

Review

Heterogeneous well-defined catalysts for metathesis of inert and not so inert bonds

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Abstract

The present short review article reports four examples of catalytic reactions realised on relatively well-defined supported catalysts. These catalysts were conceptually designed and prepared by a Surface Organometallic Chemistry (SOMC) approach. They were designed for achieving the olefin metathesis reaction, the Ziegler–Natta depolymerisation, the low temperature hydrogenolysis of alkanes and the alkane metathesis reaction. These reactions are “related” to the metathesis of inert bonds. The first example is the silica-supported rhenium (VII) carbene species $[(\equiv\text{Si}-\text{O})-\text{Re}(\equiv\text{C}-t\text{-Bu})(=\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})]$ obtained by grafting $\text{Re}(\equiv\text{C}-t\text{-Bu})(=\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ on silica. This catalyst has turned out to be very active in the propene metathesis reaction (initial T.O.F. = 0.25 mol/mol Re/s) after an initiation step involving a cross-metathesis reaction between the neopentylidene ligand and propene.

The silica or silica–alumina-supported zirconium hydride(s) catalyse(s) the “depolymerisation” of polyethylene into lower oligomers and “diesel range hydrocarbons”. The depolymerisation reaction mechanism involves a β -alkyl transfer which is the microscopic reverse of the “Cossee” mechanism of olefin insertion into a metal alkyl bond. Moreover, in the case of low-density branched polyethylenes (LDBP), the cleavage of the polymer chain occurs preferentially on the branches of the initial polymer. Therefore, the branched initial polyethylene is transformed into a linear one. Besides, recent advances in NMR spectroscopic techniques have highlighted that the zirconium hydride catalyst contains in fact two surface species: a zirconium monohydride (major) and a zirconium dihydride (minor).

The silica-supported tantalum hydride, $[(\equiv\text{SiO})_2\text{Ta}-\text{H}]$, and the silica-supported zirconium hydrides $[(\equiv\text{SiO})_2\text{ZrH}_2]$ and $[(\equiv\text{SiO})_3\text{Zr}-\text{H}]$ both catalyse the low temperature hydrogenolysis of alkanes but with a major difference between the two metals—tantalum hydride is able to cleave the C–C bond of ethane whereas zirconium hydrides are not. In fact, the C–C bond cleavage reactions go through different pathways: in the case of Zr the pathway of C–C bond cleavage obeys a β -alkyl transfer mechanism while, in the case of Ta, another pathway is required, which involves either σ -bond metathesis, oxidative addition or carbene mechanism. Notably, the tantalum hydride catalyst has also been found to be active in the alkane metathesis reaction. During this reaction, two different processes occur simultaneously: the productive alkane metathesis which leads to higher and lower alkane homologues and the scrambling of the initial alkane reagent.

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1. Introduction

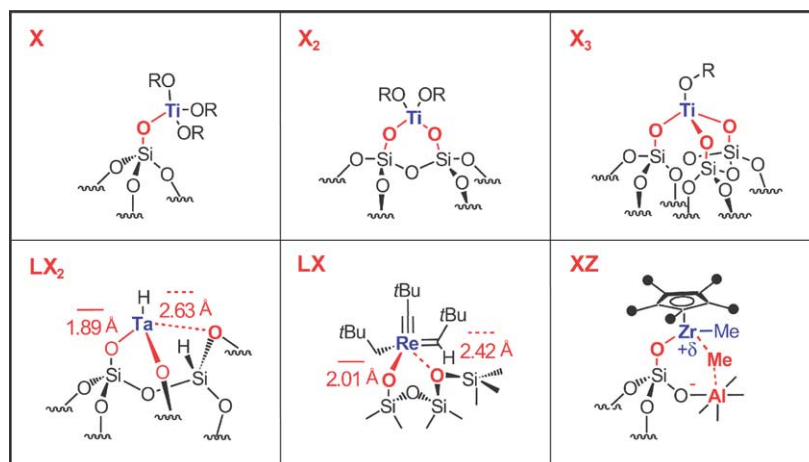
Catalysis is primarily a molecular phenomenon, since it implies the transformation of molecules into other molecules independently of phase consideration (homogeneous or heterogeneous). In heterogeneous catalysis, the level of understanding is still limited because it is usually difficult to achieve a reliable “structure–activity” relationship. This dif-

iculty arises from the small number of active site(s), a concept already introduced in 1927 by Taylor [1]. Despite the impressive number of current physico-chemical tools available to characterise surfaces at an atomic and molecular level, the detection of these active sites is extremely difficult either as such or under working catalytic conditions (detection of reaction intermediates).

In order to achieve a higher level of understanding and eventually find new catalytic systems, it is necessary to prepare on surfaces well-defined active sites uniform in composition and distribution, and thereby generate “single-site” heterogeneous catalysts. This objective is most crucial for

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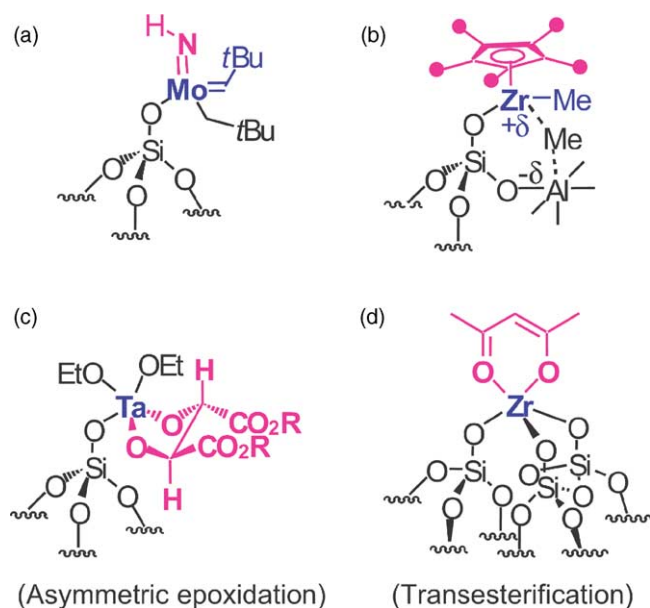
Scheme 1. X [78], X₂ [78], X₃ [78], LX₂ [73], LX [5,79], XZ [80].

the catalytic reactions, which are difficult to achieve either in homogeneous or heterogeneous catalysis, and eventually it might help to discover new catalytic reactions, which do not exist either in homogeneous, heterogeneous or even enzymatic reactions!

The strategy to make these well-defined active sites is based on a number of hypotheses:

- Firstly, it is necessary to enter the catalytic cycle via a postulated reaction intermediate (or one of its immediate precursor). Preferably it is necessary to draw a reasonable mechanism derived from molecular organometallic chemistry and focus on the crucial stable intermediate (when the sites are well-defined and in high concentrations on the surface, it is possible, in principle, to study elementary steps and determine those reaction intermediates). This concept may seem obvious in homogeneous catalysis, but it is not the general rule in heterogeneous catalysis. Classically in heterogeneous catalysis, the catalyst, which may be an oxide, a sulphide, a carbide... or a metal particle, “goes through” one or several intermediates of the “catalytic cycle” by means of the reaction of the reagents and products with the surface. A typical example is the oxidation of propene by molecular oxygen on Bi-Mo catalysts [2,3] whose mechanism has been rationalised a posteriori.
- Secondly, one has to consider the surface as a classical ligand of co-ordination chemistry such as X-, L- or Z-ligands in the Green formalism. Doing so, one has access to formal oxidation state, electron configuration and electron count of the active metal. Typical examples are given in Scheme 1. Interestingly, by considering the surface as a classical ligand of co-ordination chemistry, it is possible to make electron counts in the same way as in molecular chemistry. This is important since it allows to predict the reactivity of the active site and the mechanism by which it will operate (oxidative addition, σ -bond metathesis, etc...).

- Thirdly, one may eventually use “spectator” ligands “above” the surface in order to tune the activity, the selectivity and the life time.
- Fourthly, like for enzyme, one may also control the hydrophobicity or hydrophilicity of the local environment [4] via the presence of organic ligands on the surface at the vicinity of the catalytic site. Several examples developed in the laboratory are given in Scheme 2.
- Finally, one has to prove surface structures of relevant catalytic intermediates with the accuracy of both molecular and solid state chemistry. This is also a critical point because these two “scientific communities” have not communicated enough between each other and have implemented their own “preference” for tools. However,



Scheme 2. (a) Olefin metathesis catalyst [81], (b) olefin polymerisation catalyst [80], (c) epoxidation catalyst [82,83], (d) Lewis acid catalysis for transesterification [84].

working with well-defined surface systems allows to use physical characterisation techniques very efficiently (reliable data) since it is easier to understand a single species than a myriad of them. For example, on single site systems, EXAFS and/or XANES provide reliable coordination numbers, while it is usually a major difficulty for these techniques on ill-defined systems. Regarding solid state NMR, which is also a quite demanding technique (because of its low sensibility), it has been developed into an extremely powerful tool for structural characterisation of inorganic or organic solids, macromolecules and even proteins. Advanced solid state NMR techniques (2D HETCOR, J-resolved and DQ NMR) have been recently implemented in our laboratory in collaboration with the Laboratoire de Chimie in the Ecole Normale Supérieure de Lyon (Prof. Emsley) and has allowed us to observe surface carbenes or carbynes (2D HETCOR) [5], agostic interaction (J-resolved 2D NMR) [5] and zirconium dihydrides (DQ ^1H NMR) [6].

This approach has been called the Surface Organometallic Chemistry (SOMC) [7]. This discipline of chemistry consists in bringing the concepts and the experimental tools of molecular chemistry, especially organometallic chemistry, to surface science and heterogeneous catalysis.

Pioneering work started in the 1960 in polymer chemistry, but SOMC, in its present form, really addresses the structure of the active sites, its reactivity and its fate during catalysis in order to develop and improve catalysts through structure-activity correlation.

In relation with the meeting “metathesis of olefins and related reactions” (ISOM XV, Kyoto, July 2003), we have focused on the recent advances in *Surface Organometallic Chemistry* applied to the metathesis of olefins, but also look at the metathesis of more inert bonds, such as C–H, C–C and H–H bonds (elementary steps involved in the low temperature hydrogenolysis and metathesis of alkanes).

As examples, we describe herein the characterisation and catalytic properties of three highly active and selective catalysts prepared via the Surface Organometallic Chemistry method developed in the laboratory:

- I Silica-supported rhenium carbene species for olefin metathesis.
- II Silica–alumina-supported zirconium hydride for polyethylene depolymerisation.
- III Silica-supported tantalum hydride for alkane hydrogenolysis and alkane metathesis.

I. Silica-supported rhenium carbene species for olefins metathesis

Some of the first olefin metathesis catalysts have been prepared by British Petroleum scientists by impregnation of rhenium(VII) oxide on alumina [8–11]. These $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst has been extensively studied as it shows a high ac-

tivity in olefin metathesis at low temperatures (273–373 K) even with some functionalised olefins [12]. Noteworthy, only 2% of the supported rhenium is actually active [13] in the desired reaction. This is probably related to the very specific environment of the active site, which requires probably the proximity of the rhenium atom with a highly acidic aluminium sites of the support. This dual system is necessary both for the “initiation” reaction, formation of the metallocarbene, and the “propagation” reaction. The dramatical influence of the support acidity has been confirmed by the absence of any catalytic activity of Re_2O_7 supported on silica, a rather non acidic support [14–18].

As metallocarbenes have been recognised as key intermediates in olefin metathesis, the SOMC approach dictates the need to generate a supported rhenium carbene covalently linked to an oxide support [19–22]. This would present the obvious advantage of avoiding the initiation step of the metallocarbene, a still unknown pathway on the classical heterogeneous catalysts. As complexes of rhenium(VII) having a d^0 -configuration [23] and containing alkylidene ligands [24–30] are some of the best catalysts for olefin metathesis in homogeneous catalytic systems, it has been decided to generate a rhenium(VII) carbene supported on silica by grafting $\text{Re}(\equiv\text{C}-t\text{-Bu})(=\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ [31–33] on the surface silanol groups [34]. The choice of an alkyl precursor is particularly indicated, given the well-known clean grafting reaction undergone by such species. Typically, an alkyl precursor reacts with the silica surface’s reacting silanols, by elimination of an alkane molecule and the concomitant formation of a ($\equiv\text{Si}-\text{O}-\text{M}$) bond.

Effectively $\text{Re}(\equiv\text{C}-t\text{-Bu})(=\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ reacts with silica partially dehydroxylated at 700 °C. By using this dehydroxylation temperature, the reactive sites of the surface consist mainly in isolated silanols. As expected, the grafting reaction leads to the monografted supported species **1** (see Scheme 3(a)) by elimination of one equivalent of neopentane.

This first example of silica-supported rhenium (VII) carbene–carbyne complex **1** was fully characterized by EXAFS (see Scheme 3(b)), NMR spectroscopies (see Scheme 3(c)) (1D ^{13}C and ^1H , 2D HETCOR and J resolved solid state NMR), IR spectroscopy and elemental analysis [34].

This well-defined rhenium heterogeneous catalyst, prepared via Surface Organometallic Chemistry was found to be very active in olefin metathesis. When 500 equivalents of propene are contacted with **1** at 25 °C the equilibrium with the products of metathesis is reached within less than one hour (see Fig. 1(a), curve 1) and the initial T.O.F. is 0.25 mol/mol Re/s [34].

As reported in Table 1, these catalytic performances are comparable to those observed with the best classical heterogeneous catalysts.

Moreover, the evolution of one equivalent of a 1:3 mixture of 3,3-dimethylbutene and 4,4-dimethyl-2-pentene (see Fig. 1(a), curve 2 and 3), during the first hour of reaction,

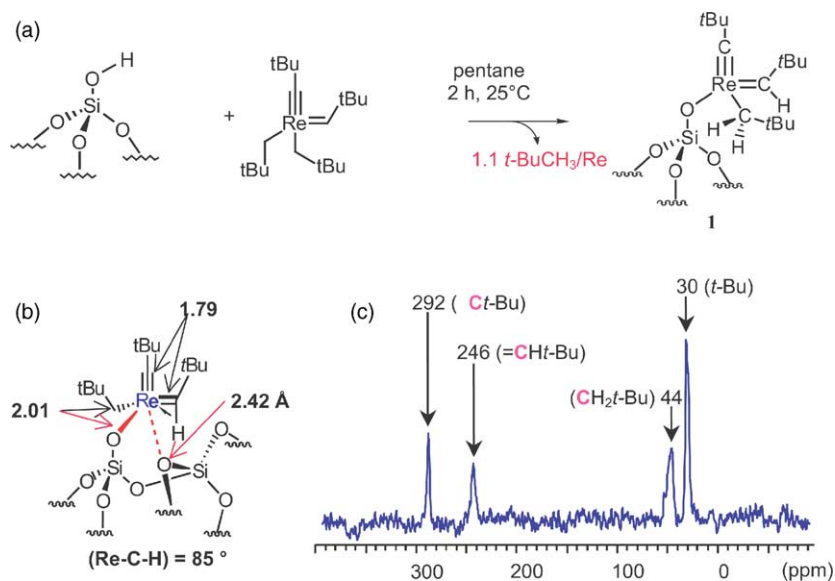
Scheme 3. (a) Chemical reaction. (b) Structure of the supported rhenium catalyst. (c) ^{13}C CP MAS solid state NMR.

Table 1

Catalyst [12]	Support	T.O.F. (mol/mol Re/s)	Temperature (°C)
MoO_3	Al_2O_3	0.20	150–250
WO_3	Al_2O_3	0.40	350–400
Re_2O_7	Al_2O_3	0.14	20–100
Re_2O_7	SiO_2	0.01	100
$\text{SiO-Re}(\equiv\text{C-t-Bu})$ $(=\text{CH-t-Bu})\text{CH}_2\text{-t-Bu}$	SiO_2	0.10–1.00	25

gives a clear molecular insight into the activation process of the rhenium catalyst by a cross-metathesis reaction between the alkylidene ligand and the propene (see Fig. 1(b)).

II. Silica–alumina-supported zirconium hydride for polyethylene depolymerisation

In the 1950's, Ziegler and Natta discovered that transition metals could catalyse the polymerisation of propylene or

ethylene giving access to new paraffinic polymers [35–38]. This discovery led to a large scale production of valuable, but non biodegradable polymers. In order to solve the environmental problem of polymer waste, the depolymerisation of these polyolefins into olefinic oligomers, monomers or useful chemicals is an important field. A SOMC approach of this subject of interest requires a molecular level understanding of the target reaction.

As the Ziegler–Natta polymerisation is based on consecutive insertions of olefins in a metal–alkyl bond [39,40], the depolymerisation reaction could involve successive de-insertions of olefins from the metal–alkyl catalyst (see Scheme 4(a)).

In terms of mechanism, the insertion of an olefin in a metal–alkyl bond (elementary step of the Ziegler–Natta polymerisation; the well known “Cossee” mechanism) is the microscopic reverse of the β -alkyl transfer [41–53] (see Scheme 4(b)). It should be, therefore, possible to use the principle of microreversibility to drive the equilibrated

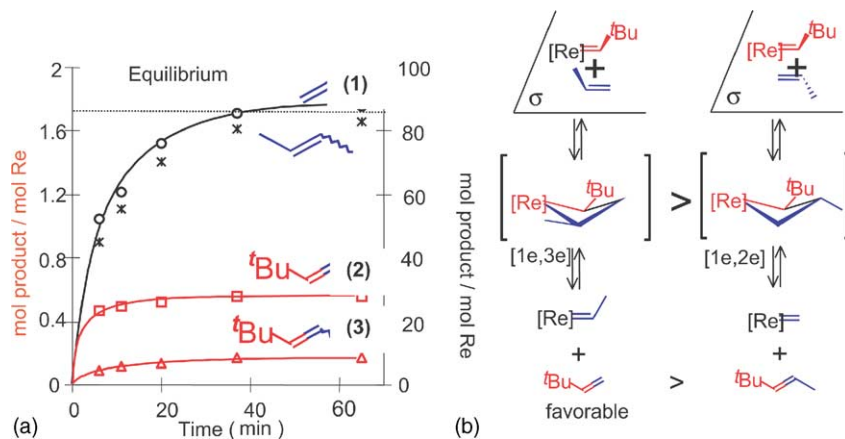
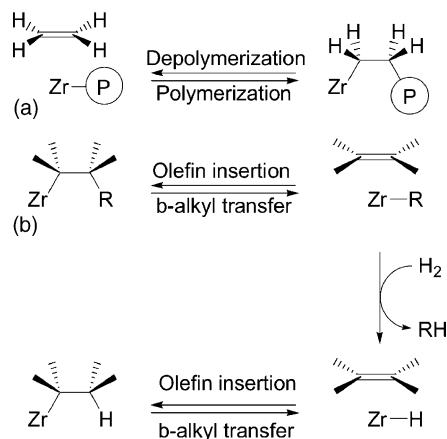


Fig. 1. (a) Amounts of products evolved in the first hour of reaction. (b) Cross-metathesis transition states.



Scheme 4. (a) Polymerisation-depolymerisation key-step. (b) Depolymerisation via β -alkyl transfer, hydrogenation and olefin insertion.

elementary step in the reverse direction: β -alkyl transfer. As the olefin polymerisation is thermodynamically very favoured at moderate temperature, the reverse reaction of depolymerisation is really disfavoured at low or moderate temperatures. Therefore, the depolymerisation of polyolefins is a very challenging goal!

In order to overcome this depolymerisation thermodynamic gap energy (see Scheme 4(b)), it is necessary to couple the desired unfavourable reaction, with a highly favoured one, which would drive the overall system in the required direction. The hydrogenation of the double bond formed in the depolymerisation can be the solution. The overall reaction would become an hydrogenolysis of an “alkane macromolecule” to produce lower alkanes. Such favourable thermodynamic balance will be the driving force for the β -alkyl transfer involved in the depolymerisation step (see Scheme 5).

The catalyst system able to achieve such kind of reaction should therefore be able to polymerise olefins. We chose a silica or silica alumina zirconium hydride-supported species, which were good candidates to fulfil these requirements (insertion of olefins [54–61], alkane hydrogenolysis [62–64]). Since 1991, the silica-supported zirconium hydrides catalyst have been obtained by the grafting of tetra-n-pentylzirconium molecular complex on partially dehydroxylated silica followed by a treatment under hydrogen [64]. These reac-

tions lead to the formation of $(\equiv\text{SiO})_3\text{ZrH}$ **3a** [62,63,65,66] as the major supported species (see Scheme 6(a)).

Zirconium hydride species has been analysed by different techniques: IR spectroscopy, EXAFS, 1D NMR spectroscopies (¹H and ¹³C solid state NMR), GC analysis [66]. Recent advances in solid state NMR spectroscopy techniques have allowed us to identify another supported species which seems to be present in smaller but nevertheless significant amounts on the surface: $(\equiv\text{SiO})_2\text{ZrH}_2$ **3b** [6].

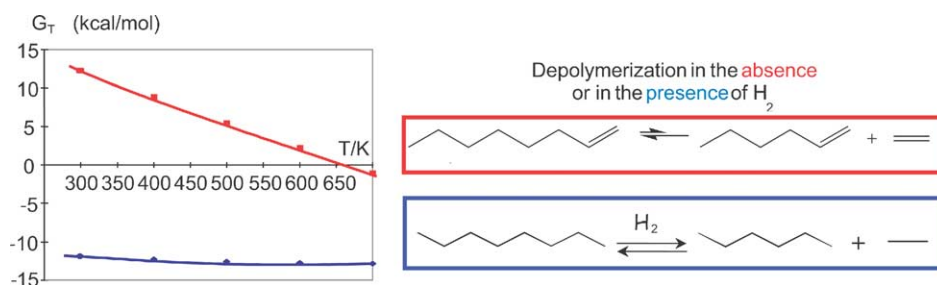
In particular, the characterisation of **3b** has been made possible thanks to the development of a ¹H 2D double quanta solid state NMR sequence, whose spectra present correlation signals for protons undergoing dipolar through-space interactions with other close spins. Therefore, such a sequence permits to identify isolated protons from non-isolated ones. For the silica-supported zirconium hydrides described above, it has been possible to identify and assign two types of hydride resonances: at 10 and 12 ppm to a monohydride and a dihydride, respectively [6].

The 2D double quanta NMR spectroscopy also highlighted the spatial proximity of the hydrogenosilane species and the zirconium monohydride. These data have ascertained the mechanism of the formation of the zirconium hydrides (see Scheme 6(b)), which involves opening the siloxane bridges and formation of (Zr–O–Si) and (Si–H) bonds close to each other.

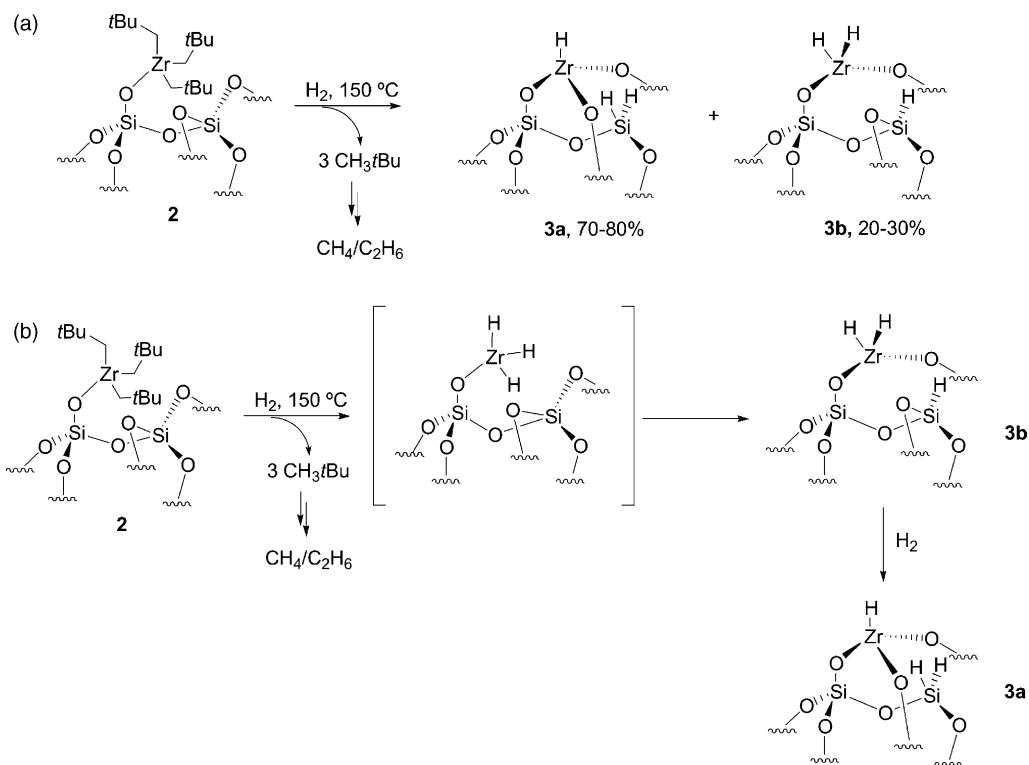
These two well-defined zirconium hydride complexes supported on silica–alumina [67], already known to catalyse ethylene or propylene polymerisation [68], have been also found to depolymerise the resulting polymers [69]. The depolymerisation reaction can readily be monitored by IR spectroscopy.

For example, a mixture of **3a** and **3b** exposed to an ethylene pressure (200 Torr, room temperature) leads to the formation of polyethylene as observed by IR spectroscopy: the appearance of very intense bands characteristic of polyethylene [70] (2970–2850 cm^{-1}) and the concomitant decrease of the band (1635 cm^{-1}) attributed to $\nu(\text{Zr–H})$ vibrations (see Fig. 2). This polymerisation takes place via the insertion of ethylene into the Zr–H bond to yield Zr–Et bond, followed by multiple insertions of ethylene into the Zr–C bond.

Upon heating this supported polymer at 150 °C overnight under H₂, the IR spectrum shows the disappearance of the aliphatic chains bands ($\nu(\text{C–H})$ 2970–2850 cm^{-1} and



Scheme 5. ΔG_{298} (kcal/mol) of the polymerisation–depolymerisation reaction.



Scheme 6. (a) Hydrogenolysis of **2**. (b) Mechanism of zirconium hydrides formation.

$\delta(\text{C-H})$ 1380 cm^{-1}) and the regeneration of the $\nu(\text{Zr-H})$ vibration band (see Fig. 2), thus demonstrating the reversibility of this process under hydrogen and the possibility to depolymerise polyolefins.

The depolymerisation properties of this catalyst have been further studied by contacting commercial low-density polyethylene (LDPE) to zirconium hydride-supported

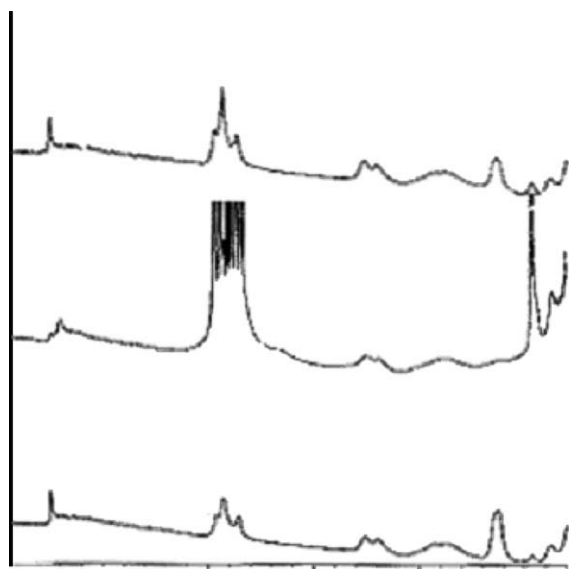


Fig. 2. IR spectra (a) starting hydrides **3a** and **3b**. (b) After exposure to ethylene overnight at room temperature. (c) After heating at 150 °C overnight under H₂.

species **3a** and **3b** under 1 bar of hydrogen at 150 °C. For example, this LDPE, initially composed of 2–3 long branches/1000 carbons and 11 butyl branches/1000 carbons with $M_n = 19,000$ and a large polydispersity index ($I_p = 7$), was transformed into a linear polymer having a higher molecular weight ($M_n = 42,000$) and a lower I_p value ($I_p = 4$). The gas phase of the reaction mixture was composed of 46% (weight) of C₁ to C₈ linear alkanes. During this process, the LDPE molecular weight number distribution becomes narrower with disappearance of the lower molecular weight numbers, which is consistent with the hydrogenolysis of the branches [71]. This was further confirmed by ¹³C NMR spectroscopy on the resulting polymer which shows the disappearance of the signals attributed to the carbons composing the butyl and the longer branches of the polymer (see Fig. 3) [71].

Based on these results, a mechanism involving a β -alkyl-transfer as the key step of the polymer cleavage can be postulated (see Scheme 7):

- activation of one C–H bond of the polymer by the zirconium hydride catalyst leading to Zr-alkyl species;
- formation of a Zr-alkyl species having a β -alkyl branch through consecutive β -H eliminations and olefin reinsertion;
- β -alkyl branch elimination to obtain an alkyl-alkene zirconium complex;
- hydrogenation of the Zr-alkyl bond to yield the Zr–H species;

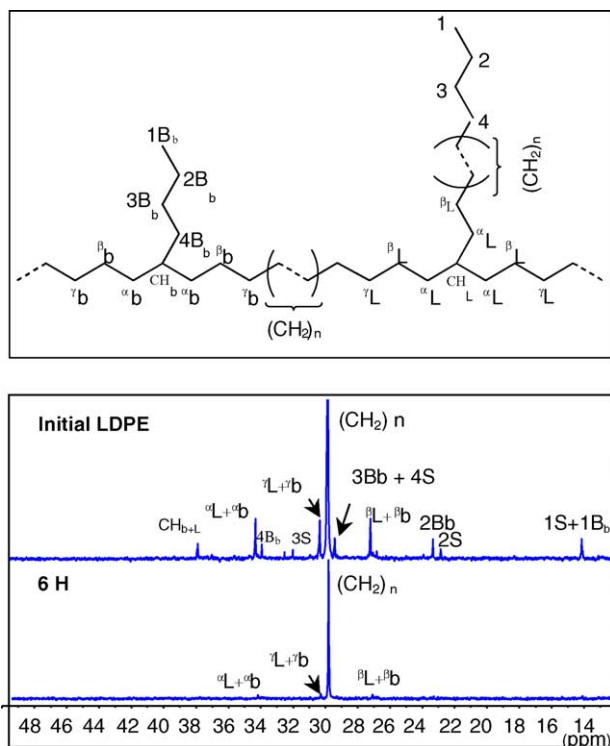


Fig. 3. ^{13}C CP MAS NMR spectra of the initial LDPE and after contact with **3a** and **3b** at 150°C under H_2 during 6 h.

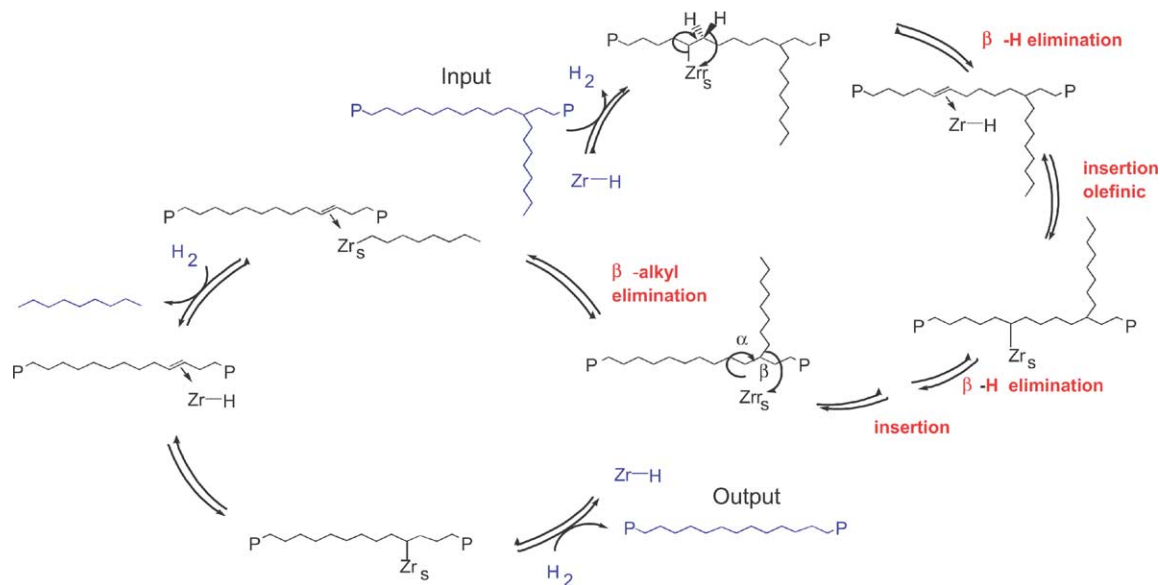
- reinsertion of the olefin into the Zr–H bond to obtain a Zr-alkyl species;
- hydrogenation of the zirconium-alkyl bond to regenerate the initial zirconium hydride catalyst.

III. Silica-supported tantalum hydride for alkane hydrogenolysis and alkane metathesis

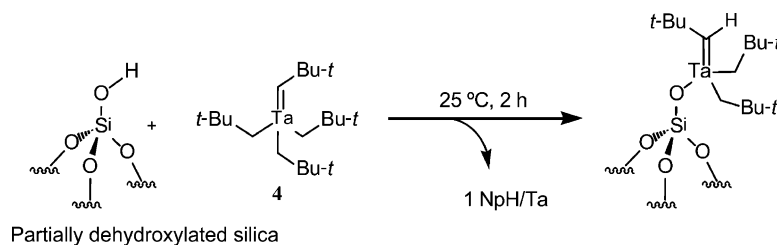
Alkane hydrogenolysis [72] and alkane metathesis [73–75] are catalysed by tantalum hydride species. Such species are prepared by impregnation of the $(\text{Ta}(\text{=CHtBu})(\text{CH}_2\text{tBu})_3)$, on partially dehydroxylated silica at room temperature (see Scheme 8). The resulted supported complex **4** has been fully characterized by IR spectroscopy, elemental analysis, GC analysis, ^1H and ^{13}C solid state NMR spectroscopies and EXAFS [73].

The well-defined tantalum hydride disiloxy-species **5** has been consecutively obtained by treatment of **4** under hydrogen at 150°C (see Scheme 9) [73] and has been characterized by IR and NMR spectroscopies.

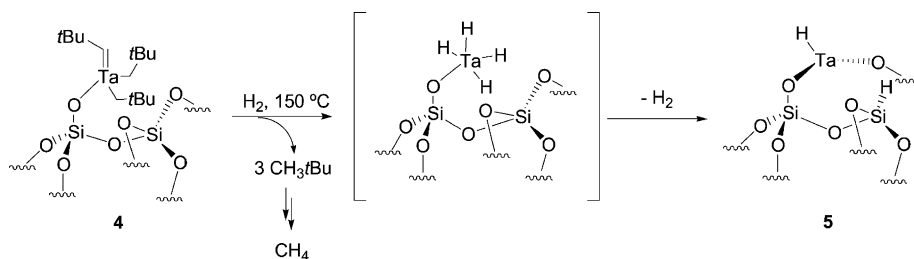
This supported species $(\text{=SiO})_2\text{TaH}$ (**5**) is an active catalyst for alkane hydrogenolysis [72], just as silica-supported group 4 hydrides $(\text{=SiO})_3\text{M-H}$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) [53,64,66,76], which readily catalyse acyclic alkane hydrogenolysis and polyethylene depolymerisation [69] (as aforementioned). In contrast with these group 4 catalysts,



Scheme 7. Polymer cleavage postulated catalytic cycle.



Scheme 8.



Scheme 9.

which yield methane/ethane mixtures as final products, the tantalum-supported species produces only methane as final product independently from the nature of the linear or branched initial alkane.

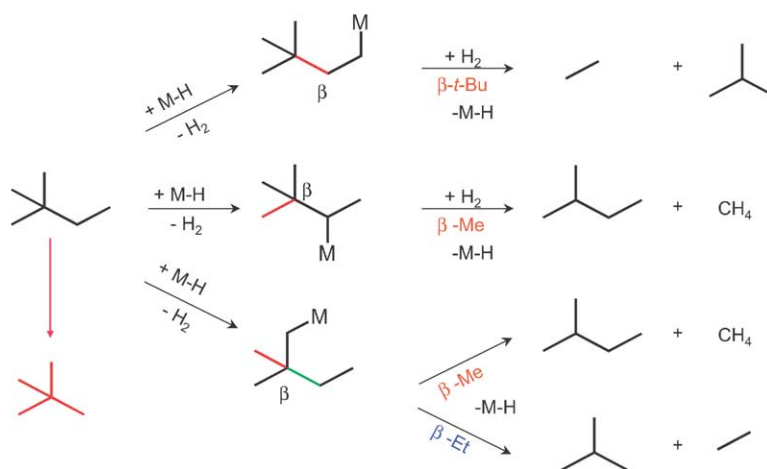
With group 4 metal hydrides, the proposed mechanism of this catalytic reaction involves a β -alkyl transfer [41–53] as the key step of the C–C bond cleavage (vida supra). Since, the tantalum hydride-supported species converts alkanes including ethane into methane at 150 °C, this rules out the β -methyl transfer as the unique C–C bond cleavage mechanism in the case of tantalum. Further confirmation of this unique reactivity was obtained by studying the hydrogenolysis of 2,2-dimethylbutane catalysed by zirconium hydrides (**3a** and **3b**) and tantalum hydride (**5**) complexes. The comparison of the primary products evolved in the gas phase showed that **3a** and **3b** lead to isopentane [77] (which can be explained by a β -methyl transfer pathway (see Scheme 10) as major product of higher alkanes while **5** produces neopentane (which can not be obtained by a β -alkyl transfer) (see Scheme 10).

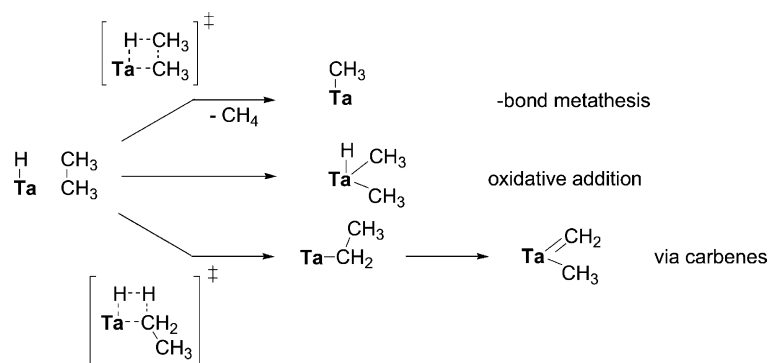
This comparison clearly shows that another process for the C–C bond cleavage takes place during the alkane hydrogenolysis reaction catalysed by a tantalum-supported species with respect to group 4 catalysts. We suggest that a possible mechanism of the C–C bond cleavage involves a four centred transition state although many other elementary steps may also be explained by an oxidative addition

followed by reductive elimination or a carbene mechanism (see Scheme 11).

Besides alkane hydrogenolysis, the silica-supported ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$)($\equiv\text{SiO}$)₂TaH [73] catalyses “alkane metathesis”, a new reaction discovered in 1996. This reaction transforms linear or branched alkanes into their higher and lower homologues [74,75]. For example, Fig. 4 represents the distribution of the various products (at 3% conversion) evolved during the metathesis of the first linear alkanes catalysed by **5** at 150 °C.

The simplest case is the metathesis of ethane. Since this molecule has only one C–C bond, it does not present any problem of selectivity. The products of the reaction are mostly propane (44%_(mol)) and methane (53%_(mol)) in nearly equal amounts with trace amounts of butane (2.4%_(mol)) and isobutane (0.6%_(mol)). Thanks to ¹³C labelling experiments using monolabelled ethane as reagent and to GC–MS analysis, the evolution of unlabelled, mono-, di- and trilateral propane during the reaction is observed. These results prove the redistribution of the ¹³C atoms in the propane molecules and thus, the cleavage of ¹³C–¹²C bond of the ethane. These experiments also reveal the presence of an additional faster process occurring simultaneously to the formation of propane. Monolabelled ethane is converted into an 1:1 mixture of unlabelled and dilabelled ethane (see Scheme 12). Such scrambling process can be considered as a “degenerative metathesis” [75], in contrast with the

Scheme 10. Fragmentation pathways via β -alkyl transfer mechanism.



Scheme 11. alkane hydrogenolysis or metathesis mechanisms via σ -bond metathesis, oxidative addition and reductive elimination pathway and carbenic species.

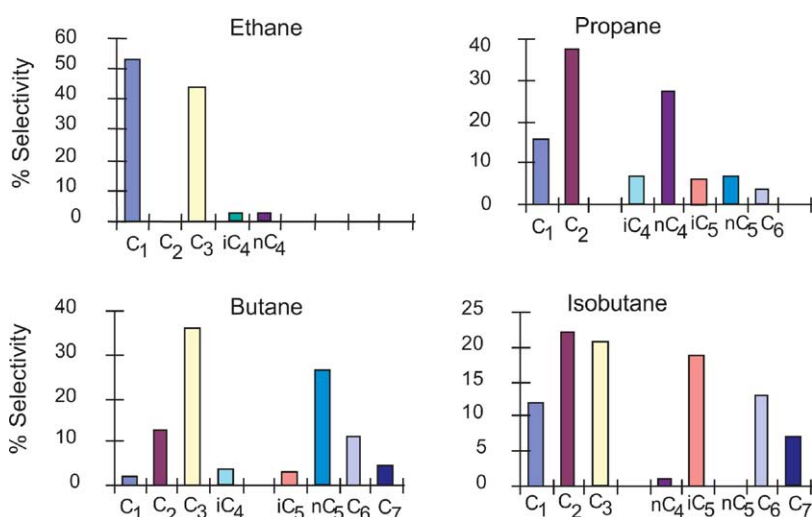
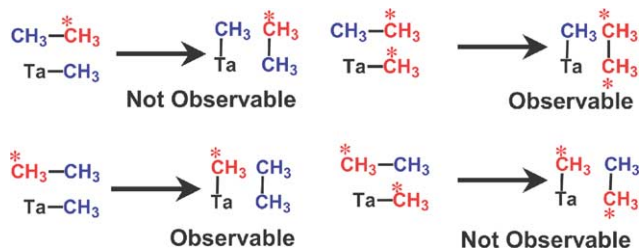


Fig. 4. Distribution of the various hydrocarbons produced during the metathesis reaction of the first linear alkenes (at 3% conversion), catalysed by [Ta]s–H complex at 150 °C (ethane, propane, butane, isobutane/Ta ratio, ≈ 800 , $P = 1$ atm).

productive metathesis which leads to higher and lower alkanes. This unproductive reaction has a rate which is ca. five times faster than the productive metathesis reaction.

In order to explain the productive and the degenerative metathesis, a specific mechanism of C–C bond cleavage and formation can be suggested such as a four centred σ -bond metathesis transition state, an oxidative addition/reductive elimination pathway or a carbenic mechanism (see Scheme 11).



Scheme 12.

2. Conclusion

The SOMC method developed in the laboratory, whose strategy is a molecular approach to heterogeneous catalysis, has allowed us to design, construct on a surface well-defined catalysts for desired reactions. Some were known and other were unknown. This approach allowed to increase the level of understanding of the mechanisms involved in various catalytic reactions.

As example, we have reported here the synthesis, characterisation and catalytic activities of three different tailored supported transition metal catalysts, as well as recent advances in the understanding of the catalyst formation and of the catalytic reaction mechanisms.

The single-site silica-supported carbenic rhenium(VII) species $[(\equiv\text{SiO})\text{Re}(\equiv\text{C}-t\text{-Bu})(=\text{CH}t\text{Bu})(\text{CH}_2-t\text{Bu})]$ has been tested in the propene metathesis reaction. Its catalytic activity has been found to be high at moderate temperatures (initial T.O.F. = 0.25 mol/mol Re/s). The reaction equilibrium is rapidly reached (within less than one hour) and

the catalyst activation process has been elucidated: it is a cross-metathesis reaction of the neopentylidene ligand with the propene.

The well-defined silica–alumina-supported zirconium monohydride (as the major species) and dihydride species [(≡SiO)₃ZrH and (≡SiO)₂ZrH₂] have been synthesised and characterized thanks to recent spectroscopic developments. These supported catalysts have been found to be very active in the polyethylene depolymerisation reaction. This depolymerisation occurs in presence of hydrogen via a mechanism involving a β-alkyl transfer elementary step. The third well-defined supported species reported above was the tantalum hydride catalyst [(≡SiO)₂TaH]. It has been tested in the alkane hydrogenolysis reaction. As the group 4 transition metal catalysts, it catalyses this reaction, but shows a particular activity: it catalytically hydrogenolyzes ethane into methane. This proves that the mechanism of the alkane hydrogenolysis reaction catalysed by tantalum hydride differs from the mechanism proposed for group 4 catalysts. The silica-supported tantalum hydride species is also active in the metathesis of alkane, which transforms an alkane into its higher and lower homologues. This catalytic reaction has been studied using a monolabelled ethane reagent. In particular, these experiments have shown the presence of a simultaneous unproductive reaction during the ethane metathesis process, which consists in a scrambling of ethane. The mechanism of the alkane metathesis (productive or not) can be related to that of the alkane hydrogenolysis catalysed by the supported tantalum hydride. It can be based on a Carbon–Carbon σ-bond metathesis and the formation of a four centred transition intermediate. Nevertheless an oxidative addition followed by a reductive elimination pathway or a carbenic mechanism cannot be excluded.

References

- [1] H.S. Taylor, Proc. Roy. Soc. (Lond.) 113A (1926) 77.
- [2] M.S. Friedrich, D.D. Suresh, R.K. Grasselli, Standard Oil Co., Ohio, USA, US19810222820; US4414134.
- [3] R.K. Grasselli, Top. Catal. 21 (2002) 79.
- [4] F. Lefebvre, A. de Mallmann, J.M. Basset, Eur. J. Inorg. Chem. (1999) 361.
- [5] A. Lesage, L. Emsley, M. Chabanas, C. Copéret, J.-M. Basset, Angew. Chem., Int. Ed. Engl. 41 (2002) 4535.
- [6] F. Rataboul, A. Baudouin, C. Thieuleux, L. Veyre, C. Copéret, J. Thivolle-Cazat, J.M. Basset, A. Lesage, L. Emsley, 2004, submitted.
- [7] J.M. Basset, B.C. Gates, J.P. Candy, A. Choplin, M. Leconte, F. Quignard, C. Santini, Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis, vol. 231, Kluwer Academic Publishers, 1988.
- [8] E.J. Howman, L. Turner, C.P.C. Bradshaw, British Petroleum Co., GB19650017222; US3424812.
- [9] B.P. McGrath, K.V. Williams, British Petroleum Co., GB19670006915; US3637890.
- [10] L. Turner, E.J. Howman, C.P.C. Bradshaw, British Petroleum Co., GB19640036722; US3641189.
- [11] B.M. Palmer, British Petroleum Co., GB19710043690; GB1377161.
- [12] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerisation Academic Press, San Diego (1997).
- [13] Y. Chauvin, D.J. Commereuc, J. Chem. Soc., Chem. Commun. 6 (1992) 462.
- [14] A.W. Aldag, C.J. Lin, A. Clark, Recl. Trad. Chim. Pays-Bas 96 (1977).
- [15] N. Tsuda, A. Fujimori, J. Catal. 69 (1981) 410.
- [16] P.S. Kirilin, B.C. Gates, J. Chem. Soc., Chem. Commun. 23–24 (1985) 277.
- [17] K. Edreva, R.M., A.A. Andreev, J. Catal. 97 (1986) 321.
- [18] L.G. Duquette, R.C. Cieslinski, C.H. Jung, P.E. Garrou, J. Catal. 90 (1984) 362.
- [19] R. Buffon, M. Leconte, A. Choplin, J.-M. Basset, J. Chem. Soc., Chem. Commun. 4 (1993) 361.
- [20] R. Buffon, M. Leconte, A. Choplin, J.-M. Basset, J. Chem. Soc., Dalton Trans. 12 (1994) 1723.
- [21] K. Weiss, G. Loessel, Angew. Chem., Int. Ed. Engl. 28 (1989) 62.
- [22] W.A. Herrmann, A.W. Stumpf, T. Priermeier, S. Bogdanovic, V. Dufaud, J.-M. Basset, Angew. Chem., Int. Ed. Engl. 35 (1996) 2803.
- [23] D.J. Commereuc, J. Chem. Soc., Chem. Commun. 7 (1995) 791.
- [24] R. Toreki, R.R. Schrock, J. Am. Chem. Soc. 112 (1990) 2448.
- [25] R. Toreki, R.R. Schrock, M.G. Vale, J. Am. Chem. Soc. 113 (1991) 3610.
- [26] R. Toreki, G.A. Vaughan, R.R. Schrock, W.M. Davis, J. Am. Chem. Soc. 115 (1993) 127.
- [27] M.H. Schofield, R.R. Schrock, L.Y. Park, Organometallics 10 (1991) 1844.
- [28] G.A. Vaughan, R. Toreki, R.R. Schrock, W.M. Davis, J. Am. Chem. Soc. 115 (1993) 2980.
- [29] A.M. Lapointe, R.R. Schrock, Organometallics 14 (1995) 1875.
- [30] B.T. Flatt, R.H. Grubbs, R.L. Blanski, J.C. Calabrese, J. Feldman, Organometallics 13 (1994) 2728.
- [31] D.S. Edwards, L.V. Biondi, J.W. Ziller, M.R. Churchill, R.R. Schrock, Organometallics 2 (1983) 1505.
- [32] D.S. Edwards, R.R. Schrock, J. Am. Chem. Soc. 104 (1982) 6806.
- [33] R. Toreki, R.R. Schrock, W.M. Davis, J. Am. Chem. Soc. 114 (1992) 3367.
- [34] M. Chabanas, A. Baudouin, C. Copéret, J.-M. Basset, J. Am. Chem. Soc. 123 (2001) 2062.
- [35] K. Ziegler, Angew. Chem. 67 (1955) 543.
- [36] K. Ziegler, H. Breil, E. Holzkamp, H. Martin, DE973626; DE973626; DE973626.
- [37] G. Natta, P. Pina, G. Mazzanti, Montedison Spa, US19550514098; US3715344.
- [38] G. Natta, J. Am. Chem. Soc. 77 (1955) 1708.
- [39] H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99.
- [40] P. Corradini, Comprehens. Polym. Sci. 4 (1988) 40.
- [41] P. Watson, C. Roe, J. Am. Chem. Soc. 104 (1982) 6471.
- [42] P.L. Watson, T. Herskovitz, ACS Symp. Ser. 212 (1983) 459.
- [43] P.L. Watson, G.W. Parshall, Acc. Res. 18 (1985) 51.
- [44] W. Kaminsky, Makromol. Chem. Rapid Commun. 5 (1984) 225.
- [45] E. Bunel, B. Burger, J. Bercaw, J. Am. Chem. Soc. 110 (1988) 976.
- [46] B. Burger, M. Tompson, D. Cotter, J. Bercaw, J. Am. Chem. Soc. 112 (1990) 1566.
- [47] L. Schrock, T.J. Marks, J. Am. Chem. Soc. 110 (1988) 7701.
- [48] J. Eshuis, Y. Tan, A. Meetsma, J. Teuben, J. Renkema, G.G. Evens, Organometallics 11 (1992) 362.
- [49] J. Eshuis, Y. Tan, J. Teuben, J. Renkema, J. Mol. Catal. 62 (1990) 277.
- [50] L. Resconi, F. Piemontesi, G. Franciscono, L. Abis, T. Fiorani, J. Am. Chem. Soc. 114 (1992) 1025.
- [51] K. McNeill, R.A. Andersen, R. Bergman, J. Am. Chem. Soc. 117 (1995) 3625.
- [52] A.D. Horton, Organometallics 15 (1996) 2675.
- [53] L. D'ornelas, S. Reyes, F. Quignard, A. Choplin, J.-M. Basset, Chem. Lett. 11 (1993) 1931.
- [54] V.A. Zakharov, Y.I. Yermakov, Catal. Rev. Sci. Eng. 19 (1979) 67.

- [55] V.A. Zakharov, Y.A. Ryndin, *Catal. Rev. Sci. Eng.* 56 (1989) 183.
- [56] V.A. Zakharov, V.K. Dudchenko, A.I. Minkov, O.N. Efrimov, L.G. Khomyakova, V.P. Babenko, Y.I. Yermakov, *Kinet. Catal.* 17 (1976) 643.
- [57] Y.I. Yermakov, V.A. Zakharov, *Co-ordination Polymerisation Academic Press, New York, 1975*, p. 91.
- [58] L.E. Firment, *J. Catal.* 82 (1983) 196.
- [59] P.J. Toscano, T.J. Marks, *J. Am. Chem. Soc.* 107 (1985) 653.
- [60] A.M. Pyle, K.J. Jens, *J. Mol. Catal.* 38 (1986) 337.
- [61] J.P. Candlin, H. Thomas, *Adv. Chem. Ser.* 132 (1976) 212.
- [62] F. Quignard, C. Lecuyer, A. Choplin, D. Olivier, J.M. Basset, *J. Mol. Catal.* 74 (1992) 353.
- [63] F. Quignard, A. Choplin, J.M. Basset, *J. Chem. Soc., Chem. Commun.* 22 (1991) 1589.
- [64] C. Lecuyer, F. Quignard, A. Choplin, D. Olivier, J.M. Basset, *Angew. Chem.* 103 (1991) 1692.
- [65] F. Quignard, C. Lecuyer, C. Bougault, F. Lefebvre, A. Choplin, D. Olivier, J.M. Basset, *Inorg. Chem.* 31 (1992) 928.
- [66] J. Corker, F. Lefebvre, C. Lecuyer, V. Dufaud, F. Quignard, A. Choplin, J. Evans, J.-M. Basset, *Science* 271 (5251) (1996) 966.
- [67] C. Thieuleux, J. M. Basset, Unpublished results.
- [68] V. Dufaud, J.-M. Basset, CPE-Lyon-FCR, FR19950008552; WO9703147.
- [69] V. Dufaud, J.M. Basset, *Angew. Chem., Int. Ed. Engl.* 37 (1998) 806.
- [70] C. Pouchert, *The Aldrich Library of Infrared Spectra*, 3rd ed., Aldrich Chem; Co; (Milwaukee, Wis.) 1981, 1873.
- [71] J.-M. Basset et al., 2003, results to be published.
- [72] M. Chabanas, V. Vidal, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, *Angew. Chem., Int. Ed. Engl.* 39 (2000) 1962.
- [73] V. Vidal, A. Theolier, J. Thivolle-Cazat, *J. Am. Chem. Soc.* 118 (1996) 4595.
- [74] V. Vidal, A. Theolier, J. Thivolle-Cazat, J.M. Basset, *Science* 276 (1997) 99.
- [75] O. Maury, L. Lefort, V. Vidal, J. Thivolle-Cazat, J.M. Basset, *Angew. Chem., Int. Ed. Engl.* 38 (1999) 13.
- [76] C. Rosier, G.P. Niccolai, J.-M. Basset, *J. Am. Chem. Soc.* 119 (1997) 12408.
- [77] C. Copéret, Unpublished results.
- [78] C. Rosier, Thesis-Université clude bernard lyon I, 1999.
- [79] M. Chabanas, A. Baudouin, C. Coperet, J.-M. Basset, W. Lukens, A. Lesage, S. Hediger, L. Emsley, *J. Am. Chem. Soc.* 125 (2003) 492.
- [80] M. Jézéquel, V. Dufaud, M. Ruiz-Garcia, F. Carrillo-Hermosilla, U. Neugebauer, G.P. Niccolai, F. Lefebvre, F. Bayard, J. Corker, S. Fiddy, J. Evans, J.P. Broyer, J. Malinge, J.M. Basset, *J. Am. Chem. Soc.* 123 (2001) 3520.
- [81] W.A. Herrmann, A.W. Stumpe, T. Priermeier, S. Bogdanovic, V. Dufaud, J.-M. Basset, *Angew. Chem.* 108 (1997) 2976.
- [82] D. Meunier, A. Piechaczyk, A. De Mallmann, J. Basset, *Angew. Chem., Int. Ed. Engl.* 38 (1999) 3540.
- [83] D. Meunier, A. Piechaczyk, A. De Mallmann, J.-M. Basset, Centre National de la Recherche Scientifique (C.N.R.S.), Fr., FR19980009328; WO0003802.
- [84] V. Capdevielle, Thesis-Université clude bernard lyon I, 1996.