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Tailoring the selectivity in 2-butene conversion over supported d^0 group 4, 5 and 6 metal hydrides: from dimerization to metathesis

Kai C. Szeto,1,5* Nicolas Merle,2 Cesar Rios,2 Pascal Rouge,3 Jessica Llop Castelbou3 and Mostafa Taoufik4,*

2-Butenes are transformed in a continuous flow reactor over metal hydrides of zirconium, tantalum and tungsten supported on silica-alumina. Exceptionally high selectivity on dimeric products is obtained over supported zirconium hydride catalyst. Supported tantalum hydride gives high selectivity in dimeric products along with small amounts of metathesis products. Conversely, supported tungsten hydride leads only to metathesis products. The unprecedented selective production of mono-branched and di-branched octenes is originated from the bi-functionality of the active sites, allowing isomerization of 2-butenes to 1-butene followed by fast insertion of 1-butene on the metal sec-butyl fragment.

Introduction

Linear and branched octenes obtained by dimerization of butenes are frequently utilized in industry, such as in the manufacture of linear low density polyethylene’s (LLDPE) comonomer, special detergents, gasoline additives, synthetic lubricating oils, etc. Branched octenes are recently widely used to replace the environmental sensitive compound MTBE in gasoline additives.1 For example, the dimerization of isobutene into 2,4,4-trimethylpentenes is generally carried out on acidic catalysts.2 Different acids have been described in the literature such as sulfuric acid, or derivatives thereof, supported phosphoric acid, ion-exchanged resins, chlorinated or fluorinated aluminas, zeolites, silica-aluminas etc.3,4 The main difficulty is to control the exothermicity of the reaction and to obtain high yield on desired dimeric products due to formation of oligomers, in particular trimers (C12 olefins) and tetramers (C16 olefins). The dimerization of 1-butene is interesting, since branched dimer (1,2-insertion) and linear dimer (2,1-insertion) can be formed, in addition to isomerization reactions and linear butenes oligomerization. For instance in homogeneous catalysis,5,6 Wasserscheid et al.7,8 and Small et al.9,10 have reported catalysts that promote linear dimerization of 1-butene. Their systems are either based on nickel complexes with fluorinated acetylatedonate ligands dissolved in buffered ionic liquids,7 or tridentate pyridine bis-imine cobalt and iron complexes after activation with MAO, can produce highly linear dimers.9 Catalysts based on vanadium and aluminum prefer to generate branched dimers.10 Nickel catalysts with phosphine ligands are generally less selective than those based on iron or cobalt for the production of linear dimers with moderate selectivity around 60%. However, the practical application has been hindered by the fact that the activity of this kind of catalysts is relatively low. Group 4 transition metal zirconium-based Ziegler-Natta catalysts have been used primarily for olefin polymerization and ethylene oligomerization.11,12 There are few reports in literature concerning the dimerization of 1-butene via zirconium-based Ziegler–Natta catalysts. A classic zirconocene, Cp2ZrCl2, activated by MAO can selectively dimerize 1-butene to 2-ethyl-1-hexene without formation of any heavier oligomer.13 On the other hand, the cationic gas phase Cp2ZrMe (obtained by electrospray ionization) reacts with 1-butene and gives multiple olefin additions.14 Furthermore, the selectivity of zirconocene catalyzed systems can be altered (from dimer to heptamers) by varying the 1-butene flow, zirconocene concentration and reaction temperature.15 These highly electrophilic systems are indeed very active, but require extensive control of reaction parameters to avoid oligomerization reactions.16–19 In order to design a selective homogeneous catalyst for linear butenes dimerization, extensive research effort in ligand tuning can be carried out. However, it is generally difficult to establish the structure-reactivity relationship on this particular system, and thereby requires multiple experimental attempts before the most promising complex is identified. A second approach is to employ 2-butene as feed to limit oligomerization reactions, as the multi-insertion of 2-butenes on metal-sec-butyl moiety is generally disfavored over β-H elimination to release dimers. Indeed, β-H elimination is generally favored compared to multiple olefin insertion at higher temperature. Nevertheless, working on higher temperature on homogeneous organo-metallic catalysts is inconvenient due to thermal decomposition or bimolecular deactivation.20 Based on these
experiences, an improved catalytic system without side reactions such as oligomerization can be designed by using either 2-butenes as feed or applying a neutral metal center based on group 4, 5 or 6 over a robust heterogeneous system. Our laboratory has established an approach to prepared supported single site catalysts, denoted surface organometallic chemistry, to avoid bimolecular decomposition. This class of heterogeneous catalysts has also resulted in the discovery of novel reactions, such as alkane metathesis, direct conversion of ethylene to propylene, non-oxidative coupling of methane etc. Heterogeneous catalysis has many advantages such as facile recycling of the catalyst, allows utilization of a continuous flow reactor in gas phase, adaptable with a wide working temperature range and give higher economic and environmental friendly process. Hence, the direct conversion of 2-butenes (major isomer and available from steam cracker or refinery based on C4 stream) is a new scientific and economical challenge for producing a wide variety of more valuable products. We have recently studied the conversion of pure 2-butene feed by metathesis catalyst ([W-H]/Al\textsubscript{2}O\textsubscript{3}). In general, applying symmetric olefins, such as 2-butenes over a metathesis catalyst gives only degenerated product. However, for this particular catalyst, 2-butenes are converted to propylene and pentenes in high yield. The driving force for this reaction is the bi-functional active specie which comprises tungsten carbene-hydride moiety that can readily isomerize 2-butenes to 1-butene (on W-H), followed by cross-metathesis (W=CHR) between 1-butene and 2-butenes. In this case, no dimeric product of 2-butenes has been observed by double insertion of 2-butenes on metal-hydride. This can be either explained by disfavor insertion of 2-butenes or even the formed 1-buten on metal-sec-butyl fragments, probably due to the low activity of tungsten complexes in oligomerization of olefins, or the fact that tungsten carbene-hydride is a very active metathesis catalyst.

Current communication reports a comparative study of 2-butene conversion into branched octenes (dimerization) or other alkenes (metathesis) by applying highly electrophilic supported metal-hydrides based on group IV (Zr), Group V (Ta) and Group VI (W).

**Experimental**

**Materials and methods**

Catalyst preparation ([ZrH/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}])\textsubscript{500}), ([TaH\textsubscript{2}/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}])\textsubscript{500}) and ([WH\textsubscript{3}/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}])\textsubscript{500}) were prepared according to published procedure reported elsewhere. The preparation consisted in two steps. The first step involved grafting Zr([CH\textsubscript{2}C(CH\textsubscript{3})\textsubscript{3}])\textsubscript{500}) Ta([CH=C(CH\textsubscript{3})\textsubscript{3}])\textsubscript{500}) and W([CC(CH\textsubscript{3})\textsubscript{3}])\textsubscript{500}) onto silica-alumina (Akzo-Nobel) dehydroxylated at 500 °C to obtain a monopodal well-defined ([Si-O])Ta([CH=C(CH\textsubscript{3})\textsubscript{3}])\textsubscript{500}) ([Si-O])Zr([CH=C(CH\textsubscript{3})\textsubscript{3}])\textsubscript{500}) and ([Si-O])W([CC(CH\textsubscript{3})\textsubscript{3}])\textsubscript{500}) fragment on the silica-alumina surface. Excess of the molecular complex was washed off with dry pentane and the solid was dried under high vacuum at room temperature. The second step comprised a treatment of the latter solids under H\textsubscript{2} at 150 °C. The catalysts were then stored in the glovebox at low temperature.

**Catalyst evaluation** Evaluation of the catalytic performance of trans-2-butene conversion was carried out in a stainless steel continuous flow microactivity reactor purchased from PID Eng&Tech. Trans-2-butene (Scott, 99%) was purified with a column of molecular sieve and activated CuO/Al\textsubscript{2}O\textsubscript{3} and was injected into the catalyst bed by a high pressure syringe pump (TOP Industrie PMHP50-500). The catalyst was charged in a glove-box. A 4-way valve allowed isolation of the charged catalyst in the reactor from the environment and extensive purging of the tubes exposed to air. The products were determined by a gas chromatograph (Varian CP 3800 connected online to the reactor with heated tube) equipped with 50 m KCl/Al\textsubscript{2}O\textsubscript{3} and 30 m HPS columns having their own FID. The conversion of butenes was calculated based on carbon number. The products were further analyzed by GC-MS (Agilent 6890/5975C) equipped with 30 m HPS-m column and NIST08 database.

**Spectroscopic characterization** DRIFT spectra were recorded on a Nicolet 6700 FTIR spectrophotometer equipped with a SMART module and MCT detector. The samples were loaded in an airtight cell with CaF\textsubscript{2} window. The spectra were composed of 64 scans and collected with a resolution of 4 cm\textsuperscript{-1}. Solid state NMR was performed in a Bruker Avance 500 spectrometer. The samples were packed in a 4 mm zirconia rotor in a glovebox and sealed with a kel-f stopper. A spinning rate of 10 kHz was applied during the acquisition.

**Results and discussion**

Catalytic performance of trans-2-butene over ([Zr-H/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}])\textsubscript{500}) was carried out in a continuous flow reactor (m\textsubscript{catalyst} = 200 mg, P\textsubscript{4He} = 20 bar, T = 180 °C, total flow rate = 10 mL min\textsuperscript{-1}). The reaction has a maximal conversion rate of 1.3 mol\textsubscript{4He}\textsuperscript{-molZr}\textsuperscript{-1}\textsuperscript{-min}\textsuperscript{-1} at the start of reaction and then undergoes a very slow deactivation, affording 1.0 mol\textsubscript{4He}\textsuperscript{-molZr}\textsuperscript{-1}\textsuperscript{-min}\textsuperscript{-1} after 86 h, yielding an overall turnover number, TON, of 5300 (Figure 1a). The obtained products are mainly octenes, along with small amounts (<5%) of pentenes, hexenes and heptenes. Importantly, no heavier alkenes (trimer and tetramer) are observed. This unprecedented reaction leads to an outstanding and fairly constant selectivity of 95% to octenes (Figure 1b), giving a maximum productivity of 30.1 mmol\textsubscript{octenes}\textsuperscript{-molZr}\textsuperscript{-1}\textsuperscript{-h}\textsuperscript{-1} after 1 h on stream. Since the selectivity is...
practically constant with time on stream (about 95%), the productivity is 23.1 mmol\textsubscript{octenes} \cdot g\textsubscript{cata}^{-1} \cdot h^{-1} after 86 h.

The formed octenes can be classified as 3,4-di-methyl hexenes (about 67.3%), 3-methyl heptenes (about 32.2%) and small amounts of linear octenes (0.5%) (Table 1, Figure S1). In addition, we observed the isomerization of 2-trans-butene into cis-2-butene (trans/cis = 2.5; thermodynamic equilibrium at 180 °C = 2.0) accompanied with small amount of isobutene and 1-butene. To understand how these products come from, the initiation and propagation steps of this reaction were elucidated by identifying the products formed while heating to the reaction conditions. It is reasonable to postulate that the initiation of the catalytic process occurs with a similar mechanism to that previously described for the cross-metathesis between isobutene and 2-butene on supported metal hydrides.\textsuperscript{36} It can be assumed that trans-2-butene inserts into the zirconium hydride precursor, affording a zirconium sec-butyl species, Zr-CH(CH\textsubscript{3})(CH\textsubscript{2}CH\textsubscript{3}), 1a. This reactivity is supported by DRIFT (Figure 2) and \textsuperscript{1}H and \textsuperscript{13}C CP MAS solid state NMR (Figure 3). After reacting the catalyst precursor with trans-2-butene at 180 °C (50 torr) for 5 min in a batch reactor, the ν(Zr-H) vibration band (1637 cm\textsuperscript{-1}) disappeared while peaks between 2850-3000 cm\textsuperscript{-1} and 1460 cm\textsuperscript{-1}, correspond to typical C-H stretching and bending bands assigned to alkyl fragments largely increased, suggesting formation of surface butyl species in addition to the small amount of neopentyl fragments remained after hydrogenolysis of the zirconium neopentyl precursor. On the other hand, the ν(Si-H) at 2248 and 2186 cm\textsuperscript{-1},\textsuperscript{37} formed during the hydrogen treatment of the supported zirconium neopentyl specie, remained intact.

\textsuperscript{1}H solid state NMR spectrum of 1 (figure 3) is in agreement with previous results\textsuperscript{38} and displays peaks correspond to supported Zr-H (10.1 ppm), ZrH\textsubscript{2} (12.0 ppm), Si-H (4.4 ppm) and remaining alkyl group (0.8 ppm). After reaction with trans-2-butene, the peaks of zirconium hydrides disappeared and a large signal centered at 0.9 ppm in the \textsuperscript{1}H NMR spectrum is observed. \textsuperscript{13}C solid state CPMAS NMR (Figure S2) shows a signal at 10 ppm, attributed to methyl group in sec-butyl fragment, and a large signal extended from 20-40 ppm, attributed to the other carbons in the zirconium butyl species. Experimental data suggest that disubstituted olefin can readily insert into zirconium hydride bond according to the Cossee-Arlman mechanism.\textsuperscript{39,40} Formation of cis-2-butene, isobutene and 1-butene can be explained by insertion of trans-2-butene followed by β-H elimination from the secondary and primary carbon, respectively (scheme 1).
As reported earlier in solution,\textsuperscript{41} the reaction of 2-butene with metal hydride initially gave the expected sec-butyl complex. However, this specie isomerizes to the more stable n-butyl counterpart, as determined by \textsuperscript{1}H NMR in C\textsubscript{6}D\textsubscript{6}. Nevertheless, experimental data based on solid state NMR are inadaptable to characterize different zirconium butyl isomers on surface after insertion of 2-butene into supported zirconium hydride at 180 °C. For further determination of the ratio between different fragments on the surface, the sample after insertion of 2-butene at 180 °C was exposed to water vapor at the same temperature. Gases given off were analyzed by GC. The products were butene isomers (trans-2-butene = 62.25%, cis-2-butene = 24.25%, 1-butene = 8.27% and isobutene = 0.20%) along with 4.99% butane, 0.04% isobutane and hydrogen. However, this result is different from the solid state NMR studies (Figure 3), showing mainly the presence of surface alkyl species. Note that the NMR spectra were taken at room temperature. When reacting the surface zirconium butyl species with water at ambient temperature, the main product was butane (76.17%), accompanied by isobutane (0.39%), trans-2-butene (13.56%), cis-2-butene (2.72%), 1-butene (6.07%) and isobutene (1.09%). These results suggest the presence of equilibrium between zirconium butyl and an olefin coordinated to zirconium hydride (scheme 1). Clearly, at 180 °C, this equilibrium is largely shifted towards the coordinated olefin species (95% butenes vs 5% butanes), and thereby confirms that β-H transfer is favored at higher temperature and the importance to employ supported zirconium catalyst to selectively produce branched octenes from 2-butenes.

The presence of zirconium isobutyl fragment on the surface can be explain either by skeletal isomerization of 2-butene on acidic sites of the support, followed by insertion on zirconium hydride, or by β-methyl transfer followed by 1,2-insertion of coordinated propylene (scheme 1).\textsuperscript{38} Several examples in the literature report utilization of metal hydrides of group 4 in low temperature hydrogenolysis of butane or polyolefin by β-alkyl elimination.\textsuperscript{34,35} It was reported that with zirconium hydride supported on silica-alumina, the mechanism of the hydrogenolysis of butane comprises C-H activation (giving species 1a and 1b), accompanied by β-alkyl transfer and liberation of the lighter alkane after hydrogen activation.\textsuperscript{34} In the present case, the very low concentration of 1c is due to the β-transfer/n-butenes insertion (scheme 1). Further product analyses provide additional insights of the dimerization mechanism. GCMS analysis reveals that the products are mainly branched C8 alkenes (linear octenes = 0.5%).

2,1-insertion begins with the surface zirconium-n-butyl species, 1b, which can insert a second 1-butene with secondary (2,1) or primary (1,2) regiochemistry to give the two zirconium-octyl species 2b and 2b’, respectively. Species 2b, which according to the product distribution represents the less likely insertion product, may then undergo β-H elimination or β-H transfer to form the linear internal olefin. This reaction is practically negligible since the products contain about 0.5% of n-octenes (scheme 2). Formation of different n-octene isomers is due to the consecutive isomerization reaction over zirconium hydride by olefin insertion followed by β-H elimination (scheme 2).

1,2-insertion of 1-butene on 1b gives 2b’ and after β-H elimination or β-H transfer releases 2-ethyl-1-hexene (scheme 2). Although isobutene comprises only traces in the gas phase, it can hypothetically insert into the zirconium n-butyl surface moiety, leading to 2-methyl heptenes (2,1-insertion) or an zirconium neo-octyl specie (1,2-insertion), which cannot liberate the corresponding branched octenes by β-H elimination. These reaction pathways can practically be excluded since the concentration of gas phase isobutene is negligible. On the other hand, 2-butenes can insert into the zirconium n-butyl fragment and release 3-methyl heptenes. However, insertion of di-substituted olefin (2-butenes) into metal α-alkyl species are generally difficult. Hence, the latter mechanism is probably less dominant for the production of methyl heptenes. These mono-branched octenes represent about 32.2% in the gas phase and can also be obtained by 2,1-insertion of 1-butene into zirconium sec-butyl surface specie, 1a, giving 3a (Scheme 3). Formation of different methyl heptenes isomers is due the consecutive β-H elimination from 3a and isomerization reaction over zirconium hydride by olefin insertion followed by β-H elimination. It is indeed impossible to identify the main mechanistic pathway for the formation of methyl heptenes. However, it is reasonable to believe that 2,1-insertion (scheme 3) is the dominating reaction due to the low gas phase concentration of 1-butene registered in the online GC. Recall that only small amount of 1-butene is observed while the thermodynamic equilibrium lies on 10% (among the linear butenes) at 180 °C.\textsuperscript{42} Current observation indicates that 1-butene is highly reactive and will easily react with surface
Scheme 3. Pathways for 1-butene 1,2-insertion on supported zirconium sec-butyl species, 1a.

1a

2,1-insertion

Scheme 4. Pathway for 2-trans-butene insertion on supported zirconium sec-butyl species, 1a.

M

1a

2a

M

M

M

M

M

M

H

H

1a

1a

M

M

M

H

H

2,5,7,8,10,11,13,17

metathesis, tantalum hydrides supported on silica-alumina has been prepared according to published methods and investigated in 2-butenes dimerization under the same conditions as the supported Zr-H catalyst. The activity curve is described by a maximal conversion of 2-butenes of 36% at the beginning of the reaction, followed by a graduate deactivation and finally converged towards 13%, affording a TON of 4400 after 86 h (Figure 4). Unprecedently, the selectivity to branched octenes is high. The dominating products are branched octenes (mainly dimethyl hexenes, along with methyl heptanes, Figure S3), as observed for the supported zirconium hydride system. In addition, metathesis products consisting linear olefins covering C2-C7 isomers are also registered. It is worth to notice that at the beginning, both dimerization and metathesis reactions are taking place. With time on stream, the selectivity to dimeric products increase (up to 80%), while metathesis products decrease from about 60% at the beginning to 20% (after 86 h). It is reasonable to assume that the initial step involves insertion of 2-butene on Ta-H to

The fact that no polymeric product is observed and the low concentration of gas phase 1-butene when trans-2-butene is fed over supported zirconium hydride indicates that the formed 1-butene (by isomerization of 2-butenes) remains coordinated to the zirconium hydride specie. Consecutively, 2-butenes can easily insert into the zirconium hydride bond, resulting in surface zirconium sec-butyl specie with 1-butene coordinated. Immediate insertion of 1-butene into the zirconium sec-butyl fragment gives mono-branched and di-branched octenes. Finally, the minor zirconium isobutyl specie can principally react with different butene isomers and provide different octenes. However, due to the low concentration of this surface specie (0.20% based on hydrolysis), the corresponding products have not been observed. By applying a supported \( d^0 \) Zr-H on silica-alumina, the present results demonstrate the first example for selective dimerization of 2-butenes in 3,4-dimethyl hexenes.

Moving to group V (Ta) species which is also known as \( \alpha \)-olefin oligomerization catalyst but poor catalysts in olefin
give tri-sec-butyl tantalum surface species. Further rapid elementary reactions, such as sec-butyl/n-butyl isomerization, β-H elimination and α-H abstraction (known in metathesis catalysts, like W-H/Al₂O₃)³³ results in Ta n-butylidene hydride surface species accompanied by n-butane release. The available Ta-H sites can undergo 2-butene/1-butene isomerization (olefin insertion/β-H elimination) and 2-butenes insertion, which offer branched octenes after a second n-butene insertion, as described above (scheme 3). In this case, the tantalum n-butylidene moiety can further reacts with 2-butenes, according to a classical metathesis pathway, to give propene and n-pentenes. Ethene and heavier olefins are formed by successive isomerization and metathesis reactions, as previously reported.⁴⁷

Supported tungsten tri-hydrides are known to be highly active in olefin metathesis and exhibit the same coordination environment (W-carbene hydride after initiation steps) as the mentioned tantalum system. When W-H₃ supported on silica alumina is exposed to 2-trans-butene under the same conditions, only metathesis products are registered. The maximal conversion was 86 % and converged towards 53%, affording a TON of 5400 after 30 h (Figure S4). The products extend from C₅-C₂ olefinic species and are due to consecutive metathesis and isomerization reactions as documented in the literature (Figure S5).⁴⁷ ⁴⁸

A clear tendency is observed in the reactivity with 2-butenes when moving from Zr, through Ta, to W hydrides supported on silica-alumina. The zirconium system affords selectively dimeric products. The tungsten system offers selectively metathesis products, while the tantalum system gives a mixture of dimeric and metathesis products (Table 1).

### Conclusions

Current work describes different methods to upgrade trans-2-butene feedstock over supported metal hydrides catalysts prepared by surface organometallic chemistry. Supported tungsten trishydride is known as a highly active metathesis catalyst and gives selectively linear olefins originated from isomerization (on tungsten hydride species) and metathesis reactions (on tungsten carbene species). The tantalum analogue results in a mixture of metathesis (minor) and dimeric (major) products. Valuable products, branched octenes, can be obtained selectively after dimerization of 2-trans-butene catalyzed by ZrH/SiO₂-Al₂O₃. Although dimerization of 1-butene is already established, no work describing the selective dimerization of 2-butenes has been reported before. This behavior is originated from the bifunctional nature of the catalysts. The most important mechanistic pathway is probably isomerization of 2-butenes to 1-butene followed by 1-butenes insertion on zirconium sec-butyl surface fragment (obtained from insertion of 2-butenes on zirconium hydride). The major products, 3,4-dimethyl hexenes are released after β-H elimination.

### References