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Bifunctional catalysts based on tungsten hydrides supported on silicated alumina for direct production of 2,3-dimethylbutenes and neohexene from isobutene

Cherif Larabi,[a] Anthony Garron,[a] Pascal Rouge,[a] Kai C. Szeto,[a] Sébastien Norsic,[a] Aimery De Mallmann,[a] Nicolas Merle[a] and Mostafa Taoufik*[a]

Abstract: Well-defined bifunctional supported catalysts comprising tungsten hydride moieties and Brønsted acid sites were successfully prepared. The catalysts showed outstanding activity and selectivity toward the formation of high value added products, 2,3-dimethylbutenes and 3,3-dimethylbutene, through combination of metathesis and dimerization reactions of isobutene. The relationship between the physicochemical proprieties of the catalysts and their activities and selectivities indicated that isobutene conversion increased from 4 % to 95 % in function of the silica content of silicated alumina (Sasol). Nevertheless, the selectivity toward branched hexenes described a volcano-shaped curve presenting a maximum for the catalyst with 5 wt% of silica. Therefore, the control of the support acidity via the silica loading on alumina resulted in an increase of the selectivity in neohexene.

Introduction

The conversion of inexpensive and readily available feedstock such as isobutene to dimethylbutenes provides an alternative route for high value added building blocks. Indeed, branched C_6 hydrocarbons are much used in various domains of petrochemical and fine chemical industries. Particularly, 2,3-dimethylbutenes and 3,3-dimethylbutene (neohexene), when hydrogenated, lead to the formation of ramified hexanes characterized by very high octane numbers.[1] Regarding environmental issues, current specifications strongly limit aromatic content in fuels. Hence, branched hexanes can be used to meet the expanding need for iso-paraffines in order to improve the fuels quality.[1] Moreover, neohexene is a common reactant for fine chemicals, such as medicament (Terbinafine®)[2] and perfumery.[3,4] 2,3-dimethylbutenes is provided by dimerization of propylene process over nickel catalysts, known as Difasol^{TM} process.[5] Due to the global growing demand for propylene which results in the rise of its price, other processes to selectively obtain dimethylbutenes have become attractive. Neohexene is currently produced by Phillips Petroleum from 2-methylpropene (isobutene) and proceeds in two separate reactors.[6] The first reaction comprises dimerization of isobutene into a mixture of 2,4,4-trimethylpent-2-ene (DIB-2) and 2,4,4-trimethylpent-1-ene (DIB-1) on acidic catalyst at fairly low temperature (Eq. 1). The second reactor contains a mixture of WO_3/SiO_2 and MgO, where MgO catalyzes the isomerization of DIB-1 to DIB-2 (Eq. 2), and the latter component undergoes cross-metathesis with ethylene added to the process over WO_3/SiO_2 at 30 bar and 370 °C (Eq. 4) to yield neohexene (Scheme 1). It is noteworthy that ethylene can be produced from the self-metathesis of isobutene (Eq. 3) over the same catalytic system.[3,4,7] More recently, another attractive approach based on a single reactor using multifunctional catalysts has been reported to be able to convert isobutene to a mixture of neohexene and 2,3-dimethylbutenes.[8,9] Moreover, this process has particularly a positive benefit in theory, as it provides an equimolar combination of 2,3-dimethyl-2-butene (DMB-2) and neohexene as shown in Scheme 1. This stoichiometric mixture can be directly used for preparation of Tonalide (1,1,3,4,4,6-hexamethyl-1,2,3,4 tetra-hydronaphthalene)[10] without the necessity for modern distillation technology to separate the products.

In the presence of well-defined alumina-supported tungsten hydride ($W\text{-}H/Al_2O_3$) catalyst, isobutene is converted into neohexene with relatively low selectivity (10%). The low selectivity is attributed to low acidity of alumina. Indeed, neohexene is formed by a cross metathesis between ethylene and DIB-2 (Eq.4 Scheme 1), which are originated from self-metathesis and dimerization of isobutene (Eq.1 and Eq. 3 of Scheme 1), respectively. The dimerization activity is linked to the surface acidity of alumina, while the metathesis is explained by tungsten-carbene fragments generated in situ.[9] Note that self-metathesis of isobutene is rare and somewhat difficult, due to a sterically hindered metallacyclobutane intermediate.[11,12]

Based on these conclusions, further study has shown that the selectivity can be altered by functionalization of the surface with well-known dimerization active species such as nickel sulfate.[13,14]. In fact, the selectivity toward neohexene was significantly improved for alumina supported tungsten hydrides catalyst containing 1 wt% of Ni.[8] Dimerization of small alkenes to higher hydrocarbons presents a considerable scientific and industrial interest.[15] Solid acids such as zeolite are recognized to catalyze these

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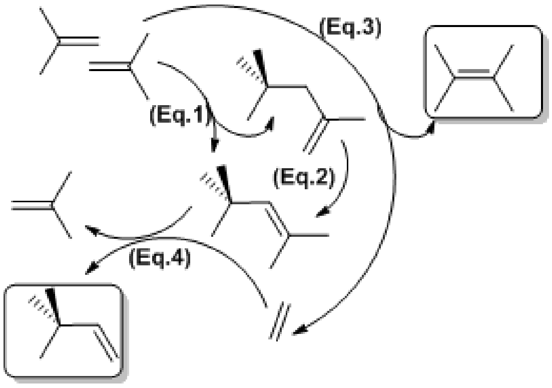
Supporting information for this article is given via a link at the end of the document reactions.[16,17]



Scheme 1. Schematic representation of different reaction steps for neohexene production starting from isobutene

Nevertheless, the activity and selectivity are closely dependent on the acid strengths. To avoid secondary reactions (oligomerizations, cracking, etc.), supports with moderate acidity are preferable.[18,19] The surface acidity of silicated-alumina can be easily tuned by the silicon content, generally the increase of silicon content results in the rise of the amount of Brønsted acid sites and decreases of the concentration of Lewis acidity and vis versa. In addition, silicated alumina have been used to obtain acidic amorphous materials active in either skeletal isomerization,[20] alcohols dehydration[21] or bifunctional hydrocracking reactions.[22,23] Moreover, it has already been shown that tungsten hydride can be successfully obtained by surface organometallic chemistry on alumina and silica-alumina support.[24] The catalysts showed interesting activity in 2-butene conversion by olefin metathesis,[25] depolymerization of waxes,[26], and in direct conversion of butane to higher hydrocarbons.[27] Lastly, the preparation of silicated alumina containing acid sites is rather simple and can be mainly classified in two methods: i) co-hydrolysis of silica and alumina sources, which results in matter commonly referred to as silica-alumina,[28] ii) controlled modification of alumina with TEOS, resulting in material which can be referred as silicated alumina or aluminosilicates.[29-31]

In order to implement this study, five samples of alumina (Siral), coated with various amounts of silica (5, 10, 20, 30, 40 wt%) were functionalized with tungsten hydrides. The obtained catalysts were characterized by different physicochemical techniques and their catalytic performances were evaluated for isobutene conversion to dimethylbutenes and neohexene under mild reaction conditions (150 °C, 1 bar).

Results and Discussion

Preparation of tungsten hydride moiety on silicated alumina

Grafting of $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$ on silicated alumina (**Siral$_{x\text{-}500}$** , x = 5, 10, 20, 30 and 40).

The main objective of the present work was to study the influence of Brønsted acidity strength provided by the support, itself, depending on the silica content, on the dimerization of isobutene. Prior to the post-synthetic modification of the supports with tunsgtenocarbyne complex, the surface functional groups and the textural proprieties of **Siral$_x$** were analyzed by BET, DRIFT spectroscopy, pyridine adsorption as well as ^{29}Si, ^{1}H and ^{27}Al solid state NMR spectroscopies.

Textural properties of the different catalysts were examined by nitrogen adsorption-desorption isotherm measurements. The BET surface areas of various supports, summarized in Table S1, indicated that the surface area as well as the porous volume depend on the silica content. Similar to what formerly reported, the surface area raised with the increase of the alumina coating by silica.[32-34] The physical adsorption isotherms (Figure. S1) correspond to type IV, according to IUPAC classification. The pores size distribution (Figure S1) tends to become larger with the increase of silica content, resulting in the rise of their volumes (Table S1).

The region of OH stretching vibration of **Siral$_x$** was analyzed by IR spectroscopy. The recorded IR spectra of the supports calcined and dehydroxylated at 500 °C under vacuum (10^{-5} mbar) are represented in Figure S2. This area results from a combination of at least four signals at 3775, 3747, 3727, and 3673 cm^{-1} characteristic of tetrahedral ν(HO-μ^1-Al^{IV}), ν(OH-Si), octahedral ν(HO-μ^1-Al^{VI}) and bridged ν(HO-μ^2-Al) respectively.[35, 36] It is noticeable that the intensities of aluminol (Al-OH) signals decrease with the silica loading and became virtually nil for silica content greater or equal to 30 wt%. Simultaneously, the intensity of silanols (Si-OH) signal increases.

NMR resonances of ^{1}H, ^{29}Si and ^{27}Al variation with the silica content of the dehydroxylated **Siral$_x$** were determined. Mainly two peaks are plainly identifiable at 0.2 and 1.8 ppm, assigned to HO-μ^1-Al and HO-Si respectively. In addition, the signal at 1.8 ppm displayed a shoulder around 4 ppm, corresponds typically to Si-(OH)Al as in zeolite.[37] Conversely, no peak at 7 ppm (related to strong Brønsted acid) was observed and is in agreement with the literature where probe molecule (TMPO) was used to highlight this signal.[38] The intensities of aluminol peaks dropped with the increase of silica content. They remained observable inherently in the form of shoulders around the peak of silanols for **Siral$_{10\text{-}500}$** and entirely disappeared for the supports (**siral$_{x\text{-}500}$**) which their amount of silica are greater than or equal to 20 wt%. ^{27}Al NMR spectra recorded after the dehydroxylation of **siral$_{x\text{-}500}$** (Figure S3 b) displayed two signals at 10 and 60 ppm attributed to the tetrahedrally coordinated Al^{IV} and octahedrally coordinated Al^{VI} respectively.[39] Note that their chemical shifts are not affected by the silica layer thickness. The ^{29}Si MAS NMR spectra of **Siral$_{x\text{-}500}$** are depicted in Figure S3 c. The broad peaks result from the combination of a multiple signals. For samples with low silica loading (5 wt%) the spectrum displayed a broad resonance centered at -85 ppm attributed to $Si(OAl)_3OH$ and $Si(OAl)_2(OH)_2$ as previously reported.[30,40] Further functionalization of alumina with 10 wt% of silica and over resulted in multiple layers which led to the formation of $Si(OSi)_4$ (Q4) sites. This explained the appearance

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of resonance between 100 and 115 ppm in ^{29}Si NMR spectra. The fraction of Q4 increases with the silica content and become dominant from 20 % and above.[40,41]

Pyridine adsorption was monitored by FTIR in order to investigate the surface acid sites of the **Siral$_{x-500}$**. Pellets of a support were exposed to vapor pressure of pyridine, then treated at 150 °C under high vacuum to evacuate the excess and physisorbed pyridine. The FTIR spectra depicted in Figure S4 showed a peak at 1540 cm^{-1} characteristic of pyridinium cations vibration consistent with the presence of Brønsted acid (B). Furthermore, two intense signal at 1454 and 1625 cm^{-1} attributable to pyridine vibration confirming the presence of Lewis acid sites (L).[42,43]. The B/L ratio evaluated from the integration area of the signals at 1454 and 1540 cm^{-1} (Figure S4) indicated that as the silica coating growth the amount of B sites increased and lowered the L acids.

As on alumina,[8] The tungsten hydride supported on a silicated alumina were prepared in two steps, the first one consist of grafting the $W(\equiv C^tBu)(CH_2{}^tBu)_3$. This procedure was conducted without solvent by reacting $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$ with the remaining surface Si-OH group of the supports. In the second step, the resulting perhydrocarbyl surface species were treated at 150 °C in the presence of anhydrous H_2 (550 Torr) for 15 h to give the corresponding supported tungsten hydrides.

The immobilization of $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$ over **Siral$_{x-500}$** performed at 65 °C (Scheme 2) were characterized by IR and NMR spectroscopies as well as mass balance analysis. The amount of the grafted W was fixed to 3.8 wt% since similar amount was reported on γ-Al_2O_3.[9] This generates identical amount of metathesis active species on various catalysts and facilitate their catalytic productivity.

As expected, after the grafting of tungsten tris(neopentyl) neopentylidyne complex, the analyses presented in Table S2 indicate the decrease of the surface area as well as the pore size distribution consequently the pores volume. Without taking into the account the uncertainties related to the measurement (ca. 5%), the materials have lost about 110±10 m²/g from their initial surfaces. In addition to the change in the sample weight triggered by the post-modification, the resulting supported tungsten complex (Scheme 2) occupied a volume in the pores, resulting in the decrease of their total free space and their specific surface area.

For example, according to the FTIR analyses (Figure 1a and S5) of tungsten tris(neopentyl)neopentylidyne complex supported on **Siral$_{5-500}$** as showed the intensity decrease of the band at 3747 cm^{-1} for the isolated silanols and the appearance of two groups of bands in the 3000-2700 cm^{-1} and 1470-1330 cm^{-1} regions assigned to ν(CH) and δ(CH) vibrations of perhydrocarbyl ligands of the grafted complexes.

^{1}H NMR spectrum of the solid (Figure 1 b) displayed broad resonance centered at 1.1 ppm assigned to the methyl protons of ^{t}Bu fragments. Moreover, two shoulders identifiable at 2.0 and 1.45 ppm are characteristics of the two diastereotopic protons as already observed for the reaction of the same complex on silica.[44] ^{13}C CPMAS solid state NMR spectrum recorded after the grafting of the $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$ complex on **Siral$_{5-500}$** is depicted in Figure 1c. The pattern displayed similarly to that previously found on silica, a sharp peak at 32 ppm, attributed to $C(CH_3)_3$, accompanied by two weak signals at 52 and 95 ppm, ascribed to (-$C(CH_3)_3$) and (-$CH_2{}^tBu$), respectively.[44] As the W organometallic precursor is un-labeled, the two latter signals remain very weak, and the triple-bonded carbon to tungsten expected at 320 ppm has not been observed.

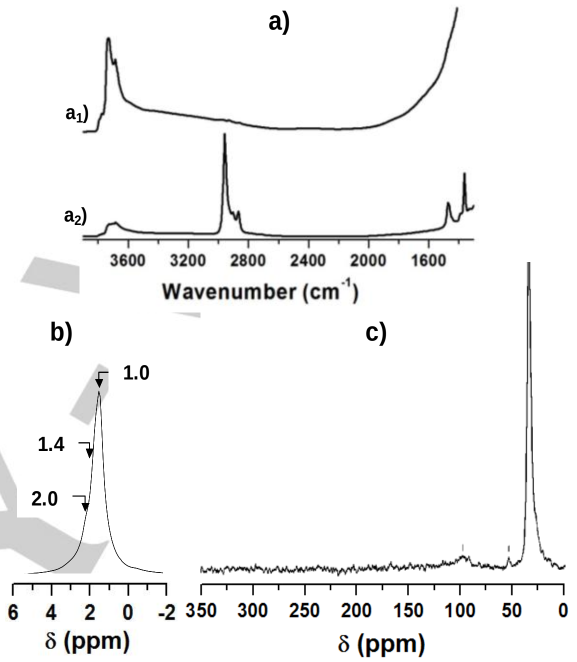
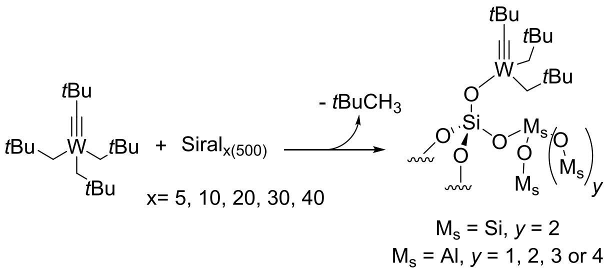


Figure 1. Monitoring the reaction of $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$ with **Siral$_{5-500}$** by a) DRIFT spectroscopy (a$_1$ **Siral$_{5-500}$** dehydroxylated at 500 °C and a$_2$ after grafting of $W(\equiv C^tBu)(CH_2{}^tBu)_3$ b) ^{1}H MAS NMR and c) ^{13}C CPMAS NMR.

Mass balance analysis. The reaction of the W complex with the surface hydroxyls was followed by the release of neopentane (^{t}BuCH$_3$) detected and evaluated by GC. For example, the elemental analyses of $W(\equiv C^tBu)(CH_2{}^tBu)_3$ supported onto Siral$_{5-500}$ indicated the presence of *ca.* 3.8 and 4.1 wt% of W and C respectively. The quantification of the volatiles emission showed the formation of *ca.* 0.19 mmol of neopentane per gram of material, this equated to 0.9 neopentane/W.



Scheme 2. Grafting reaction of $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$ onto **Siral$_{x-500}$**; x = 5, 10, 20, 30 or 40

Overall, these data are consistent with the loss of approximately one equivalent of neopentane during the grafting process, resulting in a monopodal tungsten species and leaving on average three "neopentyl-like" ligands around the metal center (Scheme 2).

The tungsten perhydrocarbyl surface species supported on the other **Siral$_{x-500}$** (x = 10, 20, 30 and 40) have also been analyzed by same characterization procedures (NMR, BET, FTIR and elemental analyses). Similar results were observed and same conclusions were found. Therefore the reaction depicted in Scheme 2 was established for all the other supports.

Hydrogenolysis of the Siral$_{x-500}$ supported tungsten perhydrocarbyl to generate tungsten hydrides

When supported tungsten perhydrocarbyl on **Siral$_{x-500}$** (x = 5, 10, 20, 30 or 40) were heated under H_2 for 15 h at 150 °C, the pale yellow solid darkens to brown. The IR spectra showed the following features : i) disappearance of up to 95% of the $\nu_{(C-H)}$ and $\delta_{(C-H)}$ bands, ii) a band at 3747 cm^{-1} associated with isolated silanols reappeared, iii) appearance of bands at 2270 cm^{-1} and in the 1980-1800 cm^{-1} area, assignable to IR spectroscopic signature of stretching ν(Si-H) and ν(W-H) respectively (Figure S6). These observations are in sharp contrast to what has already been found for the tungsten hydride supported on silica-alumina.[45]

The analyses of the gas phase revealed the formation of about 14 equiv. of methane per W and traces of ethane due to the hydrogenolysis of the neopentyl fragments, as described elsewhere.[26]

The specific surface area and the pores volume of supported tungsten hydrides on **Siral$_{x-500}$** (x = 5, 10, 20, 30 or 40) are summarized in Table S3. The measured values indicated that surface area and the structure of the support were preserved after the grafting and various thermal treatments. As expected, the surface areas and the pore volumes of the catalysts functionalized by tungsten hydrides are lower than the corresponding neat supports. Indeed the presence of about 3.8 wt% of metal on the surface of the supports affected slightly the weight as well as the size distribution of the pores impacting their volumes and the total surface area of the materials.

Catalytic conversion of isobutene

Previous studies showed that neohexene and DMB-2 can be obtained from isobutene in one single catalytic process in the presence of tungsten hydrides supported on γ-Al_2O_3. The main steps of the process are self-metathesis of isobutene, cross metathesis of DIB-2 catalyzed by tungsten hydrides and isobutene dimerization promoted by the weak acid sites of alumina. Therefore, to ensure an optimal operation of the process, both catalytic species have to act in balance. In other words, the dimerization rate must be lower than or equal to the metathesis rate activity, otherwise byproducts such as trimers would be obtained by oligomerization of isobutene to the detriment of the desired products. In the present study, several supports with various acid properties were screened in order to optimize the effectiveness of the supported tungsten hydride catalysts.

As a starting point, the catalytic activity of tungsten hydrides supported on pure alumina, **Cat1**, considered as a reference has been evaluated in the same conditions as silicated alumina ($m_{catalysts}$ = 100 mg, Flow rate$_{iC4}$ = 3 mol.mol^{-1}$_{W}$, T = 150°C, P_{iC4} = 1 bar). When isobutene was fed through a dynamic flow reactor, the reaction gives a low initial conversion of 4.4% before reaching a pseudo-plateau at 1.7% (Figure 3a). Overall, this catalytic system showed a very low catalytic activity (T.O.N = 60 after 14 h, Figure 3b).

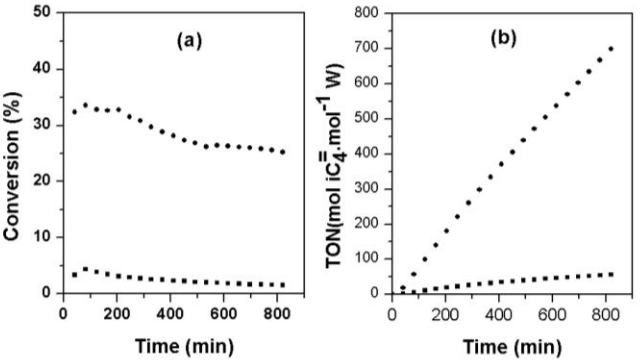


Figure 2. Evolution in function of time on stream of a) isobutene conversion and b) T.O.N (mol$_{i-C4}$/mol$_W$$^{-1}$) catalyzed by **Cat1** (W-H/Al_2O_3) (■) and **Cat3** (W-H/**Siral$_{5-500}$**) (•).

The global selectivities reached 40% for branched hexenes, 36% for ethylene and 18% for diisobutenes (Table 1 and Figure S7a). At the beginning of the reaction the selectivities in ethylene and neohexene were at about 22%. The selectivity in ethylene increased gradually with time on stream, and reached 36% after a reaction time of 14 h. Moreover, the relative selectivities for branched hexenes were 87% for DMBs (DMB-2 and DMB-1, the latter is originated from isomerization also observed previously[8]) and 13 % for neohexene (Figure 3). This low selectivity in neohexene can be explained by the gradual loss of alumina acidity, responsible of isobutene dimerization to DIB-2, intermediate for the production of neohenexe via cross-metathesis. The switch from alumina to silicated alumina resulted in a remarkable and continuous increase of isobutene conversion from 55 to 95 % with the rise of the silica coating from 10 to 40 wt% (Figure S8). The conversion of isobutene is dramatically increased with the increase of the silica content. Nevertheless the selectivity was negatively affected. Indeed, for the catalyst with 10 wt% of silica loading and over, the main compounds formed were oligomers (C_{12+}) and a very low selectivity toward branched C_6 was observed (Figure S9), as already reported on acidic supports.[46] These products distribution revealed that the isobutene dimerization rate is ensured by a strong Brønsted acidity of Siral and is much higher than the rate of cross-metathesis on tungsten hydrides.

Table 1. T.O.N and product distribution observed for the catalysts after 14 h of reaction

Catalyst	T.O.N	C_2	C_6	C_8	C_{12+}
Cat1	60	33	50	15	2
Cat2	280	14	70	14	2
Cat3	750	5	70	15	10

In the case of Siral with low silica content (5 wt%) the catalytic activity of the supported tungsten hydrides

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supported on silicated alumina was more than 12 times higher compared to the non-modified alumina. In fact after 14 h of reaction the conversion of isobutene reached 30%, much higher than for tungsten hydrides on alumina (4.4%). Overall the T.O.N has remarkably increased from 60 for the **Cat1** to 750 for the catalyst supported on the alumina modified with 5% of silica (WH/**Siral$_{5\text{-}500}$**), **Cat3**. Interestingly, the performances of this later catalyst (**Cat3**) are even higher than the one found for the tungsten hydrides support on alumina functionalized with nickel oxide (WH/Ni$_{1\%}$-Al$_2$O$_3$); **Cat2**; (T.O.N = 280, Table1).[8] In addition, the analysis of the product selectivities showed a very interesting behavior. Indeed, there has been a significant improvement for the branched hexenes selectivity (70%), compared to alumina support and maintained constant with time on stream. In parallel, the selectivity for neohexene was increased from 6% with **Cat1** to reach 40%, similar to the one measured for **Cat2** as depicted in Figure 3.

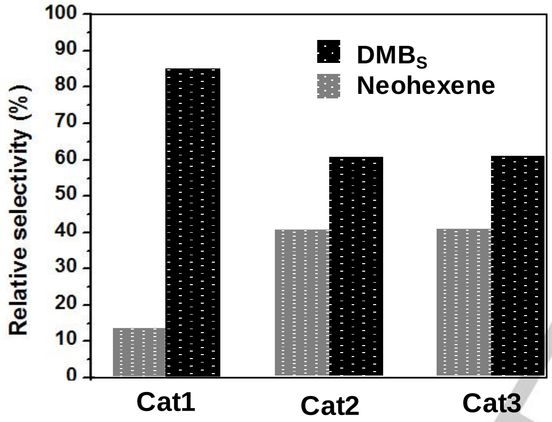


Figure3. DMBS (DMB-1 and DMB-2) and neohexene relative selectivities in the presence of the **Cat1**, **Cat2** and Cat3.

These results clearly showed that the control of Brønsted acidity of the silicated alumina by adjusting the amount of silica to 5 wt%, improved not only the activity but also the selectivity toward branched hexenes, in particular neohexene.

The comparison of the hexenes relative selectivities between the native catalyst, **Cat1**, the nickel modified catalyst, **Cat2** and the silicon modified catalyst, **Cat3**, shows the beneficial effect of the promoter on the neohexene selectivity (40% for **Cat2** and **Cat3** in comparison to 13% for **Cat1**) (Figure 4). These results along with the low selectivity in ethylene demonstrate the ability of the modified catalysts to perform both the self-metathesis and the selective dimerization of isobutene to DIB followed by cross metathesis between DIB and ethylene produced in situ. The present catalyst (**Cat 3**) exhibits higher catalytic activity, attributed to the enhanced control of the dimerization reaction catalyzed by Brønsted acids. These results highlight the importance of the dual functionality of the new W–H catalyst supported on Siral in the direct conversion of isobutene into DMBs and neohexene with improved selectivity.

Conclusions

Alumina coated by various amount of silica have been functionalized by tungsten hydride through surface organometallic chemistry methodology. Characterization of the obtained materials revealed that the structure of the supported tungsten hydrides were close to what already observed on silica-alumina. The evaluation of the catalytic activities indicated that the isobutene conversion increased with the increase of silica content. However, the selectivity in valuable branched hexenes exhibited highest value for the catalyst containing 5 wt% of silica. The drop in the selectivity reflected the fact that the rise of silica content increases the acidity strength resulting in the oligomerization of isobutene. Thus, the appropriate balance between the acidity and the metathesis activity for optimum conversion and higher selectivity was found for the tungsten hydride supported on silicated alumina with moderate acidity. In addition, current results showed that branched hexenes can be readily produced in notable yield through a simple fixed bed reactor by using only isobutene as reactant. This methodology facilitates the existing technology that involves multiple reactor system and applies a cheaper gas feed (isobutene alone versus two steps ethylene/isobutene (Phillips process) and propylene (Difasol process).

Experimental Section

General procedure

All experiments were carried out by using standard Schlenk and glove-box techniques. Solvents were purified and dried according to standard procedures. Elemental analyses were performed at the CNRS Central Analysis Department in Solaize (metal analysis) Pôle Chimie Moléculaire Faculté des Sciences Mirande (Dijon, France), using CHNS/O thermo electron flash 1112 Series elemental analyzer. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer by using an airtight DRIFT cell equipped with CaF$_2$ window. The samples were prepared in a glove-box. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm^{-1}). Solid state NMR spectra were recorded on a Bruker Avance 500. A 4mm diameter zirconia impeller (ZrO$_2$) is filled with the material and closed with a kel-f stopper. It is then transferred into the 4 mm CP Bruker probe of the spectrometer allowing rotation of the rotor at a speed of 10 kHz. The time between two acquisitions is always optimized to allow complete relaxation of the protons.

Adsorption-desorption isotherms of nitrogen at -196 °C were measured for all the materials with a Micromeritics ASAP 2020 surface and porosity analyzer. Cumulative pore volume was calculated using BJH model for the adsorption isotherm.

Preparation of the dehydroxylated support silicated alumina:

Silicated alumina (Siral® provided by Sasol) with various silica content (5, 10, 20, 30, 40 wt%) were calcined at 500 °C under dry air flow for 12 h followed by dehydroxylation under high vacuum (10^{-5} Torr) at 500 °C for 15 h. The supports referred to as **Siral$_{x\text{-}500}$** / x = 5, 10, 20, 30 or 40 were then stored in a glovebox.

Pyridine adsorption: A partial pressure of pyridine was introduced to IR cell containing a pellet of silicated alumina support at room temperature. After that the excess was evacuated under vacuum (10^{-5} Torr) at room temperature, then at 150 °C, during each step, IR spectrum was recorded.

Preparation and characterization of W-H/ **Siral$_{x\text{-}500}$**:

The molecular precursors [W(≡C^{t}Bu)(CH$_2$^{t}Bu)$_3$] as well as their grafting on **Siral$_x$** were prepared according to published procedure.[8, 9, 47] Briefly, a mixture of [W(≡C^{t}Bu)(CH$_2$^{t}Bu)$_3$] (165 mg, 0.353 mmol) and the corresponding supports (**Siral$_{x\text{-}500}$**) previously dehydroxylated at 500 °C (0.8 g) was stirred at 65 °C under Ar for 4 h. The solid was washed three times with dry pentane through filtration. All volatile compounds were condensed into another reactor (volume = 6 L) in order to quantify neopentane evolved during the grafting. The resulting yellow-brown solid was dried under vacuum (10^{-5} Torr). Then the solid previously obtained was heated at 150 °C in the presence of a large excess of anhydrous H_2 (550 Torr). After 15 h, the gaseous products were quantified by GC and the catalysts were stored in a glovebox.

Catalytic evaluation:
The evaluation of the catalytic properties of the various supported tungsten hydride material have been performed in a PID Eng & Tech® reactor. This type of reactor comprised an oven surrounded by a hotbox which allowed to pre-heat the reactant. To have a constant reactant flow, isobutene was introduced in liquid state via a high pressure liquid syringe from Top Industrie® PMPH 50-500 and vaporized in the hot box (at 120 °C) before reaching the catalyst bed. The tungsten hydride catalysts were charged in a glove box, into a stainless steel ½' cylinder reactor which can be isolated from atmosphere. After connection to the gas lines the tubes were swept with argon, then the temperature was increased to the desired value at 2.5 $°C \cdot min^{-1}$. At the reaction temperature (150 °C), isobutene (2.1 $mL.min^{-1}$) was passed through 100 mg of the catalysts (which contain 3.8 wt% of tungsten). A continuous analysis by GCMS of the product was also carried out by Gas Chromatography (Agilent technologies 7890A). The gaseous product was separated with both molecular sieve and Al_2O_3/KCl capillary column. The quantification of the product was performed in the serial connected TCD and FID.

Keywords: Metathesis • isobutene • dimethylbutenes • tungsten hydride • dimerization

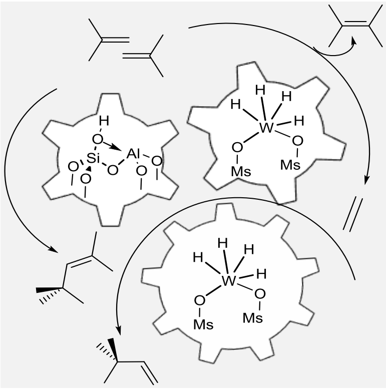
[1] J. Hancsok, S. Magyar, K. V. S. Nguyen, L. Keresztury, I. Valkai, *Pet. Coal* **2003**, *45*, 99.
[2] U. Beutler, J. Mazacek, G. Penn, B. Schenkel, D. Wasmuth, *Chimia* **1996**, *50*, 154.
[3] H. Mimoun, *Chimia* **1996**, *50*, 620.
[4] H. Sato, H. Tojima, K. Ikimi, *J. Mol. Catal. A: Chem.* **1999**, *144*, 285.
[5] H. Olivier-Bourbigou, L. Magna, D. Morvan, *Appl. Catal., A* **2010**, *373*, 1.
[6] R. L. Banks, D. S. Banasiak, P. S. Hudson, J. R. Norell, *J. Mol. Catal.* **1982**, *15*, 21.
[7] J. C. Mol, *J. Mol. Catal. A: Chem.* **2004**, *213*, 39.
[8] A. Garron, F. Stoffelbach, N. Merle, K. C. Szeto, J. Thivolle-Cazat, J.-M. Basset, S. Norsic, M. Taoufik, *Catal. Sci. Technol.* **2012**, *2*, 2453.
[9] N. Merle, F. Stoffelbach, M. Taoufik, E. Le Roux, J. Thivolle-Cazat, J.-M. Basset, *Chem. Commun.* **2009**, 2523.
[10] H. Mimoun, *Chimia* **1996**, *50*, 620.
[11] A. Motta, K. C. Szeto, M. Taoufik, C. P. Nicholas, *Catal. Sci. Technol.* **2016**, *6*, 3386.
[12] K. C. Szeto, E. Mazoyer, N. Merle, S. Norsic, J.-M. Basset, C. P. Nicholas, M. Taoufik, *ACS Catal.* **2013**, *3*, 2162.
[13] M. G. Yaocihuatl, H. L. Martin, A. C. Jorge, *Catal. Lett.* **2006**, *110*, 107.
[14] A. Sarkar, D. Seth, M. Jiang, F. T. T. Ng, G. L. Rempel, *Top. Catal.* **2014**, *57*, 730.
[15] B. Bornils, W. A. Herrmann, Editors, *Applied Homogeneous Catalysis with Organometallic Compounds, Volume 1, Second Edition: Applications*, Wiley-VCH, Weinheim, 2002, pp. 598.
[16] R. J. Quann, L. A. Green, S. A. Tabak, F. J. Krambeck, *Ind. Eng. Chem. Res.* **1988**, *27*, 565.
[17] J. F. Knifton, J. R. Sanderson, P. E. Dai, *Catal. Lett.* **1994**, *28*, 223.
[18] B. Chiche, E. Sauvage, F. Di Renzo, I. I. Ivanova, F. Fajula, *J. Mol. Catal. A: Chem.* **1998**, *134*, 145.
[19] P. Oliveira, P. Borges, R. R. Pinto, M. A. N. D. A. Lemos, F. Lemos, J. C. Vedrine, F. R. Ribeiro, *Appl. Catal., A* **2010**, *384*, 177.
[20] A. A. Davydov, M. Kantcheva, M. L. Chepotko, *Catal. Lett.* **2002**, *83*, 97.
[21] M. Trombetta, G. Busca, S. Rossini, V. Piccoli, U. Cornaro, A. Guercio, R. Catani, R. J. Willey, *J. Catal.* **1998**, *179*, 581.
[22] N. P. Makgoba, T. M. Sakuneka, J. G. Koortzen, C. Van Schalkwyk, J. M. Botha, C. P. Nicolaides, *Appl. Catal., A* **2006**, *297*, 145.
[23] R. de Haan, G. Joorst, E. Mokoena, C. P. Nicolaides, *Appl. Catal., A* **2007**, *327*, 247.
[24] N. Popoff, E. Mazoyer, J. Pelletier, R. M. Gauvin, M. Taoufik, *Chem. Soc. Rev.* **2013**, *42*, 9035.
[25] K. C. Szeto, N. Merle, C. Rios, P. Rouge, J. L. Castelbou, M. Taoufik, *Catal. Sci. Technol.* **2015**, *5*, 4765.
[26] S. Norsic, C. Larabi, M. Delgado, A. Garron, A. de Mallmann, C. Santini, K. C. Szeto, J.-M. Basset, M. Taoufik, *Catal. Sci. Technol.* **2012**, *2*, 215.
[27] K. C. Szeto, L. Hardou, N. Merle, J.-M. Basset, J. Thivolle-Cazat, C. Papaioannou, M. Taoufik, *Catal. Sci. Technol.* **2012**, *2*, 1336.
[28] D. Leckel, *Ind. Eng. Chem. Res.* **2007**, *46*, 3505.
[29] A. Corma, A. Martinez, S. Pergher, S. Peratello, C. Perego, G. Bellusi, *Appl. Catal., A* **1997**, *152*, 107.
[30] A. R. Mouat, C. George, T. Kobayashi, M. Pruski, R. P. van Duyne, T. J. Marks, P. C. Stair, *Angew. Chem., Int. Ed.* **2015**, *54*, 13346.
[31] B. P. MNilsen, J. H. Onuferko, B. C. Gates, *Ind. Eng. Chem. Fundam.* **1986**, *25*, 337.
[32] F. Jing, B. Katryniok, M. Araque, R. Wojcieszak, M. Capron, S. Paul, M. Daturi, J. M. Clacens, F. De Campo, A. Liebens, F. Dumeignil, M. Pera-Titus, *Catal. Sci. Technol.* **2016**, *6*, 5830.
[33] S. Sokolov, M. Stoyanova, U. Rodemerck, D. Linke, E. V. Kondratenko, *Catal. Sci. Technol.* **2014**, *4*, 1323.
[34] W. Daniell, U. Schubert, R. Glockler, A. Meyer, K. Noweck, H. Knozinger, *Appl. Catal., A* **2000**, *196*, 247.
[35] C. Morterra, G. Magnacca, *Catal. Today* **1996**, *27*, 497.
[36] M. Taoufik, K. C. Szeto, N. Merle, I. Del Rosal, L. Maron, J. Trebosc, G. Tricot, R. M. Gauvin, L. Delevoye, *Chem. - Eur. J.* **2014**, *20*, 3856.
[37] K. C. Szeto, A. Gallo, S. Hernandez-Morejudo, U. Olsbye, A. De Mallmann, F. Lefebvre, R. M. Gauvin, L. Delevoye, S. L. Scott, M. Taoufik, *J. Phys. Chem. C* **2015**, *119*, 26611.
[38] B. Alonso, I. Klur, D. Massiot, *Chem. Commun.* **2002**, 804.
[39] X. Li, W. Zhang, S. Liu, L. Xu, X. Han, X. Bao, *J. Catal.* **2007**, *250*, 55.
[40] T. C. Sheng, S. Lang, B. A. Morrow, I. D. Gay, *J. Catal.* **1994**, *148*, 341.
[41] Y. Cui, N. Liu, Y. Xia, J. Lv, S. Zheng, N. Xue, L. Peng, X. Guo, W. Ding, *J. Mol. Catal. A: Chem.* **2014**, *394*, 1.
[42] S. N. Delgado, L. Vivier, C. Especel, *Catal. Commun.* **2014**, *43*, 107.
[43] X. Pu, N.-w. Liu, Z.-h. Jiang, L. Shi, *Ind. Eng. Chem. Res.* **2012**, *51*, 13891.
[44] E. Le Roux, M. Taoufik, M. Chabanas, D. Alcor, A. Baudouin, C. Coperet, J. Thivolle-Cazat, J.-M. Basset, A. Lesage, S. Hediger, L. Emsley, *Organometallics* **2005**, *24*, 4274.
[45] E. Le Roux, M. Taoufik, A. Baudouin, C. Coperet, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders, G. J. Sunley, *Adv. Synth. Catal.* **2007**, *349*, 231.
[46] D. Park, S.-S. Kim, T. J. Pinnavaia, F. Tzompantzi, J. Prince, J. S. Valente, *J. Phys. Chem. C* **2011**, *115*, 5809.
[47] D. N. Clark, R. R. Schrock, *J. Am. Chem. Soc.* **1978**, *100*, 6774.

Entry for the Table of Contents

Layout 1:

FULL PAPER

This work aimed to study the influence of the acidic properties of silicated alumina on the catalytic performances of supported W-H catalysts for isobutene conversion. The positive effect of moderate doping on catalytic productivity was evidenced. Indeed, the sample with 5 wt% of SiO_2 allows obtaining high selectivities in DMBs and neohexene.



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Bifunctional catalysts based on tungsten hydrides supported on silicated alumina for direct production of branched hexenes from isobutene