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Supported metals derived from organometallics

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Abstract

This article reviews recent progress in the application of organometallic compounds for the preparation of supported metal catalysts. The approach is a very general one in that the organometallics considered are the main group element complexes, the mononuclear complexes and clusters of transition metals (in different oxidation states). The surfaces can be that of metal oxides, the internal or external surface of zeolites or the surface of supported metal particles in a zero-valent state. Volatile complexes with the right size and reactivity have been used to prepare zeolite-entrapped metals and supported catalysts via chemical vapour deposition technique. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Supported metal catalysts, 0.1–20 wt% of a metal of Groups 8–11 dispersed over the surface of a support that is typically a high-surface-area oxide, are widely used on the industrial scale and in research laboratories. The main large-scale uses of such catalysts include the hydrogenation of animal and vegetable oils, petroleum reforming for high-octane gasoline, and the treatment of vehicle exhaust fumes to minimise environmental pollution. Supported metals are effective catalysts as the active metallic phase consists of extremely small particles, their degree of dispersion being 10–100%. These particles are firmly anchored to the surface and are widely separated from each other, and hence do not readily coalesce or sinter [1].

Until a decade or so ago catalyst manufacture was more or less an art, successful recipes being acquired by trial and error rather than a scientific understanding of the processes involved. However, in the last 15 years it is the "design" of catalysts with well-defined properties that has captured the scientists' interest. Thus, controlled preparation is a necessary prerequisite and the most successful methods are those that distribute the active metal phase in a highly dispersed form onto the support surface.

Ever since Parkins [2] found that the thermal decomposition of $Ni(CO)_4$ led to the formation of nickel particles on an alumina surface, the use of zero-valent compounds for the preparation of supported metal catalysts and, more recently, for supported bimetallic catalysts, has attracted enormous attention.

Research on the use of organometallics, particularly the metal carbonyls, in producing heterogeneous catalysts can be divided in two principal areas: the first involves the production of the so-called "heteroge-

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nised molecular catalysts", the aim being a practical one from the point of view of separation, easy handling, durability, catalyst recovery and thermal stability over a wide range of reaction conditions; the second area is the use of organometallics to produce small supported metal particles.

The various processes involved in the preparation of such particles link organometallic chemistry and surface chemistry. This has led to a new field of chemistry, surface organometallic chemistry, that deals with the interaction between organometallic compounds and surfaces [3]. The approach is a very general one in that the organometallic compounds considered are the main group element complexes, the mononuclear complexes and clusters of transition metals (in different oxidation states). The surfaces can be that of metal oxides, the internal or external surface of zeolites or the surface of supported metal particles in a zero-valent or higher oxidation state. Catalyst design can be considered a promising, scientific way to prepare well-defined active surfaces with marked catalytic properties, as well as to elucidate reaction mechanisms, including dynamic changes of active sites [4]. The use of such chemically and structurally controllable surface systems, rather than conventional supported catalysts with heterogeneous metal centres, often leads to novel information about the elementary steps of catalytic processes.

2. Why metal carbonyl clusters as precursors?

Molecular metal clusters of increasing nuclearity constitute a class of organometallic complexes that almost fills the gap between the molecular state (simple metal complexes) and the metallic state (small metallic particles). Several kinds of relationship between metal clusters and metallic arrangements (e.g. comparison of the electronic characteristics and of the reactivity of ligands, chemisorbed molecules, etc.) have been discussed by a number of authors [5]. It was pointed out that the comparison of very small particles (VSP) with molecular metal clusters (MC) would require reversible poisoning of the surface of a VSP by a kind of ligand L (such as CO) that easily forms a low-valent transition metal cluster frame. Hence the interest in this respect is great in investigating thermal treatments able to regenerate the VSP according to the following equilibrium:

$$x\mathrm{L} + \mathrm{VSP} \rightleftharpoons \mathrm{MC}$$

Based on these few elegant speculations there has, in the last few years, been a large amount of work devoted to investigating the thermal and chemical behaviour of metal clusters of various nuclearities, both supported on metal oxides and trapped in the framework of zeolites. The main purpose of this approach was to prepare highly dispersed and tailor-made metallic particles [6].

Compared with conventionally prepared supported metals, clusters can offer the following advantages:

- non-aqueous catalyst preparation methods can be employed as organometallic compounds are usually soluble in organic solvents;
- catalysts are halide-free;
- high-temperature reduction (by hydrogen), required to produce reduced metal in conventional catalyst preparation, should be unnecessary since metal clusters already have the metal formally in the zero-valent state;
- spatial separation of the components and inhomogeneous composition throughout the catalyst, can be overcome by using mixed-metal cluster compounds.

Clusters are usually supported by conventional techniques such as impregnation from solutions (wet or dry); impregnation can be carried out in air, but usually an inert atmosphere is required.

3. The surface reactivity of MC

At the beginning most metal carbonyl clusters deposited on the surface of an inorganic oxide are physically adsorbed as molecular species. In such cases, the surface can be visualised as an inert dispersing agent as if it were a solvent in solution chemistry. However, supported clusters can interact also with the active sites of the surface of the support. Different types of chemical reactions will occur, often leading to well-characterised surface molecular species [7].

In fact the surface of inorganic oxides is characterised by the presence of different active sites: the acidic/basic OH groups, Lewis acidic/basic centres such as Al^{3+}, Mg^{2+} and O^{2-}. The relative amount of Brønsted or Lewis sites and their acid/base character is related to the chemical nature of the oxide and the degree of surface hydration. In addition to the simple acid–base interactions between the cluster and the surface active sites one can also observe processes of nucleophilic attack at the CO ligand, or oxidative addition of OH groups to metal–metal bonds. The chemisorption process often takes place by a single surface reaction step, eventually leading to a simple, well-defined species (Fig. 1).

The surface of inorganic oxide can therefore be represented as a multidentate ligand. This dualism of surface reactivity, an inert "solvent" or a highly active "solid ligand", is the key step in determining the final properties of the supported material.

These studies have stimulated new thoughts about the possible origin of metal–support interaction effects. For example, the oxidative addition reaction leading to the grafted species $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-OSi}{<}\}]$ models the first step in the oxidation of zero-valent metal particles on a support. It indicates that the surface hydroxyl groups can make an electrophilic attach at the metal–metal bonds of the particle, resulting in an oxidation process in a very localised region of the particle.

These oxidative processes are favoured by an oxygen atmosphere, as expected, but also by the water content of the surface. In fact $Rh_6(CO)_{16}$ interacts only weakly with alumina pre-treated at 773 K. However, upon exposure of physisorbed $Rh_6(CO)_{16}$ to a partial pressure of water at 298 K, cluster

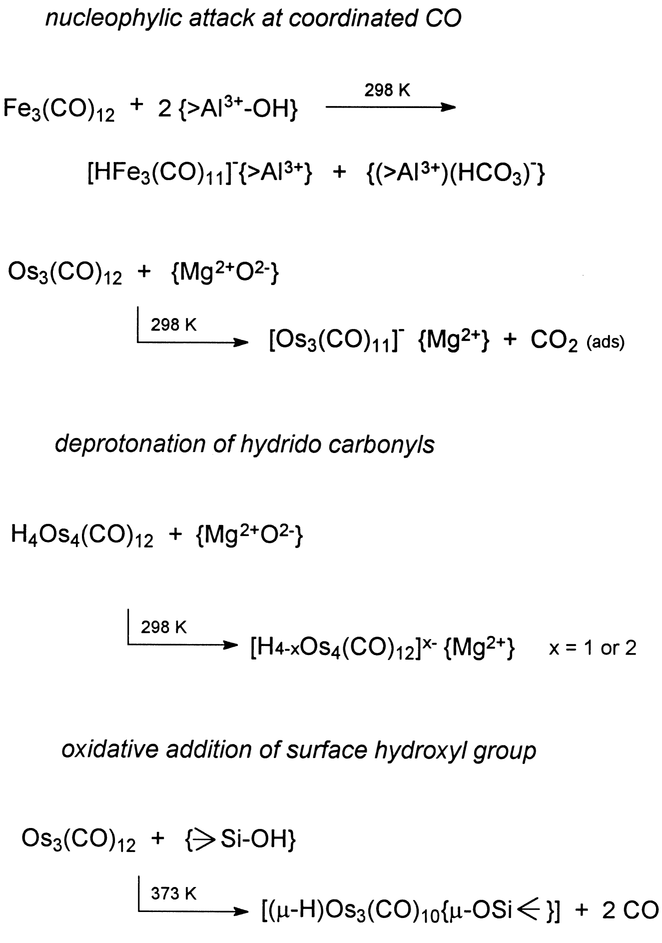

Fig. 1. Chemisorption of metal carbonyl clusters on metal oxide surfaces.

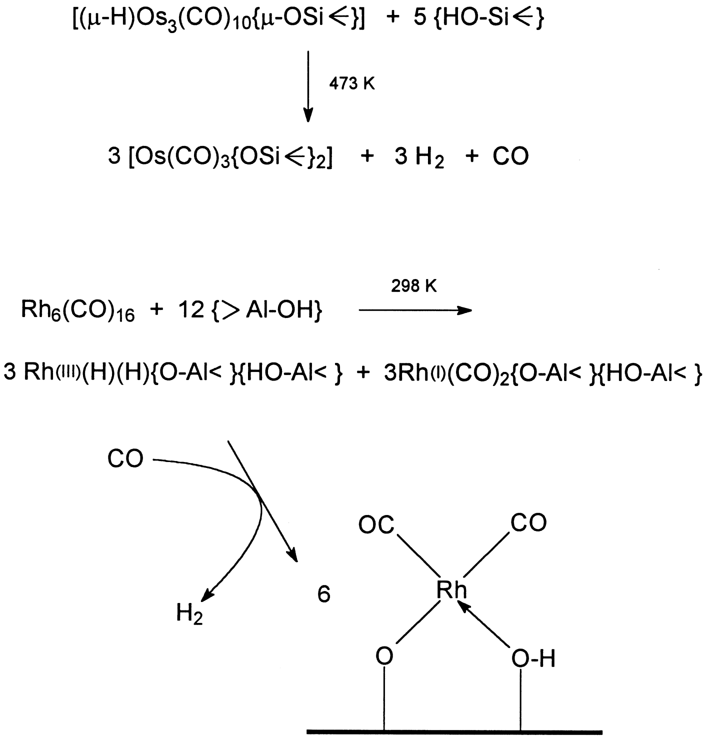

Fig. 2. Oxidative fragmentation of supported metal carbonyl clusters.

fragmentation to oxidised Rh(I) surface species occurs [8] (Fig. 2).

A similar oxidative fragmentation process has been proposed to account for the formation of $Rh^{I}(CO)_2$ species when highly dispersed rhodium on alumina is brought into contact with CO at 298 K [9]. The chemistry of supported rhodium carbonyl clusters has allowed an explanation, at the "molecular level", of the CO-induced fragmentation and oxidation of supported metal aggregates.

Generally thermal activation or decarbonylation of supported metal carbonyl clusters results in a breakdown of the metal framework, with oxidation of the metal atoms by oxidative addition of the surface hydroxyl groups.

Above 473 K, in vacuum or in inert atmosphere, the Os(II) carbonyl surface species has been obtained by oxidative fragmentation of the alumina-anchored hydrido osmium cluster (Fig. 2). The structure of this species has been elucidated by EXAFS spectroscopy [10]. On the basis of electron microscopy the existence of ensembles of three mononuclear Os(II) carbonyl species on the alumina surface has been supposed [11]. Evidence of ensembles of Re carbonyl surface species resulting from the fragmentation of MgO-supported $[H_2Re_3(CO)_{12}]^-$ has been given by catalytic test reactions and EXAFS analysis [12].

In both examples the fragmentation of the metal carbonyl clusters forms ensembles of surface mononuclear metal carbonyl complexes that retain the nuclearity of the cluster precursor.

Note also that oxidative fragmentation reactions can be reversed. The oxidised carbonyl surface species (viz. Rh(I) [13], Ru(II) [14], Os(II) [15] on silica, Rh(I) on alumina [8,16]) can be reductively carbonylated to regenerate the original physisorbed molecular clusters.

As a consequence of the strong chemical interaction between MC and oxide surfaces, only a few of these grafted oxidised species give rise to metallic particles by thermal decarbonylation (e.g. Rh(I) [13], Ru(II) [14] on silica and Rh(I) on alumina

[16]), whereas drastic treatments of hydrogen reduction at relatively high temperatures are generally required (e.g. Ru(II) [17], Os(II) species on alumina [18,19]).

4. Formation of highly dispersed metal particles

It is clear from the previous discussion that the thermal decomposition of metal carbonyls on hydroxylated supports leads to the formation of highly dispersed oxide species. The high stability and low reducibility of these oxidised species often preclude obtaining of the zero-valent species. Only with very stable metal clusters is there no evidence of any surface oxidative fragmentation reaction.

The decarbonylation of $[Ir_4(CO)_{12}]$ dispersed on γ-Al_2O_3 in He at 473 K, as indicated by infrared and EXAFS spectroscopy, takes place with little or no disruption of the tetrahedral metal frame [20]. Similarly, decarbonylation of magnesia supported $[HIr_4(CO)_{11}]^-$ and $[Ir_6(CO)_{15}]^{2-}$ takes place in helium at 573 K [20]. Decarbonylation of magnesia-supported $[Pt_{15}(CO)_{30}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$ also appears to take place without significant changes in the metal framework structures, as indicated by EXAFS [20].

There have, however, been a number of apparently successful efforts to produce small metal aggregates (between 10 and 20 Å) by decomposition and reduction in mild conditions of chemisorbed carbonyls [6], but their size is larger than that of the original metal framework because the naked cluster is unstable and some particle growth occurs.

In the case of highly dispersed rhodium catalysts prepared by deposition of $Rh_6(CO)_{16}$ on SiO_2, γ-Al_2O_3, TiO_2 and carbon, small metal entities ($\leq$10 Å) were present on the freshly prepared samples [21]. However, larger aggregates of rhodium were also present, as indicated by SAXS and TEM investigations. These results suggest that even at 298 K surface aggregation processes occur. Reduction with H_2 at 473–673 K leads to the production of larger particles (>200 Å). TEM data confirm the occurrence of metal aggregation, the changes in particle size distributions being also connected to the nature of the support [21].

The decomposition of iron carbonyls on various supports has been widely studied, because the production of small metallic particles has been found to be very difficult using conventional impregnation techniques. In particular, there was a great deal of interest in improving the selectivity of Fischer–Tropsch catalysts.

For instance highly dispersed iron catalysts were obtained from $Fe(CO)_5$ and $Fe_3(CO)_{12}$ adsorbed on various metal oxides [22,23]. With alumina as the support both catalysts gave same conversion (around 3–4%) working at 533–543 K under 10 atm ($CO:H_2=1:1$).

Lower olefins were produced with high selectivity (57% starting from $Fe(CO)_5$ and 43% from $Fe_3(CO)_{12}$); a result in marked contrast with the Schulz–Flory product distribution observed with conventional Fischer–Tropsch iron catalysts. Unfortunately the unusual selectivity is relatively short-lived: the initial product distribution is maintained after 24 h on stream, but changes after 48 h to the conventional Schulz–Flory of a traditionally prepared catalyst. An electron microscopy investigation showed that the original very small metal particles (less than 14 Å) had increased during the 48 h to 200–500 Å. Electron microscopy confirmed that sintering took place under reaction conditions at only 543 K.

The most careful studies on highly dispersed metal iron particles, prepared after low-temperature (393 K) decomposition in a flow of helium of supported iron carbonyls, were conducted by Brenner [24] and Brenner and Hucul [25].

The degree of dispersion is a function of many variables (viz. the nature of support, loading, the temperature of activation) and quite independent of the impregnation techniques and the nuclearity of the carbonyl precursor, although it is always much higher than that of conventionally prepared catalysts (Table 1).

Yermakov was a pioneer in using allylic complexes as precursors to highly dispersed supported metals [26]. At the same loading and with a reduction temperature as high as 773 K, the dispersion of palladium in samples prepared via organometallic compounds remains higher than in those prepared by conventional methods [27]. A small-angle X-ray investigation confirmed the high-metal dispersion, the size of the metal particles falling in the range 2–20 Å [28].

Table 1
The dispersion of supported iron catalysts[a] [24]

Catalyst	Loading (% Fe)	Net chemisorption (cm^3, STP)	Fe dispersion (%)
$Fe_3(CO)_{12}$	0.51	0.234	46
$Fe_2(CO)_9$	0.50	0.235	47
$Fe(CO)_5$	0.48	0.345	71
$Fe(CO)_5$[b]	0.48	0.027	5.6
Fe[b]	0.33	0.000	0.0
Fe[b]	3.6	0.030	0.83
Fe[b]	8.5	0.029	0.34

[a] The chemisorption was measured at $P(CO)=16$ Pa on 0.5 g of catalyst.

[b] Calcined in flowing O_2 at 673 K for 30 min and then reduced in flowing H_2 for 1 h at 773 K and cooled in He.

Table 2
Selected organometallic complexes for the preparation of supported metal catalysts

Cobalt	$[Co(allyl)_3]$, $[Co(AcO)_2]$, $[Co_2(CO)_8]$
Iridium	$[Ir(allyl)_3]$, $[Ir(CO)_2(acac)_2]$, $[KIr(CO)_4]$
Nickel	$[Ni(allyl)_2]$, $[Ni(acac)_2]$, $[Ni(C_5H_5)_2]$, $[Ni(CO)_4]$
Platinum	$[Pt(allyl)_2]$, $[Pt(C_4H_7)_2]$, $[Pt(acac)_2]$
Palladium	$[Pd(allyl)_2]$, $[Pd(allyl)(C_5H_5)]$, $[Pd(AcO)_2]$, $[P(acac)_2]$
Rhodium	$[Rh(allyl)_3]$, $[Rh(AcO)_2]_2$, $[Rh(C_5H_5)(CO)]_2$, $[Rh(acac)_3]$, $[Rh(CO)_2(acac)]$
Ruthenium	$[Ru(acac)_3]$, $[Ru(C_5H_5)_2]$, $[Ru(CO)_5]$

A selection of organometallic halide-free compounds useful for the preparation of monometallic catalysts is presented in Table 2.

5. Organometallic chemical vapour deposition

The technique of chemical vapour deposition of organometallic compounds (OM-CVD) [29] is now widely employed in solid state chemistry and electronics for the selective deposition of mono- or polymetallic films of high purity [30]. The advantages of CVD for integrated circuit applications have been reviewed [31], and include selectivity, conformal step coverage, high throughput and low cost. However, the technique has been little used in the field of heterogeneous catalysis; i.e. few examples have been reported on its application in the preparation of oxide-supported metal particles and films [32,33]. There are potential advantages in the case of crystalline oxides, such as zeolites. The conventionally used ion-exchange or wet-impregnation techniques have no general applicability in heterogeneous catalysis for the preparation of high-purity and high-performance materials [32].

Organometallic chemistry has made available a number of volatile complexes of all the metals of interest in catalysis (see Table 2), with the right size and reactivity to be used for the preparation of zeolite-entrapped metals via the CVD technique.

The preparation process of supported metals by this technique [34] requires two steps: (a) volatilisation and deposition inside the cavities of the zeolite of an organometallic compound; (b) thermal decomposition of the organometallic species entrapped inside the zeolite by controlled heating in hydrogen atmosphere.

The OM-CVD technique has been successfully applied to the preparation of non-acidic zeolite-supported Pd and Pt for hydrocarbon conversion. The mononuclear complexes $[(C_3H_5)Pd(C_5H_5)]$ and $[Pt(hfa)_2]$ have been found to fulfil the requirements for CVD inside large pore zeolite (NaY, KL). The achievement of a good dispersion of the metal precursor inside the zeolite pores has been shown to be critically dependent upon the deposition conditions, i.e. the sublimation temperature and the flow of the inert carrier gas. The best experimental conditions are summarised in Table 3.

A second major advantage of the CVD technique is that the preparation and activation of the catalyst can be directly carried out inside the reaction vessel. The metal phase is, in fact, simply obtained by heating the entrapped precursor in a stream of flowing hydrogen. This process does not critically depend upon the experimental conditions, but rather is governed by

Table 3
Conditions for organometallic chemical vapour deposition of Pd and Pt complexes

Organometallic precursor	Zeolite	Deposition temperature (K)	Argon flow (ml/min)	Metal loading	
				Calculated (%)	Found (%)
$[(C_3H_5)Pd(C_5H_5)]$	NaY	298	9–10	2	1.8
	KL	298	8–9	2	1.8
$[Pt(hfa)_2]$	KL	343	2	1	0.85
	HL	343	2	1	0.85

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the reactivity of ligands. All conventional drying, calcination, and reduction procedures, which traditionally affect the final properties of the catalyst, can therefore be avoided.

In addition, the CVD technique will prevent acidity being created upon formation of metal particles, since reduction is accomplished via reductive elimination of ligands. On the contrary, in the case of the conventional ion-exchange route [35], protons are formed stoichiometrically upon reduction of the metal cation

$$M^{n+} + n/2\,H_2 \rightarrow M^0 + nH^+$$

The thermal decomposition of entrapped $[(C_3H_5)Pd(C_5H_5)]$/NaY has been followed by a temperature programmed decomposition technique (TPRD), and the results are summarised as

$$[(C_3H_5)Pd(C_5H_5)]/NaY \overset{H_2}{\rightarrow} Pd^0/NaY + C_3H_8 + C_5H_{10}$$

A clean metal surface is thus formed below 473 K. In addition, the absence of any evolution of methane indicates that the complex is completely transformed into clean palladium particles in H_2 atmosphere. Any carbon adventously deposited on the metal surface would be removed as methane under TPRD conditions.

The entrapped $[Pt(hfa)_2]$/KL shows the evolution of hexafluoroacetylacetone as a single peak at about 538 K according to the reaction

$$[Pt(hfa)_2]/KL \overset{H_2}{\rightarrow} Pt^0/KL + 2hfa\,H_{(gas)}$$

The removal of ligands and the formation of entrapped metal particles is complete only at about 623 K. This temperature is higher than the one needed in the previous case involving Pd, but it is low enough to prevent fast aggregation to large metal particles and to avoid formation of carbon on metal surfaces [36]. EXAFS investigations suggest a coordination number of Pt between 5 and 6, which remains constant even after a catalytic test at 773 K, corresponding to particles of about 7–8 Å in diameter [37].

It was shown that $[Ni(CO)_4]$ can be deposited on activated carbon in a fluidised bed and in a second step can be decomposed at 523 K in a dinitrogen atmosphere; at high loadings (7–10 wt% Ni) nickel particles deposited on the support were much larger than those prepared by the impregnation method (aqueous solution of nickel acetate) [38].

In a similar way Kölher et al. [39] have obtained Pt/SiO_2, Pt/Al_2O_3 or Pt/TiO_2 catalysts starting from $[Pt(acac)_2]$ with dispersion ranging from 0.4 to 0.7 depending on the nature of the support and the metal loading. CVD of platinum acetylacetonate is a useful method for the preparation of supported platinum catalysts. The use of a fluidised-bed reactor leads to a homogeneous metal loading, which can be varied over a wide range. Even high-loaded catalysts exhibit higher dispersion than conventionally prepared samples.

Very recently, a versatile one-step method for preparing highly dispersed silica-supported rhodium catalysts using OM-CVD was described [40]. Vapour of a rhodium complex is brought into contact with silica in a fluidised-bed in a special reactor designed to work under reduced pressure (50–100 Torr). The introduction of a small amount of hydrogen allows rhodium to be deposited at low temperatures (373 K). Small aggregates (10–20 Å) and high dispersion (0.95–0.70) are obtained. Three convenient organometallic precursors $[Rh(CO)_2Cl]_2$, $[Rh(C_3H_5)_3]$ and $[Rh(acac)(CO)_2]$ were used, owing to their suitable vapour pressure under experimental conditions.

The OM-CVD technique can also be used for the preparation of unusual mono or bimetallic phases inside zeolites. Intrazeolite redox chemistry of Mn^{2+} cation is practically absent in the case of conventional ion-exchanged materials, because of the very high stability of the Mn^{2+} ion. On the contrary the neutral and volatile $Mn_2(CO)_{10}$ carbonyl species can be deposited by CVD inside NaY cavities and then decomposed via mild thermal removal of CO under inert or hydrogen atmosphere [41]. TPD experiments show that a metallic zero-valent manganese phase cannot be obtained, since the decarbonylation process is immediately followed by oxidation to MnO with parallel H_2 evolution in the presence of traces of water.

$$Mn_2(CO)_{10} \rightarrow 2Mn^0 + 10CO$$

$$2Mn^0 + 2H_2O \rightarrow 2MnO + H_2$$

A redox chemistry takes place inside the zeolite: MnO can be reduced by CO to generate quite stable intrazeolitic manganese carbonyls (probably Mn^0 or Mn^I), while oxidation of MnO to Mn_2O_3 is a facile process, which can be easily reversed by monoelectronic hydrogen reduction below 723 K. With this approach a bimetallic Rh/Mn phase, with the surface presumably enriched in Mn, can be obtained by CVD deposition of $Mn_2(CO)_{10}$ on Rh particles entrapped inside a NaY zeolite followed by reduction with H_2. Conventional H_2 reduction of the ions Rh^{3+} and Mn^{2+} exchanged inside the same zeolite leads, instead, to the formation of rhodium carbonyl species interacting with Mn^{2+} ions [42].

It follows that CVD can be a technique to prepare bimetallic particles, which cannot be easily obtained by traditional techniques.

A similar two-step approach was also used to prepare Pt–Sn bimetallic particles supported on MgO for the selective hydrogenation of unsaturated aldehydes [43]. In this case platinum is firstly introduced by solvent impregnation of $Pt(acac)_2$ while CVD is used to introduce a tetra alkyl tin precursor. A strong enhancement towards the hydrogenation of the carbonyl group is observed with respect to coimpregnated Pt–Sn/MgO catalysts.

Remarkably, the Kellog advanced Ammonia Process is based on a novel ruthenium catalyst 10–20 times more active than traditional iron catalysts. The patent clearly indicates that the catalyst is prepared by subliming $Ru_3(CO)_{12}$ onto a graphite-containing carbon support which is impregnated with an aqueous solution of rubidium nitrate [44].

6. Conclusions

Organometallic compounds, both large molecular metal clusters and volatile mononuclear species, have been demonstrated to be suitable and flexible precursors for preparing highly dispersed metal particles supported on metal oxides and zeolites. This approach is leading to new mono and bimetallic catalysts that have potential technological advantages over conventionally prepared systems [45–49] (although examples of accurate comparisons are surprisingly sparse).

The metal phase is usually obtained by simple ligand removal under mild conditions preventing, to a large extent, sintering to large crystallites or carbide formation. OM-CVD-based catalysts showed the additional advantage of a very clean metal phase, due to the absence of any contamination from solvents or anions containing halogens or sulphur.

These molecular organometallic-based catalysts are often structurally well-defined and therefore amenable to detailed spectroscopic characterisation [20]. These model materials also offer good opportunities for a better understanding of the structure and reactivity of supported metal catalysts used in industry [50].

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