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"Hydro-metathesis" of Olefins: A Catalytic Reaction Using a Bifunctional Single-Site Tantalum Hydride Catalyst Supported on Fibrous Silica (KCC-1) Nanospheres**

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Low-temperature skeletal cleavage and the formation of C−C bonds are of prime importance in the petrochemical industry because the transformation of crude oil into hydrocarbons having different numbers of carbon atoms is often necessary. In this regard, the skeletal transformation of olefins into valuable products remains an important challenge in chemistry. Any new reaction related to this challenge is important. In 1991, we discovered that the highly electrophilic early-transition-metal hydride [(≡SiO)$_3$Zr-H] supported on silica[1–4] could activate the C−H and C−C bonds of alkanes or polyolefins and could also catalyze the hydrogenolysis of these hydrocarbons into a range of gasolines.[5] Later, in 1997, we found that the highly electrophilic silica-supported tantalum hydride [(≡SiO)$_2$TaH][6,7] could transform any light alkane into its lower and higher homologues by both cleavage and formation of C−H and C−C bonds. We called this new catalytic reaction "alkane metathesis" by analogy to "olefin metathesis" [Eq. (1)].[6–8] Herein we disclose that tantalum

$$\begin{array}{l} 2\,C_nH_{2n+2} \rightleftharpoons C_{n-\mathrm{i}}H_{2(n-i)+2} + C_{n+1}H_{2(n+i)+2} \\ n \gg 2 \qquad i = 1,2,\ldots(n{-}1) \end{array} \qquad (1)$$

hydride (TaH) supported on fibrous silica nanospheres (KCC-1) can catalyze, in the presence of hydrogen, the direct conversion of olefins into alkanes having higher and lower numbers of carbon atoms; therefore we refer to the reaction as "hydro-metathesis" [Eq. (2)]. This novel reaction has

$$\begin{array}{l} 2\,(C_nH_{2n} + H_2) \rightleftharpoons C_{n-i}H_{2(n-i)+2} + C_{n+1}H_{2(n+i)+2} + C_nH_{2n+2} \\ n \gg 2 \qquad i = 1,2,\ldots(n{-}1) \end{array} \qquad (2)$$

excellent catalytic performance and unexpectedly high turnover numbers as compared to the now classical alkane metathesis. For the first time, this silica-supported tantalum hydride shows remarkable catalytic stability, with an excellent potential of regeneration.

In the case of propane metathesis, kinetic studies carried out at very low contact time, in a continuous flow reactor, revealed that the primary products of this reaction were olefins and H$_2$.[9] This observation, among many others, as well as elementary steps known in tantalum organometallic chemistry, led us to propose a mechanism based on the following key steps: 1) paraffin C−H bond activation leading to a metal/alkyl species with subsequent formation of an olefin and a metal hydride by β-hydride elimination; 2) α-hydrogen abstraction from the same metal/alkyl species leading to the formation of a metallocarbene; 3) olefin metathesis on this metallocarbene; and 4) hydrogenation of the new olefins on the metal hydride (see Scheme S1 in the Supporting Information).[9] Thus, the tantalum hydride in this metathesis reaction acts as a trifunctional single-site system (dehydrogenation/metathesis/hydrogenation).

In this work, we observed that TaH/KCC-1 not only transforms any olefin in the presence of hydrogen at moderate temperatures into the expected corresponding alkane, but also transforms the same olefin into alkanes having a higher and lower number of carbon atoms. Importantly, in our quest of nanocatalysts,[10] we used our recently discovered high-surface-area silica nanospheres having a unique fibrous morphology (KCC-1) as the catalyst support.[11]

The KCC-1-supported tantalum hydride (TaH/KCC-1) was prepared by grafting the [Ta(=CH*t*Bu)(CH$_2$*t*Bu)$_3$] complex onto fibrous silica nanospheres, and then treatment under hydrogen atmosphere at 150 °C for 12 hours. Infrared (IR) spectroscopy was used to monitor the grafting by sublimation of [Ta(=CH*t*Bu)(CH$_2$*t*Bu)$_3$] (80 °C) onto a KCC-1 silica disk, which was previously dehydroxylated under vacuum at 500 °C for 8 hours; the data indicated that the intensity of the peak corresponding to isolated silanol groups (ν(Si-OH) = 3747 cm^{-1}) was sharply reduced (more than 70%; Figure 1). At the same time, characteristic IR bands appeared at between 2700 and 3000 cm^{-1} and at 1366 and 1465 cm^{-1} which corresponded to the C−H stretching and C−H bending vibrations, respectively, and neopentane (NpH, Np = neopentyl) was evolved in the gas phase. These observations and the resistance of the IR C−H vibrations bands to a desorption process at 80 °C indicated that the Ta/hydrocarbyl complex was chemically grafted onto KCC-1. Additional treatment of the grafted Ta/hydrocarbyl complex under a

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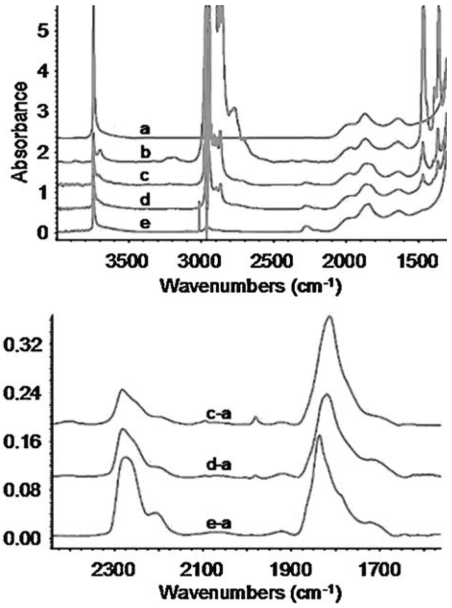


Figure 1. Upper: Transmission IR spectra of: a) KCC-1 treated at 500 °C, b) grafting of [Ta(=CHtBu)(CH$_2t$Bu)$_3$] onto a KCC-1 silica disk. The formation of the tantalum hydride on KCC-1 by treatment under hydrogen (700 mbar) at 150 °C (c), 200 °C (d), and 250 °C (e). Lower: subtracted spectra: c−a, d−a, and e−a.

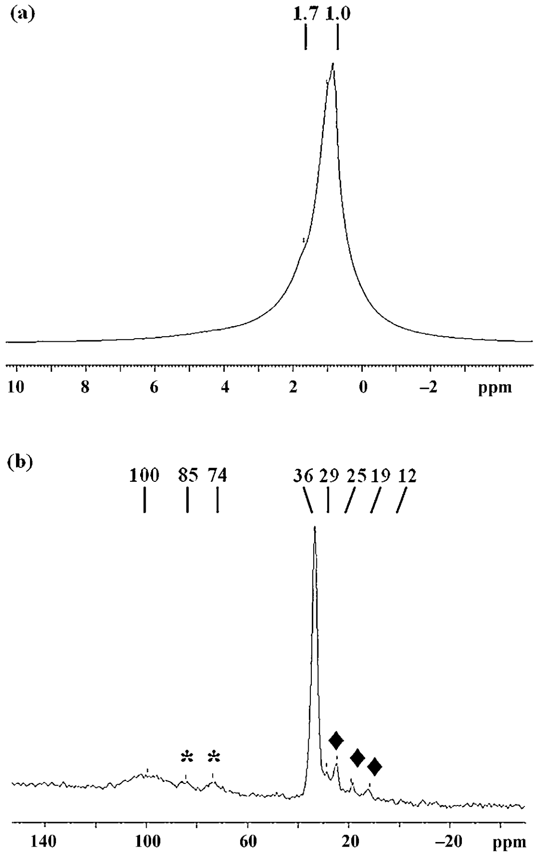


Figure 2. Solid-state NMR spectra of the [Ta(=CHtBu) (CH$_2t$Bu)$_3$]/KCC-1 complex: a) ^{1}H MAS spectrum (NS = 64, D1 = 2 s), b) ^{13}C-CP/MAS spectrum (NS = 30000, D1 = 2 s). ✲ impurities, ◆ traces of remaining template.

hydrogen atmosphere at 150 °C led to a decrease in the intensity of the IR C–H vibration bands and the appearance of ν(TaH) bands at 1815 cm^{-1} and ν(SiH) bands at 2205 and 2275 cm^{-1}, as observed on silica[7] or MCM-41.[12] Although 77 % of the C–H bands disappeared at 150 °C, heating to 250 °C was necessary to remove all the alkyl groups from the surface (Figure 1).

To scale up the preparation of the catalyst, a pentane solution of [Ta(=CHtBu)(CH$_2t$Bu)$_3$] was used to graft the complex onto a powder sample of KCC-1 silica nanospheres (pretreated at 500 °C under vacuum). Elemental analysis of the resulting [Ta(=CHtBu)(CH$_2t$Bu)$_3$]/KCC-1 indicated 7.58 wt % Ta.

The ^{1}H solid-state magic angle spinning (MAS) NMR spectrum of the [Ta(=CHtBu)(CH$_2t$Bu)$_3$]/KCC-1 complex (Figure 2 a) displays one broad signal centered on $\delta = 1.0$ ppm with a shoulder at $\delta = 1.7$ ppm, which have been assigned to alkyl C–H bands and residual OH groups, respectively. The ^{13}C solid-state CP/MAS NMR spectrum (Figure 2 b) shows two main signals at $\delta = 34$ and 100 ppm, which are assigned to $C(CH_3)_3$ and CH_2tBu, respectively. A possible signal for a carbene at around $\delta = 240$ ppm was not observed with the given natural abundance of ^{13}C.

When a 1:1 mixture of propene (3 mL min^{-1}) and hydrogen (3 mL min^{-1}) was reacted in a continuous flow reactor at 150 °C and 1 atm in the presence of TaH/KCC-1 (557 mg, 0.233 mmol Ta, in situ H_2 treated at 150 °C), the reaction proceeded efficiently with 37–40 % conversion (Figure 3 a).[13] In addition to the expected propane, butane (35–40 %) and ethane (40 %) were the major products formed, with methane, iso-butane, and pentanes as minor products (Figure 3 b). Surprisingly, the catalyst was stable even after 56 hours, affording a cumulative turnover number (TON) of up to 768, with no major change in conversion and selectivity. This is first time that we have observed such excellent catalyst stability with high turnover numbers. Also remarkable is the regenerative ability of the catalyst: after using TaH/KCC-1 in a 56 hour reaction it was regenerated by treatment with hydrogen (3 mL min^{-1}) at 150 °C for 12 hours, after which it was used in another propene hydro-metathesis under identical reaction conditions and demonstrated slightly better activity (Figure 3 a, dotted lines), selectivity (see Figure S1 in the Supporting Information), and stability. The slight increase in the catalytic activity after regeneration could result from the fact that the total elimination of alkyl groups from TaNp/KCC-1 under H_2 requires heating up to 250 °C instead of 150 °C with Degussa silica[6] or MCM-41;[9] under these conditions the regeneration could help to remove more Np groups and produce a little bit more TaH than the first run.

To make a comparison with our previously developed catalyst,[12] the propene hydro-metathesis was performed under the same conditions (150 °C, 1 atm, 3 mL min^{-1} C_3H_6, 3 mL min^{-1} H_2) using TaH/MCM-41 (11.33 wt %, 381 mg, 0.238 mmol Ta, in situ H_2 treated at 150 °C) with the same amount of tantalum in the reactor. The reaction proceeded efficiently with a conversion (35–37 %)[13] similar to that of TaH/KCC-1 and a selectivity close to that of propane

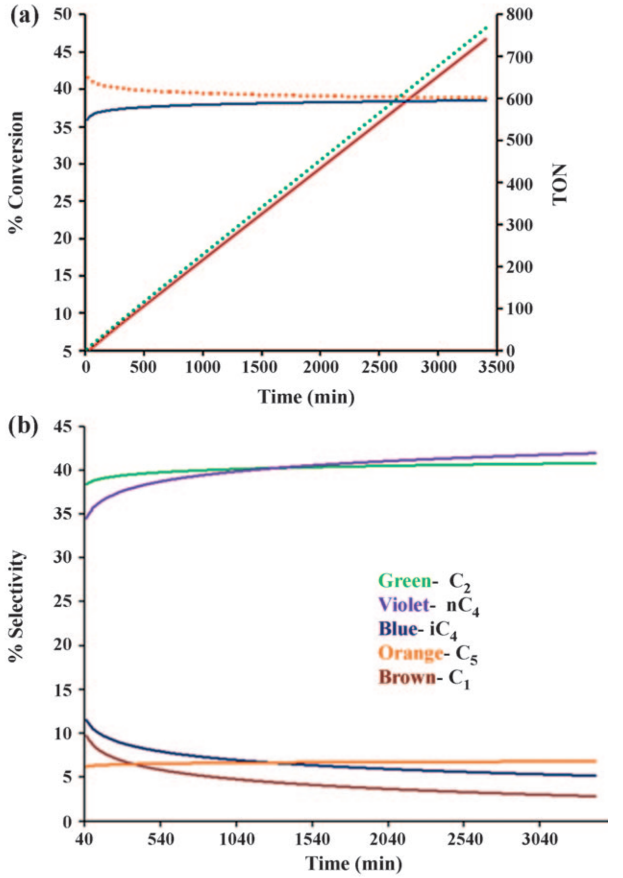


Figure 3. a) Conversion (blue and orange lines) and turnover numbers (red and green lines) and b) selectivities as a function of time obtained during the hydro-metathesis of propene (3 mL min^{-1}) catalyzed by TaH/KCC-1 (557 mg), in a continuous flow reactor (150 °C, 1 atm) in the presence of hydrogen (3 mL min^{-1}). The dotted lines indicate data for the reaction run with the regenerated catalyst.

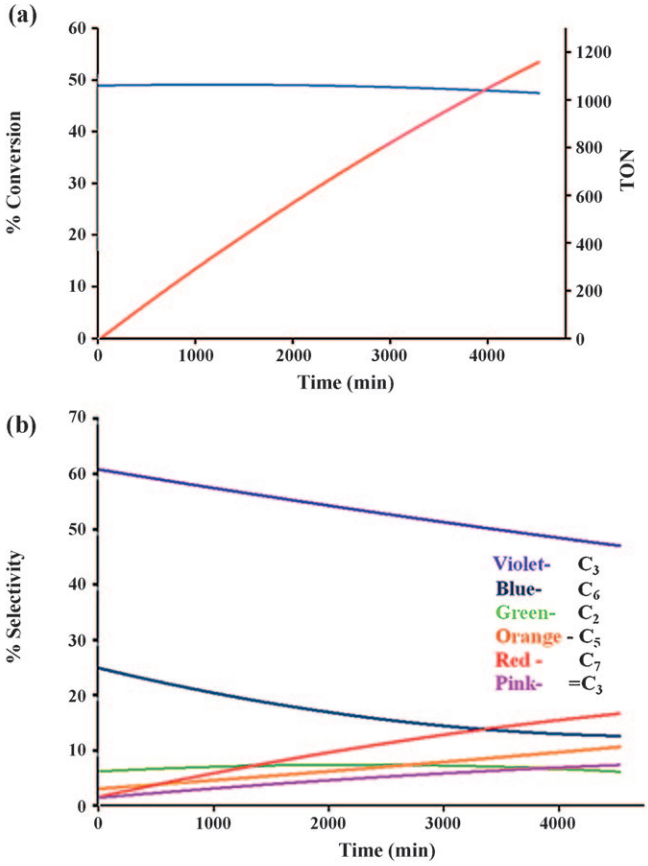


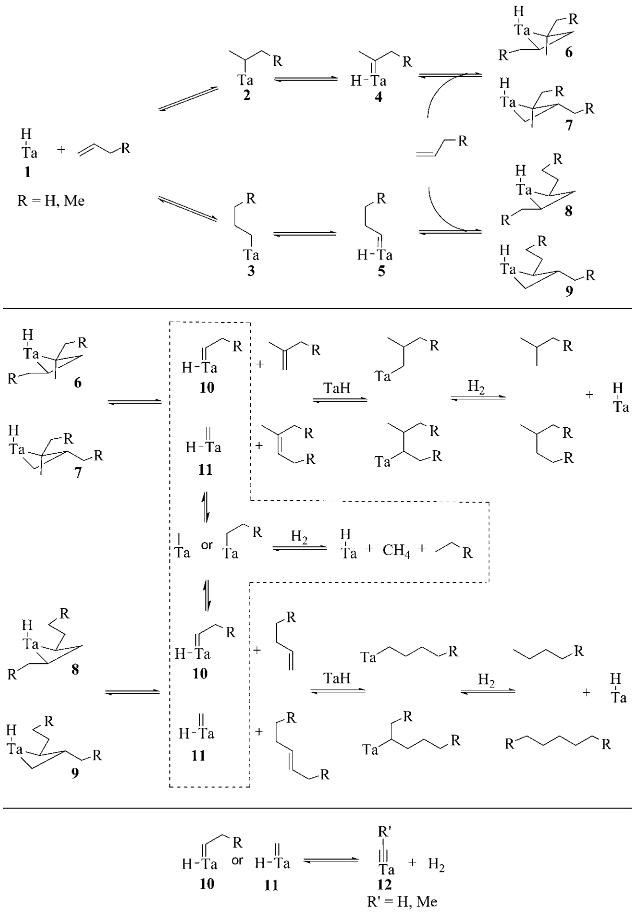
Figure 4. a) Conversions (blue line) and turnover numbers (red line), and b) selectivities as a function of time obtained during the hydro-metathesis of 1-butene (3 mL min^{-1}) catalyzed by TaH/KCC-1 (550 mg), in a continuous flow reactor (150 °C, 1 atm) in the presence of hydrogen (3 mL min^{-1}).

metathesis with TaH/SiO_2.[9] The catalyst was stable for 65 hours, affording a cumulative TON up to 750, with no major change in conversion (see Figure S2 in the Supporting Information). The regenerative ability of this catalyst (TaH/MCM-41) was also excellent; after the first run at 65 hours, the regenerated catalyst (treatment with hydrogen at 150 °C for 12 h) showed the same activity (see Figure S2 in the Supporting Information), selectivity (Figure S3), and stability for a second run of the propene hydro-metathesis.

We also conducted hydro-metathesis of 1-butene under identical reaction conditions. 1-butene (3 mL min^{-1}) and hydrogen (3 mL min^{-1}) were reacted in the presence of TaH/KCC-1 in a dynamic reactor at 150 °C and 1 atm. The reaction proceeded efficiently with good conversion (48 to 51 %; (Figure 4 a).[13] In addition to the expected hydrogenation product butane, propane (47–61 %) and hexanes (13–25 %) were formed as major products, and ethane, propene, pentanes, and heptanes formed as minor products (Figure 4 b). In this case, the catalyst was stable even after 75 hours of continuous reaction with a cumulative TON up to 1150; however, some deactivation occurred as suggested by a decrease in the conversion compared to the initial value of 51 % to 47 % (Figure 4 a).

The turnover numbers and catalyst stability observed are superior to those observed previously and to that reported by Goldman, Brookhart, et al., who conducted alkane metathesis involving tandem alkane dehydrogenation (using an iridium complex) and subsequent olefin metathesis (using a molybdenum complex).[14] They achieved good catalytic activity, however deactivation of the olefin metathesis catalyst restricted the turnover numbers. In the present study, the important outcomes were the excellent stability of our new catalyst and the high turnover numbers compared with the turnover numbers we observed for the TaH and alkane metathesis. This is very unusual because in most of our previous studies with alkanes the TaH catalyst lost activity over time. The improvement, for this catalyst, in the turnover number of about one order of magnitude can be explained on the basis of the reaction mechanism shown in Scheme 1.

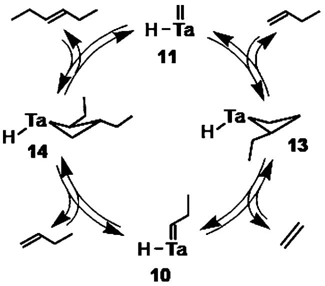
The only difference between the mechanism of alkane metathesis and that of olefin hydro-metathesis is the first step: in alkane metathesis, the C–H bond activation step by TaH produces H_2 with linear and secondary alkyl/Ta complexes (see Scheme S1 in the Supporting Information), whereas for hydro-metathesis, the same secondary (**2**) and linear (**3**) alkyl/Ta complexes are obtained by insertion of the olefin into the



Scheme 1. Mechanism of the hydro-metathesis of propene and 1-butene

TaH bond (Scheme 1). The remaining elementary steps are the same as those in alkane metathesis. Intermediates **2** and **3** undergo an α-hydrogen abstraction to form the Ta/carbene/hydrides **4** and **5**, respectively, which can react with the incoming alkene from the gas phase to produce four different tantallacyclobutanes (**6**–**9**).[15] These tantallacyclobutanes later cleave metathetically to yield higher alkenes and the hydrido tantallacarbenes **10** and **11**. The final step is the insertion of alkenes (generated in the previous step) into the tantalum hydride and then the resulting alkyl groups would be cleaved by hydrogen to liberate the corresponding alkanes. The much faster rate observed in hydro-metathesis of olefins is probably because of the ease of olefin insertion as compared to the more difficult step of C–H bond activation in alkane metathesis. Moreover, thermodynamic limitations could also explain the comparative ease of the hydro-metathesis because dehydrogenation of paraffins is thermodynamically very unfavorable at low temperatures.

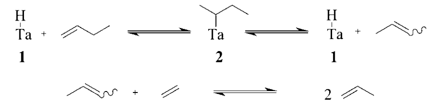
Importantly, **10** and **11** can also undergo an additional α-hydrogen elimination to form Ta/carbyne complexes **12**, which are suspected to be unreactive and potentially the cause of the catalyst deactivation. However, in the hydro-metathesis of olefins, the presence of hydrogen prevents the formation of **12**, which in turn increases the lifetime of the catalyst.



Scheme 2. Complementary reaction mechanism of the formation of two- and six-carbon hydrocarbon chains from 1-butene.

In the case of 1-butene, the observed selectivity for all products suggests the occurrence of side reactions. The mechanism depicted in Scheme 1 explains the formation of pentanes and heptanes associated as well as equimolar amounts of propane and methane. However, the unexpected but significant amount of hexanes that is formed requires another process involving the tantalum hydrido carbenes **10** and **11** (Scheme 2). In fact, **10** and **11** can also react with 1-butene to form two different tantallacyclobutanes (**13** and **14**, respectively) which will lead to their mutual regeneration and liberation of hexene and ethylene during metathetical cleavage; subsequent liberation of the alkane is similar to Scheme 1. The observation of only traces of methane (<0.7 %) among the products, which normally arises from transformation of the tantalum hydrido methylidene **11** into tantalum methyl and subsequent cleavage of the methyl (Scheme 1), supports the involvement of the intermediate **11** in another process (Scheme 2).

Nevertheless, the mechanism in Scheme 2 suggests that similar amounts of ethane and hexanes should be formed. The observed deficit of ethane compared to hexanes and the large excess of propane require the contribution of another side reaction (Scheme 3). After insertion of 1-butene into the TaH bond, as in the case of **2**, a β-hydride elimination can take place, thus leading to the liberation of *cis*- and *trans*-2-butenes, which are thermodynamically favored (Scheme 3).[16] 2-Butenes are well known to undergo cross-metathesis with ethylene to form propylene,[17] which after hydrogenation would contribute to the large excess of propane; conversely, the consumption of ethylene would explain the final lack of ethane. The presence of propylene among the products also suggests that cross-metathesis is slightly faster than the hydrogenation of olefins.



Scheme 3. Complementary reaction pathways of the formation of propylene from 1-butene.

In summary, TaH supported on fibrous silica nanospheres (KCC-1) catalyzes a new hydro-metathesis reaction of olefins with remarkable catalytic activity and stability. Conversions remain rather constant and the TONs of the reactions increase steadily. This is the first time that such a stable catalyst with such a high TON (with a gain of one order of magnitude) has been observed in tantalum hydride catalyzed reactions. Furthermore, the catalyst proved to be quite regenerable and using it in a second run yielded similar or even better results than the first run.

Mechanistically, the hydro-metathesis of olefins involves similar elementary steps as those involved in alkane metathesis, but the formation of the first alkyl/tantalum complex occurs by insertion of the olefin into the TaH, whereas in alkane metathesis the alkyl/tantalum complex is formed through C–H bond activation. The faster rate observed in hydro-metathesis of olefins is probably because of the ease of the olefin insertion as compared to the more difficult step of C–H bond activation in alkane metathesis. Moreover, thermodynamic limitations could also explain the comparative ease of hydro-metathesis because dehydrogenation of paraffins is thermodynamically very unfavorable at low temperatures. The remarkable absence of catalyst deactivation is probably because of the presence of hydrogen, which prevents the formation of unreactive carbynes.

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