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Towards a structure–activity relationship for oxide supported metals

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Abstract

The chemistry of $[RhCl(CO)_2]_2$ on rutile single crystal surfaces and high area oxides is described. Dissociative chemisorption leads to $RhCl(CO)_2$/oxide in most cases, but when the favoured site is removed, as in rutile(1 1 0)(1 × 2), reductive decomposition to the metal is rapid. In that favoured site, the surface provides a Lewis base site (O) for coordination to Rh and a Lewis acid site (Ti) for Cl. Metal particles formed by the thermolysis can attain SMSI effects.

Using energy dispersive EXAFS (EDE) in conjunction with mass spectrometry, the reactions of $Rh(CO)_2Cl$/alumina and Rh/alumina with NO have been studied in detail using the Rh K-edge. Both react rapidly with NO under mild conditions. For the dicarbonyl, the kinetics of the changes in the Rh structure and the gas phase compositions reveal two different stages in the reaction towards a bent nitrosyl complex, formulated as RhCl(NO)/alumina. For Rh/alumina, there is rapid disruption of the metal particles; O_2 similarly rapidly disrupts supported rhodium. This fluidity of the metal structures strengthens the importance of synchronous structure/reactivity observations.

It has long been the aim to derive a molecular level understanding of the heterogeneous catalysts. Such descriptions are often thwarted by the structural complexity and also by the absence of techniques that can be suitably applied to such materials under reaction conditions. We have sought to tackle this problem by a multi-facetted approach stretching from detailed studies of the chemisorption of organo-rhodium compounds onto the surfaces of single-crystal surfaces through the interaction of organometallics onto the surfaces of high area supports to the improved characterisation of oxide-supported metal catalysts. In this report, we review progress towards the elusive structure–reactivity relationship.

Keywords: Rhodium; Carbonyls; Titania; Alumina; X-ray absorption spectroscopy

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1. Introduction

The diversity and complexity of the branch of heterogeneous catalysts comprising oxide-supported transition metals has provided an enormous challenge to gaining the type of molecular level understanding that is an attainable target in homogeneous organometallic chemistry. Identifying the ensemble of metals required for a particular catalytic reaction to proceed has proven to be problematical [1]. Thus a structure insensitive reaction might display no dependence of turnover frequency against particle size. However, a "demanding", or structure sensitive reaction [2] may in principle show a turnover enhancement, maximum, or reduction with decreasing particle size. In practice, for a structure sensitive reaction like ethane hydrogenolysis, almost all types of relationship have been observed [1]. An important aspect of

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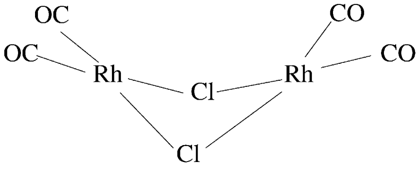
this situation is that the measurement of particle size, or fraction of metal exposed, will generally be carried out under different conditions to the catalysis.

A much closer approach to a molecular level understanding of chemisorption can be achieved by surface chemistry studies on single crystal metal surfaces [3]. Here, the effect of surface geometry on the catalytic activity can be revealed, e.g. showing that hydrogenolysis of isobutane on platinum is favoured on kinked sites on high index planes, while the competing skeletal isomerisation is preferred on sites with square arrays of platinum, as on the (1 0 0) plane. In that light, it is not surprising that the majority of examples of hydrogenolysis of cyclopentane and methylcyclopentane show antipathetic behaviour; relatively large particle sizes are required to attain a surface geometry with kinked sites. As particle sizes reduce, the metal surface facets are figured on a convex framework, such as those evident on high nuclearity metal carbonyl clusters [4]. So the localities of the sites that occur on highly dispersed metal particles may be atypical of those provided on metal single crystals.

2. Chemisorption of $[RhCl(CO)_2]$ onto TiO_2 and alumina

With this problem in mind, we (with Professor B.E. Hayden) investigated the interaction of organotransition metal complexes with single crystal oxides, carrying out parallel reactions on high area oxides, in a way similar to that previously reported by Schwartz and coworkers [5]. The MOCVD method could be applied to both substrate materials and $[RhCl(CO)_2]_2$ (**1**) proved to be an effective adsorbate.



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The rhodium carbonyl chloride readily binds to dried titania. Three possible surface sites could be proposed for a mononuclear rhodium site (Fig. 1). The strongest evidence for the dissociative chemisorption into monomeric species came from IR spectroscopic studies of the ν(CO) region. As for the $Rh(CO)_2$ species formed by the oxidative fragmentation of $Rh_4(CO)_{12}$ on alumina [6], enrichment with isotopically labelled CO demonstrated the six IR bands expected from three isotopomers, which was the diagnostic for a monomeric $Rh(CO)_2$ centre [7]. Differentiating between **2a** and the other two sites could be achieved by Rh K-edge X-ray absorption spectroscopy (XAS) [7]. This demonstrated the presence of both Rh–O and Rh–Cl bonds, so eliminating **2a** as an option. However, on a powdered sample, there was no means of distinguishing **2b** from **2c**.

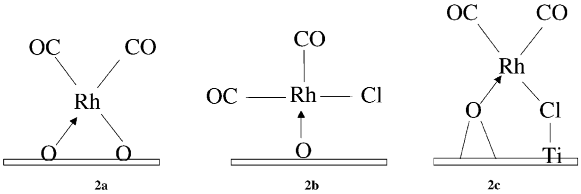


Fig. 1. Three possible surface sites for the dissociative chemisorption of $[RhCl(CO)_2]_2$ onto a TiO_2 surface.

A similar adsorption process was also identified on the rutile (1 1 0) single crystal surface [8,9]. The Rh species was identified by XPS and RAIRS, both being consistent with a $Rh^I(CO)_2$ centre. The reflectivity in the ν(CO) region demonstrated that the symmetric stretch was polarised perpendicular to the oxide surface, with the asymmetric mode polarized parallel the surface. This would be consistent with sites **2a** or **2c**, but for **2b** both modes would be polarized at a dihedral angle close to 45° to the surface. The Cl XPS results indicated a marked change in the environment of chlorine from that in **1**, but was not definitive between **2a** or **2c**.

The idealised (1 1 0) surface of rutile is shown in Fig. 2. STM images show some non-idealities of step edges and point defects [10]. The relative sizes of a $Rh(CO)_2$ unit and the surface oxygens is consistent with the observed maximum Rh surface coverage of ca. 1/3. The surface is anisotropic, and in principle the orientation of the $Rh(CO)_2$ unit can be probed by observing the intensity variation of the asymmetric stretch. About 85% of the sites have been shown to be oriented in the ⟨1 1 0⟩ direction, with a minority of sites oriented differently [11]. Given the likelihood of a square planar geometry for this $4d^8$ Rh(I) site, this would suggest that **2c** is the preferred site, with

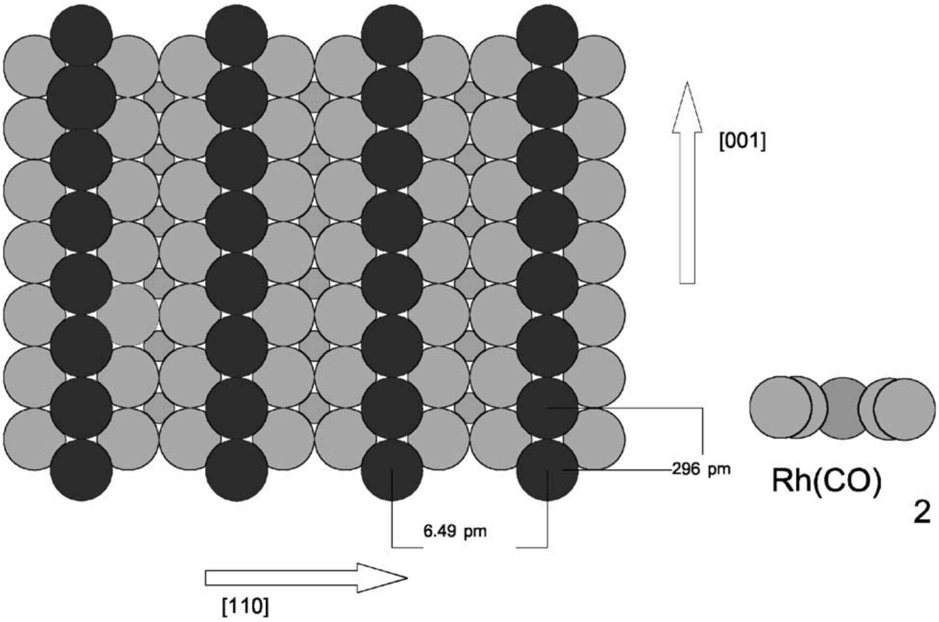


Fig. 2. The (1 1 0) plane of rutile. Each $Rh(CO)_2$ unit will cover three surface oxygen atoms.

the chlorine being stabilised by coordination to the 5-coordinate Ti(IV) surface site. STM images of the adsorbed complex show very little surface order initially [10], but this increases with time. Interestingly, on a surface where the amphoteric site in **2c** is broken, as in a (2×1) reconstruction obtained by different pretreatment conditions, the first observed sites do not contain these $Rh(CO)_2$ centres, rather small metallic particles are identified [12].

When heated to high temperatures (>600 K), $RhCl(CO)_2$/titania forms large, ordered f.c.c. metal particles [7]. Under UHV conditions, $RhCl(CO)_2$/rutile(1 1 0) also forms metal particles, above 400 K [13]. After heating to 800 K, these particles show a strong SMSI effect, reducing their ability to adsorb CO [9]. Interestingly, STM studies showed that rhodium particles actually formed on the (1 1 0) plane of rutile at room temperature during the period when the organometallic generates a more ordered phase. There is preferential metal formation at step and defect sites on the oxide; this minority process was probably not apparent in the previous IR and XPS monitoring methods. On the more reducing (1×2) surface, in place of the $Rh(CO)_2$ centres, smaller metal particles form on the terraces.

$RhCl(CO)_2$/rutile(1 1 0) also reacts with NO at 300 K [14]. A dispersed $Rh(NO^+)$ centre is evident ($\nu(NO) = 1920\,cm^{-1}$). This is considerably more thermally stable than the carbonyl, which can be regenerated from it by exposure to CO. Similar sites are also observed on titania. The Rh/titania formed by thermal decomposition of $RhCl(CO)_2$/titania will also react with NO, initially forming an additional surface nitrosyl. Interestingly, continued exposure to NO was thought to disrupt the metal particles, as indicated by monitoring NO as a probe molecule with IR spectroscopy.

These results show strong parallels between the chemistry on single-crystal and high area TiO_2, though there are important differences between single crystal surface type that indicate a potential surface dependence of some of the rhodium reactivity.

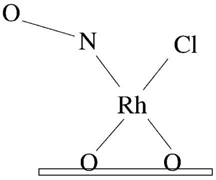
3. Energy dispersive EXAFS as an in situ technique for heterogeneous catalysis

Trying to establish a structure–reactivity relationship ideally requires both the studies to be simultaneous. XAS has become established as an important structural technique, particularly for materials of low crystallographic order [15,16]. However, in its normal scanning mode, the acquisition time required (>10 min) renders it only appropriate for steady state studies. In principle with a curved monochromator, the points in a X-ray absorption spectrum of an element's edge could be acquired simultaneously using a fast, position sensitive detector [17]. This was applied to catalyst studies relatively early in the development of the technique [18], but for in situ studies on heterogeneous catalysts, improvements in optics and detectors were necessary [19,20]. At the SRS, acquisition of Pt L_{III} edge X-ray absorption spectra of $Pt(acac)_2/H_1–SiO_2$ was demonstrated to be feasible at faster than 1 s, so allowing real-time studies of the local structures of oxide supported metals [21]. The mesoporous silica was used to achieve a high spatial loading of the metal [22]. Using a temperature ramp (4°/min), it was possible to demonstrate that a clean conversion of the metallo-organic complex into metallic platinum occurred between 111 and 124 °C under hydrogen, the reaction being complete within 12 min. As an extension of the technique, the Pt L_{III} and Ge K-edges were monitored simultaneously to follow the structural changes during the thermolysis of $Pt(acac)_2–GeBu_4/H_1–SiO_2$ [23]. This has allowed new insights into the formation of a supported alloy by hydrogen reduction. It is apparent that platinum particle formation occurs initially, but the presence of $GeBu_4$ retards this process. Alloying occurs at a higher temperature, but is accompanied by a reduction in the mean metal particle size. There is some evidence for the formation of a GeR_2 centre as an intermediate in the decomposition of the supported organometallics.

4. In situ studies of $RhCl(CO)_2$/alumina

Having achieved relatively rapid scanning of the EXAFS energy range (rather than just the near edge features), the simultaneous monitoring of the gas phase species was included in quartz-tube microreactor operation for in situ monitoring of the chemistry of oxide supported rhodium. This could be achieved on beamline ID24 of the ESRF using a Si(1 1 1) monochromator in a Laue geometry (Fig. 3), with the cell also shown in position (Fig. 4).

The reaction between $RhCl(CO)_2$/alumina and NO was found to be relatively quick. The nature of the resulting nitrosyl was dependent upon the pretreatment of the oxide surface. Hydroxylated alumina afforded a species with ν(NO) value typically of bent nitrosyls (~1730 cm^{-1}). EXAFS analysis of this material was consistent with structure **3**. Both CO and N_2O were observed as reaction products, and a kinetic analysis of the mass spectrometry and XAS features indicated that they were revealing two different stages of the reaction [24]. Mass spectrometry afforded the kinetic



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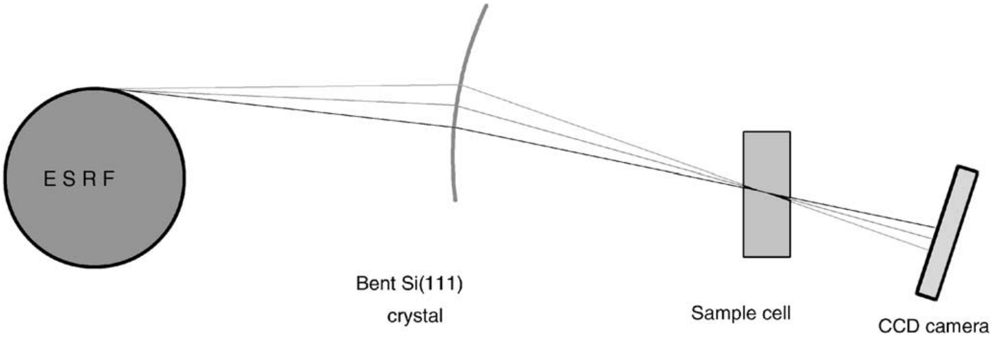

Fig. 3. Optical outline for the acquisition of energy dispersive X-ray absorption spectra at the Rh K-edge on ID24 at the ESRF.

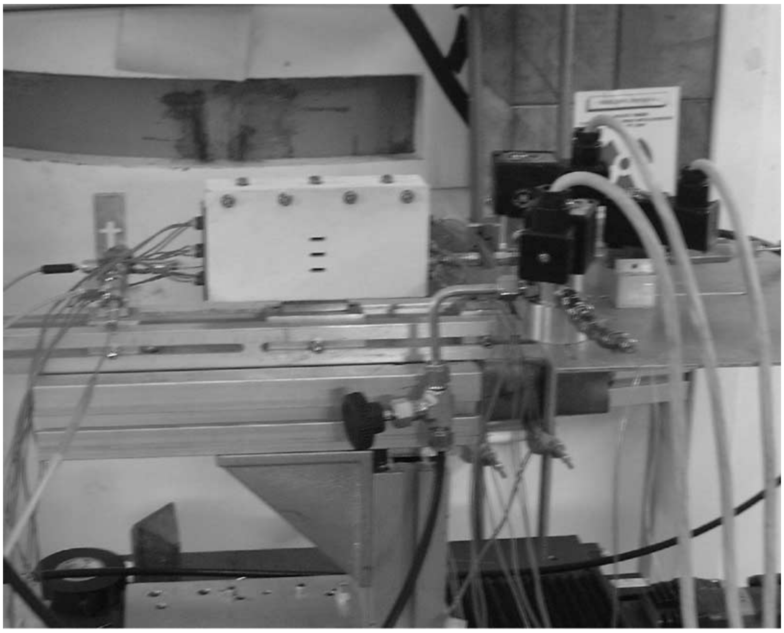

Fig. 4. The in situ microreactor on ID24 showing gas controls (right), heating elements, thermocouple and capillary leak valve to a mass spectrometer (left).

parameters of reaction (1). It is believed that this linear nitrosyl species would be difficult to distinguish from the starting material by XAS, both having very similar coordination geometries. The second stage of the reaction (2) is thought to evolve N_2O and generate a highly reactive intermediate, which rapidly coordinates a third NO molecule (3). The multiple scattering features of a linear nitrosyl are lost at this stage; analysis suggests a Rh–N–O angle of 135°.

$$2NO(g) + Al(O){-}Rh(CO)_2Cl \overset{E_{act} \sim 11\,(\pm 1.25)\,kJ\,mol^{-1}}{\Rightarrow} Al(O){-}Rh(NO)_2Cl + 2CO(g) \tag{1}$$

$$Al(O) {-}Rh(NO)_2Cl \overset{E_{act} \sim 40.6\,(\pm 3.5)\,kJ\,mol^{-1}}{\Rightarrow} Al(O){-}Rh(O) * Cl + N_2O(g) \tag{2}$$

$$NO(g) + Al(O){-}Rh(O) * Cl \overset{fast}{\Rightarrow} [Al(O)]_2{-}Rh(NO)^{-}Cl(\mathbf{3}) \tag{3}$$

Species **3** also reacts with CO, reforming the dicarbonyl site, albeit more slowly.

This reaction sequence differs from that on rutile(1 1 0) and on titania under very high vacuum conditions [14]. Under some pretreatment conditions, a linear nitrosyl can also be formed on alumina, the hydroxyl content appearing to be very important in determining the reaction route.

5. In situ Rh/alumina

When Rh/alumina, formed by ex situ reduction of $RhCl_3$/alumina under H_2, was examined within reactor by Rh K-edge EDE, the EXAFS pattern did not resemble that of metallic rhodium. Analysis indicated a mean coordination site of ~3 Rh–O (2.00 Å) and ~2 Rh–Rh (2.71 Å) [25]. Exposure to H_2 in situ did reform the metal, with the mean Rh–Rh coordination number increasing with reduction temperature. Exposure to O_2 at 373 K caused a two-stage reaction, the rapid step being complete in seconds, and a slower step requiring about 10 min. The analysis of this material showed strong similarities in the initially loaded material. The rapid step is accompanied by the evolution of CO_2, indicating rapid dissociation of O_2.

The reaction with NO follows a similar two-stage process, but is even more rapid and highly exothermic

[26]. Again, the metal particles are cleaved by the NO, with N_2 and O_2 being the first gaseous products formed. This demonstrates again a very fast disruption of metal particles on admission of a reactive gas.

6. Conclusions

This combination of approaches shows that it is still very difficult to establish the coordination site of an organometallic centre beyond the coordinated atoms. In favoured cases, such as the chemisorption of **1** on rutile(1 1 0), the orientation and specific adsorption site may be inferred, but not proven. The stability of the surface organometallic is shown to be highly dependent upon the surface structure of the oxide. Studies on the single crystal plane show that the route to metal particles (MOCVD and thermolysis versus MVD) strongly impacts on the reactivity of the metals so formed. Nevertheless, parallel chemistry, such as the reaction of $RhCl(CO)_2/TiO_2$ with NO, can be identified.

The combination of structural information, concentrations of gaseous reactants and products and kinetic analysis provides new insights into the reaction pathways of oxide supported metals. The rapid formation of metal particles from organometallics ($Pt/H_1–SiO_2$), the dependence of those particles on a co-adsorbate ($GeBu_4$), and the fragility of rhodium particles under oxidising conditions clearly demonstrate that the nature of the small metal particles of highly dispersed catalysts may be constantly changing. This places severe constraints on the previous analyses of the structure sensitivity of catalytic reactions and also on the appropriateness of single-crystal metal surfaces as catalytic models.

The rapid reaction of NO with Rh/alumina shows that dissociative chemisorption of NO is a fast process at room temperature. The nitrosyl species so formed is a poisoned form of rhodium. What is problematic for catalytic conversion reactions on rhodium is the maintenance of metal particles for the reaction to proceed.

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