Molecular metal carbonyl clusters and volatile organometallic compounds for tailored mono and bimetallic heterogeneous catalysts

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Abstract

Specific studies carried in Milan laboratory in the application of metal carbonyl clusters to preparation of supported catalysts are reviewed. Examples are reported of catalysis by heterogeneous organometallic surface species, such as 1-butene isomerisation catalysed by silica-anchored osmium carbonyl species, or of catalysis by very small metal particles produced under catalytic conditions, such as ethylene hydroformylation using silica supported $[Rh_{12}(CO)_{30}]^{2-}$ as precursor. Highly active bimetallic FeIr/MgO catalysts for methanol synthesis, have been prepared by controlled reductive decomposition of physisorbed $[Et_4N]_2[Fe_2Ir_4(CO)_{16}]$ and $[Et_4N]_2[Fe_2Ir_2(CO)_{12}]$ clusters. In these examples, evidence of the nature of the catalytic entities is reached by in situ DRIFTS characterisation under catalytic conditions or using EXAFS measurements. Metal particles deposited inside the zeolitic cavities have been obtained by mild reduction conditions of entrapped organometallic compounds introduced by chemical vapour deposition (CVD). In this way, non-acidic Pt/KL, Pd/NaY catalysts for hydrocarbon reforming have been prepared. Bimetallic Pt/Re and Rh/Mn particles, entrapped inside a NaY zeolite, have been easily obtained by CVD of $M_2(CO)_{10}$ carbonyls (M = Re, Mn) on pre-reduced metal particles.

Keywords: Tailored metal catalysts; Inorganic oxides; Zeolites; Metal carbonyl clusters; Volatile complexes; Organometallic complexes

1. Introduction

In the last 15 years the original idea of studying supported molecular clusters as 'heterogenized homogeneous catalytic systems' [1] has evolved into the concept of supported clusters as precursors of metallic catalysts [2]. In order to give further support to this approach to new metallic catalysts, the chemical behaviour of molecular metal carbonyl fragments bound to the surface of

an inorganic oxide has been rationalised through the concept of 'surface organometallic chemistry' involving specific sites of the support, regarded as a rigid mono or multidentate ligand [3]. This new preparative approach has been extended, although less extensively, to the surface of carbon [4] or to the cavities of zeolites [5]. Highly dispersed metal crystallites, as well as surface bound molecular species of specific nuclearity, can be obtained by reaction of metal carbonyl clusters with different surfaces or inside the cages and cavities of zeolites [6]. With zeolites, the problem of the

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penetration inside the cavities of rather large solvated molecular species such as metal carbonyl clusters can be avoided by chemical vapour deposition (CVD) of volatile organometallic species, which can be a metal carbonyl or a traditional organometallic compound. The process of preparation of a heterogeneous metal catalyst by this technique [7] requires two steps: (a) volatilisation and deposition inside the cavities of the zeolite of a metal carbonyl or of an organometallic compound, which must fulfil the requirements of small size, well defined shape and a certain thermal stability; (b) thermal decomposition of the organometallic species entrapped inside the zeolite by controlled heating in hydrogen atmosphere.

In this way metal particles are produced by mild removal of ligands such as CO or hydrocarbon moieties or other volatile ligands. This process is quite simple when compared to the traditional calcination/reduction cycles for the decomposition of supported metal salts or of metal ions exchanged inside a zeolite.

The catalysts so obtained are characterised by the total absence inside the cavities of residues of halides or other anions and of protonic acidity. In addition, it is possible to obtain unusual alloys or cherry crystallites by CVD of an organometallic species on the top of particles of another metal [8].

This article will summarize and describe some investigations carried out in our laboratories on the properties of heterogeneous mono and bimetallic catalysts obtained either by decomposition of metal carbonyl clusters supported on inorganic oxides or of volatile organometallic compounds deposited inside zeolites.

2. Catalytic reactions with heterogeneous metal catalysts obtained from supported metal carbonyl clusters

We first studied the catalytic behaviour of the silica-anchored hydrido cluster $Os_3(CO)_{10}(\mu$-$H)(\mu$-$OSi\leqslant)$ which, under inert atmosphere or under vacuum, is stable up to about 438 K [9].

This surface species interacts reversibly with olefins which can be hydrogenated [10] or isomerised [11,12] under very mild conditions.

This interaction has been first studied by transmission IR spectroscopy on pressed disc. However, diffuse reflectance FT-IR spectroscopy (DRIFTS) allows observation directly on the catalyst in granular form, working under real catalytic conditions (gas composition, temperature, gas pressure). In this way, many of the problems associated with studies in situ with the pressed disc approach can be avoided [13].

We have carried out in situ DRIFTS studies on the interaction at 343 K of 1-butene with the surface anchored osmium cluster, using a porous silica as support. A slow formation of an adduct with 1-butene occurs after 30 min of contact, characterised by the replacement of the weak band at 2112 cm^{-1} with a new one at 2104 cm^{-1}. In addition, a modification of the intensity ratio of the bands at 2077 and 2065 cm^{-1} takes place (Fig. 1-a). Both the original anchored cluster and
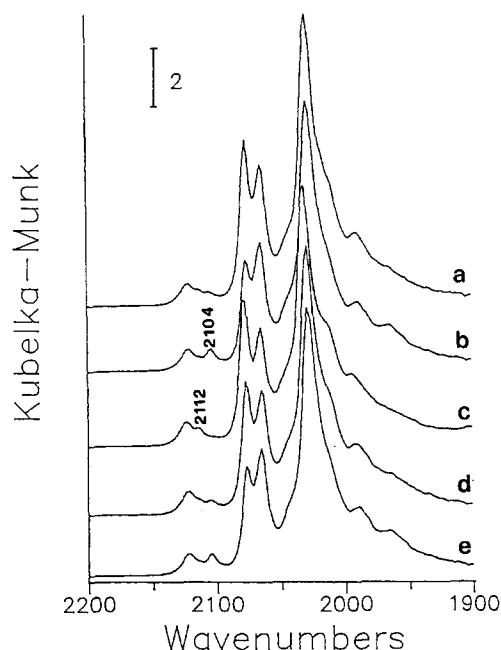

Fig. 1. Sequential DRIFT spectra in the ν(CO) region of $Os_3(CO)_{10}(\mu$-H)(μ-OSi$\leqslant$): (a) after 30 min in flow of 1-butene at 343 K; (b) as in a after 3 h; (c) as in b after 30 min of N_2 purging at 343 K; (d) as in c after 30 min in flow of 1-butene at 343 K; (e) as in d after 3 h.

an intermediate olefin adduct are simultaneously present, in agreement with previous findings of Basset et al. [10]. After 3 h at 343 K the concentration of the olefin adduct is the highest (Fig. 1-b). Spectral changes are completely reversed at 343 K by purging in nitrogen (Fig. 1-c), with quantitative regeneration of the original anchored cluster, suggesting that the adduct does not involve any CO replacement.

$$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\!\!<) \overset{C_4H_{10}}{\underset{N_2}{\rightleftharpoons}} Os_3(CO)_{10}$$

$$(\mu\text{-}H)(OSi\!\!<)(C_4H_{10})$$
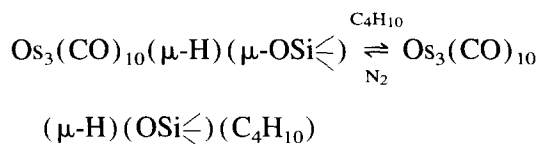
A subsequent treatment in 1-butene at 343 K quantitatively regenerates the olefin adduct (Fig. 1-d, 1-e). Our spectroscopic results strongly support the mechanism of the reversible opening of an Os–O–Os bond, proposed by Basset et al. [10].

The isomerisation of 1-butene was also investigated working at higher reaction temperature, viz. 388 K. At the beginning of the catalytic reaction, the anchored cluster being still intact, a rather low initial conversion is observed. After a long induction period (14 h) a final steady state conversion value of about 36% was reached, with parallel change of the cis/trans ratio from 0.9 to 0.7. Both FT-IR and XPS studies identified the oxidised surface species $[Os(CO)_x(OSi\!\!<)_2]_n$ ($x=2,3$) as the real catalytic entity under steady state conditions and that the oxidative fragmentation process of the anchored cluster was favoured by the presence of the olefin [12].

In situ DRIFTS studies in flow of N_2 at 388 K indicate that this surface fragmentation is complete after only 8 h (Fig. 2). On the contrary previous studies in transmission mode on pressed disc indicated that after 58 h bands characteristic of the anchored cluster were still present in the infrared spectrum [12]. DRIFTS spectra reported in Fig. 2 clearly establish that the surface oxidative fragmentation process occurs without involvement of intermediates as evidenced by the presence of few isosbestic points.
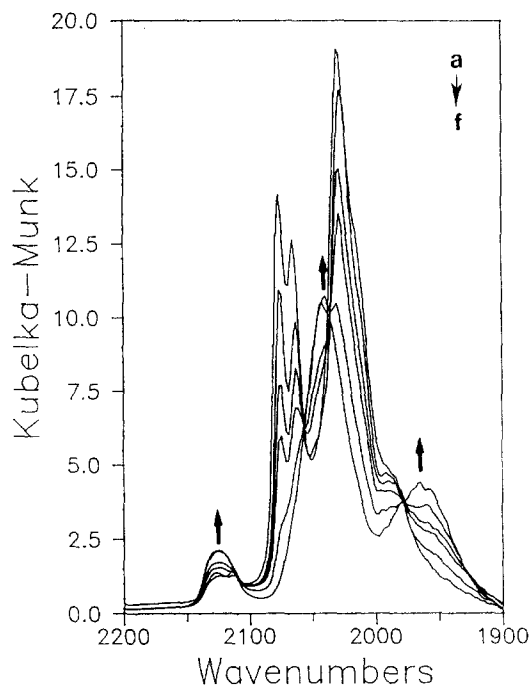

Fig. 2. Sequential DRIFT spectra in the $\nu(CO)$ region of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\!\!<)$ in flow of N_2 at 383 K: (a) after 30 min; (b) after 1 h; (c) after 2 h; (d) after 3 h; (e) after 5 h; (f) after 8 h.

By this investigation it is confirmed that, in the presence of 1-butene, cluster degradation proceeds faster, with the involvement of olefin intermediates as shown by the absence of isosbestic points (Fig. 3).

DRIFTS spectra recorded for over 100 h at 388 K under catalytic atmosphere confirm the good stability of the oxidised species. These molecular surface metal catalysts can be poisoned by CO and activated by hydrogen. On the contrary, silica-supported metallic catalyst, prepared by reducing the osmium surface oxidised species in H_2 at 573 K, are characterised by a very different activity and selectivity, which are not influenced by addition either of CO or H_2 [12].

Therefore we have strong spectroscopic and catalytic evidence of a surface catalysis at molecular level, involving carbonyl osmium species grafted to the silica surface, as the anchored cluster at lower temperature or as oxidised species.

The observed inhibition effect of CO on the catalytic activity on both kind of catalysts is not simply due to preferential saturation of the free
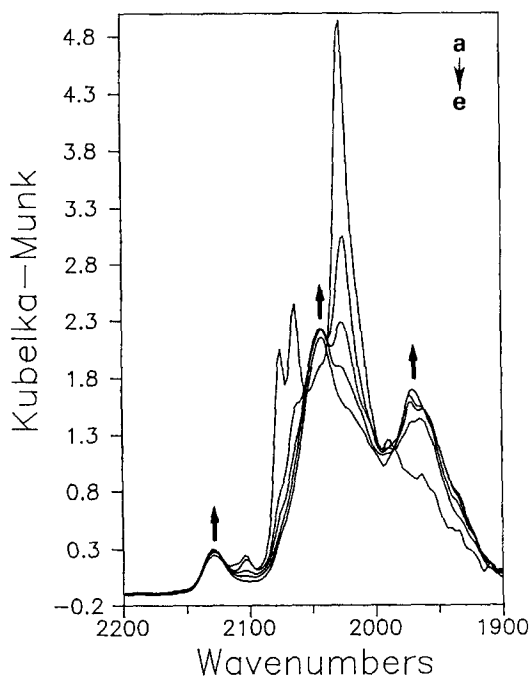
Fig. 3. Sequential DRIFT spectra in the ν(CO) region of $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}\lessapprox)$ in flow of 1-butene at 383 K: (a) after 10 min; (b) after 1 h; (c) after 2 h; (d) after 3 h; (e) after 5 h.

coordination sites of the surface osmium centers in competition with 1-butene. Significant structural modifications of the osmium surface molecular species are already observed at 388 K: in situ IR studies gave evidence of a partial reconstruction of the original cluster moiety via reductive carbonylation of the oxidised species. At higher reaction temperatures the formation of volatile $Os_3(CO)_{12}$ was observed [14]. This is likely to constitute a severe limitation in using this kind of molecular heterogeneous catalysts in reactions involving CO as reagent.

We confirmed such a statement by studying vapour phase ethylene hydroformylation at 453 K, using as catalyst either the anchored osmium cluster or the oxidised surface osmium carbonyl fragments. Formation of oxygenated products is not observed but only a very moderate hydrogenation to ethane. Complete deactivation occurs after only 2 h, due to the quantitative transformation of the surface-grafted osmium carbonyls into the volatile $Os_3(CO)_{12}$ and $H_4Os_4(CO)_{12}$ clusters. The metal leaching from the support into

the gas phase, as volatile carbonyl species, is prevented on basic surfaces, such as MgO [15]. For instance, anionic Os carbonyl clusters generated in situ at 548 K during catalytic CO hydrogenation are stabilised by strong ionic interactions with the support.

With this point in mind we studied the $[Rh_{12}(CO)_{30}]^{2-}$ cluster anion supported on silica as a potential molecular heterogeneous catalyst for vapour phase ethylene hydroformylation [16]. In addition to the expected low volatility under catalytic conditions of this anionic species, the presence of metal cations associated with the Rh_{12} framework was likely to offer a further advantage at molecular level. In fact it was known the promotion effect for CO insertion by addition of Zn^{2+} [17] and Na^+ [18] to conventional oxide-supported metallic rhodium catalysts.

A selectivity of about 32% to propanal was observed with silica supported $Na_2[Rh_{12}(CO)_{30}]$ working at 453 K, without any induction period [19]. The parallel reaction was ethylene hydrogenation to ethane. The absence of any induction period, together with the constant activity to hydroformylation for over 100 h suggested that the cluster framework could be stable under reaction conditions as the catalytically active species. This stability under reaction conditions is likely to be explained with the presence of $CO + H_2$ atmosphere, preventing any oxidative fragmentation processes at 453 K. This first hypothesis has been supported by in situ infrared studies, carried out on a pressed disc of the freshly prepared catalyst, immediately exposed to hydroformylation mixture under catalytic conditions [16].

There is no evidence of sintering to large rhodium crystallites during the catalytic process, because XRD studies on used catalysts did not detect the presence of metallic particles larger than 20 Å [19]. The unpromoted catalyst, prepared from $[Rh_4(CO)_{12}]$, was still active but the selectivity to propanal was 25% only. The very low activity of supported metallic rhodium, conventionally prepared from $RhCl_3$, could be explained in terms of metal dispersion, because XRD studies

on used catalyst indicate the presence of particles of at least 40 Å [19].

The selectivity to propanal can be increased, as expected, to 50% working at lower temperature, 393 K instead of 453 K. At this temperature, however, a long induction period (20 h) was observed to reach a steady state conversion suggesting a slow transformation of the starting anionic cluster into more active species. In agreement with this hypothesis, when the fresh catalyst was pre-treated in Ar flow at 393 K for 3 h before the admission of the hydroformylation mixture, a significant increase of the catalytic activity, was observed without any induction period [20].

In agreement with the well-known chemistry of supported rhodium cluster carbonyls [21], DRIFT investigations indicate that during the pre-treatment at 393 K a disruption of the Rh_{12} cluster framework into the isolated Rh^I gem-dicarbonyl species takes place. A DRIFT investigation under real catalytic conditions showed only a broad band around 2035 cm^{-1} characteristic for CO linearly bonded on metallic particles suggesting that a fast surface restructuring by reductive carbonylation of the isolated $Rh^I(CO)_2$ sites has thus occurred [20].

Our findings seem to indicate an important role of small metallic particles as active species for olefin hydroformylation. As already pointed out by other authors [22] for the Rh-Y zeolite systems, we confirm that $Rh^I(CO)_2$ species itself would not be considered to be the active species.

We extended our investigations to the hydrogenation of carbon monoxide. Recent studies have shown that uniformly dispersed alloys having a predetermined composition can be obtained by controlled thermal decomposition of supported mixed metal carbonyl clusters [23]. Therefore we studied the catalytic properties of bimetallic Fe–Ir particles supported on MgO in methanol synthesis from syn-gas, using the mixed Fe–Ir clusters $[Et_4N]_2[Fe_2Ir_4(CO)_{16}]$ or $[Et_4N]_2[Fe_2Ir_2(CO)_{12}]$ as precursors. Both clusters are only weakly physisorbed on MgO, as suggested by both their infrared spectra as adsorbed

species and their easy extraction from the surface with the solvent used for the impregnation.

Treatment of the physisorbed species with a flow of H_2 from 298 K to 623 K is needed for the removal of the tetraethyl ammonium cations and of carbonyl ligands with formation of a catalytically active bimetallic phase [24].

These cluster-derived catalysts were tested in methanol synthesis from $CO + H_2$ (2:1) working at 3.1 MPa and 503 K, and compared to mono-metallic MgO-supported Ir and Fe catalysts prepared starting from physisorbed $Ir_6(CO)_{16}$ and $Fe(CO)_5$ carbonyls, respectively. The selectivities after 20 h on stream are showed in Fig. 4.

Monometallic iron and iridium catalysts are characterised only by Fischer–Tropsch and water–gas shift activities; on Ir/MgO the selectivity to oxygenates below 27%. On bimetallic cluster-derived catalysts the rate of methanol production is increased by two orders of magnitude when respect to monometallic catalysts, whereas methane is produced to a limited extent. Upon raising the Fe to Ir ratio in the cluster precursor from 2:4 to 2:2, the rates of carbon monoxide conversion and methanol formation almost doubled, the selectivity to oxygenates remaining around 80%.

It follows that bimetallic clusters seem to be unique precursors for bimetallic Fe–Ir catalysts characterised by high activity and selectivity to methanol. In fact, by optimising the process conditions (temperatures between 488–523 K and
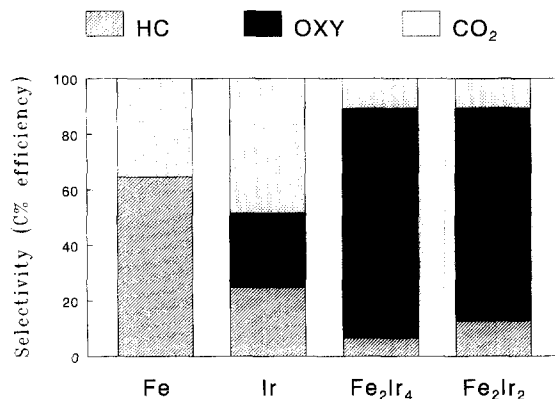

Fig. 4. Selectivity of MgO-supported mono and bimetallic Fe and Ir cluster-derived catalysts in CO hydrogenation at 503 K, 3.1 MPa, $H_2/CO = 2$.

total pressure of 6.1 MPa) a selectivity for oxygenates above 90% can be reached. Carbon monoxide conversion ranges from 6 to 15% according to temperatures with methanol productivity of more than 100 mol/mole$_{Ir}$·h [24].

In order to explain these observations, the nature of the active sites were investigated by different surface techniques [24]. H_2 chemisorption data on catalysts obtained from bimetallic clusters by hydrogen reduction at 673 K suggest that iridium is highly dispersed, without any significant coverage by iron species. Accordingly, preliminary EXAFS investigations on in situ pre-reduced Fe_2Ir_2–MgO give coordination numbers of around 7.5 for Ir–Ir and 1.4 for Ir–Fe. No evidence for Ir–O contributions is observed. The Ir–Ir coordination number is significantly lower than the corresponding bulk value, which is 12, confirming a high dispersion of iridium particles of dimension around 7–8 Å. The presence of Ir–Fe contributions indicates the presence of bimetallic clusters; the difference between Ir–Ir and Ir–Fe coordination numbers suggests that only a small fraction of the iridium atoms is interacting with iron atoms; the absence of Ir–O contributions is consistent with a structural hypothesis of very small iridium particles stabilised on the MgO surface by interfacial iron atoms.

The role of the basic MgO surface is likely to stabilise the anionic cluster precursor, preventing an initial disruption of cluster framework with segregation of iron during the thermal pretreatment.

In agreement with this hypothesis, the [$Et_4N]_2[Fe_2Ir_4(CO)_{16}$] anionic cluster was found to have very low stability when supported on silica. Upon H_2 pre-treatment, the final cluster-derived catalysts shows only classical Fischer–Tropsch activity and a very low selectivity to methanol (Fig. 5). This remarkable difference from MgO-supported catalyst is probably due to the quick fragmentation on silica of the bimetallic clusters, before the metal particles are formed, with parallel oxidation of the iron fragments by oxidative addition of the surface hydroxyl groups.
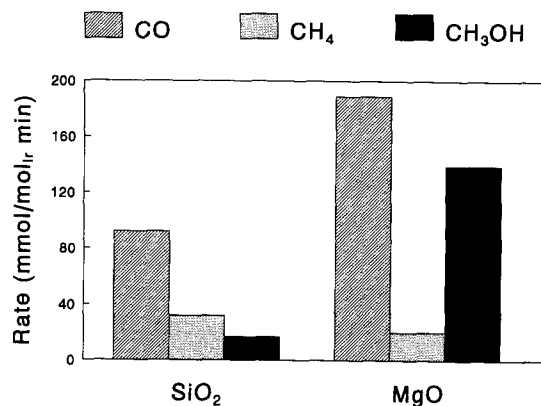

Fig. 5. Influence of the support on the activity and selectivity of supported catalysts derived from [EtN$_4$]$_2$[Fe$_2$Ir$_4$(CO)$_{16}$] in CO hydrogenation at 523 K, 1.1 MPa, H_2/CO = 2.

3. Chemical vapour deposition in the preparation of mono and bimetallic particles inside zeolite cages

The chemical vapour deposition (CVD) has long been used in material science and electronics, but is only slowly gaining acceptance in the catalysis community [25].

Clean and relatively flat surfaces of monocrystalline electronic materials have to be replaced by a complex network of small channels in porous, high surface area supports or by the very reactive surfaces of highly basic or highly acidic materials. In addition, the deposition and decomposition steps need to be separated because a proper choice of the decomposition process is required for the optimisation of the topological and electronic properties of the supported metal particles. It follows that chemical vapour deposition as a technique for catalyst preparation is a much more demanding and less controlled task than the clean formation of a thin metallic film on a silicon surface. With this in mind we have been able to find few volatile organometallic compounds of the right size and shape which are chemically and thermally stable enough to be deposited from the vapour phase inside the porous structure of zeolites.

Many features appear to be particularly promising in the catalysis field. First is the complete absence of protonic sites formed during the reduc-

tion process. In ion exchanged catalysts, zeolite protons are generated upon hydrogen reduction of the exchanged cations; according to the reaction:

$$M^{n+} + n/2H_2 \rightarrow M^0 + nH^+ \quad (M = Pt, Pd \text{ etc.})$$
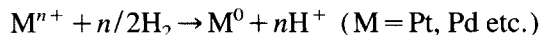
leading to a bifunctional catalyst, with acidic properties.

Post neutralisation with aqueous NaOH or by reaction with NaN_3 is usually required [26], however it is rarely complete and a strict control of experimental conditions is needed for preventing modification of the topology and electronic properties of metallic particles. The second key feature is the absence of any contamination from the impregnation solvents or from undesired dopants

Fig. 6. Activity and selectivity to ring opening (R.O.) and ring enlargement (R.E.) in MCP reforming at 623 K and 0.1 MPa of Pd/ NaY catalysts obtained: (a) from chemical vapour deposition (CVD) of [Pd(C_3H_5)(C_5H_5)]; (b) from ion-exchange (I.E.) of [Pd(NH_3)$_4$] (NO_3)$_2$.

coming from the counter-anions of the added salt (e.g. chlorine or sulphur). The third issue is that the conventionally used steps in supported metal catalyst preparation such as drying, calcination and finally reduction, can be avoided, being substituted by a rather mild reduction process, which can be carried out in situ in the catalytic reactor. This should help to reduce the migration of metal atoms or small metal particles outside the channel, favouring the formation inside the zeolite structure of metal particles with clean surfaces and well controlled size and topology.

For instance [Pd(η^3-C_3H_5)(η^5-C_5H_5)] (where η^3-C_3H_5 is a π-allyl ligand and η^5-C_5H_5 is a π-cyclopentadienyl ligand) is a well suited organometallic precursor for CVD inside large-pore zeolites (NaY, KL, NaMor and their acidic counterparts) [27].

Once deposited inside the zeolite structure it can be decomposed to metallic palladium by mild reduction in flowing hydrogen according to the reaction:

$$[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)] \xrightarrow{H_2} Pd^0 + C_3H_8 + C_5H_{10}$$
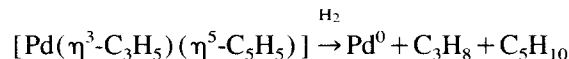
which can be followed by temperature programmed decomposition technique (TPRD) [7]. The highly dispersed, highly active palladium particles produced during the decomposition are efficient catalysts for hydrocarbon reforming reactions. In particular, methylcyclopentane (MCP) conversion at 623 K and atmospheric pressure was chosen as model reaction, since it can differentiate monofunctional (metal-only) catalysts from bifunctional ones, where both acidic and metal functions are present [28].

CVD-derived Pd/NaY, which have no acidic sites, shows a quite constant activity and 100% selectivity to ring opening of MCP to n-hexane, 2-methylpentane and 3-methylpentane. Pd/ NaHY obtained by ion-exchange has instead higher initial activity, followed by a faster deactivation rate, whilst ring enlargement is the predominant reaction as expected for a true bifunctional catalyst (Fig. 6).
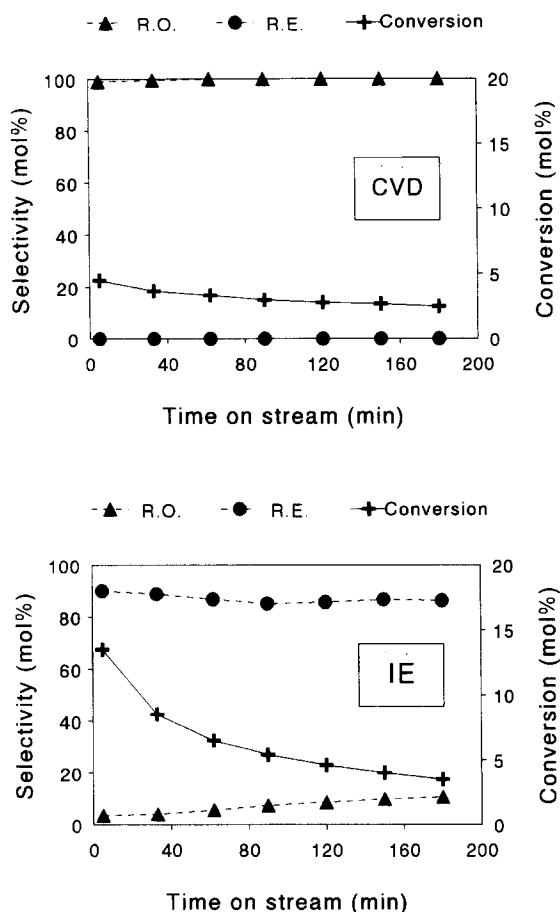
With a neutralised Pd/NaY catalyst obtained by ion-exchange, and subsequent post neutralisation of the protonic acidity, the initial activity is slightly higher with respect to the CVD-based Pd/NaY catalyst, but a fast deactivation is observed. Selectivity for ring opening is always higher than 96%.

In fact, the deactivation process must be ascribed to coke deposition only in the case of bifunctional Pd/NaHY catalyst as shown by a TPO investigation, but another process must be involved in the case of Pd/NaY catalyst obtained by ion exchange followed by neutralisation [27].

It must be recalled that small Pd clusters are formed and stabilised in the presence of surface protons, which should act as chemical anchors for the growing particles [29]. The neutralisation process removes such anchors; therefore sintering of the original small Pd clusters can become appreciable during actual catalysis at elevated temperatures explaining the decrease in activity for the neutralised Pd catalysts.

The same CVD methodology has been applied for the preparation of truly non-acidic Pt/KL catalyst for hydrocarbon aromatization. The complex [Pt(hfa)$_2$] (where hfa is the hexafluoroacetylacetonate ligand) has size and shape, volatility and thermal stability good enough to be an excellent molecular precursor for Pt particles.

The TPRD investigation in a flow of H$_2$/He shows the evolution of hexafluoroacetylacetone as a single peak at around 538 K according to the reaction:

$$[Pt(hfa)_2]/KL \xrightarrow{H_2} Pt^0/KL + 2hfaH_{(gas)}$$
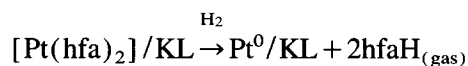
The removal of ligands and the formation of entrapped metal particles is complete only at around 623 K. This temperature is higher than that needed in the previous case involving Pd, but it is low enough to prevent fast aggregation to large metal particles and to avoid formation of carbon on metal surfaces [30].

EXAFS investigations suggest a coordination number of Pt between 5 and 6, which remains constant even after a catalytic test at 773 K, cor-responding to particles of about 7–8 Å in diameter [31]. The structure of entrapped Pt particles was investigated by DRIFTS using chemisorption of CO as a probe. The infrared spectrum is characterised by a fine structure and by location of carbonyl bands at relatively low frequencies, suggesting the formation of carbonyl cluster anions, similar to those of general formula $[Pt_3(CO)_6]_n^{2-}$ ($n = 1$–4) obtained in basic solutions [32]. Therefore it was proposed that very small and electron-rich particles of platinum are formed by the CVD technique in KL zeolites, which are characterised by rather basic sites, which can behave as electron donors.

The catalytic activity of Pt/KL in MCP reforming is that expected for a platinum catalyst, with total absence of acidic sites. At 623 K the only reaction is the ring opening; while at 773 K benzene formation is the major reaction, with an activity rather constant with time on stream. No coke deposition, in agreement with a monofunctional metallic catalyst, is observed by TPO investigation on a used catalyst. This catalyst shows a very high stability, even after two sequential regeneration cycles of oxidation at 673 K and reduction at 773 K [31]. Recent EXAFS investigations [31] show a striking similarity of the structure of the metallic particles before and after the regeneration cycle, confirming the high stability of entrapped Pt particles. In the oxidised sample it appears that metal particles are still located inside the zeolite cavities, but they are only partially oxidised to PtO$_2$. The oxidised part seems to be anchored to the zeolite structure thus inhibiting diffusion of PtO$_2$ and large clustering phenomena.

The CVD technique can be used also 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 [33]. TPD experiments show that a metallic

zerovalent 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.

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

$$2Mn^0 + 2H_2O \rightarrow 2MnO + H_2$$
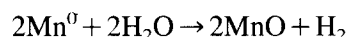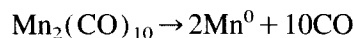
A redox chemistry takes place inside the zeolite: MnO can be reduced by CO to generate rather stable intrazeolitic manganese carbonyls (probably Mn^0 or Mn^I), while oxidation of MnO to Mn_2O_3 is a facile process, which can be easily reversed by monoelectronic hydrogen reduction below 723 K. With this 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 [34].

It follows that CVD can be a technique to prepare bimetallic particles, which can not be easily obtained by traditional techniques. For instance CVD proved to be the most convenient way for preparing zeolite-entrapped rhenium particles from $Re_2(CO)_{10}$, since exchange of the bulky cation $[ReO_2(en)]^+$ (en = ethylendiamine) is a slow process and carbide species are formed upon drastic reduction poisoning the metal surface [35].

Bimetallic Pt/Re particles, entrapped inside the supercages of a NaY zeolite, are easily obtained by CVD deposition of $Re_2(CO)_{10}$ on prereduced Pt particles acting as nucleation sites for the decomposition of the metal carbonyl [8].

These alloy particles are characterised by a high selectivity for deep hydrogenolysis of n-heptane to methane, much higher than that of the single Re and Pt metal catalyst. Interestingly the bimetallic $PtRe_2(CO)_{12}$ cluster carbonyl can not be used as precursor of alloy particles. It is too big to easily enter the windows interconnecting the supercages and most is left at the external surface of the zeolite crystals, where phase separation and Re segregation occur as on an Al_2O_3 surface [36].

4. Conclusions

Organometallic compounds, either large molecular metal clusters or volatile mononuclear species, are 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.

The metal phase is usually obtained by simple ligand removal under mild conditions, preventing, at a large extent, sintering to large crystallites or carbide formation. 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 characterization. These model materials are also offering good opportunities for understanding structure and reactivity in industrial supported metal catalysts.

Acknowledgements

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