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Surface organometallic chemistry: a molecular approach to surface catalysis

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Abstract. – The study of the reactions of organometallic complexes with the surfaces of inorganic oxides, zeolites and metals constitutes a new aspect of the coordination chemistry of organometallic compounds. We will demonstrate that the basic rules of organometallic chemistry are often valid when applied to surfaces, using as an example the chemistry of bis(allyl)rhodium grafted onto silica. In addition, concepts can be developed which are new both in molecular chemistry and in surface science (unusual oxidation state, coordination number and electron count). These new concepts allow the design of a new generation of catalysts with unexpected activity and/or selectivity. Two examples will be presented: the low temperature activation of the C–H and C–C bonds of alkanes by a zirconium hydride supported on silica, and the regioselective hydrogenation of citral to geraniol with a metallic surface of Rh covered with alkyltin fragments.

Introduction

Modern organometallic chemistry has had an enormous impact on homogeneous catalysis in the last two decades. Soluble metal complexes bind organic substrate molecules, which then undergo a large variety of transformations in the coordination sphere of the metal. The strategy for developing new homogeneous catalysts is based on knowledge of the series of elementary steps which constitute the catalytic mechanism. This governs the choice of the central metal atom, oxidation state, ancillary ligands and reaction conditions. Mechanistic studies carried out with well-defined organometallic complexes have identified key intermediates in many catalytic processes. However, the efficiency of homogeneous catalysts is often limited by instability caused by irreversible ligand dissociation and side reactions such as bimolecular reactions of unsaturated (highly reactive) intermediates. Separation and recovery of the catalyst, which sometimes contains an expensive metal such as Rh or Ir, is usually not efficient (note that biphasic systems are an important exception).

A recent development in homogeneous catalysis involves immobilizing the organometallic complex directly on a surface [1]. This approach is called Surface Organometallic Chemistry (SOMC). Site isolation and limited mobility of catalytically active molecules prohibit bimolecular decomposition reactions, and catalyst recovery becomes a simple matter of phase separation. An additional and considerable advantage is that unsaturated intermediates are readily formed and stabilized by the surface, which acts as a large and rigid ligand to trap them. Although the supported organometallic complexes superficially resemble heterogeneous catalysts, their relatively uniform structure, reactivity and distribution on the support material make them essentially homogeneous in nature. The similarities between molecular species and supported organometallic complexes are illustrated by the example of allylrhodium(III) complexes, discussed below.

The potential benefit to catalysis is now beginning to be realized. Catalyst active sites can be custom-designed with the ligand environment, oxidation state and other chemical properties desired for a given reaction. Any organometallic material can be used (transition metal, main group, rare earths) with a large variety of supports (inorganic oxides, zeolites, metal surfaces). The activity of these SOM catalysts is often very high, since the concentration of active sites is controlled by the level of organometallic loading. The SOM catalysts may possess enhanced selectivity usually associated with traditional homogeneous catalysts.

Two such systems have been thoroughly characterized in our laboratory [2]. Tetra(neopentyl)zirconium, when supported on silica, has been converted into a hydride which catalyses the low-temperature C–C bond hydrogenolysis of alkanes, activates C–H bonds (even of methane) and performs the stoichiometric functionalisation of alkanes to aldehydes, alcohols and longer alkanes. The reaction of tetra(*n*-butyl)tin with highly dispersed Rh metal supported on silica gives a new generation hydrogenation catalyst which selectively activates C=O bonds in the presence of C=C bonds. It has been demonstrated that the high chemoselectivity is directly related to the presence of organotin fragments grafted onto the surface of the metallic particles.

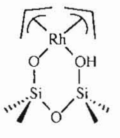
Rules of surface organometallic chemistry

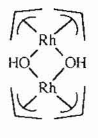
Grafting of $Rh(\eta^3\text{-}C_3H_5)_3$ onto silica

Removal of surface water from silica (Aerosil, 300 m^2/g) by treatment in vacuum (10^{-4} torr) at 200°C creates a surface covered with exposed hydroxyl groups. $Rh(\eta^3\text{-}C_3H_5)_3$ reacts via the gas phase with these hydroxyl groups, which results in the formation of a grafted organometallic complex and propene, eq. 1 [3].

$$\equiv Si - OH + Rh(\eta^3\text{-}C_3H_5)_3$$
$$\rightarrow \equiv Si - O - Rh(\eta^3\text{-}C_3H_5)_2 + C_3H_6 \qquad (1)$$

This reaction has been studied in detail by IR spectroscopy [4]. Sublimation of $Rh(\eta^3\text{-}C_3H_5)_3$ onto silica, which originally contains no ν(CH) bands, results in bands due to physisorbed (3063, 3004 cm^{-1}) and chemisorbed (3049, 2990 cm^{-1}) species. Evacuation of the sample at room temperature removes physisorbed $Rh(\eta^3\text{-}C_3H_5)_3$ from the surface. During the grafting reaction, the intensity of the ν(OH) band at 3750 cm^{-1}, attributed to free silanol groups, decreases. At the same time, a new type of hydroxyl group, characterized by a sharp band at 3636 cm^{-1}, appears. This band was attributed to a silanol which is strongly perturbed by the grafted organometallic fragment. The following structure, which provides a stable 18 electron configuration to the grafted species, has been proposed:





This structure is a monomeric form of the well-characterized molecular analogue, $[Rh(\eta^3\text{-}C_3H_5)_2OH]_2$ [5], and is consistent with molecular modelling [4] and theoretical calculations [6] on the surface complex.

Reaction of $(\equiv SiO)(\equiv SiOH)Rh(\eta^3\text{-}C_3H_5)_2$ with CO

The reaction of the molecular complex $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$ with CO induces the $\eta^3 \rightarrow \eta^1$ shift of the allyl ligands followed by reductive elimination of 1,5-hexadiene, eq. 2 [7, 8].

$[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2 + 4\ CO$

$\rightarrow [Rh(CO)_2Cl]_2 +$  (2)

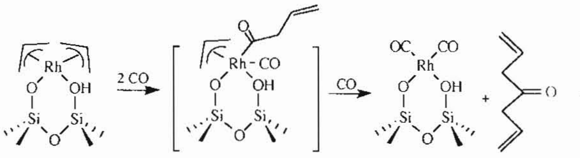
The surface interaction between $(\equiv SiO)(\equiv SiOH)Rh(\eta^3\text{-}C_3H_5)_2$ and CO on silica(400) is exactly analogous to the homogeneous reaction. Quantitative formation of 1,5-hexadiene was observed when $(\equiv SiO)(\equiv SiOH)Rh(\eta^3\text{-}C_3H_5)_2$ was exposed to 0.1 torr CO [7].

$(\equiv Si\text{-}O)(\equiv Si\text{-}OH)Rh(\eta^3\text{-}C_3H_5)_2 + 4\ CO$

$\rightarrow [(\equiv Si\text{-}O)Rh(CO)_2]_2 +$  (3)

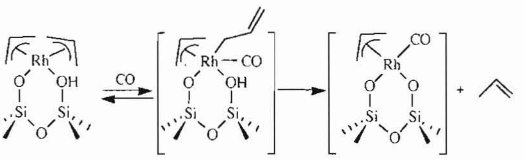
The same reaction was observed for bis(allyl)rhodium(III) grafted onto alumina and titania.

However, the reaction was found to depend strongly on the CO pressure and the proton content (extent of dehydroxylation) of the silica surface. At higher CO pressure ($\geq$10 torr), insertion of CO into a Rh–C bond precedes reductive elimination of 1,6-heptadien-4-one, eq. 4.

 (4)

When the proton content of the surface is higher, as in silica(200), the major gaseous product is proprene instead of 1,5-hexadiene. Insertion of CO into the remaining Rh–C bond gives an acyl complex (ν(CO) = 1692 cm^{-1}). Reductive elimination of the acyl ligand with a siloxy ligand leads to the formation of a silyl ester, strongly bound to the surface.

The monomeric dicarbonylrhodium(I) product ultimately dimerizes on silica, as shown by the evolution of the IR spectrum in the ν(CO) region. The two bands at 2012 and 2087 cm^{-1} which characterize the monomeric species are replaced (over 30 min at room temperature) by three bands at 2109, 2092 and 2035 cm^{-1}, characteristic of



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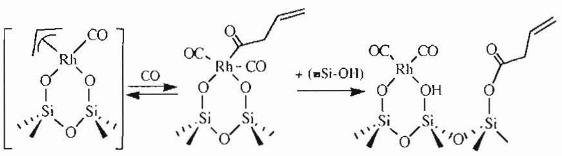
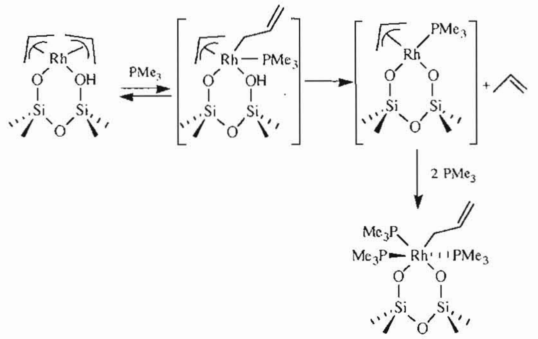


(6)

a nonplanar dicarbonylrhodium dimer. The dimer is strongly bound to the surface, and so is formulated as $[(\equiv \mathrm{SiO})\mathrm{Rh}(\mathrm{CO})_2]_2$.

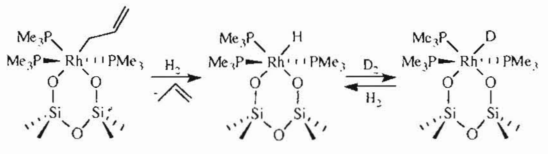
Reaction of ($\equiv$ SiO)($\equiv$SiOH)Rh(η^3-C_3H_5)$_2$ with PMe_3

Coordination of PMe_3 to the bis(allyl)rhodium(III) complex on silica(400) results in formation of 1,5-hexadiene, as in the reaction with CO. On silica(200), the exclusive gas phase product is propene. The second allyl ligand remains bound to Rh, as shown by the appearance of a band at 1 612 cm^{-1} in the IR, characteristic of the ν(C=C) stretch of a σ-allyl group [9]. This ligand can be removed from the surface as allyl alcohol by reaction with H_2O.



(7)

Reaction of the grafted allyltriphosphinorhodium species with H_2 causes the disappearance of the band at 1 612 cm^{-1} and the appearance of a new band at 1 938 cm^{-1}, attributed to $\nu(\mathrm{Rh}-\mathrm{H})$. The latter is displaced to 1 390 cm^{-1} in the presence of D_2, consistent with exchange to form Rh–D. The exchange is completely reversible when D_2 is replaced by H_2. These reactions are summarized in eq. 8.



(8)

A surface organometallic catalyst for the low temperature C–H and C–C bond activation of alkanes

Grafting of $Zr(CH_2C(CH_3)_3)_4$ onto silica

Sublimation of $Zr(CH_2C(CH_3)_3)_4$ onto silica partially dehydroxylated at 500°C results in the electrophilic cleavage of a Zr–C bond by surface protons, with formation of a grafted species described as $\equiv \mathrm{Si-O-Zr(CH_2C(CH_3)_3)_3}$, eq. 9.

$$\begin{aligned}&\equiv \mathrm{Si-OH} + \mathrm{Zr(CH_2C(CH_3)_3)_4}\\ &\rightarrow \equiv \mathrm{Si-O-Zr(CH_2C(CH_3)_3)_3} + \mathrm{C(CH_3)_4}\end{aligned} \tag{9}$$

Thus the intensity of the ν(OH) vibration at 3 750 cm^{-1} attributed to surface silanols disappears during the reaction, and ν(C–H), $\delta(\mathrm{CH_2})$ and $\delta(\mathrm{CH_3})$ bands appear which are stable to prolonged exposure to dynamic vacuum. The surface species has also been characterized by ^{13}C CP-MAS NMR (33.9 ppm, $\mathrm{CH_2C(\underline{C}H_3)_3}$) and elemental analysis, which shows that, on average, 3 alkyl groups remain bound to the surface after grafting [10].

Formation of a grafted Zr hydride

The reaction of $\equiv \mathrm{Si-O-Zr(CH_2C(CH_3)_3)_3}$ with dry H_2 (450 torr, 150°C) leads to hydrogenolysis of the Zr–C bonds with formation of mixture of Zr hydrides, eq. 10 [11].

$$\begin{aligned}&(\equiv \mathrm{SiO})\mathrm{ZrR_3} + \mathrm{H_2} \rightarrow (\equiv \mathrm{SiO})\mathrm{ZrR_2(H)} + \mathrm{RH}\\ &\rightarrow \rightarrow (\equiv \mathrm{SiO})_n\mathrm{Zr(H)}_x + 3\mathrm{RH}\end{aligned} \tag{10}$$

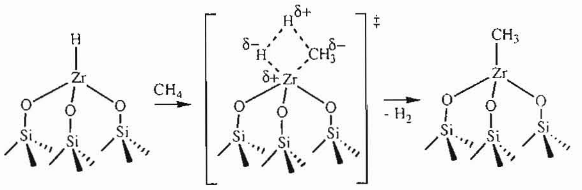
The grafted Zr hydride complexes are highly oxophilic, reacting with siloxane bridges to give silicon hydrides, eq. 11. The ν(Si-H) vibrations appear at 2 253 and 2 191 cm^{-1}, and do not shift in the presence of D_2. The ν(Zr-H) bands are observed in the region of 1 635 cm^{-1}. They disappear in the presence of D_2 (90 torr, 25°C), however, the ν(M–D) bands are obscured by the strong absorption of silica below 1 200 cm^{-1} [12].

$$\begin{aligned}&(\equiv \mathrm{SiO})_n\mathrm{Zr(H)}_x + 2 \equiv \mathrm{Si-O-Si} \equiv\\ &\rightarrow (\equiv \mathrm{SiO})_3\mathrm{ZrH} + 2 \equiv \mathrm{Si-H}\end{aligned} \tag{11}$$

The reaction of the grafted metal hydride with CH_3I (400 torr, 25°C) liberates CH_4.

C–H bond activation by a supported Zr hydride

The grafted hydride ($(\equiv SiO)_3ZrH$ is highly electrophilic, having formally only 8 electrons (neglecting the pπ-dπ interaction between surface oxygens and Zr), as well as being sterically unhindered. These properties are undoubtedly responsible for the ability of the grafted hydride to react with unactivated C–H bonds in CH_4 (150°C) and cyclooctane (25°C). The reaction has been proposed to proceed by a 4-centre σ-bond metathesis mechanism, eq. 12 [13].



(12)

This mechanism has been demonstrated in homogeneous chemistry for alkane activation by d^0 transition metal complexes of Sc and Y [14, 15].

The selectivity of stoichiometric activation of propane by the Zr hydride species has been studied [16]. When the Zr hydride was converted to propylzirconium under propane, then oxidized with dry O_2 , the resulting propoxide ligands were extracted with HCl/ether. The ratio n-propanol/2-propanol was determined quantitatively by GC to be >37. Therefore, activation occurs predominantly at the primary carbon. In a separate experiment, the propylzirconium species was hydrolysed with D_2O and the resulting propane-d_1 was analysed by mass spectroscopy. The isotopic pattern for the primary fragment peaks indicated that the ratio $CH_3CH_2CH_2D/CH_3CHDCH_3$ was approx. 49.

Catalytic exchange of propane C–H bonds with D_2 revealed that propane activation is extremely rapid at room temperature (70 turnovers/min) [16]. The kinetics of the exchange reaction were biphasic, corresponding to primary and secondary C–H exchange with a rate constant ratio $k_{1°}/k_{2°} = 6.4$. Taking into account the number of primary and secondary C–H bonds, this corresponds to a total kinetic selectivity for primary C–H activation of 19. At room temperature, hydrogenolysis of propane is not significant (see below).

Stoichiometric alkane functionalisation

To alcohols

The grafted metal alkyls react with dry O_2 to give alkoxy ligands, which can be hydrolysed with HCl to the corresponding alcohol, eq. 13-14 [10].

$$\equiv Si-O-Zr(CH_2C(CH_3)_3)_3 + 3/2O_2 \rightarrow \equiv Si-O-Zr(OCH_2C(CH_3)_3)_3 \quad (13)$$

$$\equiv Si-O-Zr(OCH_2C(CH_3)_3)_3 + 3HCl \rightarrow \equiv Si-O-ZrCl_3 + 3HOCH_2C(CH_3)_3)_3 \quad (14)$$

The mechanism of oxygen insertion into the Zr–C bond remains unclear.

To aldehydes

The grafted metal alkyls insert CO into the M–C bond to form acyl species. At room temperature, the first step is the coordination of CO to Zr, accompanied by a color change from white to yellow and the appearance of two new bands at 2027 and 1938 cm^{-1} in the IR spectrum [16]. No CO insertion occurs at this temperature. At 100°C, insertion of CO into the alkylzirconium bond results in the appearance of a $\nu(C=O)$ band in the IR spectrum at 1652 cm^{-1} (cyclooctyl) and 1643 cm^{-1} (n-propyl). Treatment with HCl gives the product aldehyde, eq. 15-17.

$$(\equiv SiO)_3ZrCH_2CH_2CH_3 + CO \rightarrow (\equiv SiO)_3Zr(CH_2CH_2CH_3)(CO)_2 \quad (15)$$

$$(\equiv SiO)_3Zr(CH_2CH_2CH_3)(CO)_2 \rightarrow (\equiv SiO)_3Zr(C(O)CH_2CH_2CH_3) + CO \quad (16)$$

$$(\equiv SiO)_3Zr(C(O)CH_2CH_2CH_3) + HCl \rightarrow (\equiv SiO)_3ZrCl + CH_3CH_2CH_2CHO \quad (17)$$

To longer-chain alkanes

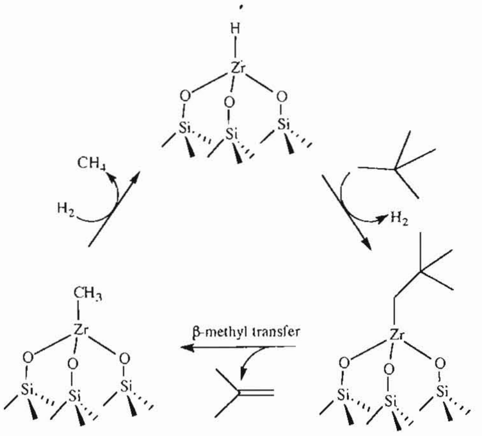
The grafted metal alkyls will insert ethylene into the M–C bond, effectively extending the alkyl chain, eq. 18 [13].

$$\equiv Si-O-Zr(CH_2C(CH_3)_3)_3 + n\ CH_2CH_2 \rightarrow \equiv Si-O-Zr(CH_2)_nCH_2C(CH_3)_3)_3 \quad (18)$$

This is a route to polymers. Indeed, the polymerisation activity of organozirconium catalysts is enhanced by immobilization on an alumina surface [17, 18].

Catalytic low temperature C–C bond hydrogenolysis of alkanes: a unique example of catalysis by σ-bond metathesis and β-methyl transfer

In the presence of H_2, the grafted Zr hydride cracks hydrocarbons into smaller fragments. Thus, 40 torr neopentane was converted into isobutane and methane by the catalyst ($\equiv SiO)_3ZrH$ in the presence of 230 torr H_2 at 50°C [19]. The mechanism is proposed to involve the formation of a $Zr - CH_2C(CH_3)_3$ species by σ-bond metathesis, as in eq. 12, followed by β-methyl transfer to give isobutene and a $Zr-CH_3$ species. The latter is converted to methane by H_2, with regeneration of the Zr–H catalyst, Scheme I.

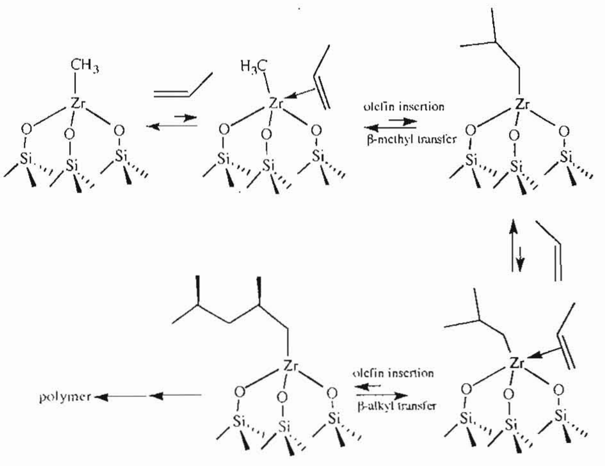


Scheme I. – Catalytic hydrogenolysis of neopentane by silica-supported zirconium hydride.

The primary product isobutene was not identified because the catalyst converts it rapidly to isobutane under H_2. Ultimately, isobutane undergoes further hydrogenolysis to propane and methane. Likewise, propane becomes ethane and methane. Ethane is not cleaved, presumably because the ethylzirconium intermediate lacks a β-methyl group.

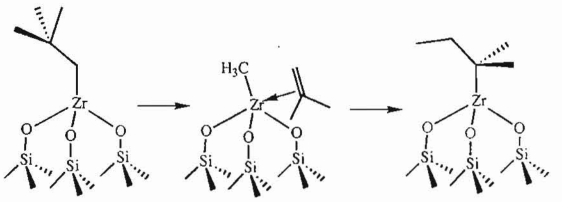
Relationship between elementary steps of C–C bond cleavage in alkane hydrogenolysis and C–C bond formation in olefin polymerisation

β-alkyl transfer corresponds to the microscopic reverse of olefin insertion into a metal-alkyl bond, presumed to be a crucial step in polymerization of olefins catalysed by early transition metals, which are often d^0 systems. For example, in the hydrogenolysis of isobutane, propene and a methylzirconium species are the proposed primary products, Scheme II. The reverse reaction is precisely what occurs in the polymerisation of propene catalysed by supported zirconium complexes [20, 21].



Scheme II. – Analogy between alkane hydrogenolysis and olefin polymerisation.

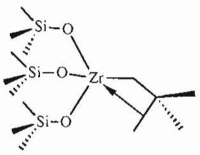
In support of this hypothesis, a small amount of 2-methylbutane was observed during the hydrogenolysis of neopentane [19], arising from the anti-Markovnikov insertion of isobutene into the $Zr-CH_3$ bond, eq. 19.



(19)

Recently, β-methyl transfer has been identified as a chain termination step in propene polymerization catalyzed by homogeneous group IV metal complexes [22, 23]. In this respect, the mechanisms of alkane hydrogenolysis and olefin polymerisation are consistent with each other. Key parameters which control the direction of the reaction are temperature and H_2 pressure. Low temperatures favor C–C bond formation whereas high H_2 pressure favors C–C bond cleavage. It is well-known that H_2 is a molecular-weight regulator in catalysed olefin polymerisation [24].

The reason why β-methyl transfer rather than β-hydrogen elimination occurs with supported and homogeneous Zr catalysts is unclear. Steric effects in the ground state have been proposed to be important [22]. The importance of electronic effects has also been suggested [25]. Thus the highly electrophilic nature of the Zr center is thought to favor β-methyl transfer. Although direct evidence is lacking, an agostic C−C interaction with the early transition metal center can be envisaged.



A surface organometallic catalyst for the selective hydrogenation of conjugated C=O bonds

Reaction of Sn(n-Bu)$_4$ with metallic Rh dispersed on silica

From an applied perspective, metals are probably the most important surfaces in SOMC. The controlled reaction of organometallic compounds with the surfaces of metals can lead to bimetallic particles whose properties are significantly different from those of the monometallic materials [26-28]. Our investigations of transition metal/main group metal combinations have proved particularly fruitful.

The possibility of coordinating an organometallic fragment to the surface of a metal particle is highly relevant to the field of heterogeneous catalysis. Metals, whether supported or in the bulk, present at their surfaces a variety of crystallographic planes, edges and corners. The relative ratios of these sites depends on the particle size. Even particles which are fairly uniform in size are heterogeneous in terms of surface composition. Selective grafting of an organometallic fragment onto a specific surface site (e.g. low coordination sites) leads to selective poisoning of that site. The nature of the ligands on the surface organometallic fragment also influences the properties of the modified metal particle.

Small particles of Rh (1.4 nm mean diameter), dispersed on silica (Aerosil, 300 m^2/g), were reduced under flowing H$_2$ at 673 K to ensure complete reduction of the surface to the metallic state. Rh surface atoms are covered with dissociated hydrogen under these conditions. The reaction with Sn(n-Bu)$_4$ from the physisorbed state evolves BuH in a stepwise hydrogenolysis reaction, leading eventually to a Sn/Rh alloy [29]. Depending on the experimental conditions, the reaction can be intercepted at an intermediate stage. At 100°C, a species with the empirical formula (SnBu$_2$)Rh/SiO$_2$ is present on the surface.

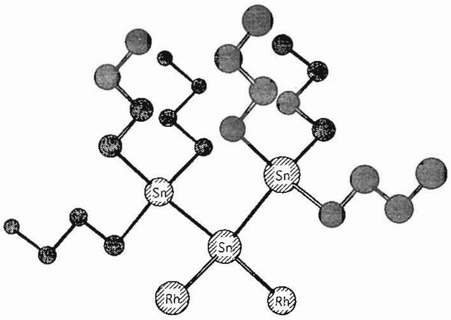
A possible side reaction, the protolytic cleavage of a Sn−C bond by surface silanols, has been studied independently [30]. Chemisorption begins when the temperature is raised to 100°C, and the surface complex is stable up to 200°C.

$$\begin{aligned}&\equiv \mathrm{Si}-\mathrm{OH}+\mathrm{Sn}(n-\mathrm{C_4H_9})_4\\&\rightarrow \equiv \mathrm{Si}-\mathrm{O}-\mathrm{Sn}(n-\mathrm{C_4H_9})_3+n-\mathrm{C_4H_{10}}\end{aligned} \qquad (20)$$

This reaction can be minimized by avoiding an excess of SnBu$_4$ (relative to exposed Rh atoms) and by removing unreacted SnBu$_4$ with a cold trap. Thus by IR, the band attributed to free silanol, ν(OH) = 3 748 cm^{-1}, is fully restored after heating the sample to 100°C. The ^{13}C CP/MAS NMR spectra shows no signal attribuable to $\equiv \mathrm{Si-O-Sn}(n-\mathrm{C_4H_9})_3$ if $\mathrm{Sn/Rh_s} < 1.5$.

The organometallic fragment described as (SnBu$_2$) Rh/SiO$_2$ has been characterized by several techniques [31]. Electron microscopy revealed an increase in average particle diameter to 2.2 nm, consistent with the formation of 1-2 monolayers of alkyltin on the Rh surface. However, adsorption measurements showed that 1/3 of the surface Rh atoms are still accessible for binding of CO. XPS and Mössbauer spectroscopy identified the oxidation state of the organometallic fragment, corresponding to 75% Sn(II or IV) and 25% Sn(0). By EXAFS, Sn has an average of 2 light neighbours (C or O) at 0.217 nm and 2 heavy neighbours (Sn or Rh) at 0.268 nm.

Molecular modelling of the grafted surface organometallic fragment demonstrated that it is impossible to fit enough SnBu$_2$ entities around the Rh particles to satisfy the ratio $\mathrm{Sn/Rh_s} = 1$ without unreasonable steric interference. An alternate model was proposed, Scheme III, which is consistent with the spectroscopic data and results in a sterically accessible structure: (Bu$_3$Sn)$_2$SnRh/SiO$_2$.

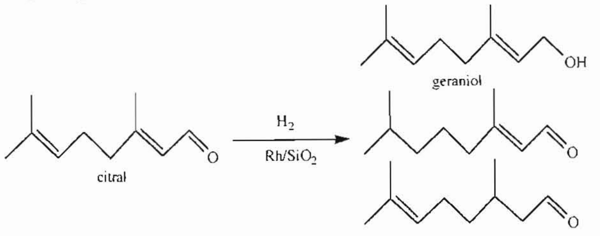


Scheme III. – Proposed structure for SnBu$_4$-modified Rh.

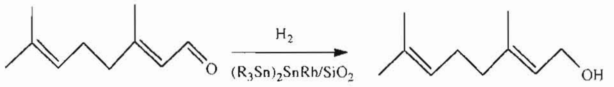
Organometallic modification of Rh has proved promising for the molecular control of chemo-, regio- and enantioselectivity in Rh-catalysed reactions. One example is discussed below.

Chemoselective hydrogenation of citral

Hydrogenation of citral, an α, β-unsaturated aldehyde, on a conventional supported Rh catalyst leads to a variety of products, because Rh is fairly unselective for the site of hydrogenation.



In the presence of the grafted butyltin fragment, the yield of unsaturated alcohol, geraniol, is 96% at 100% conversion [32]. This increase in selectivity is attributed to (1) an electronic effect, in which coordination and activation of the aldehydic function of citral is enhanced by the presence of butyltin moieties, and (2) a steric effect, in which limited access to the metal surface favors hydrogenation at the less hindered double bond of citral, i.e., the aldehyde function.



Conclusion

In the long term, the systematic study of the reactivity of organometallic compounds with surfaces may have an impact on surface catalysis rivalling that of organometallic chemistry on homogeneous catalysis. Compared to the direct study of heterogeneous systems, the SOMC approach offers several advantages, including the preparation of well-defined active sites, the possibility of observing elementary reaction steps and the development of a fundamental basis for the synthesis of tailor-made catalysts.

The impact of SOMC on the methodology of heterogeneous catalysis is still limited by the difficulty of applying the technology of organometallic chemistry (e.g., preparation of the catalyst in a controlled atmosphere) to large-scale operations. However, this is merely a matter of approach, and should not be an insurmontable obstacle. There are already examples of catalysts prepared by the SOMC technique which are being used in industry. For example, the dehydrogenation of 2-butanol to methyl ethyl ketone is now performed in Japan with a Raney nickel catalyst covered with alkyltin fragments. In five years of use, no sign of aging or loss of selectivity has become apparent.

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