsorption of $^{13}C_3^=$ on supported $(CH_3)_3ReO_3$/alumina followed by evacuation and titration at room temperature with $C_2^=$ gave ~15% activated rhenia sites.[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.[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_2O_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.[6] This approach, however, ignores the fact that the activated supported rhenia/Al_2O_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_x/Al_2O_3 and $ReO_x/TaO_x/Al_2O_3$ catalysts were prepared by impregnation of 65−70 wt % aqueous solution of perrhenic acid, $HReO_4$

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(Sigma-Aldrich) and toluene solution of tantalum ethoxide (Ta-$(OC_2H_5)_5$, Alfa Aesar, 99.999%) onto the Al_2O_3 support (Engelhard batch no. H5433C), respectively. The rhenia loading is expressed as wt % ReO_4 on Al_2O_3, and the notation 15.6 ReAl corresponds to 15.6 wt % ReO_4/Al_2O_3. 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 ($m/z = 27$), 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 % O_2/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 % $C_4^=$ (trans-2-butene)/Ar (30 mL/min) (Praxair, Purity 99.9%), and titration of the surface intermediates were performed with flowing 1 vol % $C_2^=$ (ethylene)/Ar (Praxair, Purity 99.9 vol %) to yield $C_3^=$. After the constant temperature titration, the remaining surface intermediates were reacted during TPSR (10 °C/min) in flowing 1 vol % $C_2^=$/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 $C_4^=$ and Titration with $C_2^=$. Titration of the surface intermediate(s) formed by 2-$C_4^=$ activation of the supported 15.6% ReO_4/Al_2O_3 catalyst with $C_2^=$ 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 $C_4^=$ adsorption and $C_2^=$ 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 $C_4^=$ adsorption and $C_2^=$ titration (0 min), the ratio of propylene produced at low temperature to high temperature was ∼7.5 (corresponding to a total $C_3^=$/Re ratio of 0.087). After 240 min of an Ar purge between $C_4^=$ adsorption and $C_2^=$ titration, the ratio of propylene produced at low temperature to high temperature was only ∼0.7 (corresponding to a $C_3^=$/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 $C_4^=$ from the gas phase by an Ar purge produces additional gas-phase 2-butene from the surface intermediates on the catalyst.

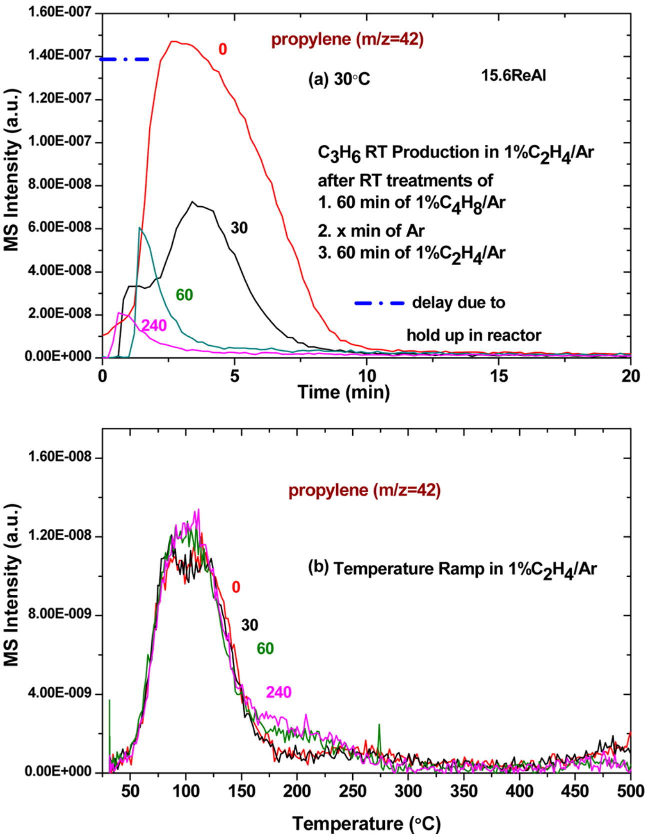

Figure 1. Production of $C_3^=$ from $C_2^=$ titration of surface intermediates resulting from $C_4^=$ activation (1 vol % $C_4^=$/Ar for 60 min at 30 °C) of the supported 15.6ReAl catalyst as a function of Ar flushing time (0−240 min) between $C_4^=$ adsorption and $C_2^=$ titration (1 vol %/Ar), (a) as a function of time at 30 °C (*x*-axis corresponds to the time of $C_2^=$ flow) and (b) during temperature-programmed surface reaction (TPSR) spectroscopy in flowing 1 vol % $C_2^=$/Ar.

In addition to the production of propylene during ethylene titration of the surface intermediates resulting from 2-butene activation, desorption of $C_4^=$ also takes place. Upon switching from a $C_4^=$/Ar flow to an Ar flow, $C_4^=$ desorption continues for several minutes reflecting the equilibrium between the surface intermediates and gas-phase $C_4^=$ (see Figure S1). A minor amount of $C_4^=$ desorbs again from the catalyst upon switching to a flow of $C_2^=$/Ar (see Figure S1). This is especially evident when $C_2^=$ is introduced after flowing inert Ar, and the amount of desorbed $C_4^=$ increases (see 30, 60, and 240 min experiments of Figure S1). Additional modest amounts of $C_4^=$ also appear at higher temperatures during TPSR (indicated by an * in Figure S1) and may be related to adsorption of $C_3^=$ product during the titration (self-metathesis of propylene forms $C_4^=$ and $C_2^=$). Desorption of $C_4^=$ upon exposure to $C_2^=$ was not observed for the Refree Al_2O_3 support, and thus, the desorbed $C_4^=$ is associated with the surface ReO_x 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 ReO_x/Al_2O_3 catalysts.

3.2. Contribution of Propylene Formed by Cross-Metathesis of $C_2^=$ and $C_4^=$. 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% ReO_4/Al_2O_3 catalyst. The simultaneous introduction of 2-butene (1 vol % $C_4^=$/Ar) and ethylene (1 vol % $C_4^=$/Ar) in the reactor only accounted for a maximum of ~14% of the propylene formed during the $C_2^=/C_4^=$ titration experiment without an Ar purge. The actual contribution is actually much lower since the gas-phase concentrations of $C_2^=$ and $C_4^=$ are much lower when both gases are present during the titration measurement. This shows that the propylene formed by $C_2^=$ titration of the surface intermediates from $C_4^=$ adsorption dominates the titration results even when both gases are present.

3.3. Effect of $C_2^=$ Partial Pressure on Number of Surface Reaction Intermediates. The influence of the titrant $C_2^=$ partial pressure on production of $C_3^=$ by reaction with the surface intermediates formed from initial $C_4^=$ 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 $C_2^=$ (0, 0.33, and 0.67 vol %) and saturating at ~1 vol % $C_2^=$. Quantitative analysis indicates that the number of $C_3^=$ molecules formed varies as ~ first-order in $C_2^=$ partial pressure for the 0 to 0.67 vol % $C_2^=$ concentration range (Figure S3). The number of $C_3^=$ molecules produced from the strongly bound surface intermediates between 50 and 150 °C, however, is relatively constant and independent of the $C_2^=$ 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 $C_2^=$ titrant partial pressures sufficiently high where the number of titrated surface intermediates is independent of $C_2^=$ partial pressure.

The amount of $C_4^=$ desorbing during the titration is also dependent on $C_2^=$ partial pressure (see Figure S4). This trend suggests that the desorbing $C_4^=$ is mostly related to desorption of weakly bound surface reaction intermediates as increasing $C_2^=$ partial pressure consumes more of these intermediates. The faster $C_4^=$ elution times with increasing $C_2^=$ partial pressure reflects displacement of weakly bound surface intermediates in the presence of gas-phase $C_2^=$ and supports the conclusion that this 2-butene product 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 $C_4^=$ activation temperature on the number of $C_3^=$ molecules produced during $C_2^=$ titration is presented in Figure S5. The number of $C_3^=$ molecules formed at 30 °C decreases as the $C_4^=$ activation temperature is raised, especially above 70 °C (Figure S5a). This reflects the facile reaction among the surface intermediates to yield $C_4^=$ and the resulting lower coverages of the surface intermediates at elevated temperatures during the catalyst activation stage. The number of $C_3^=$ molecules formed during $C_2^=$ 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 $C_4^=$ activation temperature is plotted in Figure S6. The number of $C_3^=$ 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 $C_3^=$ indicate that even more strongly bound surface intermediates are created from higher $C_4^=$ 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 temperatures.[1−3,8]

3.5. Effect of ReO_x Loadings on Number of Surface Reaction Intermediates. The time-dependent evolution of $C_3^=$ molecules produced from $C_2^=$ titration of weakly bound surface intermediates created from $C_4^=$ activation at 30 °C are shown in Figure 2 as a function of ReO_4 loading on alumina. For most of the catalysts, almost all of the surface intermediates created by $C_4^=$ activation react within 10 min of $C_2^=$ 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).

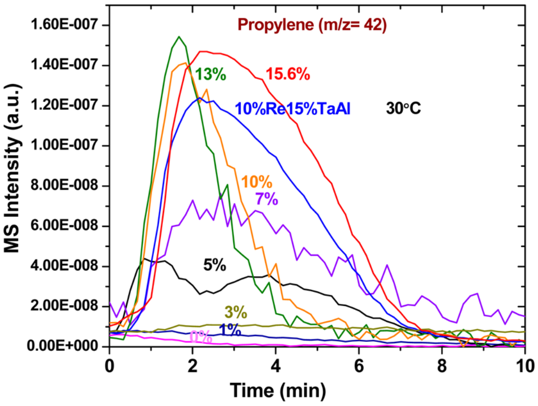

Figure 2. Evolution of $C_3^=$ during $C_2^=$ titration of surface intermediates resulting from $C_4^=$ adsorption (60 min at 30 °C) as a function of ReO_x loading and time at 30 °C (x-axis corresponds to the time of $C_2^=$ flow).

The total number of $C_3^=$ molecules produced by $C_2^=$ titration at 30 °C monotonically increases with rhenia loading on alumina (Figure 3-right axis). The percentage ratio of $C_3^=$ molecules produced to surface ReO_4 sites, however, strongly depends on surface rhenia coverage (Figure 3-left axis). For low rhenia loadings (<7% ReO_4), the $C_3^=$/Re percentage ratio monotonically increases with surface rhenia coverage on alumina. At high rhenia loadings (>7% ReO_4), the $C_3^=$/Re percentage ratio becomes relatively independent of surface rhenia coverage on alumina. The $C_3^=$/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 TaO_x promoter that blocks formation of inactive surface ReO_4−I sites (elaborated upon below).[9]

4. DISCUSSION

4.1. Number of Activated Surface Rhenia Sites on Alumina. Titration Methods. The new findings demonstrate that the number of reactive surface intermediates on supported ReO_x/Al_2O_3 catalysts measured by initial activation with $C_4^=$ and subsequent titration with $C_2^=$ 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

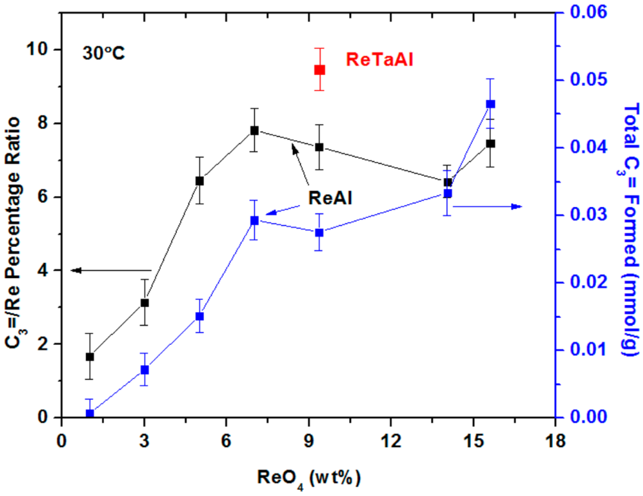

Figure 3. Number of $C_3^=$ molecules produced from reaction of surface intermediates created by $C_4^=$ activation (1 vol % $C_4^=$/Ar for 60 min at 30 °C) with $C_2^=$ titration as a function of ReO_4 loading on Al_2O_3 (right *y*-axis). The left *y*-axis is normalized by taking the number of $C_3^=$ molecules produced and dividing by the total number of surface ReO_4 sites to yield a percentage of $C_3^=$/Re. The RaTaAl catalyst consisted of 9.4Re10TaAl.

experimental variables. Evacuation 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 evacuation 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 evacuation or flushing step[1−3,8] and the order of magnitude higher number of titrated surface intermediates in studies not evacuating 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 rhenia 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 rhenia 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 Rhenia Sites on Alumina. Spectroscopic Method. Direct monitoring with *in situ* Raman spectroscopy reveals that there are two surface rhenia sites anchored at basic (ReO_4−I) and acidic (ReO_4−II) surface hydroxyls of the Al_2O_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.[9] Consequently, a small fraction of surface rhenia sites is activated during olefin metathesis below ~7% ReO_4/Al_2O_3 (0.98 Re/nm^2), where the noninteracting surface ReO_4−I sites dominate, whereas the majority of surface rhenia sites is activated above ~5% ReO_4/Al_2O_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 rhenia sites become activated because they are bonding to the adsorbed hydrocarbons.[9]

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_2O_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 rhenia/alumina catalysts with surface rhenia 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 $C_3^=$/Re values.

5. CONCLUSIONS

In conclusion, the number of surface rhenia sites on alumina participating in olefin metathesis is dependent on the surface rhenia coverage on alumina. At low surface rhenia loadings (<0.98 Re/nm^2), noninteracting surface ReO_4−I sites dominate. At high surface rhenia loading (>0.74 Re/nm^2), interacting surface ReO_4−II dominate. Consequently, the proper value for the number of surface rhenia sites (Ns) participating in olefin metathesis is the total number of surface ReO_4−II sites. The accepted olefin titration method undercounts the number of surface reaction intermediates by factors of 10^1−10^2 because of many invalid assumptions. These new fundamental insights finally resolve the long-standing debate about the number of surface rhenia 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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