Recent applications in catalysis of surface organometallic chemistry

Frédéric Lefebvre, Jean-Marie Basset *

Laboratoire de Chimie Organométallique de Surface, UMR CNRS-CPE 9986, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne Cedex, France

Abstract

This paper reviews recent applications of well-defined silica-supported hydrides of the group 4 and 5 transition metals in the field of carbon—carbon and carbon—hydrogen bonds activation of alkanes. The synthesis and characterization of the zirconium hydride is presented. The monohydride ($\equiv$SiO)$_3$Zr–H is obtained by hydrogen treatment at ca. 150°C of the well-defined surface species $\equiv$Si–O–ZrNp$_3$ (Np = CH$_2$C(CH$_3$)$_3$). This surface complex is formally an 8 electron species and is consequently very electrophilic. Similarly, hafnium and titanium hydrides are obtained by treatment under hydrogen of $\equiv$Si–O–MNp$_3$ (M = Hf,Ti). In the case of titanium the reaction is not quantitative in the sense that a non-negligible amount of titanium(III) is formed. The tantalum hydride ($\equiv$SiO)$_2$Ta–H is obtained by hydrogen treatment at ca. 150°C of ($\equiv$Si–O)$_x$Ta(=CHC(CH$_3$)$_3$)(CH$_2$C(CH$_3$)$_3$)$_{3-x}$ (x = 1,2), prepared by reaction of Ta(=CHC(CH$_3$)$_3$)(CH$_2$C(CH$_3$)$_3$)$_3$ with the hydroxyl groups of silica. Examples of applications of these hydrides in the field of the activation of alkanes at moderate temperatures are then given. All these surface hydrides can achieve the hydrogenolysis of alkanes at low temperature. When the titanium hydride is used, a simultaneous reaction of skeletal isomerization occurs. In all cases, the mechanism of C–C bond cleavage passes through an elementary step of β-alkyl transfer. The mechanism of hydroisomerization observed with the titanium hydride passes also by an elementary step of β-alkyl transfer but, in this case, the β-H elimination-olefin reinsertion occurs quite rapidly so that a skeletal isomerization also occurs. The zirconium hydride can also catalyze under olefin pressure the olefin polymerization and under hydrogen pressure the polyolefin hydrogenolysis. Here the equilibrium between the olefin insertion into a metal alkyl and the β-alkyl transfer is shown to occur with the same catalyst in agreement with the concept of microreversibility. A new catalytic reaction called 'alkane metathesis' has been discovered with the tantalum hydride. By this reaction, alkanes are catalytically transformed into higher and lower alkanes. The mechanism by which this reaction occurs is not fully understood. The products distribution, especially with labeled alkanes, is explained by a concerted mechanism by which a Ta–C bond and a C–C bond of the alkane can be cleaved and reformed simultaneously via a kind of four centered σ-bond metathesis which has no precedent in classical organometallic chemistry. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last 30 years, homogeneous catalysis has considerably progressed, due to the high level of comprehension reached by molec-

* Corresponding author. Tel.: +33-472-431792; Fax: +33-472-431795; E-mail: basset@coms1.cpe.fr

ular organometallic chemistry. In fact, these two sciences have progressed in parallel, resulting in new concepts which make it possible to predict, in several cases and for a given reaction, what will be the best homogeneous catalyst (the metal, its oxidation state, its ligands and the reaction conditions) [1].

In contrast, the heterogeneous catalysis, which is much more important for an industrial point of view, has progressed more slowly and even now it remains a highly empirical science [2]. One reason of this was the difficulty to characterize the surfaces before, during and after the catalytic reactions. This resulted in a great development of physicochemical methods which, often, do not take into account the diversity of the sites on the surface and the low concentration of the active ones. As a consequence, up to now only few elementary steps are understood at the molecular and atomic level (e.g., ammonia synthesis, CO oxidation, etc.). So, as the reaction mechanisms are not known, it is not always possible to have a predictive approach.

One of the purposes of surface organometallic chemistry is to determine if the concepts developed for homogeneous catalysis by the molecular organometallic chemistry can be applied to heterogeneous catalysis [3–5]. Is it possible to synthesize, on a surface, active sites with a uniform distribution on all the solid and in a high concentration? The first objective of surface organometallic chemistry is to try to understand what happens when an organometallic complex reacts with a surface and what are the surface reaction products. In a second step, the concept of molecular organometallic chemistry can be transposed to the supported complexes whose structure is relatively well defined and thus the reactivity of surface organometallic fragments can be tentatively predicted on the bases of what is known in molecular (coordination and organometallic) chemistry. For this purpose, all steps of the interaction of the starting organometallic complex with the surface must be well understood. The resulting grafted organometallic fragment is usually characterized by numerous techniques such as chemical analysis, infrared spectroscopy, solid-state NMR and EXAFS. It is thus possible to study the stoichiometric and catalytic reactivities of this 'well-defined' surface organometallic species and to interpret the results with the concepts of organometallic chemistry and surface science. This field combines the advantages of homogeneous catalysis where the knowledge is good enough to allow in several cases a prediction of the catalytic properties of an organometallic complex and those of heterogeneous catalysis with, e.g., its easy separation of the catalyst from the reactional medium and the isolation of the reactive sites preventing their deactivation by bimolecular processes.

Surface organometallic chemistry has been the subject of a number of reviews [3–10]. In this paper, we will focus on the catalytic activation of carbon–carbon and carbon–hydrogen bonds of alkanes by oxide supported transition metal hydride complexes. We will first describe the synthesis and the characterization of well-defined surface hydrides on oxides, mainly silica, and we will then give applications of these materials in catalysis. Examples of hydrogenolysis, hydroisomerization and metathesis of alkanes will be given together with applications in polymerization/depolymerization.

2. One example of surface organometallic chemistry: the synthesis of surface hydrides

As mentioned in Section 1, the main purpose of surface organometallic chemistry is the synthesis of relatively well-defined complexes on the surface of oxides or metals, which can then be used in catalysis in a conceptual way. A typical example of this methodology is the synthesis of supported metal hydrides. Numerous metals can lead to quite the same reaction, for example zirconium, hafnium, titanium and tantalum. These four metals lead to quite similar chemistry and so we will more extensively de-
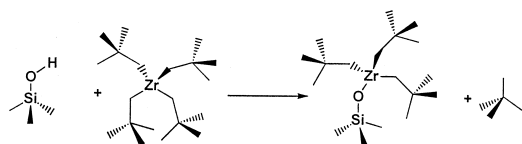
Scheme 1.

scribe the synthesis of one of them, the zirconium hydride. We will then discuss briefly what are the differences between these four metals.

2.1. Synthesis and characterization of the silica supported zirconium hydride ($\equiv Si–O$)$_3$Zr–H

Sublimation of tetraneopentyl zirconium onto the surface of a silica dehydroxylated at 500°C results in the electrophilic cleavage of one Zr–C bond by a surface proton, with formation of the tris neopentyl zirconium $\equiv$Si–O–Zr(CH$_2$C-(CH$_3$)$_3$)$_3$ grafted species [9] (Scheme 1).

This supported organometallic complex has been fully characterized by numerous methods [11] such as solid-state NMR, EXAFS, qualitative and quantitative analysis of evolved gases, chemical analysis of the surface compound, etc. The formation of only one bond between the metal fragment and the surface is evidenced by the use of a deuterated silica: only one equivalent of monodeuterated neopentane per mole of grafted zirconium is evolved during the grafting reaction (it is necessary to use a deuterated silica in order to be sure that the neopentane arises from the grafting reaction and not from a partial decomposition of the complex). The C/Zr molar ratio of the grafted complex determined by chemical analysis as well as the amount of neopentane evolved during the hydrolysis of the surface complex agree also well with the $\equiv$Si–O–Zr(CH$_2$C(CH$_3$)$_3$)$_3$ formula. Another proof of this reaction is obtained by infrared spectroscopy which shows a decrease of the ν(O–H) vibrations of silica at 3647 cm^{-1} and the appearance of ν(C–H) (around 2900 cm^{-1}) and δ(C–H) (around 1400 cm^{-1}) bands characteristic of the neopentyl groups. ^{13}C CP-MAS NMR of the supported complex shows

two peaks at 95.5 ppm (Zr–CH$_2$) and 33.9 ppm (–CH$_3$), the quaternary carbon being not observed due to the lack of protons directly bonded to it. EXAFS analysis of this complex is also in agreement with the proposed structure: The zirconium atom is surrounded, on average, by 3.2 carbon atoms at 0.2219(4) nm and 1.1 oxygen atom at 0.1956(3) nm [12].

Reaction of this well-characterized species with dry hydrogen at 150°C leads to the formation of a zirconium hydride and evolution of alkanes [11–13]. Surprisingly, only methane and ethane are evolved at this temperature while the reaction should form neopentane. This result is in fact due to the hydrogenolysis of the evolved neopentane, as it will be described more extensively in the next part of this review. Other interesting features are observed [12]: (i) the amount of hydride per zirconium, as determined by reaction with methyl iodide is not 3 as expected but 1; (ii) infrared spectroscopy shows the disappearance of all ν(C–H) bands and the appearance of a ν(Zr–H) band at 1625 cm^{-1} and of two other bands at 2263 and 2196 cm^{-1}, not exchangeable by deuterium and attributed to Si–H vibrations; (iii) the amount of Si–H bonds, determined with reaction with KOH, formed during the reaction with hydrogen is exactly 2 per grafted zirconium; (iv) ^{29}Si CP-MAS NMR and a careful interpretation of the infrared spectra show that in fact there is formation of $=$SiH$_2$ groups; (v) finally, EXAFS shows that the zirconium atom is surrounded by three σ-bonded oxygen atoms at 0.1945(3) nm and one π-bonded oxygen atom at 0.268 nm. All these results can only be explained as follows (Scheme 2): In a first step, hydrogen reacts with the supported tris-neopentyl zirconium leading to
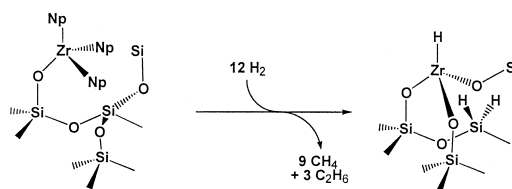
Scheme 2.

the evolution of neopentane, further hydrogenolyzed into methane and ethane (see below) and a hypothetical zirconium tris-hydride. This tris-hydride zirconium complex should be highly oxophilic (zirconium is known for this) as so highly reactive. Simple molecular modeling studies show that this tris-hydride will have Zr–H bonds pointing to silicon bridges. It can then easily proposed that a hydride will break one ≡Si–O–Si≡ bridge, leading to a Zr–O bond and a Si–H bond. Molecular modeling studies show that this new surface bis-hydride zirconium can further react with another ≡Si–O–Si≡ bridge leading finally to a monohydride zirconium complex and a silicon bis-hydride. This can also be seen by examination of Scheme 2 and replacement of the neopentyl groups of the starting complex by hydrogen atoms. Note also that the zirconium monohydride cannot further react as there is no mobility of the Zr–H bonds which points vertically to the surface. A further proof of such an explanation is given by EXAFS data. Indeed, a careful examination of the structure as deduced from molecular modeling studies shows that there is one oxygen atom, not directly bound to zirconium but just below it (the oxygen atom bound to the silicon dihydride on the scheme). EXAFS data have shown that there is such an oxygen atom around zirconium, at c.a. 0.26 nm from zirconium [12].

This formation of a surface hydride by treatment of a 'well-characterized' surface species by hydrogen is relatively general and has been observed with numerous metals. However, some discrepancies were observed between zirconium, hafnium, titanium and tantalum. These differences are resumed below.

2.2. Titanium, hafnium and tantalum hydrides

Titanium, hafnium and tantalum display a chemistry quite similar to that of zirconium. However there are differences from one metal to another. The first difference can be observed if we compare the starting organometallic complexes. If titanium and hafnium can be found as tetraneopentyl complexes, the corresponding tantalum complex, which should be tantalum pentaneopentyl, does not exist. Indeed, in this hypothetical complex the steric crowding would be so high that it transforms, via a α-H abstraction, into a carbene complex, $Ta(=CHC(CH_3)_3)$ $(CH_2C(CH_3)_3)_3$ [14]. These three complexes react with the hydroxyl groups of silica but, as the starting tantalum is different and contains a carbene ligand, its reactivity is different from that of hafnium and titanium tetraneopentyl. Hafnium and titanium tetraneopentyl react as zirconium tetraneopentyl, leading to the formation of a monografted ≡Si–O–M(CH_2C-$(CH_3)_3)_3$ (M = Hf,Ti) complex and evolution of 1 mol of neopentane per grafted metal [15–18]. Treatment under hydrogen at 150°C of these two complexes leads to the formation of hydrides like that for zirconium. However, if the chemistry of hafnium is quite similar to that of zirconium, a monohydride being obtained quantitatively [15,16], the situation is rather more complicated for titanium. Indeed, ESR experiments show that, in addition to the monohydride, there is a formation of a titanium(III) species (≡Si–O)Ti^{III} [18–20] in a relatively large amount (ca. 30%).

The tantalum complex $Ta(=CHC(CH_3)_3)$ $(CH_2C(CH_3)_3)_3$ reacts also with the hydroxyl groups of silica, leading to the formation of a supported tantalum complex. However, in contrast to what is observed for zirconium, titanium or hafnium, the first step of the reaction, as evidenced by the use of a deuterated silica, is an addition of the silica surface O–H group across the Ta=C double bond of the carbene moiety, followed by a neopentane elimination, by the same mechanism as that leading to the formation of $Ta(=CHC(CH_3)_3)(CH_2C(CH_3)_3)_3$ [21] (Scheme 3).

The main difference compared to the reaction of tetraneopentyl zirconium is that there is an evolution of more than one neopentane molecule per grafted tantalum (NpH/Zr = 1.3) [21]. This result is also confirmed by chemical analysis and reaction of the grafted complex with water.
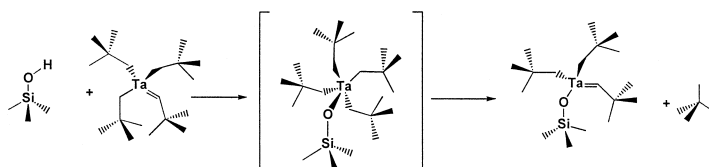
Scheme 3.

Reaction with acetone (pseudo-Wittig reaction) shows that there is on average one carbene function per grafted complex. All these data, combined with infrared and MAS NMR characterizations, were interpreted by assuming that two species were present on the surface, a mono-grafted $\equiv$Si–O–Ta(=CHC(CH$_3$)$_3$)(CH$_2$C-(CH$_3$)$_3$)$_2$ species and a digrafted ($\equiv$Si–O)$_2$Ta-(=CHC(CH$_3$)$_3$)(CH$_2$C(CH$_3$)$_3$) species in relative proportions 65/35 [21].

Most interesting is the reaction of this mixture of two surface complexes with hydrogen. Indeed, as in the above, there is a formation of a tantalum hydride, as evidenced by an infrared band at 1830 cm^{-1} and of silicon hydride (infrared bands in the 2200–2300 cm^{-1} region) [22]. Titration of the tantalum hydride by reaction with methyl iodide or di(*tert*-butyl)ketone shows that there is one hydride per grafted tantalum, as for zirconium. However, titration of the Si–H groups by KOH shows that there is a formation of only 0.65 Si–H per grafted tantalum. An EXAFS study of the tantalum hydride

gave a first coordination sphere of two oxygens at 0.189 nm for tantalum and one oxygen at ca. 0.263 nm. These results and the amount of oxygen consumed during the oxidation of the complex show that there was a formation of a tantalum(III) hydride as depicted in Scheme 4 [22].

It must be noted that this system displays a quite unexpected behavior as the two different precursor surface species lead to the formation of the same tantalum hydride. As observed in the case of group 4 metal, the transformation of the first precursor leads to the breaking of a neighboring $\equiv$Si–O–Si$\equiv$ bridge and formation of a corresponding Si–H group.

3. Hydrogenolysis of alkanes by the zirconium and hafnium hydrides

The stoichiometric hydrogenolysis of the neopentyl ligands was first observed during the reaction under hydrogen of the tris neopentyl zirconium grafted onto silica [12]. Indeed, no neopentane was evolved but only methane and ethane, in a 3:1 ratio, were observed at 150°C. The catalytic hydrogenolysis reaction was then studied in more details on the zirconium, titanium and hafnium hydrides. Various alkanes were studied such as neopentane, isobutane and *n*-butane [12,17,23–25]. Quite the same results were observed on zirconium and hafnium, while titanium led to a slightly different behavior, which will be explained in the next part of this review.

When neopentane was reacted with the zirconium or hafnium hydrides, it was observed that
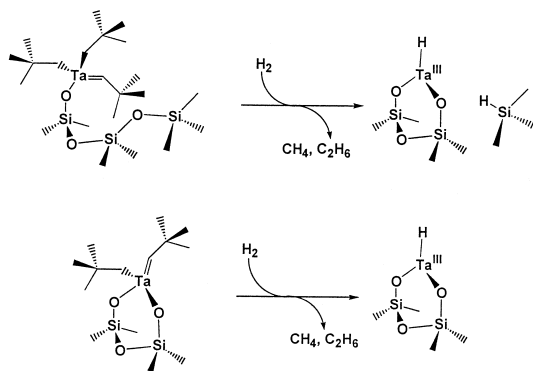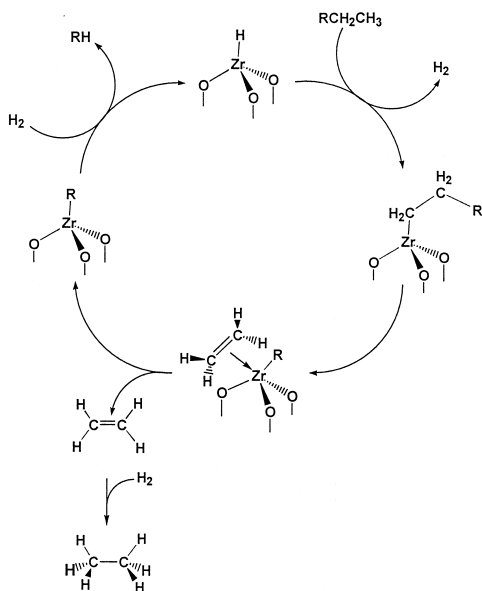

Scheme 4.

isobutane and methane were the primary products of the reaction. As a function of the reaction time, methane was further evolved and ethane was only formed during the last stages of the reaction. These results can easily be explained by the well-known β-alkyl transfer mechanism, which occurs with both high-valent early transition and low-valent late transition metal systems [26–28]. It can be described as an equilibrium between a metal alkyl and metal–olefin complexes (Scheme 5).

The catalytic cycle deduced from several stoichiometric reactions carried out on the zirconium hydride as well as from elementary steps of β-alkyl transfer is shown below (Scheme 6).

The observed activation of the C–H bond of several alkanes at low temperature (even at room temperature) by the zirconium and hafnium hydrides is not surprising. Indeed, these three supported hydrides are formally 8-electron complexes which are then expected to be very electrophilic. A second reason is that, on silica, these complexes are 'trapped' on the surface (they have three M–O bonds which link strongly the metal to the silica surface) avoiding coupling reactions between two hydrides which should result in a deactivation of the catalyst. The surface can thus be considered as a stabilizing agent. A third reason is a matrix effect of silica which imposes to zirconium a tetrahedral geometry whereas zirconium tends to be hexa-, hepta- or octa-coordinated. As a result, empty orbitals are directed through space with a tetrahedral hybridization which apparently favors quite strongly σ-bond metathesis of the C–H bonds of alkanes with the zirconium hydride. A fourth reason, logically deduced from the molecular modelling studies, is that the hydride, located above the oxide, is very accessible to
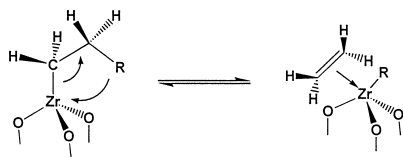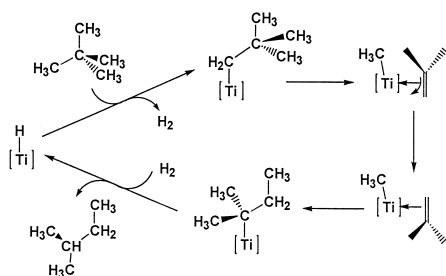

Scheme 6.

the reagents and there is a place for the coordination of other ligands on the zirconium or hafnium atom.

4. Hydroisomerization of alkanes by the titanium hydride

It had been observed during the synthesis of the silica supported titanium hydride that methane and ethane were not formed in a 3:1 ratio, but rather in a 1:1 ratio. A detailed study of the hydrogenolysis of neopentane and isobutane performed on this system showed that this unexpected result was due to the isomerization of neopentane during the hydrogenolysis cycle [17]. In the case of neopentane, methane, isobutane and *n*-butane are primary products. The main difference compared to the previous case was then the obtention of isobutane. Although isopentane was not observed, the presence of isobutane (and it is a major product early in the reaction) was a clear indication of a carbon rearrangement prior to the formation of the products. Quite the same results were obtained during the hydrogenolysis of isobutane with

Scheme 5.

Scheme 7.

hydrogen at 150°C [17]. Ethane was a primary product and the isomerization product *n*-butane was observed in the gas phase.

The skeletal alkane isomerization is easily explained by the same mechanism as the above. The first step of the reaction is the C–H bond activation of the alkane by the titanium hydride, leading to the surface alkyl titanium complex. This complex can undergo a β-methyl elimination leading to a titanium–methyl–olefin complex. But, in contrast to what is observed for zirconium and hafnium, this intermediate has a relatively long lifetime allowing the olefin to rotate before reinsertion into the metal–carbon bond. This mechanism is depicted below for neopentane (Scheme 7).

5. Polymerization / depolymerization on zirconium

We have seen above that, in the proposed mechanism of hydrogenolysis of alkanes, there is formation by β-alkyl transfer of an olefin 'coordinated' to a hydride or to an alkyl zirconium. However, no olefin could be detected because it was quickly inserted into the hydride to give an alkyl and then an alkane. It was then logical to study the reaction of olefins with the zirconium hydride in the absence of hydrogen. When the zirconium hydride was exposed to an ethylene pressure of 200 Torr at room temperature, the IR spectrum of the solid showed the immediate disappearance of the Zr–H band at 1625 cm^{-1} [29]. Simultaneously, very intense

bands appeared in the region of 2970–2850 cm^{-1} and at 1380 cm^{-1}, which are characteristic of polyethylene. The same catalyst was also able to polymerize propylene at room temperature into polypropylene, as evidenced by infrared spectroscopy. Such a result was not surprising as the polymerization of ethylene and propylene has been reported to occur on zirconium hydrides supported on alumina [30–32]. The mechanism of this reaction can be easily deduced from the above studies: There is first the insertion of the olefin into the metal hydride bond and later the insertion into the metal–alkyl bond. This can also be schematized by the equilibrium between the metal–alkyl and the metal–olefin complexes (Scheme 5).

Interestingly, the polyethylene produced by this polymerization could be fully transformed into methane and ethane under hydrogen at 150°C [29]. This hydrogenolysis of polyethylene regenerated simultaneously the zirconium hydride. This experiment was a strong support in favor of the equilibrium between insertion polymerization and β-alkyl transfer. Even if polymerization reaction is interesting from an academic point of view, the main interest of the zirconium hydride is to perform this inverse reaction of the polymerization. Polyethylene (or polypropylene) can be considered as alkanes of high molecular weight and so they undergo hydrogenolysis in the presence of hydrogen. The reaction was performed with the zirconium hydride supported on various oxides but silica–alumina led to the best results [29]. Samples of polyethylene of low molecular weight (C_{18} to C_{50}) were brought into contact with the zirconium hydride supported on a Ketjen silica–alumina (25% Al, 375 m^2 g^{-1}) under hydrogen ($P = 1$ atm) at 150°C for varying periods of time. The oligomer composition was determined by gas chromatography and showed a shift to lower molecular weights as a function of time. After 62 h of reaction, only light alkanes ($< C_6$) could be detected in the reaction mixture showing that all the polymer had depolymerized. Quite similar results were obtained with

Scheme 8.
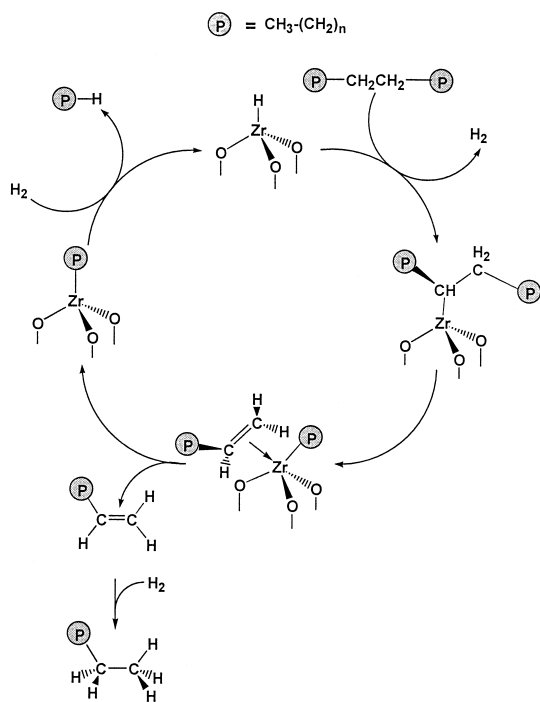
polypropylene ($M = 250\,000$) and higher molecular weight polyethylene ($M = 125\,000$), showing in all cases a hydrogenolysis and formation of light hydrocarbons.

The mechanism of this reaction is quite similar to that proposed for the hydrogenolysis of alkanes and is depicted below (Scheme 8).

Unfortunately, this reaction is not selective in the sense that all C–H bonds of the polymer can be activated by the zirconium hydride, resulting in a broad distribution of the reaction products. However, it is potentially interesting for plastic recovery and their transformation into valuable products instead of burning them as it is actually made.

6. Metathesis of alkanes by the tantalum hydride

All catalytic applications described above are mainly related to the equilibrium between the

olefin insertion and the β-H or β-alkyltransfer. However, the surface hydrides are also active catalysts for a new catalytic reaction, the metathesis of alkanes which does not involve this equilibrium. This reaction has been called 'metathesis' by analogy with the olefin metathesis. By this reaction, carbon–carbon and carbon–hydrogen bonds seem to be reversibly broken and formed allowing transformation of C_n alkanes to higher and lower alkanes.

A typical example is the metathesis of ethane. As we have seen it above, ethane cannot undergo hydrogenolysis as it does not have an alkyl group in β-position. It can only undergo an olefin insertion /β-H transfer equilibrium and on the zirconium hydride in the presence or absence of hydrogen it does not react whatever the temperature. However, when it was contacted with the tantalum hydride (ethane/Ta molar ratio of 800) at 150°C in the absence of hydrogen there was apparition of methane and propane in quite similar amounts and of traces of *n*-butane and isobutane ($n/\text{iso} = 4$) [33]. When ethane was ^{13}C-monolabelled, the resulting propane contained from 0 to 3 carbon-13 atoms (in a ratio 1:3:3:1 ratio) probing the cleavage of the [13]C–[12]C bond of ethane and the redistribution of the carbon-13 atoms into the propane molecules.

When higher alkanes were used, a distribution of higher and lower alkanes was obtained, showing that the reaction was not fully selective even if the C_{n+1} and C_{n-1} alkanes were always the major products. For example, the metathesis of *n*-butane led to methane (2%), ethane (12.5%), propane (36%), *n*-pentane (26.5%), *n*-hexane (10%), heptanes (4.5%), the other products (8.5%) being mainly iso-alkanes. In the case of isobutane, propane and the higher iso-alkanes were the major products, *n*-butane being formed only in very small amounts (less than 0.6%), showing that there was only very little isomerization of the alkane in this case [33]. The formation of iso-alkanes during the metathesis of *n*-alkanes can be explained easily if we assume that the first step of the reaction is
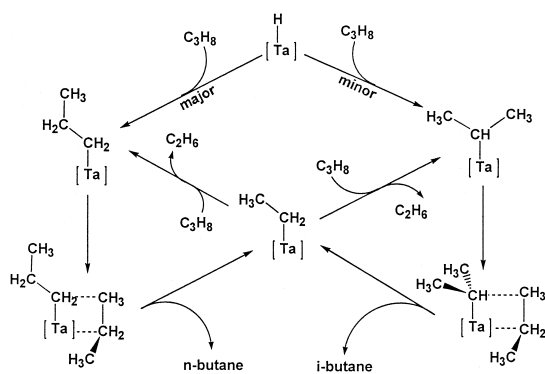
Scheme 9.

a C–H bond activation of the alkane by the tantalum hydride, as evidenced by infrared spectroscopy and solid-state NMR and as in the first step of the hydrogenolysis reaction. Indeed, the activation could occur both on primary or secondary carbon atoms, leading to the formation of *n*-alkyl and iso-alkyl tantalum surface species [33]. A study performed elsewhere on the zirconium hydride system had shown that in the case of the activation of propane there was a formation of the *n*- and isopropyl zirconium complexes, in a 15:1 ratio, showing that the most stable alkyl–zirconium complex was the linear one, even if there was a non-negligible amount of the iso-isomer [25].

The mechanism of the metathesis reaction from the tantalum alkyl complex still remains unknown even if numerous studies were performed on this system. Scheme 9 shows a proposition of catalytic cycle for the metathesis of propane and the formation of the C_{n+1} and C_{n-1} hydrocarbons. Its main aspect is the formation of a four-center intermediate, quite similar to that is proved for the metathesis of olefins.

This simple drawing of the catalytic cycle explains most of the experimental data. For example, for the metathesis of propane, *n*-butane and isobutane were formed in a 4:1 ratio, in agreement with the fact that activation of propane occurs preferentially on the primary carbon atoms.

7. Conclusion

In the course of this short review, we have shown various catalytic applications of well-defined surface hydrides supported on oxides. These hydrides are obtained by reaction of an alkyl–metal with the hydroxyl groups present on the surface of the oxide, leading to a mono- or di-grafted surface species, well characterized by numerous physico-chemical methods. This surface complex is then treated under hydrogen at 150°C leading to the formation of a highly reactive metal hydride and a restructuring of the surface of the oxide. For all metal studied (zirconium, hafnium, titanium, tantalum) there is always a formation of a monohydride, even if in the case of titanium a non-negligible amount of the metal is found as inactive titanium(III).

This surface supported hydride depicts quite interesting catalytic properties mainly explained by the equilibrium between β-alkyl transfer and olefin insertion. For example, they can achieve hydrogenolysis of alkanes at moderate temperature (below 150°C). A potentially interesting application of this catalytic reaction is the polymerization/depolymerization of polyolefins, which can also be synthesized with these catalysts. In the case of the titanium hydride, the lifetime of the coordinated olefin is long enough to allow rotation of this molecule and then a resulting isomerization of the alkanes. Finally, tantalum hydride has been shown to perform a new catalytic reaction, called 'alkanes metathesis', in which alkanes are converted into higher and lower alkanes.

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