# Industrial Aspects of Cluster Chemistry

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# Industrial aspects of cluster chemistry

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The reasons for industrial interest in metal clusters and cluster catalysis are described. These may be summarized as attempting to bridge the gap between homogeneous and heterogeneous catalysis, specifically by combining the high selectivities typical of the former with the high activities associated with the latter. Progress towards the realization of this objective is illustrated by using examples of our work in both areas. Thus, some results from an investigation of homogeneous ruthenium and rhodium catalysts (as both separate components and mixtures) for the synthesis of oxygenated products from CO–$H_2$ are summarized and correlated with high-pressure infrared spectroscopic measurements. The cluster anion $[Rh_5(CO)_{15}]^-$ is shown from spectroscopic evidence to be very closely related to the catalytically active species in the rhodium-catalysed reactions. Also, the distinction between the behaviour of supported catalysts derived from Group VIII metal cluster compounds and those obtained by more conventional methods of heterogeneous catalyst preparation is discussed. For example, in the case of ruthenium, cluster-derived catalysts are shown to display greatly enhanced activity for the complete hydrogenolysis of straight-chain aliphatic hydrocarbons to methane and provide a temperature advantage of 150 °C relative to conventionally prepared ruthenium catalysts, where only moderate hydrocarbon conversions are noted. The increased activity superficially correlates with the smaller metal crystallite sizes (15–20 Å; 1.5–2.0 nm) reproducibly obtainable with metal cluster compounds as catalyst precursors.

## Introduction

Industrial interest in metal clusters is centred around their application as catalysts, either directly in the form of homogeneous systems or indirectly by acting as precursors to novel heterogeneous catalysts (Whyman 1980). A recent paper has described cluster catalysis as an important new research area (Haggin 1982). In that report the current situation has been accurately summarized in terms of the importance of cluster catalysis deriving more from the promise of future commercial successes than from any demonstrated use or indeed ability to solve existing problems. Most industrial research laboratories are now said to maintain major efforts in cluster research with emphasis on developing selective catalysts for $C_1$ chemistry.

Metal clusters are of interest as potential catalysts principally because they may be considered to represent the interface between the traditional disciplines of homogeneous and heterogeneous catalysis. Thus, on the one hand, the presence of adjacent metal sites in polynuclear complexes makes available coordinative, electronic and steric situations that cannot be duplicated at the single metal site typical of most conventional homogeneous catalysts. Catalysts derived from supported metal clusters, on the other hand, can represent one extreme, namely that of the very small particles in which almost every atom is a surface atom, of classical heterogeneous supported metal catalysts. The situation is summarized in figure 1. The areas 'cluster catalysis' and 'supported clusters' are of course very diffuse and may be further subdivided. For example, in addition to catalysis by molecular metal clusters, catalysis by colloidal metal particles should also be considered under the former heading. Molecular metal clusters may act either as catalysts in their own right *or* simply as catalyst precursors, possibly with subsequent fragmentation under reaction conditions to highly reactive species of lower nuclearity. Distinction between these two possibilities is difficult. Under the 'supported clusters' heading a distinction should be drawn between those materials in which most of the original attached ligands are retained (i.e. catalysis by supported molecular metal clusters) and those in which the ligands have been removed in an activation process (i.e. catalysis by very highly dispersed metal particles). Homogeneously catalysed processes are frequently characterized by high selectivity, whereas high activities tend to be associated with heterogeneous catalysts. It is therefore an attractive hypothesis to pursue that operation in this interfacial area between homogeneous and heterogeneous catalysis may provide a means of combining the high selectivity associated with the former with the high activity characteristic of the latter.

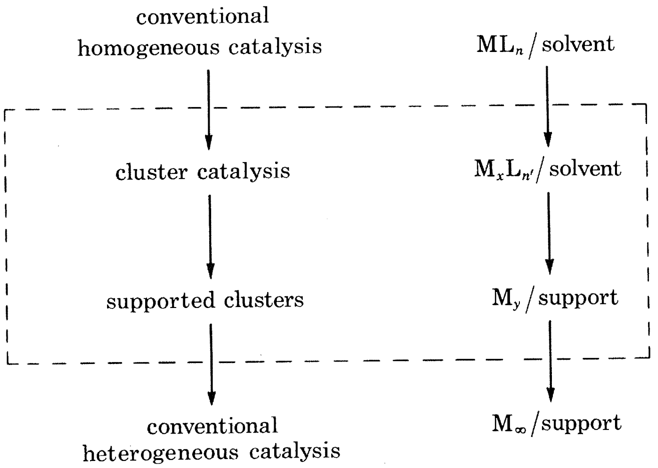

FIGURE 1. The relation between metal clusters, homogeneous and heterogeneous catalysis.

The subject of particle size effects in heterogeneous catalysis, in particular the dependence or otherwise of catalytic activity and selectivity on metal particle size in the range 1–10 nm is of considerable interest to both industrial and academic circles. General trends that have emerged suggest that transformations such as those involving the reactions of unsaturated hydrocarbons, e.g. catalytic hydrogenation and isomerization, are independent of metal particle size, i.e. are structure-insensitive. In contrast the energetically more demanding reactions such as those that involve the activation of C–H and C–C bonds in saturated hydrocarbons, and the hydrogenation of carbon monoxide and of nitrogen, are structure-sensitive. The latter are also rarely observed in the presence of conventional mononuclear homogeneous catalysts. It is conceivable that they may be facilitated by the presence of adjacent metal centres in a multinuclear cluster.

In attempting to assess whether the elegant chemistry of the type described in this Discussion Meeting can be profitably developed and applied to real industrial situations it is important to at least consider the following questions as they relate to the subject on either side of the interface. First, do homogeneous catalysts derived from metal clusters provide catalytic activities or selectivities that are not attainable by using mononuclear catalyst precursors? Secondly, do heterogeneous catalysts derived from metal clusters show genuinely different properties from supported metal catalysts prepared by traditional routes? In this paper I shall attempt to answer these questions at least in part by using two aspects of our work as illustrations. The first is related to homogeneous catalysts for the reduction of carbon monoxide and the second to reactions of saturated hydrocarbons over catalysts derived from supported metal clusters.

## HOMOGENEOUSLY CATALYSED REDUCTION OF CARBON MONOXIDE

The development of catalysts for the selective synthesis of high added value oxygenated molecules such as alcohols, diols and polyols directly from $CO–H_2$ (or other $C_1$ molecules such as methanol) is of considerable commercial potential (see, for example, Pruett 1981) and therefore the scene of intense industrial activity. Extensive studies have been made on a rhodium-based homogeneous catalyst for the production of ethylene glycol and methanol directly from synthesis gas (Pruett & Walker 1974, 1976). High pressures (in the range 50–125 MPa) and temperatures (473–513 K) are necessary for significant conversions, the greatest selectivity to ethylene glycol being observed at higher pressures. Although both mononuclear and polynuclear rhodium complexes may be used as catalyst precursors, i.r. spectroscopic evidence has been presented to suggest the involvement of polynuclear rhodium carbonyl anions as the catalytically active species (Vidal & Walker 1980; Whyman 1980). Some of our spectroscopic results are summarized in table 1.

TABLE 1. CONVERSION OF $CO–H_2$ TO ETHYLENE GLYCOL: REACTION SEQUENCES OBSERVED BY HIGH-PRESSURE I.R. SPECTROSCOPY

| catalyst precursors | species present at 90 MPa and 473 K |
|---|---|
| $Rh(CO)_2acac \xrightarrow{\text{no base}} Rh_6(CO)_{16}$ | $Rh_6(CO)_{16} + [Rh_5(CO)_{15}]^-$ (tr.) |
| $Rh(CO)_2acac \xrightarrow{\text{2-OHpy}} [Rh_5(CO)_{15}]^-$ | $[Rh_5(CO)_{15}]^-$ |
| $\begin{tikzcd} {[Rh_{12}(CO)_{30}]^{2-}} \arrow[rr, "\text{no base}"] \arrow[dr, shift left, "H_2"] & & {[Rh_5(CO)_{15}]^- + Rh_4(CO)_{12}} \\ & {[HRh_6(CO)_{15}]^-} \arrow[ul, shift left] \arrow[ur, "CO–H_2"'] & \end{tikzcd}$ | $[Rh_5(CO)_{15}]^- + Rh_6(CO)_{16}$ |
| $[Rh_{12}(CO)_{30}]^{2-} \xrightarrow{\text{2-OHpy}} [Rh_5(CO)_{15}]^-$ | $[Rh_5(CO)_{15}]^-$ |
| $[Rh_6(CO)_{15}]^{2-} \rightleftharpoons [Rh_5(CO)_{15}]^- + [Rh(CO)_4]^-$ | $[Rh_5(CO)_{15}]^- + [Rh(CO)_4]^-$ |
| $Ir(CO)_2acac \xrightarrow{\text{2-OHpy}} Ir_4(CO)_{12}$ | $Ir_4(CO)_{12}$ |

$[Rh_{13}(CO)_{24}H_3]^{2-}$ also observed, but only under CO-deficient conditions

TABLE 2. CONVERSION OF $CO–H_2$ TO OXYGENATES BY RHODIUM AND RUTHENIUM CATALYSTS

(Catalyst composition: Rh added as $Rh(CO)_2acac$, Ru added as $Ru(acac)_3$; 2-hydroxypyridine (2.25 mmol), caesium benzoate (0.125 mmol) in 50 ml *N*-methylpyrrolidone–tetraglyme (1:4). Reaction conditions: 86.1 MPa $CO–H_2$ (1:1), 503 K, 4 h)

| metal added/mmol | | products formed/mmol | | |
|---|---|---|---|---|
| Rh | Ru | $CH_3OH$ | $C_2H_5OH$ | $\begin{array}{c}CH_2OH\\ \vert \\ CH_2OH\end{array}$ |
| 0.75 | 0 | 47.1 | 2.6 | 101.3 |
| 0.75 | 0.25 | 4.5 | 0.6 | 5.0 |
| 0.75 | 0.75 | 5.8 | 1.0 | 9.8 |
| 0 | 0.75 | 22.5 | 3.5 | 0.9 |

The use of ruthenium catalysts for the formation of methanol under similar reaction conditions has been described (Bradley 1979). No ethylene glycol is produced. In contrast to the observations on the rhodium system, the use of either polynuclear or mononuclear ruthenium complexes as catalyst precursors results in the formation of mononuclear $Ru(CO)_5$ under reaction conditions. In neither case has the nature of the active catalyst been established unequivocally.

We have studied the catalytic properties of closely related rhodium and ruthenium systems, together with their mixed-metal combinations in different proportions. In the presence of a nitrogen base and alkali-metal promoter, rhodium complexes form active catalysts for the production of ethylene glycol and methanol at 86 MPa total CO–$H_2$ pressure and 503 K (see table 2). An ethylene glycol–methanol molar selectivity of 2.2 : 1 is observed. Analogous ruthenium catalysts are less active under these reaction conditions and produce significant quantities of methanol but only traces of ethylene glycol. The addition of up to equimolar amounts of ruthenium to the optimum rhodium catalyst for the production of ethylene glycol results in a dramatic suppression of the overall catalytic activity.

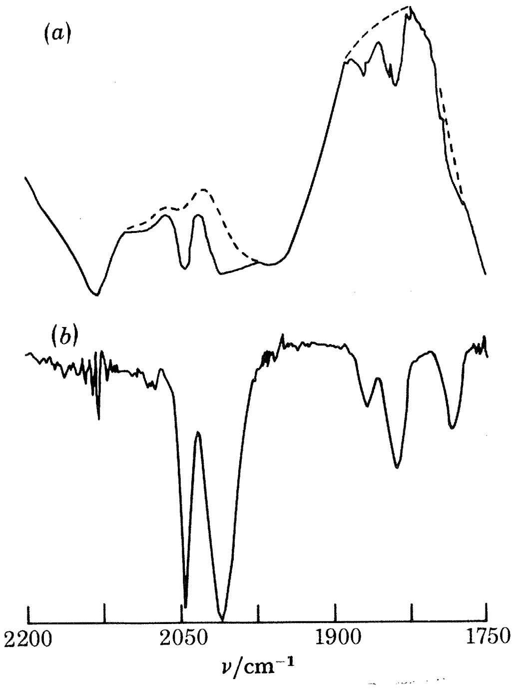

FIGURE 2. Fourier transform i.r. spectra (in the region 2200–1750 $cm^{-1}$) of the catalyst composition initially containing $Rh(CO)_2acac$ (0.3 mmol), 2-hydroxypyridine (0.9 mmol), caesium benzoate (0.05 mmol) in 20 ml *N*-methylpyrrolidone–tetraglyme (1 : 4) measured at 31.1 MPa CO–$H_2$ (1 : 1) and 323 K. (*a*) Spectrum of reaction mixture (——); reference spectrum of the system in the absence of rhodium complex (– – –). (*b*) Spectrum of the rhodium-containing species after subtraction of (– – –) from (——).

These changes in catalytic activity have been correlated with Fourier transform infrared spectroscopic measurements under similar reaction conditions and under which the major species present in solution have been identified. Spectroscopic studies on the rhodium-based catalyst are consistent with the formation of the polynuclear anion $[Rh_5(CO)_{15}]^-$ (Fumagalli *et al.* 1980) at 31.1 MPa CO–$H_2$ and 323 K (see figure 2), and this remains the only detectable species present in solution at 65.9 MPa and 503 K. The less complex system $Rh_4(CO)_{12}$–*N*-methylpyrrolidone–tetraglyme, which is also catalytically active for the formation of oxygenated products, shows very similar features. In the ruthenium system (see figure 3), which produces significant quantities of methanol but only minor amounts of ethylene glycol, the metal is predominantly present in the form $[HRu_3(CO)_{11}]^-$ (Johnson *et al.* 1979) at 54.0 MPa CO–$H_2$ and 503 K. The intermediate formation of $Ru(CO)_2(acac)_2$ ($\nu$(CO) 2054, 1983 $cm^{-1}$) (Calderazzo *et al.* 1969) is observed at 423 K, but above 473 K the spectrum shows absorptions at 2010s, 1985s and 1953m $cm^{-1}$, which correspond closely to the spectrum of the polynuclear hydridoruthenium carbonyl anion. In the Ru–Rh mixed system $[Rh_5(CO)_{15}]^-$ is initially observed in solution at 30.4 MPa CO–$H_2$ and 293 K. Tris-acetylacetonatoruthenium is unreactive under these conditions and is reduced to $Ru(CO)_2(acac)_2$ only when the temperature approaches 423 K. At this stage the spectrum (figure 4*a*) is consistent with the presence of a mixture of $Ru(CO)_2(acac)_2$, $[Rh_5(CO)_{15}]^-$ and a small amount of $[Rh(CO)_4]^-$ (absorption at 1896 $cm^{-1}$). Above this temperature the distinctive bridging $\nu$(CO) absorptions at 1868, 1837 and 1784 $cm^{-1}$, characteristic of $[Rh_5(CO)_{15}]^-$, and the peak due to $[Rh(CO)_4]^-$ decrease in intensity and are replaced by a single band at 1844 $cm^{-1}$. At 63.5 MPa and 503 K the species $[Rh_5(CO)_{15}]^-$ is *not* present in detectable concentrations in solution. Under these conditions the infrared spectrum comprises absorption bands at 2053m, 2036sh, 2016vs, 1984s, 1953mw and 1844 $cm^{-1}$ (see figure 4*b*). The most probable interpretation of this spectrum is in terms of the presence of a mixture of $[Rh_{13}(CO)_{24}H_3]^{2-}$ ($\nu$(CO) 2016, 1844 $cm^{-1}$) (Albano *et al.* 1975) and $[HRu_3(CO)_{11}]^-$ ($\nu$(CO) 2016, 1984, 1953 $cm^{-1}$) together with smaller concentrations of $Ru(CO)_2(acac)_2$ ($\nu$(CO) 2053, 1984 $cm^{-1}$) and possibly $Ru(CO)_5$ ($\nu$(CO) 2036 and 1995 $cm^{-1}$, the latter band being obscured). An alternative explanation could arise from the presence of at present unidentified mixed Ru–Rh species such as $[RuRh_4(CO)_{15}]^{2-}$, although the above i.r. spectrum does not resemble that reported for the related complex $[RuIr_4(CO)_{15}]^{2-}$ (Fumagalli *et al.* 1981). The apparent lack of

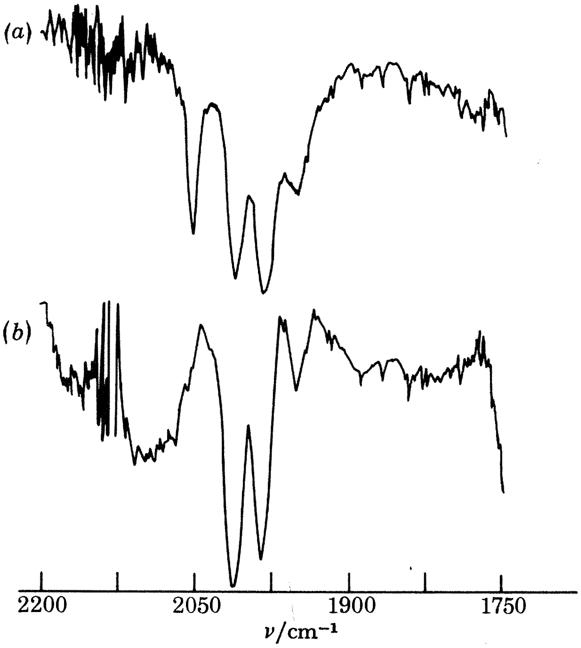

FIGURE 3. Fourier transform i.r. spectra of ruthenium-containing catalyst composition (after subtraction of background absorptions due to solvents and additives) initially comprising $Ru(acac)_3$ (0.3 mmol), 2-hydroxypyridine (0.9 mmol) and caesium benzoate (0.05 mmol) in 20 ml *N*-methylpyrrolidone–tetraglyme (1:4). (*a*) Spectrum recorded at 50.0 MPa CO–$H_2$ and 423 K. (*b*) Spectrum recorded at 54.0 MPa CO–$H_2$ and 503 K.

evidence for the presence of mixed Ru–Rh species under reaction conditions is at first sight surprising. However, our knowledge of the stability of anionic mixed-metal carbonyl clusters with respect to pressures of CO or $H_2$, or both, is extremely limited, although fragmentation to homonuclear species has been reported to occur quite readily with neutral analogues (Fox *et al.* 1980). For example, $HCoRu_3(CO)_{13}$ in hexane reacts completely in 1 h with 0.1 MPa CO to give $Ru_3(CO)_{12}$, $Ru(CO)_5$, $Co_2(CO)_8$ and hydrogen. It is therefore quite conceivable that mixed Ru–Rh complexes would be unstable with respect to their homonuclear counterparts under severe reaction conditions.

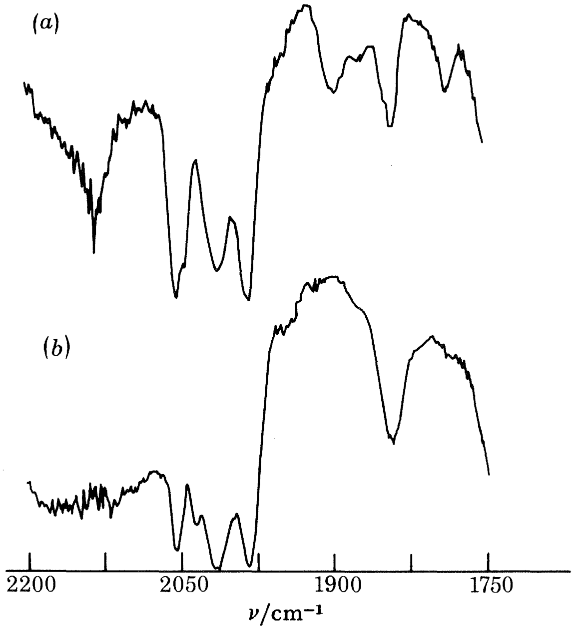

FIGURE 4. Fourier transform i.r. spectra of ruthenium–rhodium catalyst composition (after subtraction of background absorption due to solvents and additives) initially comprising $Ru(acac)_3$ (0.3 mmol), $Rh(CO)_2acac$ (0.3 mmol), 2-hydroxypyridine (0.9 mmol) and caesium benzoate (0.05 mmol) in 20 ml *N*-methylpyrrolidone–tetraglyme (1:4). (*a*) Spectrum recorded at 54.0 MPa CO–$H_2$ and 423 K. (*b*) Spectrum recorded at 63.5 MPa CO–$H_2$ and 503 K.

TABLE 3. CONVERSION OF CO–$H_2$ TO OXYGENATES

(High-pressure F.t. i.r. results on Rh and Ru catalysts at 60.0 MPa and 293–503 K.)

*rhodium*

$Rh(CO)_2acac$–2-OHpy–CsOBz–NMP–TG

$$Rh(CO)_2acac \xrightarrow{293\ \mathrm{K}} [Rh_5(CO)_{15}]^- \xrightarrow{503\ \mathrm{K}} \text{no change}$$

*ruthenium*

$Ru(acac)_3$–2-OHpy–CsOBz–NMP–TG

$$Ru(acac)_3 \xrightarrow{423\ \mathrm{K}} Ru(CO)_2(acac)_2 \xrightarrow{>463\ \mathrm{K}} [HRu_3(CO)_{11}]^-$$

*ruthenium–rhodium*

$$Rh(CO)_2acac \xrightarrow{293\ \mathrm{K}} [Rh_5(CO)_{15}]^- \xrightarrow{>423\ \mathrm{K}} [Rh_{13}(CO)_{24}H_3]^{2-}$$

$$Ru(acac)_3 \xrightarrow{423\ \mathrm{K}} Ru(CO)_2(acac)_2 \xrightarrow{>463\ \mathrm{K}} [HRu_3(CO)_{11}]^-$$

The interpretation of the spectroscopic data is summarized in table 3, and a comparison between this and the results from the catalytic studies clearly suggests that the presence of $[Rh_5(CO)_{15}]^-$ in solution is to be closely associated with the generation of catalysts forming ethylene glycol and methanol. This is not to suggest that it is the active catalyst but merely a closely related precursor. The role of $[HRu_3(CO)_{11}]^-$ is less clear, although in the monometallic system at least it acts as a precursor to a methanol-forming catalyst.

If $[Rh_5(CO)_{15}]^-$, the major species present in solution, is indeed the actual catalyst, the total activity of the system (based on rhodium concentration) is far too low for commercial application. This appears to be a general feature of homogeneous catalysts so far reported for the reduction of carbon monoxide. Under the reaction conditions described here, the addition of ruthenium to the rhodium system results in a very marked catalytic deactivation. Equally marked synergistic effects are well documented (Thompson 1975 and references therein), and the search for promotional effects (additional metal(s), ligands, bases, etc.) offers much scope for future research in this area of chemistry, irrespective of whether mononuclear, dinuclear or polynuclear metal centres are involved.

## ACTIVATION OF SATURATED HYDROCARBONS OVER HETEROGENEOUS CATALYSTS DERIVED FROM SUPPORTED METAL CLUSTERS

As far as the development of heterogeneous catalysts derived from metal cluster compounds is concerned, such catalysts will be valuable only if they exhibit activities and selectivities that differ from those afforded by materials prepared conventionally. Unfortunately, it is a deficiency of much of the work so far reported that such comparisons have not been made. In an attempt to clarify this situation we initiated a programme of work to compare the catalytic activity of supported metal clusters of known particle size (prepared by the impregnation and activation–decomposition of metal cluster compounds on supports) with that displayed by catalysts containing the typical crystallite sizes available from conventional methods of heterogeneous catalyst preparation, namely halide impregnation or ion exchange, followed by hydrogen reduction. Ruthenium was selected as the initial metal for investigation, with silica as support. The precursor complexes used and eventual catalyst type are summarized in table 4.

TABLE 4. CATALYST PRECURSOR COMPLEXES

| type | Ru complex |
|---|---|
| cluster | $Ru_3(CO)_{12}$<br>$Ru_6C(CO)_{17}$ |
| ion exchange | $[Ru(NH_3)_5N_2]Cl_2$ |
| impregnation | $RuCl_3.xH_2O$ |

The cluster compounds were supported on silica by impregnation from organic solvents. The ‘conventional’ catalysts, produced by ion exchange and halide impregnation were usually supported from aqueous solutions. After drying, all materials were activated–reduced by treatment with a nitrogen–hydrogen mixture at 573–623 K for several hours. Activated catalysts were characterized by transmission electron microscopy for the measurement of metal particle size distributions both before and after catalyst testing. Typical metal particle size distributions for catalysts prepared by the different methods are summarized in table 5. From these results it is clear that the use of cluster compounds as catalyst precursors leads to the formation of particles of smaller crystallite size than those obtained from conventional methods of catalyst preparation.

However, it is equally clear that significant aggregation of the initial $M_3$ and $M_6$ cluster units has occurred during the overall supporting–activation process.

As indicated previously, the catalyst test reaction used was the activation of saturated hydrocarbons and in the results described here, specifically *n*-heptane. To effect this reaction a nitrogen–hydrogen–*n*-heptane mixture (volume ratio 100:10:1) at atmospheric pressure was passed over a silica-supported ruthenium catalyst obtained from $Ru_3(CO)_{12}$ contained in a tubular silica reactor. The temperature was increased in 50 K increments and the hydrocarbon products monitored by gas chromatography. The results (see table 6) demonstrate that *n*-heptane is completely hydrogenolysed to methane at 523 K, with no evidence for the formation of any other products.

TABLE 5. METAL PARTICLE SIZES (NANOMETRES) OF SILICA-SUPPORTED RUTHENIUM CATALYSTS

| precursor complex | Ru (%) | particle size/nm |
|---|---|---|
| $Ru_3(CO)_{12}$ | 1.7 | 1.5–2.0 |
| $Ru_6C(CO)_{17}$ | 1.4 | 1.5–2.0 |
| $[Ru(NH_3)_5N_2]Cl_2$ | 2.3 | 2.5–3.0 |
| $RuCl_3.xH_2O$ | 0.5 | 3.5–4.5 |

TABLE 6. HYDROGENOLYSIS OF *n*-HEPTANE OVER SILICA-SUPPORTED RUTHENIUM CATALYST

(Catalyst precursor, $Ru_3(CO)_{12}/SiO_2$; activation, $N_2$–$H_2$(4:1) at 623 K for 4 h; metal content, 1.0%; $H_2$:*n*-heptane, 10:1.)

| temperature/K | heptane conversion (%) | products |
|---|---|---|
| 373 | <1 | — |
| 423 | 7 | — |
| 473 | 87 | $CH_4 + C_2H_6$ |
| 523 | 100 | $CH_4$ |

TABLE 7. HYDROGENOLYSIS OF *n*-HEPTANE OVER SILICA-SUPPORTED RUTHENIUM CATALYSTS: CONVERSIONS AND METHANE SELECTIVITIES AS A FUNCTION OF TEMPERATURE

| catalyst precursor | Ru (%) | temperature/K | conversion (%) | selectivity to methane (%) |
|---|---|---|---|---|
| $Ru_3(CO)_{12}$ | 1.7 | 473 | 90.0 | 93.0 |
| | | 523 | 100 | 100 |
| $Ru_6C(CO)_{17}$ | 1.4 | 523 | 96.0 | 90.0 |
| | | 573 | 100 | 100 |
| $[Ru(NH_3)_5N_2]Cl_2$ | 2.3 | 523 | 26.0 | 65.0 |
| | | 623 | 78.5 | 72.0 |
| $RuCl_3.xH_2O$ | 0.5 | 523 | 18.0 | 65.0 |
| | | 623 | 22.2 | 72.0 |

A comparison between the activities of various supported ruthenium catalysts derived from $Ru_3(CO)_{12}$, $Ru_6C(CO)_{17}$, $[Ru(NH_3)_5N_2]^{2+}$ and $RuCl_3 \cdot xH_2O$ and activated–reduced under the same conditions is presented in table 7. There is clearly a very significant difference between the cluster-derived and conventional catalysts. With the former *n*-heptane is completely hydrogenolysed to methane at 473–523 K, whereas temperatures greater than 623 K are required to give 78 % and 25 % conversions over the catalysts based on $[Ru(NH_3)_5N_2]Cl_2$ and $RuCl_3 \cdot xH_2O$ respectively.

The new catalysts show a very high selectivity towards methane formation. In the temperature range 473–823 K no unsaturated derivatives, e.g. ethylene, are formed, and the only other product observed, in minor amounts, is ethane.

The key point to emerge from this work is that supported ruthenium catalysts derived from cluster compounds show significantly higher activity than conventionally prepared materials for the hydrogenolysis of hydrocarbons. This effect provides the opportunity to operate at as much as 150 °C below the temperature necessary to give even moderate activity over conventionally prepared catalysts. The increased activity observed with the cluster-derived catalysts bears at least a superficial relation to the smaller metal crystallite size of these materials. In addition to providing highly active ruthenium catalysts for the destructive cleavage of C–C bonds in saturated hydrocarbons, this work has led to the development of a system for the selective removal of ethylbenzene (by hydrogenolysis to toluene and methane) from aromatic $C_8$ fractions containing the various xylene isomers (Simpson & Whyman 1981; Whyman 1982).

Although I have shown that metal cluster-derived catalysts can display significantly different properties from their conventionally prepared counterparts, clearly considerably more detailed work is necessary to assess such features as (i) the nature of the initial interaction between the cluster compound and the support; (ii) the sequence of events that occurs on ligand removal during the catalyst activation process; (iii) the temperature at which the molecular clusters are transformed into small metal crystallites; and (iv) determination of the mildest reaction conditions under which catalytic activity can be detected.

As a start in this direction we have, jointly with workers at Hull University, studied the interactions of $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ with silica, alumina and titania. Such materials, when activated under milder reaction conditions than discussed earlier (vacuum, 523 K), give rise to a lesser degree of aggregation and the formation of clustered entities that retain some carbonyl groups. These materials are catalysts for the hydrogenolysis of ethane, the hydrogenation of ethylene and the hydrogenation of carbon monoxide and carbon dioxide. Moreover the activity of these materials is unaffected by exposure to air, in complete contrast to the behaviour of conventional ruthenium and osmium catalysts (Hunt *et al.* 1982). This further emphasizes the difference between metal cluster-derived and conventional supported metal catalysts.

## CONCLUSIONS

In this paper I hope that I have been able to demonstrate that (*a*) homogeneous catalysts derived from metal clusters can display novel selectivities particularly in the area of CO–$H_2$ chemistry and that (*b*) heterogeneous catalysts derived from metal clusters – in the form of either molecular aggregates or very highly dispersed metal particles – display properties that distinguish them from conventionally prepared materials. In the former case the overall catalytic activity of such systems is currently too low for commercialization, but development of the latter area could lead to a new generation of heterogeneous catalysts, provided that novel activities and selectivities can be maintained under the more forcing conditions typical of industrial use.

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