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Understanding the Hydro-metathesis Reaction of 1-decene by Using Well-defined Silica Supported W, Mo, Ta Carbene/Carbyne Complexes

Aya Saidi, Manoja K. Samantaray*, Mykyta Tretiakov, Santosh Kavitate and Jean-Marie Basset*

Abstract:

Direct conversion of 1-decene to petroleum range alkanes was obtained using hydro-metathesis reaction. To understand this reaction we employed three different well-defined single site catalysts precursors; $[(\equiv\text{Si-O})\text{W}(\text{CH}_3)_5]$ **1**, $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{C}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2]$ **2** and $[(\equiv\text{Si-O})\text{Ta}(\equiv\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2]$ **3**. We witnessed that in our conditions olefin metathesis/isomerization of 1-decene occurs much faster followed by reduction of the newly formed olefins rather than reduction of the 1-decene to decane, followed by metathesis of decane. We found that Mo-based catalyst favors 2+2 cycloaddition of 1-decene forming metallocarbene, followed by reduction of the newly formed olefins to alkanes. However, in the case of W and Ta-based catalysts, a rapid isomerization (migration) of the double bond followed by olefin metathesis and reduction of the newly formed olefins were observed. We witnessed that silica supported W catalyst precursor **1** and Mo catalyst precursor **2** are better catalysts for hydro-metathesis reaction with TONs of 818 and 808 than Ta-based catalyst **3** (TON of 334). This comparison of the catalysts provides us a better understanding that, if a catalyst is efficient in olefin metathesis reaction it would be a better catalyst for hydro-metathesis reaction.

Introduction

Direct transformation of a given alkanes to fuel range alkanes is a value-added process and will always remain a challenge considering the inertness of the C-C and C-H bonds towards most of the organometallic compounds.^[1] Our daily life is influenced by the ups and downs of the price of petroleum products and will continue as such because they are natural resources and hence limited. To overcome this challenge, there is an urgent need for an artificial synthesis of the petroleum products, in particular, transportation fuel.

Practically, two main processes are known for artificial synthesis of diesel or gasoline range alkanes. Fischer-Tropsch synthesis (conversion of syngas to diesel range alkanes)^[2] and alkane

metathesis (conversion of a given alkanes to lower and higher homologues and eventually diesel or gasoline range alkanes).^[3] Our group mainly focuses on alkane metathesis reaction at low temperature.^[3f, 4] After the discovery of a single-site silica supported Ta-H catalyst by our group in 1997, we are continuously searching for better catalysts for conversion of alkanes.^[5] During our research, we understood from the reaction mechanism that olefin and hydrogen are the primary products in alkane metathesis.^[6] The olefins which are formed, undergo olefin metathesis reaction with formation of lower and higher olefins, after reduction of the newly formed olefins, new alkanes are produced.^[7]

Considering the above facts, we explored the retrosynthesis of higher and lower alkanes using olefin as a reactant along with hydrogen and named it **hydro-metathesis** reaction.^[8] We moved on from Ta to W and found out that W catalyst is better than the Ta counterpart.^[9] We suspected it might be because it has been known that W is a better metal for olefin metathesis reaction than Ta.^[10] Not only we changed the metal, but also we explored the ligand environment around the metal center to generate the better catalyst for alkane metathesis reaction. For example, we compared the activity of metal hydrides with their parent metal neopentyl catalysts, and we observed that metal hydrides are better catalysts than the metal alkyls.^[9] The reason for the enhanced activity of the metal hydride is first, its strong ability to react with C-H bond of alkane by sigma bond metathesis, the most difficult step, leading to hydrogen and a metal alkyl. The subsequent elementary steps produce from the resulting metal alkyl, a metallocarbene (by α -hydrogen abstraction), and an olefin (β -hydride elimination).

This concept led us to think alternatively, where we can use olefin and hydrogen along with metal catalyst to convert it to transportation fuel range alkanes. Based on this concept our first try was to use Ta-H as hydro-metathesis catalyst for conversion of propene and butene.^[8] Recently we developed a well-defined silica supported $\text{W}(\text{Me})_5$ catalyst for alkane metathesis reaction.^[11] We observed that this catalyst precursor and its corresponding hydrides are much more reactive in alkane metathesis reaction than the previously used Tantalum based catalyst.^[3e] With various single site catalysts based on Ta, Mo and W in our hands, we compared them in hydro-metathesis reaction taking liquid olefin as a reactant and tried to determine which catalyst produces better conversion and what is the possible reason for it.

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Supporting information for this article is given via a link at the end of the document.

In this paper, we disclose direct conversion of an olefin to diesel range alkanes in a single step and compare the reactivity of the

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various metal neopentyl/methyl (Figure 1) catalysts in the hydro-metathesis reaction.

Figure 1. Well-defined silica supported $[(\equiv\text{Si-O})\text{W}(\text{CH}_3)_5]$ **1**, $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{C}'\text{Bu})(\text{CH}_2'\text{Bu})_2]$ **2** and $[(\equiv\text{Si-O})\text{Ta}(\equiv\text{CH}'\text{Bu})(\text{CH}_2'\text{Bu})_2]$ **3**.

Results and Discussion

In a typical reaction, in a batch reactor under Ar, 40 mg of catalyst precursor **1** was introduced and 1 mL of dried 1-decene was added inside the glovebox into a 265 mL reactor tube which was frozen later in liquid nitrogen. After pumping the argon under vacuum, 0.8 mbar of hydrogen was introduced into the reactor. The reaction mixture was heated at 150 °C for 3 days, after the completion of the reaction, the reactor was cooled down under liquid nitrogen and quenched with a fixed amount of dichloromethane. After filtration, the products were analyzed by GC/GC-MS.

Figure 2. **2A** represents the product distribution (absolute values in mmols of Alkanes vs. Carbon number of Alkanes) obtained from neat **1-decene** hydro-metathesis reaction whereas **2B** represents the distribution of alkanes obtained

by neat **n-decane** metathesis reaction using **1** $[(\equiv\text{Si-O})\text{W}(\text{CH}_3)_5]$ as catalyst precursor.

The GC chromatogram of the hydro-metathesis reaction of 1-decene displays a wide distribution of products ranging from C_3 to C_{34} alkanes with a few unreacted olefins (Figure 2A). We also observed 100 % conversion of the reactant with an overall TON of 910 (alkanes + olefins) and 818 for only alkanes except n-decane.

We observed a nearly similar distribution of alkanes what we observed in case of n-decane metathesis using catalyst precursor **1** (Figure 2B), except higher conversion and TON (150). Looking at the product distribution of the alkanes we became curious to understand the reaction mechanism of this particular reaction. We believed that the reaction might go through olefin metathesis followed by reduction of the double bond to form alkanes, though we are not completely eliminating the possibility of reduction of the olefin to alkane and then alkane metathesis. If we follow the second point and believe it could reduce the olefin bond and carryout alkane metathesis, then it is difficult to believe that it produces a very high TON (818) as compared to normal alkane metathesis with n-decane (TON 150) with catalyst precursor **1**.^[3b] To understand fully, we thought to carryout olefin metathesis reaction and monitor the reaction with specific time.

Figure 3. Product distribution (absolute values in mmols of Olefins vs. Carbon number of the Olefins) of neat 1-decene metathesis reaction using **1** $[(\equiv\text{Si-O})\text{W}(\text{CH}_3)_5]$ at 150 °C for different intervals of time (30 minutes, 2 hours, 4 hours and 72 hours). It is clearly visible that the primary products are lower olefins rather than C_{18} olefin.

For olefin metathesis reaction we maintain similar reaction conditions as that of hydro-metathesis reaction except for the dihydrogen as a reactant. In a batch reactor, we kept the ratio of reactant to catalyst identical to that of hydro-metathesis reaction,

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and the reaction mixture was heated at 150 °C for 3 days. The reaction was monitored by GC at specific intervals of time (Figure 3). From the graph, we could understand that after 30 minutes of reaction the major products are C₉, C₁₁, C₁₇, and C₁₈. The formation of the product C₁₈ is understandable as it is coming from the direct olefin metathesis of 1-decene. C₉, C₁₁, and C₁₇ come from the isomerization of the double bond from 1,2 position to 2,3 position (formation of 2-decene) followed by cross metathesis of the 1-decene and 2-decene.

It was also observed that the concentration of the C₉ and C₁₁ is higher as compared to C₁₈ which confirms that isomerization is much faster than metathesis of 1-decene in our reaction conditions resulting C₃ to C₁₈ olefins. At the end of the reaction, after 3 days, we could observe a higher amount of the lower olefins as compared to higher olefins with a TON of 900, which again corroborates our results that double bond migration followed by olefin metathesis is much faster (chain walking process)^[12] than the reduction of the olefin to alkane followed by alkane metathesis, resulting in a high TON in hydro-metathesis of 1-decene.

We understood these data by assuming that in the liquid phase hydro-metathesis, an olefin metathesis occurs first followed by reduction of the newly formed olefins to alkanes, although we cannot eliminate fully the possibility of alkane metathesis of the newly formed alkanes.

To further understand the reaction mechanism and the effect of other metals on the hydro-metathesis reaction, we choose well-defined catalysts **2** and **3** to compare them with the parent tungsten catalyst **1**. To begin with, we carried out the hydro-metathesis reaction with catalyst precursor **2**, in a typical reaction in a batch reactor, we kept reactant to catalyst ratio as well as the amount of added hydrogen almost similar as with that of catalyst **1** and the reaction was heated up to 150 °C for 3 days (Table 1).

Table 1. 1-decene hydro-metathesis reaction under 0.8 bar of H₂ and 150 °C for 72 hours having similar reactant to catalyst ratio (1010) for all the complexes (TONs are expressed in mol of n-alkane formed per mol of catalyst)

	Catalyst	Conversion (%)	TON	TON	Time (h)
		(Based on C ₁₀)	(alkanes+Olefins)	(alkanes except C ₁₀)	
1	[(=Si-O)-W(CH ₃) ₅]	100	910	818	72
2	[(=Si-O)-Mo(=C ^t Bu)(CH ₂ ^t Bu) ₂]	100	942	808	72
3	[(=Si-O)-Ta(=CH ^t Bu)(CH ₂ ^t Bu) ₂]	100	820	334	72

We could observe that the activities of catalysts **1** and **2** are almost similar with TONs of 818 and 808 (Note that TONs are calculated based on the number of mol of n-alkanes formed except n-decane per mol of catalyst), whereas catalysts **3** is less active with a TON of 334 in hydro-metathesis reaction (SI Figures S1 to S5).

Figure 4. Represents the product distribution (absolute values in mmols of Alkanes vs. Carbon number of Alkanes) of neat 1-decene hydro-metathesis reaction using **2** [(=Si-O)-Mo(=C^tBu)(CH₂^tBu)₂] under 0.8 bar of H₂ and 150 °C for 72 hours

In the hydro-metathesis reaction employing catalyst **2** we could observe a very good TON with a broad distribution of alkanes from C₃ to C₃₄ (Figure 4). We observed that the formation of the C₁₈ is more pronounced as compared to other alkanes.

In order to understand the reaction mechanism in hydro-metathesis reaction, we carried out olefin metathesis reaction of 1-decene with catalyst **2** (Figure 5).

Figure 5. Represents the product distribution (absolute values in mmols of Olefins vs. Carbon number of Olefins) of neat 1-decene metathesis reaction using **2** [(=Si-O)-Mo(=C^tBu)(CH₂^tBu)₂] at 150 °C for 72 hours

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To our expectation, we got C₁₈ as a major product with a TON of 774 (olefin metathesis) along with other olefins which convey us that with molybdenum catalyst **2**, olefin metathesis of the 1-decene takes place much faster than the isomerization of the olefinic double bond. The other olefins are generated via isomerization of double bond followed by cross metathesis of the newly formed olefins.

Additionally, metathesis of 1-decene was tested with catalyst **3** to see if isomerization is much faster than the olefin metathesis in the case of Ta catalyst. To our expectations, we observed that isomerization of the double bond occurs with the formation of other olefins than metathesis of the decene itself (SI Figures S6A and S6B). Based on the above reaction we tried to chalk out a plausible mechanism for this reaction (Figure 6).

Figure 6. Proposed catalytic mechanism of 1-decene hydro-metathesis using M-catalyst (M: W, Mo, and Ta)

Looking at the catalytic results of 1-decene hydro-metathesis reaction with 3 different well-defined silica supported catalysts, we observed that there are 3 competing reaction cycles (A, B and C) are going on simultaneously (Figure 6). **A**- Metathesis of the olefin, **B**-Isomerization of the olefins to newly formed olefins and **C**-Reduction of the olefins to newly formed alkanes in hydro-metathesis reaction. W and Ta silica supported catalysts favor isomerization of the olefins (cycle **B**) followed by cross metathesis (cycle **A**) of the inner olefin with 1-decene resulting lower olefins. Subsequently, newly formed alkanes are generated by reduction (cycle **C**) of the newly formed olefins (Figure 2A and SI Figure S1). Whereas silica supported Mo catalyst favors metathesis of the 1-decene followed by reduction of the newly formed olefins to alkanes (Figures 4, 5 and SI figure S3). Although W and Ta favor isomerization of the double bond over metathesis and Mo favors metathesis over isomerization, we cannot fully eliminate the possible reduction of the 1-decene to n-decane and the metathesis of the n-decane to various alkanes. Additionally, to understand the catalyst behavior after hydro-metathesis reaction solid-state NMR and IR of the catalyst **1** was carried out. As

expected we only observed the alkyl chain on the support (SI figures S7 and S8).

Conclusions

We tested for the first time 3 different catalysts in liquid phase hydro-metathesis reaction. Our aim was to convert liquid olefin to diesel range alkanes. To our expectations, we successfully converted 1-decene into diesel range alkanes. Additionally, we observed that a better metathesis catalyst could convert olefin to alkanes efficiently in the presence of hydrogen. We also observed that different metals approach differently towards olefin: with Mo, olefin metathesis is faster than isomerization whereas with W and Ta isomerization of the double bond is much faster. Comparing this with n-decane metathesis, we witnessed that we could get better conversion, as well as TON, starting from 1-decene to diesel range alkanes than n-decane. We believe this study will open up many directions to efficiently use the olefins for various organic transformation reactions.

Experimental Section

General procedure:

All experiments were carried out by using standard Schlenk and glove box techniques under an inert argon atmosphere. The syntheses and the treatments of the surface species were carried out using high vacuum lines ($< 10^{-5}$ mbar) and glove-box techniques. Pentane was distilled from a Na/K alloy under Ar and dichloromethane from CaH₂. Both solvents were degassed through freeze-pump-thaw cycles. SiO₂₋₇₀₀ prepared from Aerosil silica from Degussa (specific area of 200 m²/g), which was partly dehydroxylated at 700 °C under high vacuum ($< 10^{-5}$ mbar) for 24 h to give a white solid having a specific surface area of 190 m²/g and containing around 0.5-0.7 OH/nm². 1-decene purchased from Aldrich, Hydrogen (99.999 %) gas was purchased from Specialty Gases Center of Abdullah Hashim Industrial Gases & Equipment Co. Ltd. (Saudi Arabia). W(CH₃)₆,^[13] [Mo(=C'Bu)(CH₂'Bu)₃]^[14] and [Ta(=CH'Bu)(CH₂'Bu)₂]^[15] (SI Figures S9 – S14) and supported *pre*-catalyst [(≡Si-O-)W(CH₃)₅]^[11] **1**, [(≡Si-O-)Ta(=CH'Bu)(CH₂'Bu)₂]^[16] **3** and [(≡Si-O-)Mo(=C'Bu)(CH₂'Bu)₂]^[17] **2** were prepared according to literature procedures (SI Figures S15 – S17).

IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer by using a DRIFT cell equipped with CaF₂ windows SI figures S9 – S11. The IR samples were prepared under argon within a glove box. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm⁻¹). Elemental analyses were performed at Mikroanalytisches Labor Pascher (Germany) and Core Lab ACL KAUST.

GC measurements were performed with an Agilent 7890A Series (FID detection). Method for GC analyses: Column HP-5; 30m length x 0.32mm ID x 0.25 μm film thickness; Flow rate: 1 mL/min (N₂); split ratio: 50/1; Inlet temperature: 250 °C, Detector temperature: 250 °C; Temperature program: 40 °C (3 min), 40-250 °C (12 °C/min), 250 °C (3 min), 250-300 °C (10 °C/min), 300 °C (3 min); 1-decene retention time: *t*_R = 9.5 min, n-decane retention time: *t*_R = 9.6 min.

GC-MS measurements were performed with an Agilent 7890A Series coupled with Agilent 5975C Series. GC/MS equipped with capillary column coated with none polar stationary phase HP-5MS was used for molecular weight determination and identification that allowed the separation of hydrocarbons according to their boiling points differences. GC response

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factors of available C₅-C₁₀ *n*-alkanes standards were calculated as an average of three independent runs. The plot of response factor versus *n*-alkanes carbon number was determined, and a linear correlation was found, then we extrapolated the response factors for other *n*-alkanes.

Hydro-metathesis of 1-decene:

A mixture of species **1**, **2**, and **3** (5.2×10⁻³ mmol W, Mo or Ta) and dry 1-decene (5.28×10⁻³ mmol) were mixed inside the glovebox in a glass reactor (V= 265 ml) with water circulation. The reaction mixture was frozen, evacuated under vacuum, and 0.8 bar of dry hydrogen was added to it. The reactor is warmed up to the room temperature, connected to a chiller (T= 16 °C), immersed in an oil bath and heated at 150 °C for a set time. Then, the catalytic run was quenched by addition of a fixed amount of CH₂Cl₂, and after filtration, the resulting solution was analyzed by GC and GC/MS.

Metathesis of 1-decene:

A mixture of species **1**, **2**, and **3** (5.2×10⁻³ mmol W, Mo or Ta) and dry 1-decene (5.28×10⁻³ mmol) were mixed inside the glovebox. The ampoules were sealed under vacuum, immersed in an oil bath, and heated at 150 °C for a set time. At the end of the reaction, the ampoules were frozen under liquid nitrogen. Then, the catalytic run was quenched by addition of a fixed amount of CH₂Cl₂, and after filtration, the resulting solution was analyzed by GC and GC/MS.

Liquid State Nuclear Magnetic Resonance Spectroscopy:

All liquid state NMR spectra were recorded on Bruker Avance 600 MHz spectrometers. All chemical shifts were measured relative to the residual ¹H or ¹³C resonance in the deuterated solvent: CD₂Cl₂, 5.32 ppm for ¹H, 53.5 ppm for ¹³C.

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Keywords: Hydro-metathesis • Catalysis • Organometallics • Surface organometallic chemistry • Carbyne

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