Supramolecular approach to metal–support interactions: reactivity of silica-supported bis(allyl)rhodium(III) and the influence of surface hydroxyl groups

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Abstract

The structure and stoichiometric reactivity of a surface organometallic fragment, bis(allyl)rhodium(III) on silica, has been studied in order to identify concepts of molecular chemistry which can be applied to mechanisms of heterogeneous catalysis. The reactions with electrophiles and Lewis bases are examined. The similarity of the 'supramolecular' surface chemistry to molecular chemistry was limited since the surface hydroxyl groups of silica were found to participate. A hydroxyl group in the coordination sphere of rhodium is a source of electrophilic protons, and neighbouring hydroxyl groups facilitate surface mobility of grafted organometallic fragments.

Keywords: Hydroxyl groups; Metal–support interactions; Rhodium; Silica; Supported catalysts

1. Introduction

Metal catalysts are often prepared by dispersing small metal particles on a high surface area oxide support. However, the nature of the metal–support interaction and its influence on heterogeneous reactivity is not well-understood. For example, product selectivity in the Fischer–Tropsch conversion of syn gas ($CO + H_2$) towards either hydrocarbons or oxygenates (alcohols, aldehydes and carboxylic acids) depends strongly on the transition metal catalyst and the nature of the oxide support on which it is dispersed [1]. Thus the catalyst Rh/TiO_2 or ZrO_2 produces more oxygenates than Rh/SiO_2 or Al_2O_3, which favour hydrocarbons [2]. Hydrocarbons were suggested to be formed on fully reduced metal particles, while alcohols may be formed on rhodium ions [3,4]. It is known that CO exerts a strong disruptive effect on rhodium crystallites, leading to the formation of isolated and oxidized $Rh^I(CO)_2$ species [5,6]. It is also known that highly dispersed zerovalent rhodium atoms derived from molecular clusters can be oxidized by protons on the surface of hydroxylated oxides, Eq. 1 [7,8].

$$Rh_6(CO)_{16} + 6[Al]-OH \rightarrow 6[Al]-O-Rh(CO)_2 + 3H_2 + 4CO \qquad (1)$$
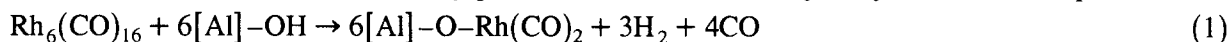
It has been suggested that 'chemical anchoring' of metal particles to oxide surfaces via oxidized

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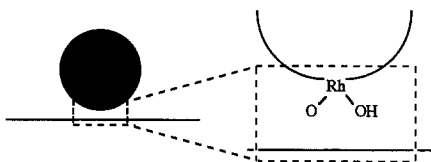
Scheme 1. Metal–support interaction in an oxide-supported rhodium particle.

surface metal atoms, Scheme 1, stabilizes small metal particles supported on oxide surfaces [9]. It is also expected that some crucial elementary steps of catalysis might occur at the interface between the small metal particles and the support. The reactivity may not be determined uniquely by the collective properties of the metal atoms which form the metal particle, but also by the 'molecular-like' species at the metal–support interface.

Molecular analogues of supported metal particles have been prepared and structurally characterized [10,11]. They model at a molecular level the nature of the bonding between a transition metal and a surface:
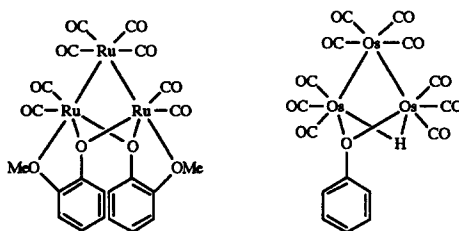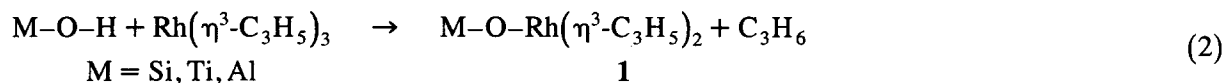

The surface oxygen atoms of an oxide may behave towards a metal particle as the oxygen atoms of the aryloxy ligands in these model compounds, oxidising the metal atoms at the interface with the oxide.

In this contribution, we describe a supramolecular approach to the investigation of heterogeneous mechanisms, using the reactivity of bis(allyl)rhodium species grafted on a silica surface to model elementary steps of C–C and C–O bond formation. The advantage of this approach, relative to direct study of heterogeneous systems, is that the starting point is a relatively well-defined surface organometallic fragment.

2. Grafting of Rh(allyl)₃ on oxide surfaces

With silica, titania, and partially dehydroxylated (> 200°C) alumina, $Rh(\eta^3\text{-}C_3H_5)_3$ reacts rapidly at room temperature to give a bis(allyl)rhodium complex and one equivalent of propene according to Eq. 2 [12]:

$$M\text{-}O\text{-}H + Rh\left(\eta^3\text{-}C_3H_5\right)_3 \quad \rightarrow \quad M\text{-}O\text{-}Rh\left(\eta^3\text{-}C_3H_5\right)_2 + C_3H_6$$
$$M = Si, Ti, Al \qquad\qquad\qquad\qquad \mathbf{1} \tag{2}$$

The surface organometallic fragment **1** is a well-defined surface complex. Three microenvironments

were proposed for **1** on the silica surface, based on the known structure of a molecular analogue, **1́**, [13] IR evidence [12] and theoretical calculations [14].
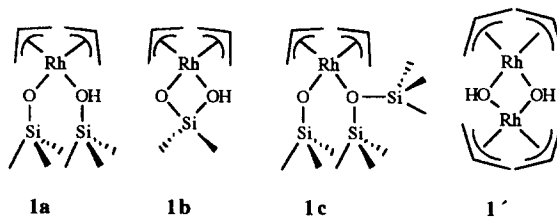

The presence of a hydroxyl group in the coordination sphere of rhodium in at least some of the surface organometallic complexes was observed experimentally: a sharp IR band at 3636 cm^{-1} was assigned to the γ(OH) vibration of a rigid silanol group perturbed by coordination to Rh (species **1b**), whereas a broad IR band in the same region was ascribed to a less rigid coordinated silanol such as in **1a** [12]. Both bands shift by the expected amount when the silica surface is labelled with oxygen-18.

The presence or absence of the hydroxyl group in the coordination sphere of Rh is expected to have a profound influence on the reactivity of the surface organometallic fragments. Thus the knowledge of the structure of **1** creates an opportunity to observe stoichiometric surface reactions and to judge the importance of the presence of surface oxygen and hydroxyl groups.
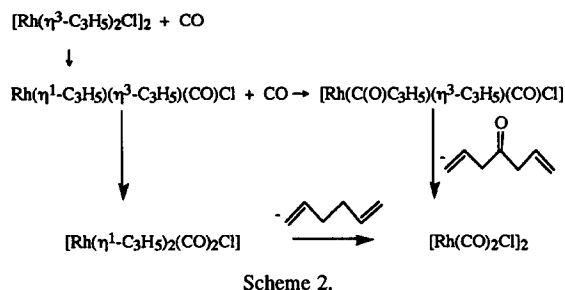
3. Reaction with Lewis bases

When **1** is prepared on a silica surface dehydroxylated at 550°C, few hydroxyl groups remain after grafting. In this case, the predominant species is believed to be **1c**, whose reactivity towards Lewis bases resembles that of molecular analogues. For example, when **1$_{550}$** is exposed to PMe$_3$ or CO, 1,5-hexadiene is formed by reductive elimination of two allyl ligands from the coordination sphere of Rh, Eq. 3.
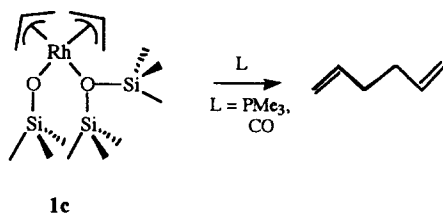

$$(3)$$

Formation of 1,5-hexadiene has precedent in the reactions of the molecular analogue [ICo(η^3-C$_3$H$_5$)$_2$]$_2$ [15]. The organometallic product, in the case of L = PMe$_3$, is $\equiv$SiORh(PMe$_3$)$_3$, which was characterised by ^{31}P MAS NMR and elemental analysis, and was prepared independently the reaction of CH$_3$Rh(PMe$_3$)$_3$ with silica [16]. We can consider $\equiv$SiORh(PMe$_3$)$_3$ to be a 'supramolecular' analogue of Wilkinson's catalyst. In the case of L=CO, the organometallic product of Eq. 3 is [$\equiv$SiORh(CO)$_2$]$_2$ [17,18]. The fact that the product is a dimer while the starting complex **1c** is monomeric has important implications for the mobility of surface organometallic fragments (vide infra).

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

$\downarrow$

$Rh(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)(CO)Cl$ + CO $\rightarrow$ $[Rh(C(O)C_3H_5)(\eta^3\text{-}C_3H_5)(CO)Cl]$

$[Rh(\eta^1\text{-}C_3H_5)_2(CO)_2Cl]$ $\xrightarrow{\hspace{2cm}}$ $[Rh(CO)_2Cl]_2$

Scheme 2.

When L=CO, insertion of CO into the metal–allyl bond is also possible. In addition to 1,5-hexadiene, we observed traces of 1,6-heptadien-4-one in the gas phase. We suggest that this product is formed by reductive elimination from an (allyl)(acyl)rhodium intermediate, Eq. 4.

1c
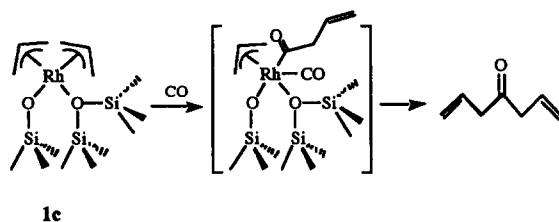
$$(4)$$

Reductive elimination of 1,6-heptadien-4-one was observed in the reaction of molecular bis(allyl)nickel complexes with CO [19]. Homogeneous (alkyl)(acyl)Rh^{III} complexes such as $[RhR(C(O)R)(CO)(Cl)L_2]$ are unstable and rapidly eliminate ketone [20].

In summary, when few surface hydroxyl groups are present, the reactivity of 1 towards Lewis bases is very similar to the reactivity of molecular analogues. This point is additionally illustrated by comparison to the chemistry of the molecular compound, $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$. Addition of CO induces the $\eta^3 \rightarrow \eta^1$ shift of the allyl ligand, followed by reductive elimination of 1,5-hexadiene or CO insertion and reductive elimination of 1,6-heptadien-4-one, Scheme 2 [18].

By increasing the surface hydroxyl content (using SiO$_{2(200)}$ or a low Rh coverage on SiO$_{2(400)}$), we increase the proportion of species 1a and 1b with respect to 1c. Reaction with Lewis bases no longer produces 1,5-hexadiene. Instead, propene is the major product [16,18]. We propose that it is formed by the electrophilic attack of a surface proton on a σ-allyl ligand, Eq. 5.

1a   2
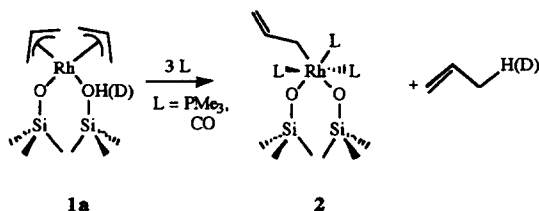
$$(5)$$

The proposed mechanism is supported by an experiment in which the surface hydroxyl groups were partially deuterated by exchange with D$_2$O. The amount of monodeuterated propene liberated by the reaction of 1 with L was equal to the amount of deuterium incorporated into surface silanol groups.

The coordination of L forces a π-allyl ligand of **1** to adopt a σ-allyl configuration, which in general renders the metal–carbon bond susceptible to electrophilic cleavage [21].

The elimination of propene and coordination of L to Rh is followed by the $\eta^3 \rightarrow \eta^1$ shift of the second allyl ligand, Eq. 5. In the case of L = PMe₃, we observed IR bands at 3072 and 1612 cm⁻¹ which are characteristic of a σ-allyl group coordinated to a metal atom [22]. These bands are assigned to the $\nu(=C–H)$ and $\nu(C=C)$ modes, respectively, of **2**. The $\eta^3 \rightarrow \eta^1$ shift was inferred in the reaction of **1** with CO, Eq. 5, however, rapid insertion of CO into the Rh–C bond to give an acyl complex ($\nu(C=O)$ 1692 cm⁻¹) prevented the characterisation of a σ-allyl complex comparable to **2** [18].

2   3
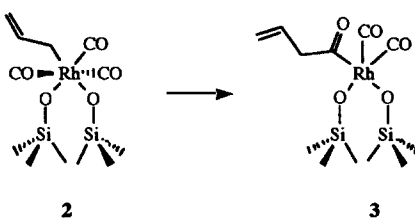
(6)

4. C–O bond formation

The acylrhodium complex **3** undergoes reductive elimination of the acyl ligand with a siloxy ligand coordinated to Rh to give the silyl ester of 3-butenoate, Eq. 7.


4
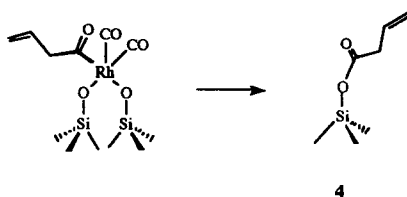
(7)

In molecular chemistry, this type of inner-sphere reductive coupling is a viable final step in ester synthesis [23]. On the silica surface, the $\nu(CO)$ mode of **4** was observed at 1713 cm⁻¹ (on SiO₂(₂₀₀)) or 1747 (on SiO₂(₄₀₀)). The shift to higher frequency on the more dehydroxylated silica is consistent with less H-bonding of the acyl carbonyl to adjacent silanols [24]. The silyl ester was extracted from the surface as the methyl ester with both (CH₃)₂SO₄ and CH₃I, and identified by GC [18].

The σ-allyl ligand of **2** (L = PMe₃) also undergoes insertion of CO into the metal-carbon bond followed by reductive elimination with a siloxy ligand to give the silyl ester, **5**, with $\nu(CO)$ and $\nu(C=C)$ modes at 1765 and 1643 cm⁻¹, respectively.
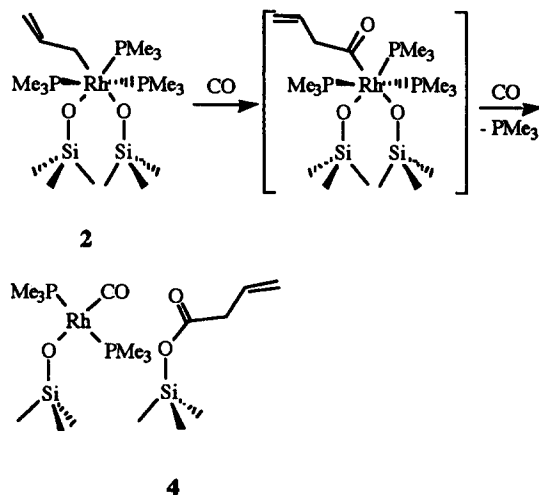
$$(8)$$

Although the reaction of **1** with PMe_3 on $silica_{200}$ gives almost exclusively propene as the gas phase product, the σ-allyl complex **2** is not the major surface product. The ^{31}P NMR spectrum shows the presence of $\equiv$SiORh$(PMe_3)_3$ [16]. We propose that a portion of the initially-formed product, **2**, is transformed by a subsequent reaction into $\equiv$SiORh$(PMe_3)_3$ by reductive elimination of the σ-allyl ligand with a siloxy ligand to give surface ether **5**, Eq. 9.
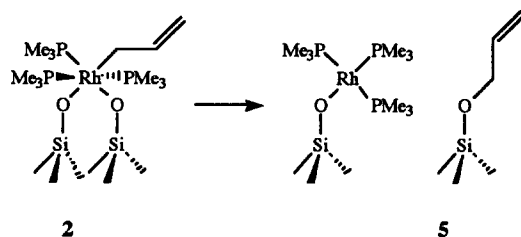
$$(9)$$

Indeed, allyl alcohol was extracted from the surface and identified by GC [16,25].

The surface ether **5** is readily transformed into allyl alcohol in the presence of surface hydroxyl groups. The alcohol is then decarbonylated on the surface, Eq. 10.
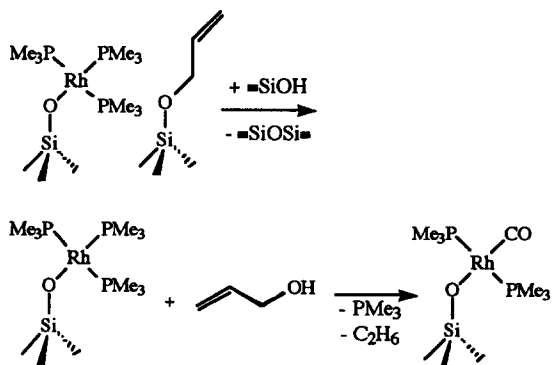

$$(10)$$

The mechanism of C–O bond formation is depicted as a reductive elimination of a σ-allyl ligand with a siloxy ligand. Decarbonylation of allyl alcohol by the tris(phosphine)rhodium(I) complex then leads

to evolution of ethane and formation of the carbonylrhodium complex, which was characterised by IR, ^{31}P MAS NMR and elemental analysis [25]. It was also prepared independently by the reaction of $\equiv$SiORh(PMe$_3$)$_3$ with CO. A similar decarbonylation reaction was reported between allylic alcohols and ClRh(PPh$_3$)$_3$, yielding ClRh(PPh$_3$)$_2$(CO) [26].

The origin of the carbonyl oxygen was suspected to be oxygen atoms of the silica surface. Therefore we partially exchanged the surface oxygen atoms with ^{18}O, by repeated treatment of the silica with H$_2^{18}$O prior to dehydroxylation [27]. Subsequent reaction of the grafted bis(allyl)rhodium fragment with PMe$_3$ gave two carbonyl peaks at 1957 and 1915 cm^{-1}, corresponding to the isotopically different products of Eq. 11:
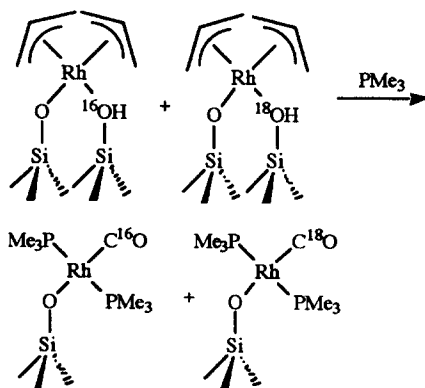
$$(11)$$

The appearance of the 1960 cm^{-1} band is faster on more hydroxylated silica, implying that surface hydroxyl groups are involved in the mechanism of decarbonylation.

5. Influence of surface hydroxyl groups on the mobility of surface organometallic fragments

The reactions described above demonstrate that surface hydroxyl groups influence the chemistry of 1 by direct participation in the coordination sphere of rhodium. We have also observed that the extent of surface hydroxylation influences the fate of organometallic products.

The initial Rh product from the reaction of 1 with CO is monomeric ($\equiv$SiO)($\equiv$SiOX)Rh(CO)$_2$, X = H or Si$\equiv$, as shown by the presence of two ν(CO) bands in the IR spectra, and six ν(CO) bands in the presence of a ^{12}CO/^{13}CO mixture [18]. Over the course of several minutes, the monomer dimerizes, Eq. 12.
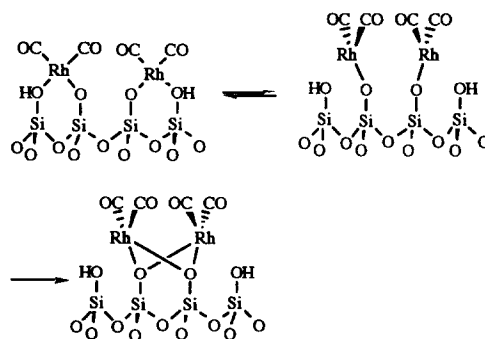
$$(12)$$

During this reaction, the $\nu(CO)$ bands shift and a third $\nu(CO)$ band appears at higher frequency, typical of non-planar dicarbonylrhodium dimers. A probable structure for the dimer contains bridging siloxy ligands [17], as in the molecular complex $[Rh(CO)_2(\mu\text{-OSiMe}_3)]_2$. Dimerization requires migration of $Rh^I(CO)_2$ fragments, a process which has been demonstrated on oxide surfaces during the formation of zerovalent Rh clusters [28,29]. The presence of surface hydroxyl groups is thought to be crucial to the mobility of the dicarbonylrhodium fragments [6]. The mechanism of mobility probably may be hopping of surface protons and reversible coordination of surface silanols to rhodium, Eq. 13.
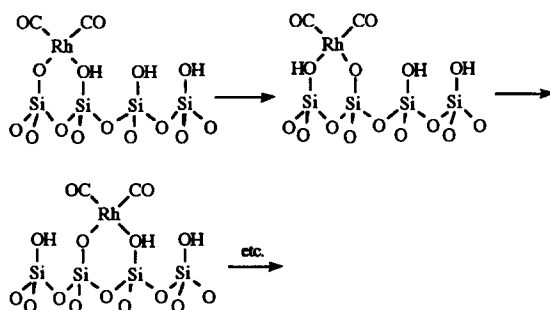
$$(13)$$

The facile exchange of alkoxy ligands −OR on rhodium in the presence of R′OH has been reported [30].

Finally, in the presence of H_2, the surface dimers $[Rh(CO)_2(\mu\text{-OSi}\equiv)]_2$ are reduced to zerovalent rhodium atoms which migrate to form CO-covered metal particles [16]. The principle of surface mobility has been used in the surface-mediated synthesis of rhodium clusters [31,32].

6. Conclusion

We have shown that coordinated OH groups participate in the reactivity of monomeric surface organometallic fragments, and non-coordinated OH groups facilitate the migration of surface species. The latter phenomenon makes bimolecular surface reactions possible, and may lead to the formation of higher nuclearity clusters.

Only the OH groups of silica, which are neither highly acidic nor nucleophilic, were studied in this work. We anticipate that the reactivity of OH groups on other oxides, such as alumina and titania, will show a different reactivity due to their different properties of acidity and nucleophilicity. The study of the reactions of surface organometallic fragments supported on these oxides will undoubtedly lead to more discoveries of unique surface reactions.

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