

# Mechanistic Aspects of a Surface Organovanadium(III) Catalyst for Hydrocarbon Hydrogenation and Dehydrogenation

David M. Kaphan,\*<sup>®</sup> Magali S. Ferrandon, Ryan R. Langeslay,<sup>®</sup> Gokhan Celik,<sup>®</sup> Evan C. Wegener, Cong Liu,<sup>®</sup> Jens Niklas,<sup>®</sup> Oleg G. Poluektov,<sup>®</sup> and Massimiliano Delferro\*<sup>®</sup>

Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave., Lemont, Illinois 60439, United States

Supporting Information

ABSTRACT: Understanding the mechanisms of action for base metal catalysis of transformations typically associated with precious metals is essential for the design of technologies for a sustainable energy economy. Isolated transitionmetal and post-transition-metal catalysts on oxides such as silica are generally proposed to effect hydrogenation and dehydrogenation by a mechanism featuring either  $\sigma$ -bond metathesis or heterolytic bond cleavage as the key bond activation step. In this work, an organovanadium(III) complex on silica, which is a precatalyst for both olefin hydrogenation and alkane dehydrogenation, is interrogated by a series of reaction kinetics and isotopic labeling studies in order



to shed light on the operant mechanism for hydrogenation. The kinetic dependencies of the reaction components are potentially consistent with both the  $\sigma$ -bond metathesis and the heterolytic bond activation mechanisms; however, a key deuterium incorporation experiment definitively excludes the simple  $\sigma$ -bond metathesis mechanism. Alternatively, a twoelectron redox cycle, rarely invoked for homologous catalyst systems, is also consistent with experimental observations. Evidence supporting the formation of a persistent vanadium(III) hydride upon hydrogen treatment of the as-prepared material is also presented.

**KEYWORDS:** heterogeneous catalysis, supported organometallic catalysis, mechanistic study, hydrogenation, organovanadium

# INTRODUCTION

The development of nonprecious-metal-based catalysts for hydrocarbon hydrogenation and dehydrogenation increases in importance, in conjunction with the shift of the energy economy toward shale gas feedstocks.<sup>1</sup> Platinum nanoparticles, usually employed as a bimetallic alloy with tin, zinc, gallium, or other promoting metals, are the most widely used catalysts for light hydrocarbon dehydrogenation.<sup>2</sup> Chromium oxide supported on silica or alumina is a viable nonprecious-metal alternative, and it has been adopted for industrial applications.<sup>2a,3</sup>

Vanadium oxides have also shown promise as catalysts for dehydrogenation, primarily in the context of oxidative dehydrogenation, but also under anaerobic conditions.<sup>4</sup> These catalysts, typically synthesized by impregnation or sol-gel processes, are characterized as a mixture of onedimensional and two-dimensional polymers and oligomers, as well as some isolated vanadium sites.<sup>5</sup> Recent work in this area suggests that dehydrogenation occurs at the isolated sites; however, the low abundance of these sites in catalytically relevant material complicates the confirmation of this hypothesis.4b,6

The application of supported transition-metal complexes synthesized via the chemisorption of well-defined molecular precursors has emerged as a compelling tool for the study of both isolated and polyatomic metal oxide active sites, and they have shown promise as active and selective catalysts in their

own right.<sup>7</sup> Isolated surface transition-metal and posttransition-metal catalysts for hydrogenation and/or dehydrogenation are extensively studied and have been synthesized from scandium,<sup>8</sup> yttrium,<sup>8</sup> titanium,<sup>9</sup> zirconium,<sup>9,10</sup> hafnium,<sup>9</sup> vanadium,<sup>4c,11</sup> chromium,<sup>12</sup> iron,<sup>13</sup> cobalt,<sup>14</sup> zinc,<sup>15</sup> gallium,<sup>16</sup> and indium<sup>17</sup> inorganic and organometallic molecular precursors.

Mechanistic study of supported organometallic catalysts is complicated by heterogeneity, mass-transfer effects, as well as an increase in the kinetics of oxidative and hydrolytic decomposition, relative to analogous solvated or solid-state organometallics, as a result of their dispersion on high-surfacearea support materials.<sup>7b</sup> Nevertheless, significant effort has been devoted to understanding these mechanisms.<sup>14</sup> Broadly, hydrogenation and dehydrogenation over isolated metal catalysts, both those synthesized from organometallic precursors, as well as those synthesized by other methods, generally proceeds through one of two mechanistic manifolds: heterolytic bond activation (Scheme 1A) and metal hydride  $\sigma$ bond metathesis (Scheme 1B).

Isolated Cr, Co, Fe, Zn, Ga, and In are catalytically active in the hydrogenation and dehydrogenation of light hydrocarbons and likely proceed via the heterolytic bond activation

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Scheme 1. Mechanisms of Hydrogenation and Dehydrogenation for Isolated Transition-Metal and Post-Transition-Metal Catalysts on Silica: (A) Heterolytic Cleavage Mecahnism and (B)  $\sigma$ -Bond Metathesis Mechanism

**A** Heterolytic cleavage mechanism:



mechanism. The commercial  $CrO_x/Al_2O_3$  catalyst for propane dehydrogenation (the CATOFIN process)<sup>2a</sup> is thought to initiate the catalytic cycle by heterolytic C–H bond activation, based on labeling and operando studies; however, it is not clear if catalytic turnover occurs via the heterolytic bond activation or  $\sigma$ -bond metathesis mechanism once the Cr–H is generated.<sup>3,12</sup> Copéret and co-workers provide strong evidence for the heterolytic bond activation mechanism for isolated Co on silica, synthesized by the thermolytic molecular precursor approach,<sup>18</sup> including a para-hydrogen-induced polarization experiment consistent with pairwise hydrogen incorporation, as well as a detailed study of the kinetics of H/D exchange and the hydrogenation process.<sup>14</sup> This mechanism has also been validated computationally for Cr, Co, and Zn, among others.<sup>12,15a,17,19</sup>

Supported group III (Sc and Y) and IV (Ti, Zr, and Hf) organometallic catalysts are proposed to hydrogenate olefins by metal hydride insertion into the C=C double bond, followed by direct hydrogenolysis of the resulting metal alkyl by  $\sigma$ -bond metathesis with dihydrogen to regenerate the metal hydride. These d<sup>0</sup> metal centers are highly electrophilic and feature unusually low electron counts, because of the low coordination number enforced by the structure of the oxide surface. The mechanism of bond activation for these catalysts is generally inferred by analogy to the homogeneous literature.<sup>20</sup> In support of this inference, it was demonstrated that, while bipodal Sc and Y alkyls are competent hydrogenation catalysts, authentically prepared isolated tripodal Sc and Y sites on silica were incapable of effecting olefin hydrogenation, presumably because of their inability to heterolytically activate dihydrogen across the M-O bond. These hydride catalysts are only metastable and undergo

hydride transfer to the surface under conditions where appreciable thermal dehydrogenation is thermodynamically favorable (>450 °C).<sup>8,21</sup> In order to rationalize the kinetic incompetence of the heterolytic activation mechanism for these metals, Hock and co-workers draw analogy to gas-phase diatomic M–O bond dissociation energies, which are more than 50 kcal/mol higher for Sc and Y than for metals known to undergo heterolytic bond activation, such as Cr, Fe, and Co.<sup>11</sup> Notably, while many of the isolated transition-metal catalysts for hydrogenation and dehydrogenation have the filled *d*-orbitals required for a mechanism involving activation of C–H or H–H bonds by oxidative addition, no experimental or computation evidence for this mechanism has been reported for these systems.

It is not clear a priori if isolated vanadium on silica should behave more similar to the group III and IV transition metals and favor the  $\sigma$ -bond metathesis mechanism, or if it is more likely to follow the heterolytic bond activation mechanism by analogy to the later first-row transition-metal catalysts. In 2013, Taoufik and co-workers described the synthesis of a well-defined V(V) oxo mesityl complex on silica (( $\equiv$ SiO)<sub>2</sub>V<sup>V</sup>(O)-Mes), and its application as a catalyst for selective non-oxidative propane dehydrogenation (Scheme 2A).<sup>4c</sup> Our group

Scheme 2. (A)  $(\equiv SiO)_2 V^V(O)$ Mes Catalysis of Propane Dehydrogenation Reported by Taoufik and Coworkers,<sup>4c</sup> and (B)  $(\equiv SiO)_2 V^{III}(THF)$ Mes Catalysis of Propylene Hydrogenation Reported by Delferro and Co-workers<sup>11a</sup>



later found that the V(III) homologue on silica  $((\equiv SiO)_2 V^{III}(THF)Mes, 1)$  was active at room temperature for olefin and alkyne hydrogenation (Scheme 2B).<sup>11a</sup> However, little mechanistic information pertaining to these systems has been reported. In 2018, Taoufik and co-workers reported that, when the vanadium(V) catalyst system was employed for hydrogenation above 200 °C, some pairwise hydrogen incorporation occurred based on a *para*-hydrogen-induced polarization study; however, it was inconclusive if this was a dominant reaction pathway, because of potential relaxation from the paramagnetic vanadium metal center.<sup>22</sup> In this work, a detailed investigation of the mechanism of olefin hydrogenation catalyzed by V(III) catalyst 1 is reported and interpreted in the context of its activity as a catalyst for both hydrogenation and dehydrogenation.

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#### RESULTS AND DISCUSSION

Bipodal organovanadium(III) sites on silica  $((\equiv SiO)_2V (THF)Mes, 1)$  were shown in our previous report to display activity as a precatalyst for olefin hydrogenation;<sup>11a</sup> however, the activity of this material as a precatalyst for alkane dehydrogenation, and its performance relative to the vanadium(V) analogue, was unknown.<sup>4c</sup> When the hydrogenation of propylene was performed in a plug flow reactor at 22 °C with 100 mg of 1 (2.8% V (w/w)), and a 20 mL/min flow rate of 1.2% propene and 42% hydrogen, an initial conversion of 92% was observed, with gradual deactivation over a 20 h period, in which time ~120 turnovers had occurred (see Figure 1A).<sup>23</sup> When the hydrogenation was run under



Figure 1. (A) Hydrogenation of propylene in a plug flow reactor catalyzed by 1. (B) Dehydrogenation of propane in a plug flow reactor catalyzed by 1.

differential conversion at 22 °C, a rate of  $6.1 \times 10^{-4} \text{ s}^{-1}$  was obtained (see Figure S1 in the Supporting Information). Dehydrogenation of propane was then performed at 550 °C with 200 mg of 1 (1% V (w/w)), and a 5 mL/min flow rate of 2.3% propane, resulting in an initial turnover frequency  $6.5 \times 10^{-5} \text{ s}^{-1}$ . The dehydrogenation, while modest in activity, was very stable, decreasing only from 8.1% conversion to 4.6% conversion over 200 h on stream, with high selectivity (94% to 92% propylene selectivity and >99% mass balance) (see Figure

1B). When the reaction profile for dehydrogenation with catalyst 1 is compared to that of the vanadium(V) oxo species reported by Taoufik and co-workers, 1 displays a significantly shorter induction period and a comparable turnover frequency.<sup>4c</sup> Based on these observations, it is plausible that the vanadium(V) precatalyst is reduced in its induction period and converges on the same active species that is generated from the vanadium(III) precatalyst. This is also consistent with the suggestion by Taoufik and co-workers that their catalyst is reduced to V(III) under high-temperature hydrogenation conditions (>250 °C).<sup>11b</sup>

Alternating between hydrogenation and dehydrogenation in the plug flow reactor without recovering the catalyst revealed that subjection to dehydrogenation conditions deactivates the catalyst for hydrogenation, suggesting that the low-temperature hydrogenation is effected by a thermally metastable catalyst structure, not persistent at temperatures required for dehydrogenation. Thus, insights from the hydrogenation reaction cannot be applied to infer mechanistic details about the dehydrogenation by the concept of microscopic reversibility. Nonetheless, the catalytic mechanism of the hydrogenation was intriguing, as there are very few well-defined molecular vanadium complexes capable of promoting the hydrogenation of unsaturated hydrocarbons. Gambarotta and co-workers reported a V(II) hydride dimer that affected olefin hydrogenation by a bimetallic V(II)/V(III) redox cycle.<sup>24</sup> Toste and co-workers later reported a V(V) bisimido complex, which was a catalyst for selective semihydrogenation of alkynes, and activated dihydrogen by heterolytic cleavage across the V=N double bond.<sup>25</sup> For this reason, a mechanistic study on the low-temperature hydrogenation was pursued in order to elucidate the nature of this process in the context of the existing literature regarding isolated metal ion catalysis.

The nature of supported organometallic catalysts leads to increased oxygen and moisture sensitivity, relative to molecular analogues, mass-transfer effects, and surface heterogeneity, each of which represent intrinsic complications for detailed mechanistic study, and as a result, relatively few such studies have appeared to date. In order to understand the mechanism of action of our recently reported supported organovanadium-(III) catalyst (1), conditions were required for reproducible batch olefin hydrogenation that could be validated as free from mass-transfer effects, and therefore kinetically pertinent to the mechanism of hydrogenation. Hydrogen uptake was the targeted as the method of kinetic reaction monitoring in order to minimize the analytical load of the kinetic study, compared to overhead sampling and analysis by gas chromatography. The hydrogen uptake kinetics were validated relative to the reaction sampling method in the hydrogenation of 4-<sup>t</sup>Bu-styrene (2) run in triplicate in an eight-well highthroughput parallel pressure reactor, with two reactions monitored by overhead sampling and the third by gas uptake (see Figure 2). The reactions were run with 0.25 M 4-<sup>t</sup>Bustyrene and 0.35 mol % of 1 at 50  $^{\circ}$ C under 200 psi of H<sub>2</sub> with 1,3,5-tri-tert-butylbenzene as an internal standard.

The reaction profile from hydrogen uptake obtained by monitoring pressure changes in the reactor headspace are in good agreement with the kinetic profile from overhead sampling. Periodic discontinuities in this hydrogen uptake profile correspond to roughly 60 s settling intervals during which the common overhead stirring for the three reactors was halted to allow the catalyst to settle and prevent obstruction of the sampling needle. During this period, hydrogen dissolution



Figure 2. Comparison of overhead sampling and  $H_2$  uptake as a method for tracking the kinetics of hydrogenation by catalyst 1.

is slow and the catalyst is not suspended in the reaction mixture, arresting the progress of the reaction. The reaction proceeded with an approximate half-life of 45 min, with no sign of styrene polymerization or side-product formation on the time scale of the hydrogenation process.

Having validated the hydrogen uptake analytical method, the reaction was repeated without overhead sampling in order to remove the periodic discontinuities in the rate. The reaction profile obtained from this experiment (Figure 3, blue trace)



Figure 3. Comparison of the hydrogen uptake reaction profile for 1 as-prepared (blue) and with a 30 min hydrogen pretreatment (orange).

deviated significantly from simple first-order kinetic behavior, with a slight increase in rate over the first 15% conversion, suggestive of an induction period. When the reaction was immediately preceded by a 30 min hydrogen treatment prior to the addition of the substrate, the initial rate of the reaction increased and the induction period was not observed (Figure 3, orange trace). The initial rate the reaction was  $(1.22 \pm 0.07) \times 10^{-4}$  M/s under standard conditions  $(0.25 \text{ M 4-'Bu-styrene}, 200 \text{ psi of H}_2, 25 \text{ mg of 1 [1.4 mmol, 0.35 mol %], 50 °C; for a discussion of error, see page S7 in the Supporting Information). Elimination of the induction period upon hydrogen treatment is consistent with the hydrogenolysis of the vanadium mesityl occurring with a higher kinetic barrier than the subsequent catalytic turnover of the reaction.$ 

The initial product of hydrogenolysis of the bipodal vanadium(III) mesityl precatalyst is likely to be the analogous vanadium(III) monohydridide complex; however, further reactivity could plausibly furnish either hydride transfer to the silica surface, generating a tripodal vanadium(III) species, or, alternatively, oxidative addition of a further equivalent of dihydrogen could generate a vanadium(V) trihydride species. Hydride transfers to open surface siloxane rings are commonly observed for early transition-metal hydrides, and silica supported tantalum(III) monohydrides reversibly form small amounts of tantalum(V) tridhydride under an atmosphere of dihydrogen.<sup>26</sup>

Several spectroscopic methods were employed to further characterize the species generated upon exposure of 1 to a hydrogen atmosphere. A hydrogen-treated sample of 1 (hereafter referenced as 4) was first interrogated by CW Xband EPR spectroscopy (see Figure 4). The resulting spectrum



Figure 4. CW X-band EPR spectrum of 4 (1 after hydrogen treatment) and 4 after brief exposure to atmospheric oxygen. (See spectrum of 1 in Figures S5 and S7 in the Supporting Information.)

showed only weak EPR signals, a broad peak at  $g \approx 4$ , and a relatively minor contribution of more narrow signals at  $g \approx 2$ , which we attribute to a small amount of V<sup>4+</sup> (d<sup>1</sup> configuration). This small amount of V<sup>4+</sup> is likely due to adventitious oxidation of the more-reduced vanadium, while V<sup>3+</sup> (d<sup>2</sup> configuration) is EPR silent, because of a large zero-field splitting.<sup>27</sup> Upon exposure to air, sample 4 showed an intense EPR signal typical of V<sup>4+</sup> in vanadyl complexes.<sup>27,28</sup> Since dioxygen is strongly oxidizing and generated V<sup>4+</sup>, the majority of the vanadium in hydrogen-treated 4 is likely composed of a more-reduced state. Since V<sup>2+</sup> is expected to give substantial EPR signals which were not observed, the majority of vanadium in sample 4 is inferred to be in the V<sup>3+</sup> oxidation state.

Vanadium K-edge X-ray absorption measurements were performed on 1 and 4 to gain further information on effect of hydrogen treatment on the local coordination environment and oxidation state of the precatalyst. Changes in the pre-edge and main absorption feature in the X-ray Absorption Near Edge Structure (XANES) spectra (Figure 5, top) indicate a change to the local coordination environment of V after hydrogen treatment. However, the edge energy of 4 and 1 overlap to within the error of the measurement (5472.8  $\pm$  0.1 eV), providing further evidence that the vanadium center remains in the 3+ oxidation state.<sup>29</sup> The decreased intensity of the feature at ~1.5 Å observed in the Extended X-ray



Figure 5. Vanadium K-edge XANES (top) and EXAFS (bottom) spectra of 1 and 4 showing a decrease in the magnitude of the major feature at  $\sim 1.5$  Å potentially consistent with a decrease in nonhydrogen coordination number.

Absorption Figue Structure (EXAFS) spectrum of 4, compared to 1 suggests a decrease in nonhydrogen coordination number, consistent with the hydrogenolysis of the mesityl group to form a vanadium hydride, although changes in symmetry at the vanadium center may also account for this decrease in magnitude (Figure 5, bottom).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed in search of vanadium hydride stretching resonances for hydrogen-treated 1 both in situ and ex situ; however, these studies were inconclusive. This is not surprising as early transition-metal hydrides are difficult to characterize via infrared (IR) analysis, because of their sensitivity and low molar absorptivity (see Figure S17 in the Supporting Information).<sup>21</sup> It is also possible that partial activation to generate a low concentration of the isolated metal hydride species explains the difficulty in spectroscopic characterization.

More information about the nature of the species generated by hydrogen treatment of 1 was obtained by indirect chemical means. A hydrogen-treated sample of 1 was decomposed with methanol- $d_4$ , which resulted in a complex mixture of species by <sup>1</sup>H NMR spectroscopy, including both HD and H<sub>2</sub>, likely from proteolytic decomposition of a vanadium hydride, although it is conceivable that hydrides transferred to the surface could also lead to the generation of HD/H<sub>2</sub> (Figure S8 in the Supporting Information; note that the formation of H<sub>2</sub> may be explained by rapid H/D exchange between methanol and Brønsted acidic residual silanol sites). Furthermore, it was reasoned that a surface vanadium hydride species 4 would be active for insertion and oligomerization of ethylene, while a tripodal vanadium species, lacking a hydride or alkyl for insertion, would be relatively sluggish or inactive in this transformation. Indeed, when 1 was subjected to 1 atm of hydrogen for 1 h in a J. Young NMR tube, followed by degassing and replacing the atmosphere with ethylene, rapid oligomerization was observed with no apparent induction period (see Figure S9 in the Supporting Information). Interestingly, when vanadium mesityl complex 1 was subjected to an atmosphere of ethylene without any hydrogen pretreatment, an induction period was observed, followed by the formation of a similar profile of oligomerization products, concomitant with the formation of 2,4,6-trimethylstyrene (5), presumably from the insertion of ethylene into the vanadiummesityl bond, followed by rapid  $\beta$ -hydride elimination (see Scheme 3, as well as Figure S9). This oligomerization behavior

Scheme 3. Generation of Vanadium Hydride 2 by Hydrogenolysis of 1 or Insertion of Ethylene Followed by  $\beta$ -H Elimination



is consistent with the characterization of the hydrogen-treated material as a vanadium(III) hydride (4), although it does not specifically rule out the possibility of a tripodal species, as silica-supported tripodal Ta(III) complexes have also been shown to polymerize ethylene under certain conditions.<sup>30</sup> Each of these pieces of data based on spectroscopic and chemical reactivity experiments are individually inconclusive but, taken together, suggest the formation of vanadium hydride 4 upon hydrogenolysis of mesityl complex 1.

In order to gain more information about the mechanism of the reaction by probing the kinetic dependence on various reaction components, it was first necessary to demonstrate that the rate of the reaction was intrinsic to the chemistry occurring at the organovanadium sites, and was not dominated by masstransfer effects. Mass-transfer limitations at the gas/liquid interface could be ruled out by comparing the rate of hydrogen dissolution to that of the reaction. By omitting the substrate and catalyst from the reactor, the kinetics of dissolution could be directly observed by monitoring the pressure of the reactor headspace immediately after dosing hydrogen (see Figure S10 in the Supporting Information). The resulting hydrogen pressure profile displayed first-order kinetics with an approximate half-life of 18 s ( $k = 3.78 \times 10^{-2} \text{ s}^{-1}$ , or an



**Figure 6.** Kinetic dependencies of 4-<sup>t</sup>Bu-styrene hydrogenation catalyzed by 1. (A) Rate dependence on loading of 1. (B) Double log plot showing first-order kinetics, with respect to 1. (C) Rate dependence on the initial concentration of 4-<sup>t</sup>Bu-styrene. (D) Double reciprocal plot showing saturation kinetics, with respect to styrene concentration. (E) Rate dependence on H<sub>2</sub> pressure. (F) Double reciprocal plot showing saturation kinetics with H<sub>2</sub> pressure. (G) Rate dependence on the concentration of THF added to the reaction mixture. (H) Reciprocal plot consistent with THF dissociation kinetics at high THF concentrations. (I) Rate dependence on H<sub>2</sub> pressure in the saturation regime, with respect to substrate concentration.

approximate initial rate of  $1.43 \times 10^{-3}$  M/s), which is more than an order of magnitude faster than the rate of a representative hydrogenation  $(1.22 \times 10^{-4} \text{ M/s})$ . Furthermore, the observation of first-order kinetic dependence, with respect to catalyst loading, is inconsistent with gas-liquid masstransfer limitations (vide infra). If mass-transfer limitations at the bulk liquid/particle interface controlled the kinetics of the reaction, then decreasing the catalyst particle size would increase exterior particle surface area and, by extension, reaction rate. To evaluate this, the catalyst was prepared with silica sieved to three different ranges of particle size-125-177  $\mu$ m, 177–250  $\mu$ m, and 250–500  $\mu$ m—and no effect on reaction rate was observed (rates of 2.03  $\times$  10<sup>-4</sup> M/s, 1.96  $\times$  $10^{-4}$  M/s, and 2.00  $\times$   $10^{-4}$  M/s, respectively, were observed<sup>31</sup>). These experiments suggest that the kinetics of the reaction are not governed by mass-transport limitations at

the gas/liquid or bulk liquid/particle interface, and the kinetic dependencies of the reaction components should faithfully reflect the reaction occurring at the vanadium active site.<sup>32</sup>

Having validated that the hydrogenation of 4-<sup>t</sup>Bu-styrene (2) with 1 was not mass-transfer-limited, the kinetic dependence of the reaction was evaluated with respect to H<sub>2</sub>, 4-<sup>t</sup>Bu-styrene, 1, and THF (see Figure 6).<sup>33</sup> A first-order rate dependence on the loading of vanadium precatalyst 1 was observed over a loading range of 0.35 mol% to 1.38 mol% (see eq 1 and Figure 6A). This is confirmed by a double logarithmic plot with a slope of 1.07 (ln[rate] vs ln[mol% 1]; see Figure 6B). The rate dependence, with respect to the concentration of 4-<sup>t</sup>Bu-styrene, was nonlinear, with close to first-order behavior at low substrate loading, and only marginal increases in rate observed after ~1 M substrate concentration (Figure 6C). This kinetic dependence could be linearized by

plotting the reciprocal of rate versus the reciprocal of the styrene concentration, which is consistent with saturation kinetics (see eq 2 and Figure 6D). Varying the pressure of hydrogen in the reactor between 50 psi and 400 psi also led to a nonlinear kinetic response; however, this deviation from firstorder behavior was much more subtle than that observed in the study of substrate dependence (Figure 6E). Nonetheless, the rate dependence on hydrogen pressure could also be linearized in a double reciprocal plot, suggesting a similar saturation mechanism for hydrogen (eq 3 and Figure 6F). The effect of the addition of THF to the reaction mixture was then studied in order to determine if THF dissociates from the vanadium metal center between the resting state and rate-determining transition state of the reaction. If THF dissociation is relevant to the catalytic mechanism of the reaction, then added THF should inhibit the reaction, and the reciprocal of the rate of the reaction should be proportional to the concentration of THF. Indeed, added THF was found to inhibit the reaction (Figure 6G); however, the reciprocal plot deviated from linearity at low concentrations of THF--that is, THF inhibition is more extreme than expected at low concentrations of THF, based on a simple dissociation mechanism (see eq 4 and Figure 6F). Two scenarios could account for this deviation from simple dissociative kinetic behavior (see Figure S13 in the Supporting Information): the first equivalents of THF could result in an increase in coordination number, forming a bis(THF) vanadium adduct, which then must dissociate one THF molecule to perform the chemistry; alternatively, there may exist a minority of highly active lower-coordinate vanadium sites lacking in THF, which are transformed back to the  $[(\equiv SiO)_2V(THF)Mes]$  structure upon the addition of small amounts of THF. The latter hypothesis is consistent with the observation of small amounts (<5 mol%, relative to grafted vanadium) of THF that are liberated upon chemisorption of  $(THF)VMes_3$  in the synthesis of 1.

Order in catalyst:

$$\frac{\mathrm{d}(3)}{\mathrm{d}t} \propto [\mathbf{1}] \tag{1}$$

Order in substrate:

$$\frac{\mathrm{d}(\mathbf{3})}{\mathrm{d}t} \propto \frac{[\mathbf{2}]}{(C + [\mathbf{2}])} \tag{2}$$

Order in hydrogen:

$$\frac{\mathrm{d}(\mathbf{3})}{\mathrm{d}t} \propto \frac{[\mathrm{H}_2]}{(\mathrm{C} + [\mathrm{H}_2])} \tag{3}$$

Order in THF:

$$\frac{\mathrm{d}(\mathbf{3})}{\mathrm{d}t} \propto \frac{1}{(C + [\mathrm{THF}])} \text{ at high [THF]}$$
(4)

In order to evaluate the reversibility of the migratory insertion step of the reaction, the hydrogenation of styrene was conducted in a J. Young NMR tube under an atmosphere of  $D_2$ . The reaction was followed by both <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy. As the reaction progressed, the signals for the protons in the  $\beta$ -position of the styrene starting material diminished more rapidly than the signals associated with the proton at the  $\alpha$ -position or those associated with the aromatic ring, suggesting that deuterium was incorporated into the

residual starting material during the reaction by reversible hydride insertion (Figure 7, top). Deuterium incorporation at



**Figure 7.** (Top) Profile of <sup>1</sup>H NMR signals for residual styrene during hydrogenation catalyzed by **1** under an atmosphere of  $D_2$ . (Bottom) <sup>2</sup>H NMR spectrum at partial conversion showing deuterium incorporation into the ethyl group of the product, as well as the  $\beta$ -position of the residual styrene.

the  $\beta$ -position of the styrene was verified by the observation of new resonances at 5.2 and 5.7 ppm in the <sup>2</sup>H NMR spectrum at partial conversion (260 min, Figure 7, bottom). Upon completion of the reaction, ethyl benzene was afforded with 50% deuterium incorporation at the benzylic methylene, and 82% deuterium incorporation at the terminal methyl position based on integration of the resulting <sup>1</sup>H NMR spectrum. If the insertion were irreversible, the expected deuterium incorporation would be 50% at the methylene and 33% at the methyl position. The observation of exactly 50% deuterium incorporation at the methylene position and excess deuterium incorporation at the methyl group implies that vanadium hydride insertion occurs with complete regiospecificity, affording the vanadium alkyl only at the more-substituted benzylic position. This regiochemical outcome is in contrast with several recently reported first-row transition-metal-based catalysts for olefin hydrogenation, which add the deuteride at

both the  $\alpha$ - and  $\beta$ -position of styrenyl substrates.<sup>34</sup> One hypothesis to explain this observation is that the surface may enforce a lower coordination number<sup>21</sup> than would typically be obtained for a molecular organometallic intermediate, increasing the stabilization from developing  $\eta^2$  or  $\eta^3$  binding modes when the vanadium is entering the benzylic position.

Based on these observations, consistent mechanisms can be drawn for both the  $\sigma$ -bond metathesis mechanism (Scheme 4)

Scheme 4. Plausible  $\sigma$ -Bond Metathesis Mechanism of Hydrogenation Consistent with Kinetic Data, But Inconsistent with Deuterium Incorporation Pressure Dependence



and the heterolytic bond activation mechanism (Scheme 5) of hydrogenation over isolated transition-metal sites on oxide supports. In the  $\sigma$ -bond metathesis mechanism, a bipodal

Scheme 5. Plausible Heterolytic Bond Activation Mechanism of Hydrogenation Consistent with Kinetic Data and with Pressure Independent Deuterium Incorporation



vanadium hydride (4, A) represents the resting state at low concentrations of the styrene, transitioning to vanadium alkyl species B at high concentrations of styrene, which would explain the saturation kinetics in styrene concentration. Dihydrogen would then cleave the vanadium alkyl through a  $\sigma$ -bond metathesis mechanism, possibly through a lowercoordinate intermediate, such as C. The nonlinearity of the kinetic dependence on hydrogen may be taken into account by a partial change in the rate-determining step from hydrogenolysis by  $\sigma$ -bond metathesis at low hydrogen concentration, to olefin insertion at higher pressures of hydrogen.

The heterolytic cleavage mechanism starts with bipodal or tripodal species  $D(L_n = hydride, alkyl, silanol, or other X-type$ ligand), which reversibly binds the styrenyl substrate as an olefin complex (intermediate E), followed by heterolytic activation of hydrogen to afford intermediate G. Reversible migratory insertion generates vanadium alkyl H, which then undergoes 1,2-elimination, releasing the hydrogenated product and regenerating D. In this mechanism the resting state of the cycle is species **D** at low concentration of styrene, shifting to  $\pi$ complex E at elevated styrene concentration, resulting in saturation kinetics. Vanadium alkyl complex H can be ruled out as the resting state at high styrene concentration for this mechanism by the observation that the reaction is roughly first order in hydrogen under saturation conditions, with respect to the styrene (2.5 M  $4^{-t}$ Bu-styrene; see Figure 6I). If H were the resting state at high styrene concentration, then, under those conditions, the reaction would be zero order in hydrogen, as incorporation of H<sub>2</sub> into the active site is prerequisite for the formation of H. In contrast, the observation of a positive rate dependence in hydrogen is consistent with the assignment of E as the resting state, as hydrogen has yet to be incorporated at that point in the catalytic cycle. The nonlinearity in hydrogen pressure dependence is rationalized in this mechanism by a buildup of intermediates F and/or G in the speciation of the resting state, in which hydrogen has already been activated. While direct evidence for each of the elementary steps in this mechanism and those below is not obtained for this system, these processes are precedented and commonly proposed for well-defined homogeneous organometallic complexes. For general rate laws and derivations for the  $\sigma$ -bond metathesis and heterolytic bond activation mechanisms, see pages S19 and S20, respectively, in the Supporting Information. In order to evaluate if THF displacement by various ligands in the system is energetically plausible, the thermodynamics of displacement of THF by styrene (to form a  $\pi$ -complex) and by dihydrogen (to form a  $\sigma$ -complex) was examined. The displacement of THF from the vanadium complex following heterolytic activation of dihydrogen was found to be 10.7 kcal/mol uphill (see Figure S19 in the Supporting Information). This is a very reasonable value for a reversible pre-equilibrium to generate a high-energy intermediate in this system. Note that the lowervalent vanadium(III) metal center is expected to be significantly less oxophilic than its vanadium(V) analogue, which contributes to the relatively low energetic cost for THF dissociation. Dissociative ligand displacement is well-precedented for this class of organometallic complex, including for the molecular precursor to 1, (THF)VMes<sub>3</sub>.<sup>35</sup> Displacing THF from the bipodal vanadium monohydride with dihydrogen was found to be uphill by 27.0 kcal/mol. This is value would be too large for a high-energy intermediate in a reaction pathway that proceeds at a reasonable rate at room temperature; however, we do not discount the plausible intermediacy of a dihydrogen

sigma complex, since the variable coordination-site geometries present on the amorphous surface may decrease the thermodynamic penalty of this equilibrium sufficiently to bring it into the accessible range for a reaction between room temperature and 50  $^{\circ}$ C. For further discussion of the viability of THF displacement in these mechanisms, including computational thermodynamic data, see page S17 in the Supporting Information.

While mechanisms for the hydrogenation reaction by both the  $\sigma$ -bond metathesis and heterolytic bond activation pathways are both plausible and consistent with the kinetic data, inspection of these reaction networks reveals a key difference in the reaction sequences that can be leveraged for their differentiation: the extent of excess deuterium incorporation is predicted to have a different pressure dependence for the two mechanisms. When the hydrogenation is performed with  $D_{2}$ , the fraction of deuterium labeling at the  $\beta$ -position in the product is governed by the ratio of product formation to  $\beta$ hydride elimination from the vanadium alkyl intermediate (C/ H). For the  $\sigma$ -bond metathesis mechanism, hydrogenolysis of the alkyl group in intermediate C is first order in hydrogen, whereas hydrogen is not involved in the  $\beta$ -hydride elimination, making that elementary step zero-order, with regard to hydrogen. This mechanism predicts that increasing the D<sub>2</sub> pressure should decrease the amount of excess deuterium incorporated in the product. In contrast, for the heterolytic bond activation mechanism, the hydrogen molecule has already been incorporated in vanadium alkyl intermediate H. Both the 1,2-elimination step to form the hydrogenated product, and the  $\beta$ -hydride elimination to reform the styrene are zero-order in D<sub>2</sub>, which suggests that the extent of excess deuterium incorporation should be independent of  $D_2$ pressure. When the reaction was performed under one, two, and four atmospheres of  $D_2$ , no discernible changes in the extent of excess deuterium incorporation were observed, with a measured deuterium fraction at the  $\beta$ -methyl group of 82%, 83%, and 81%, respectively (see Table 1). The independence

# Table 1. Effect of $D_2$ Pressure on Excess Deuterium Incorporation at the $\beta$ -Position



of the amount of excess deuterium incorporation on the pressure of deuterium requires that the elementary steps of the catalytic cycle forward and backward from the vanadium alkyl intermediate must have the same order, with regard to hydrogen. This is inconsistent with the  $\sigma$ -bond metathesis mechanism, as drawn in Scheme 4, and this mechanism can be ruled out for the hydrogenation of styrenyl substrate by vanadium catalyst 1.

This deuterium pressure dependence study on the extent of deuterium incorporation is consistent with the heterolytic bond activation mechanism, as both the forward and backward steps from the vanadium alkyl intermediate  $(\mathbf{H})$  are zero-order, with regard to hydrogen; however, this observation would also

be consistent with a mechanism in which both hydrogenolysis and  $\beta$ -hydride elimination were first-order, with regard to D<sub>2</sub>. If, instead of  $\sigma$ -bond metathesis, the mechanism of vanadium alkyl cleavage in Scheme 4 proceeded via oxidative addition of dihydrogen to form vanadium(V) intermediate J, followed by C-H reductive elimination (Scheme 6), it is possible that  $\beta$ -

Scheme 6. Plausible Redox Mechanism of Hydrogenation Consistent with Kinetic Data



hydride elimination from the oxidized species, J, could be faster than  $\beta$ -hydride elimination from vanadium(III) alkyl **B**. If this were the case, then both the forward hydrogenolysis step and backward  $\beta$ -hydride elimination step would be first-order, with regard to hydrogen. Since these two steps have the same order in hydrogen, no effect on the extent of deuterium incorporation upon varying D<sub>2</sub> pressure would be predicted, which is consistent with the experimental outcome. In this mechanism, vanadium alkyl intermediate B sits off-cycle and represents the resting state at high styrene concentration. The deviation from linearity in the rate dependence on hydrogen pressure may be taken into account by a buildup of vanadium(V) hydride species I and/or J. Such a redox-based mechanism for olefin hydrogenation has not been proposed for other isolated transition-metal ions on silica that catalyze hydrogenation. However, many of these catalysts have a d<sup>0</sup> electron configuration and are incapable of oxidative addition, particularly those based on group III and IV transition metals. While this redox cycling mechanism would require a delicate balance of elementary rate constants, it is consistent with experimental observations. While no direct precedent for the intermediacy of vanadium(V) trihydride complexes has been reported in the literature, some support for the kinetic accessibility of this complex may be inferred from the observation of the homologous tantalum(V) trihydride on silica by Bassett and co-workers.<sup>30</sup> While the paramagnetic vanadium(III) hydride would be difficult to detect by solidstate <sup>1</sup>H NMR spectroscopy, the vanadium(V) trihydride would be diamagnetic and, therefore, would be observable if it were persistent and low enough in energy to be significantly populated in the resting state. When the hydrogen-treated material was inspected by <sup>1</sup>H NMR spectroscopy, no hydride resonances were detectable; however, this does not discount their mechanistic relevance as high-energy intermediates (see Figure S21 in the Supporting Information). For a general rate law and rate law derivation for the redox mechanism of hydrogenation, see page S22 in the Supporting Information.

# **ACS Catalysis**

# CONCLUSIONS

Of the two classes of mechanisms commonly proposed for hydrogenation and dehydrogenation catalyzed by isolated transition-metal and post-transition-metal complexes on silica, for organovanadium precatalyst 1, the heterolytic bond activation mechanism is consistent with the kinetic and isotope labeling data reported, while the  $\sigma$ -bond metathesis mechanism is excluded. The key experiment to differentiate these mechanisms was the observation that the amount of excess deuterium incorporation in the product was independent of the D<sub>2</sub> pressure under which the reaction was run. An alternative mechanism based on a vanadium(III)/vanadium-(V) redox cycle is also consistent with the experimental data. This mechanism, typically associated with late-transition-metal molecular catalysts, is generally not favored for homologous isolated transition-metal or post-transition-metal catalysts on oxides such as silica.

Propane dehydrogenation catalyzed by 1, although not studied in depth in this report, displays activity and selectivity reminiscent of other isolated first-row transition-metal sites on silica (such as Cr, Fe, and Co), plausibly suggesting a common mechanism, for which heterolytic cleavage is typically proposed. The active catalyst for low-temperature hydrogenation must be a metastable structure that follows a different mechanism than the dehydrogenation (vide supra). Although the data for the hydrogenation reaction presented above are consistent with both the heterolytic cleavage mechanism and the redox cycling mechanism, one possibility is that the vanadium hydride redox cycling mechanism occurs at low temperatures, while under conditions required to drive the thermodynamics of dehydrogenation, the more active catalytic species is not persistent and the heterolytic cleavage mechanism dominates. The interpretation of data in the context of multiple possible mechanisms and then selection of those that most simply explain the experimental observations is consistent with recent direction from the editorial office of this journal.<sup>36</sup>

Differentiation of the heterolytic cleavage mechanism and the redox cycling mechanism may be possible by in situ spectroscopic techniques in the presence of elevated pressures of dihydrogen; however, the sensitivity of 1 has thus far complicated these experiments. Nonetheless, efforts to this end are ongoing, in addition to efforts to describe these energetic landscapes, from a computational perspective. Understanding the mechanisms by which base transition metals catalyze reactions typically associated with precious metals such as hydrogenation and dehydrogenation is of great importance to the development of a new generation of sustainable catalyst materials. Well-defined vanadium catalysts are less wellstudied, compared to some of their first-row transition-metal neighbors; however, this element has a range of properties that make its chemistry unique, and increased attention to its catalytic applications is warranted.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b02800.

XYZ coordinate files for computational assessment of ligand displacement from vanadium to support mechanistic discussion. Jmol files (ZIP)

General discussion of synthetic and experimental procedures, instrumentation, characterization of materials, and rate laws and their derivations (PDF)

# AUTHOR INFORMATION

#### **Corresponding Authors**

\*E-mail: kaphand@anl.gov (D. M. Kaphan). \*E-mail: delferro@anl.gov (M. Delferro).

#### ORCID 0

David M. Kaphan: 0000-0001-5293-7784 Ryan R. Langeslay: 0000-0003-2915-9309 Gokhan Celik: 0000-0001-8070-5219 Cong Liu: 0000-0002-2145-5034 Jens Niklas: 0000-0002-6462-2680 Oleg G. Poluektov: 0000-0003-3067-9272

Massimiliano Delferro: 0000-0002-4443-165X

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The authors declare no competing financial interest.

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(31) For the study of particle size effects, 50 mg of catalyst was used, instead of the standard conditions (25 mg).

(32) Rate-limiting diffusion of physisorbed substrates is not excluded by these experiments, but is generally inconsistent with the kinetic experiments described below.

(33) In lieu of performing each reaction in triplicate, the error associated with the reaction was evaluated under standard conditions both in parallel on the same day, and when performed on different days with separate batches of reagents (see Figure S4 in the Supporting Information). Five reactions run in parallel under the identical conditions were found to have an average initial rate of  $1.22 \times 10^{-4}$  M/s with a standard deviation of  $0.07 \times 10^{-4}$  M/s. The same conditions performed on five different days was found to have an average initial rate of  $1.26 \times 10^{-4}$  M/s with a standard deviation of  $0.16 \times 10^{-4}$  M/s. When possible, directly compared rates were collected in parallel, to minimize error. By studying the error of the standard conditions, a more complete understanding of this error is obtained, and a wider set of conditions can be evaluated, with respect to each reaction variable.

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