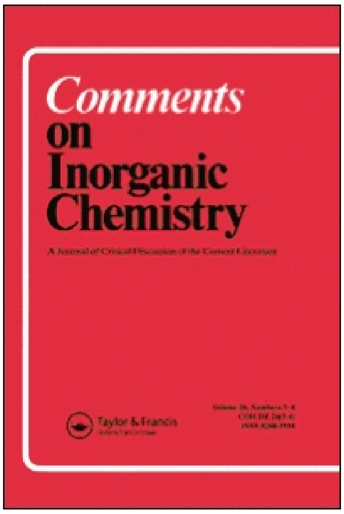

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Advances in the Application of Mössbauer Spectroscopy with Less-Common Isotopes for the Characterisation of Bimetallic Supported Nanoparticles: ^{193}Ir Mössbauer Spectroscopy

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Advances in the Application of Mössbauer Spectroscopy with Less-Common Isotopes for the Characterisation of Bimetallic Supported Nanoparticles: ^{193}Ir Mössbauer Spectroscopy

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A detailed picture of the state of iridium in materials of interest in heterogeneous catalysis can be obtained by ^{193}Ir Mössbauer spectroscopy. This technique can yield unique information on the chemical state of iridium on going from the molecular precursors and its adsorption on the surface of the support. It allows the estimation of the composition of the Ir-containing alloys that are possibly formed during the activation treatments of supported bimetallic systems. In order to point out the possibilities of this technique, the main results obtained in the application of ^{193}Ir Mössbauer spectroscopy to two Ir-containing bimetallic supported nanoparticles, i.e., the Pt-Ir on amorphous silica and the Fe-Ir on magnesia, will be presented and discussed relative to their synthesis and the influence of the preparation methods.

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1. INTRODUCTION

The use of Mössbauer spectroscopy as a tool for the investigation of catalytic systems has been introduced rather recently, starting around 1970. By the end of 1989, over 600 scientific papers had been published.[1] Notwithstanding this, the application of Mössbauer spectroscopy for the characterisation of heterogeneous catalysts has been limited, mainly because only few elements relevant in catalysis are suitable for Mössbauer studies. Iron, tin, iridium, ruthenium, gold, platinum and antimony are the most important Mössbauer elements that are also of importance in catalysis. However, only the Mössbauer resonances of iron and tin have been used extensively in studies of catalytic systems. This is principally due to two favourable features of these two Mössbauer resonances:

1. The low energies of the Mössbauer transitions in ^{57}Fe and ^{119}Sn allow measurements at ambient temperature, and
2. The relatively long half life of the respective ^{57}Co and ^{119m}Sn, the parent nuclides feeding the respective Mössbauer transitions, allows the use of commercial Mössbauer sources for many months.

For elements like iridium, gold and platinum, the high energy of the nuclear transitions allows measurements only at cryogenic temperatures, while the short half life of the respective sources requires the vicinity of a nuclear reactor for the frequent reactivation of the Mössbauer sources.

A major focus in the research carried out in the field of heterogeneous catalysis is to correlate the catalytic properties of a material with its structure (i.e., relationship between particle size and structure, structure sensitivity and metal-support interactions).[2] In this view, Mössbauer spectroscopy is, when it can be applied, a quite powerful method. In fact, it has been of help in the identification of phases, the determination of oxidation states, the attainment of structural information, the determination of particle sizes and the study of the kinetics of solid state reactions. Even though most of the Mössbauer work on catalysts deals with ^{57}Fe and ^{119}Sn, the other elements mentioned above have been used as well, although only sporadically. Several excellent books on Mössbauer spectroscopy[3-8] and reviews on the application of the technique to catalysis are available.[9-12]

In the present paper, we discuss the application of ^{193}Ir Mössbauer spectroscopy in the characterisation of materials of interest in heterogeneous catalysis. With the exception of osmium, iridium is the least abundant of the six platinum group metals. It is of crucial importance in a number of high technology applications and, at least in the past, has been regarded as a strategic material mainly for military purposes and stockpiled by major governments. In recent years it has become more available, the reduced strategic demand for iridium was matched by a decrease in its price, prompting renewed interest by researchers, including those seeking to develop more efficient catalysts.

Supported iridium has been proposed as a catalyst for the partial oxidation of methane to synthesis gas,[13] as well as for the water gas shift reaction.[14] Cativa®, an iridium-based catalyst, is the most significant breakthrough in acetic acid technology for over 25 years.[15] Developed in-house by BP Amoco Chemicals for the acetic acid carbonylation process, Cativa® offers high selectivity, high reaction rates and reduced by-products. Russian scientists[16] developed iridium-based catalysts having specific characteristics, which are unique among the platinum group metals for the selective hydrogenation of organic compounds. Mixed-metal platinum-iridium catalysts have long been known for the reforming of petroleum naphthas[17], and a large interest for iridium-iron catalysts has been shown recently in the synthesis of methanol from synthesis gas.[18–25] Being highly specific to this metal, ^{193}Ir Mössbauer spectroscopy is a rather promising technique, which can be largely applied to the study of the structure of iridium-containing catalytic materials and of their precursors.

In the first part of this paper, we describe the main properties of the ^{193}Ir Mössbauer resonance. In the second part the results obtained up to now in the field of catalysis are discussed.

2. THE 73.0 keV MÖSSBAUER TRANSITION OF ^{193}IR

Both stable isotopes of iridium, ^{191}Ir and ^{193}Ir, have a Mössbauer transition with sufficient resolution for studies of hyperfine interactions. There are, however, several factors, that make the 73.0 keV transition in ^{193}Ir preferable to the 82.4 keV transition in ^{191}Ir. Among them are its slightly narrower natural linewidth, the weak emission of gamma rays from the ^{191}Pt or ^{191}Os source feeding the ^{191}Ir transition and the strong

K-shell photo absorption of gamma rays by the iridium in the absorber in the case of ^{191}Ir, the K absorption edge of iridium being at 76.1 keV. The latter effect imposes major limitations to the absorber thickness.[26] For these reasons, almost all data in the literature have been acquired with the 73 keV transition of ^{193}Ir, which is also the focus of the current study.

^{193}Ir occurs with a natural isotopic abundance of 67.3 %. The nuclear ground state has spin 3/2, whereas the 73.0 keV excited state has spin 1/2 and a half-life of 6.20 ns, yielding a natural linewidth of 0.30 mm/s (Fig. 1). The observed experimental linewidths therefore are at least 0.60 mm/s.

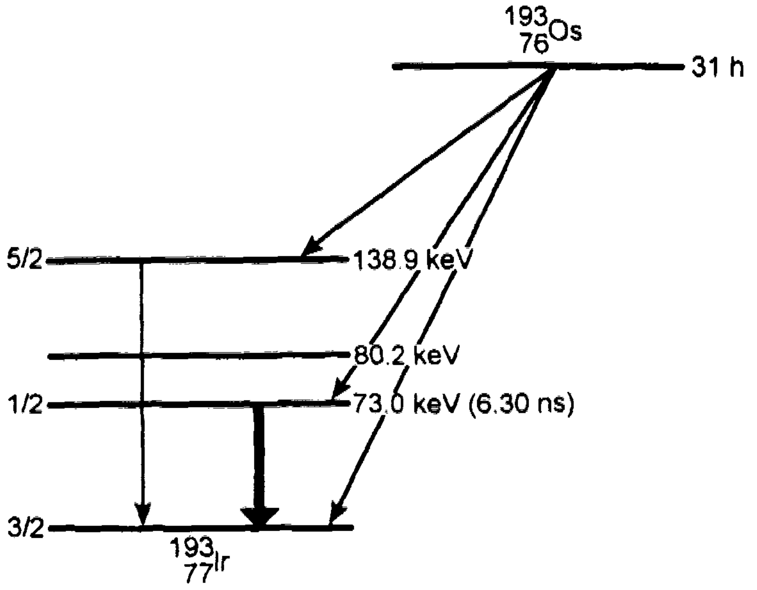

FIGURE 1 ^{193}Ir nuclear energy level diagram

The isomer shift of ^{193}Ir allows the distinction of the oxidation states of iridium (Fig. 2). An increase in isomer shift corresponds to an increase of s-electron density at the nuclei, since the relative change of the nuclear radius between the excited and the ground state $\Delta\langle r^2\rangle/r^2$ is

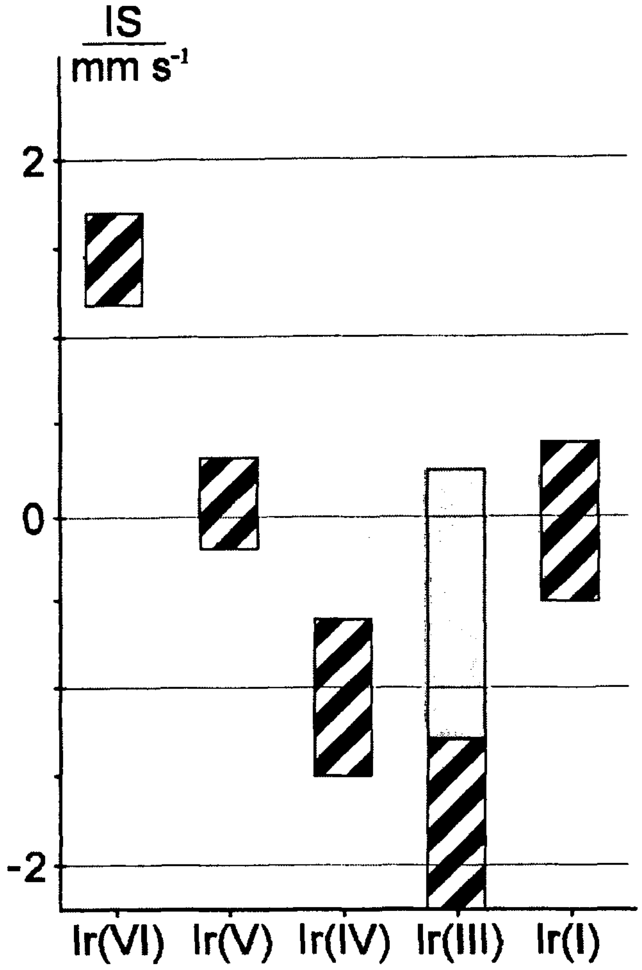

FIGURE 2 ^{193}Ir Mössbauer isomer shift ranges for different oxidation states of iridium

positive. The increase in isomer shift with the oxidation state that is observed for many iridium compounds and is attributed to a decrease of the shielding effect of the 5d electron population on the s-electron density at the nucleus[27] and to an increase of the 6s electron population due to an increasing covalency. This approach is usually valid for the high oxidation states (Ir(III) through Ir(VI)), whereas a different range of isomer shift is obtained for compounds containing iridium in low oxidation state like Ir(I). In particular, most of the Ir(I) compounds are stabilised by ligands which are very good π acceptors, like CO and NO^+. The π back-donation from the iridium to the ligands allows a higher occupation of the 6s orbitals via direct σ-donation to the iridium and hence an increase of the electron population at the nucleus.[28] The combination of isomer shift and quadrupole splitting, however, often allows the easy identification of different iridium compounds (cf. Table I).

TABLE I ^{193}Ir Mössbauer parameters of some iridium compounds at 4.2 K

Compound		*Oxidation State of Ir*	*QS [mm/s]*	*IS^a [mm/s]*	*Ref.*
$H_2[IrCl_6]\cdot 6H_2O$		Ir(IV)	0.19(2)	−1.02(2)	27
IrO_2		Ir(IV)	2.71(1)	−0.85(1)	43
$IrCl_3$		Ir(III)	0.55(2)	−1.94(1)	43
$Na_3[IrCl_6]\cdot 12H_2O$		Ir(III)	0.60(4)	−2.16(3)	26
$IrCl_3\cdot xH_2O$		Ir(III)	1.01(2)	−2.02(1)	43
$[Ir(NH_3)_5Cl]Cl_2$		Ir(III)	2.06(6)	−1.63(2)	26
Ir metal		Ir(0)	0	0.00(1)	43
$Ir_4(CO)_{12}$		Ir(0)	1.62(1)	0.27(1)	43
$[Et_4N]_2[Fe_2Ir_2(CO)_{12}]$	Ir[1]	–	2.40(1)	0.12(1)	45
	Ir[2]	–	0.70(7)	0.01(2)	

a. The isomer shift scale is relative to iridium metal.

The ^{193}Os activity feeding the ^{193}Ir Mössbauer transition is obtained by neutron activation of ^{192}Os through the reaction $^{192}Os(n,\gamma)^{193}Os$. Although natural osmium could be used for preparing the sources, the background of iridium K_β X-rays from the beta-decay of ^{191}Os decreases the line-to-background ratio considerably. Therefore, enriched ^{192}Os is preferably used as the source material. Since osmium metal has a hexagonal lattice structure, the emission line of such sources is split into a doublet with a separation of 0.48 mm/s.[27] This splitting has to be taken into account in the least squares fits of the spectra.

The high energy of the nuclear transition of ^{193}Ir allows the measurement of Mössbauer spectra only at liquid helium temperature (4.2 K). Due to the short half-life (31 h) of the ^{193}Os parent nuclide, the source is usually recycled and irradiated again every three or four days in order to achieve good count rates and signal-to-noise ratios.

The reference for the isomer shift scale is iridium metal, which has an isomer shift of –0.54 mm/s relative to the source of ^{193}Os in Os metal.

3. MÖSSBAUER SPECTROSCOPY OF CATALYTIC MATERIALS

The 73.0 keV Mössbauer transition of ^{193}Ir has been used until now for the study of the two main iridium-containing catalytic systems, i.e., the Ir-Pt and the Ir-Fe catalysts. In both bimetallic supported nanoparticles, a second Mössbauer isotope is present, so that is possible to study the chemical state of both metals at the same time. The presence of two Mössbauer isotopes makes these couples very interesting for the application of this technique.

3.1 Iridium-platinum catalysts

Wagner and co-workers studied silica supported Ir-Pt catalysts both by ^{193}Ir and ^{197}Au Mössbauer spectroscopy.[29–33] In fact, the Mössbauer resonances of ^{195}Pt are not very well suited for studying Pt catalysts, the 99 keV resonance having insufficient resolution and the 129 keV resonance being very difficult to observe.[26] On the other hand, it is possible to make platinum accessible to the Mössbauer investigation by irradiating the specimens in a reactor and using the ^{197}Pt thus produced as the source for ^{197}Au Mössbauer experiments. The latter resonance has a good resolution for both isomer shifts and electric quadrupole interactions and rather large effects can be observed.

Both the ^{193}Ir and the ^{197}Au Mössbauer resonances could be used in the investigation of the bimetallic character of the supported metal particles in relation to the precursors and the pretreatments of the catalysts. In the case of ^{193}Ir Mössbauer spectroscopy, the isomer shift varies linearly from zero in pure Ir metal to –0.67 mm/s for diluted Ir in platinum metal. In this way, from the isomer shift it is possible to detect to what extent Ir and Pt are alloyed and to get an estimate of the composition of the alloy.[34] In addition, the adsorption of the precursors and the formation of different iridium species can be followed through the several activation treatments.

Ir-Pt catalysts on amorphous silica were prepared either by impregnation with solutions of $[Ir(NH_3)_5Cl]Cl_2$ and $[Pt(NH_3)_4]Cl_2 \cdot H_2O$[29–32] or by impregnation with solutions of H_2IrCl_6 and H_2PtCl_6 in ethanol,[33] and subsequent calcination and/or reduction treatments (Fig. 3). In samples made by impregnation of amorphous silica with solutions of $[Ir(NH_3)_5Cl]Cl_2$ and $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, the decrease of the Mössbauer absorption indicates a lower Debye temperature of the complex Ir ions adsorbed on the silica surface compared to the crystalline salt. Slight changes in the quadrupole splitting of the adsorbed species, together with the rather narrow lines, suggest that the complex ions are adsorbed on the substrate individually and in a rather well defined position, whereas the oxidation state of the iridium and the molecular structure of the complex seem to be preserved. A slightly different picture emerges for samples prepared by impregnation with solutions of H_2IrCl_6 and H_2PtCl_6 in ethanol (Fig. 3). Interestingly, a reduction from Ir(IV) to Ir(III) occurs in this case during the adsorption on the silica, the adsorbed species being presumably $[IrCl_6]^{3-}$.

For both methods of preparation, the calcination of the catalyst in air at 723 K produces mainly IrO_2 (Fig. 3). It is noteworthy, however, that the IrO_2 component is often rather broad and not symmetrical, contrary to what is observed for crystalline IrO_2. This asymmetry indicates that the spectrum is the sum of a series of quadrupole doublets with a distribution of Mössbauer parameters, suggesting that the iridium is present in a range of slightly different environments. It is interesting to notice that this broadening is weakest in samples containing only iridium, suggesting that some Pt present as impurities in the IrO_2 lattice might cause this effect.

After reduction in flowing H_2 at 473 K, the spectra measured in-situ of the samples obtained from both precursors show the presence of the metallic component only, except for a very weak spectral contribution due to some unreduced oxidic iridium (Fig. 3). From the estimate of the alloy composition obtained from the variation of the isomer shift, one concludes that the majority of the platinum is not in contact with the iridium, but the two metals are rather segregated. Apparently, the use of a different precursor does not give rise to substantial differences in the segregation behaviour. It is interesting to notice that, if the samples are exposed to air, part of the iridium (up to 20 %) oxidises to IrO_2, showing that the characterisation of catalyst should always be carried out in situ.

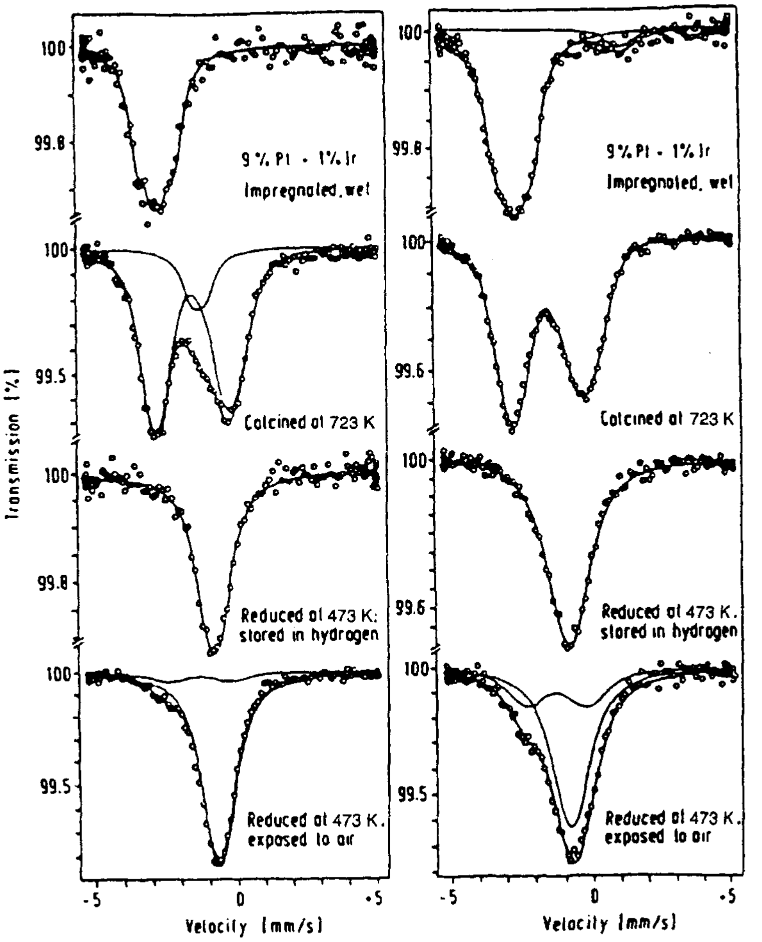

FIGURE 3 ^{193}Ir Mössbauer spectra of amorphous silica impregnated with H_2IrCl_6 and H_2PtCl_6 and treated in different ways. The samples contain 9 % Pt plus 1 % Ir. The spectra on the right represent the specimens in which the Pt was calcined before Ir was deposited (from ref. 33)

A slightly different alloying behaviour of the two metals is found if the samples are not prepared by coimpregnation. Some catalysts, in fact, were also prepared in two steps, first by impregnation of the support with a solution of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ and calcination at 725 K, and subsequently by impregnation with a solution of $[Ir(NH_3)_5Cl]Cl_2$and re-calcination at 525 K before reduction. For these samples, the platinum content of the bimetallic particles is slightly higher than that found in samples prepared by coimpregnation with the same nominal composition. For instance, for samples containing 9 wt. % Pt and 1wt. % Ir, the preparation by coimpregnation led to particles containing 20 % of Pt and 80 % of Ir, while the sequential impregnation produced bimetallic particles containing 40 % of Pt and 60 % of Ir.

In all cases, however, the iridium content of the bimetallic particles turns out to be higher than the ratio determined by plasma emission and EXAFS analysis, indicating that, independent of the preparation method, the catalysts contain iridium rich alloy particles, whereas most of the Pt is unalloyed. These results confirm the strong tendency towards segregation of iridium and platinum in bimetallic Pt-Ir catalysts. This behaviour is probably caused by the low-temperature miscibility gap in the Ir-Pt phase diagram,[35] together with the different surface mobility of the two metals (the Hutting temperatures $T_H=T_m/3$ of pure Ir and Pt metals are 895 and 680 K, respectively).

3.2 Iridium-iron catalysts

Due to their interesting catalytic properties in the associative hydrogenation of carbon monoxide, supported Fe-Ir catalysts have been studied by many techniques, including Mössbauer spectroscopy. Although in the last 15 years the much more common ^{57}Fe Mössbauer transition was mostly used to study such catalysts (for the main results, cf. ref.[20,24,36–39]), a few studies were also performed with the 73 keV Mössbauer resonance of ^{193}Ir in addition to ^{57}Fe Mössbauer spectroscopy. The ^{193}Ir Mössbauer isomer shift of iron iridium alloys with an iron concentration up to 80 %, i.e., in the range of existence of the fcc γ structure, increases linearly with the iron concentration (Fig. 4).[40] In the case of supported metal catalysts, it is therefore possible to obtain a rather accurate estimate of the average composition of the Fe-Ir alloy particles from the isomer shift.

In the early work[41,42] of Berry and Jobson, ^{193}Ir Mössbauer spectroscopy was used simply to distinguish between the state of iridium after calcination and after subsequent reduction of Fe-Ir catalysts prepared by impregnation of both silica and alumina with appropriate solutions of

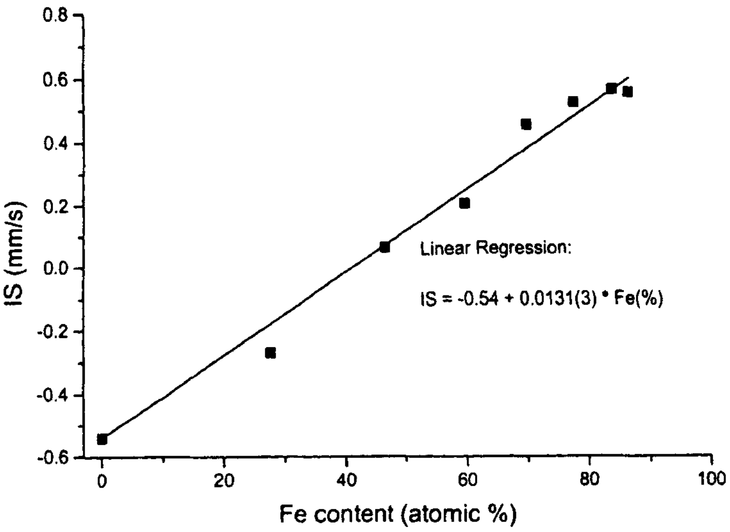

FIGURE 4 ^{193}Ir isomer shift in bcc iron-iridium alloys (data from ref. 40)

iron nitrate and $IrCl_3$. In this case, calcination at 725 K in air produced tetravalent iridium oxide on both supports. After reduction at 475 K in flowing H_2, zerovalent iridium in the form of an Fe-Ir alloy was produced on the samples supported on silica, as confirmed also by the ^{57}Fe Mössbauer results. This result is in accord with the reduction of the initial Fe(III) at lower temperatures in the presence of zerovalent iridium and the easy formation of the supported Fe-Ir alloy. A slightly different behaviour is found for the samples supported on alumina. In this case, reduction at a much higher temperature is necessary to obtain the metallic phase. ^{193}Ir Mössbauer spectroscopy indicates the formation of the alloy phase after reduction at 875 K. These results indicate that iridium induces the low temperature reduction of the iron via a spillover mechanism.

More recently, a comprehensive study of magnesia-supported iron-iridium catalysts was performed, including the investigation by both by ^{57}Fe and ^{193}Ir Mössbauer spectroscopy.[43] The interest for the thorough characterisation of these materials has been raised by the remarkable catalytic properties of magnesia-supported Fe-Ir catalysts prepared from organometallic cluster precursors in the synthesis of methanol.[21,22,25] Catalysts prepared by impregnation from inorganic salts reach the favourable steady state activity and selectivity only after an activation period of the about 50 hours,[24] whereas the cluster-derived catalysts attained the highest activity readily after the activation treatment in H_2 and showed only a small decrease of the activity during the first hours of reaction.[24] In particular, a comparison with other systems derived from bimetallic clusters on MgO and having different Fe/Ir ratios showed that samples prepared with $[Et_4N]_2[Fe_2Ir_2(CO)_{12}]$, i.e., with an atomic Fe/Ir ratio of 1:1, are the most active.[22,25]

To study the relation between the structure of the catalysts obtained from different precursors and the development of the catalytic properties, a series of Fe-Ir/MgO catalysts was prepared both through the conventional wetness impregnation technique from inorganic salts and by organometallic compounds. The samples were studied after impregnation and after activation in hydrogen at 625 K. In addition, the molecular precursor $[Fe_2Ir_2(CO)_{12}]^{2-}$ cluster compound was also studied together some other reference materials (Table I).

^{193}Ir Mössbauer spectroscopy identified two non-equivalent iridium sites in crystalline $[Et_4N]_2[Fe_2Ir_2(CO)_{12}]$ (Fig. 5), in agreement with the refined structure of the cluster.[44] The relative intensity of the two components is slightly different from the expected 1:1 ratio, most probably because a small fraction of iron substitutes for iridium in the Ir[1] position.[45] The spectra of $[Et_4N]_2[Fe_2Ir_2(CO)_{12}]$ adsorbed on MgO are largely similar to that of the crystalline cluster compound, indicating that most of the bimetallic cluster is physisorbed intact onto the MgO surface, as confirmed by FT-IR data.[45] The high stability of the cluster on the support is very important if one wants to obtain well-dispersed bimetallic particles with a homogeneous composition. In fact, the nature of the adsorption of a molecular metal cluster is known to influence strongly the resulting metal dispersion.[46] After reduction, the ^{193}Ir Mössbauer spectrum of the sample obtained from the bimetallic cluster is a single broadened line (Fig. 6) with an isomer shift of 0.38(2) mm/s with respect to Ir metal. The increase of the isomer shift indicates the formation of metallic particles consisting of an iron iridium alloy with an iron content of about 30%.[40] That only part of the iron is alloyed with Ir is confirmed by ^{57}Fe Mössbauer spectroscopy, which shows that about half of the iron is in the oxidised state.

A different picture emerges if the samples are prepared by coimpregnation from a solution of $IrCl_3{\cdot}xH_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$. In this case

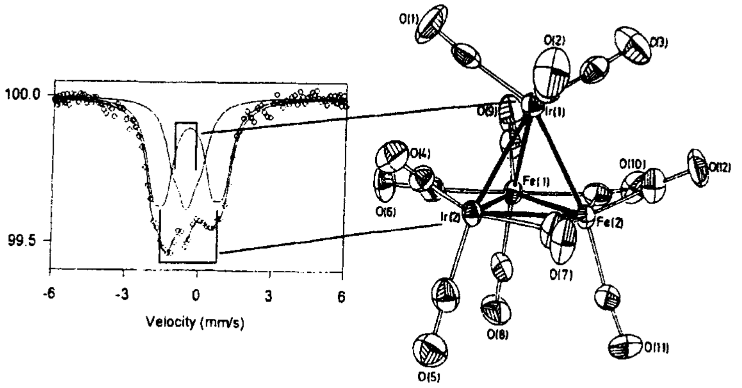

FIGURE 5 Attribution of the ^{193}Ir Mössbauer spectral components to the two different iridium sites in the $[Fe_2Ir_2(CO)_{12}]^{2-}$ anion (ORTEP drawing from ref. 44)

^{193}Ir Mössbauer spectroscopy indicates that after the impregnation the iridium is deposited on the support as the $IrCl_3 \cdot xH_2O$ salt. After reduction (Fig. 6), the Mössbauer spectrum is a single line with an isomer shift virtually identical to that of iridium metal. ^{57}Fe Mössbauer spectroscopy and EXAFS measurements confirm that no Fe-Ir alloy is formed. This contrast with the situation of SiO_2, where bimetallic particles are more easily obtained starting from inorganic salts an even by reduction at a rather low temperature.[24,41]Our results clearly show how the use of organometallic compounds with the preformed metal-metal bonds as molecular precursor, in contrast to the conventional coimpregnation methods, offer good opportunities for the preparation of MgO-supported Fe-Ir catalysts with maximised bimetallic interactions and well-defined, highly dispersed structures.

The ^{193}Ir Mössbauer line of the metallic particles is found to be very broad, having a width of about 3 and 2 mm/s for the samples obtained from clusters and from inorganic salts, respectively. Such widths, in fact, are much larger than the natural width of 0.60 mm/s for ^{193}Ir.[26] In an effort to understand the reason for this broadening, monometallic MgO-supported samples obtained from $Ir_6(CO)_{16}$ clusters and from $IrCl_3 \cdot xH_2O$ have also been studied after reduction in H_2 at 625 K. The ^{193}Ir Mössbauer spectrum of the sample prepared from the monometal-

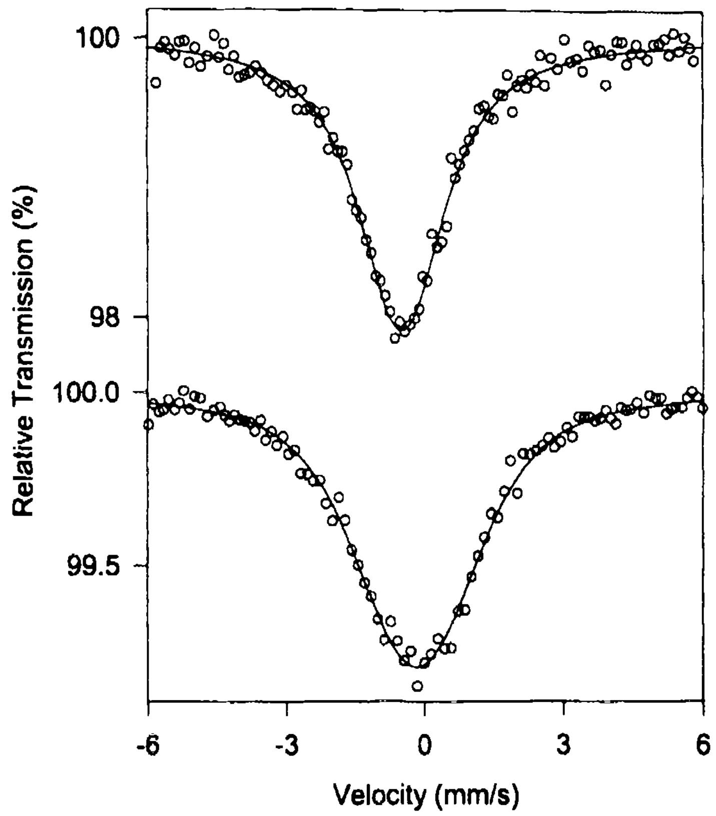

FIGURE 6 ^{193}Ir Mössbauer spectra of the bimetallic Fe-Ir/MgO catalysts reduced in H_2 at 623 K for 2 h: samples obtained from inorganic salts (top) and from the bimetallic cluster $[Et_4N]_2[Fe_2Ir_2(CO)_{12}]$ (bottom)

lic cluster is again a broadened single line with practically no isomer shift, as expected for metallic iridium, and with a linewidth of 3 mm/s, as for the sample prepared from $[Et_4N]_2[Fe_2Ir_2(CO)_{12}]$. On the other hand, the spectrum of the sample prepared from $IrCl_3{\cdot}xH_2O$ has same shift and width as the sample obtained by coimpregnation from a solution of the inorganic salts of both Ir and Fe. The similar linewidths observed in the spectra of both bimetallic and monometallic samples obtained by the same preparation routes suggests that the cause of this broadening is not an inhomogeneous distribution of the concentration of iron, which might cause a distribution of the isomer shift.

The line broadening therefore must have a non-trivial cause. One explanation could be a collective motion or oscillation of the metal particles on the support. A similar line broadening has, indeed, been observed in the ^{197}Au Mössbauer spectra of sintered copper-gold alloys and has been explained by the occurrence of low-frequency vibrational modes of the metal particles.[47] Another cause could be the small particle size. When the particle size decreases to the nanometer range, the contribution of the atoms on the surface of the metallic nanoparticles becomes visible and may give additional components in the Mössbauer spectra. Such components are, in general, different from those of bulk metal atoms and might therefore contribute to the observed envelope. Such an effect has recently been observed for gold nanoparticles in mylar studied by ^{197}Au Mössbauer spectroscopy.[48] It is remarkable, however, that in both hypotheses an increase of the width of the Mössbauer line would correspond to a decrease of the particle size. In this case, such an information can be used to study either the occurring of the quantum size effect with decreasing particle sizes, which might influence the catalytic properties, or the strength of interaction of the metal particles with the support and its dependence on the particle size. Further studies at variable temperatures, however, are needed to deepen the knowledge on the nature of this phenomenon.

4. CONCLUSIONS

In the present work, we have reported the results obtained up to know by ^{193}Ir Mössbauer spectroscopy in the characterisation of heterogeneous catalytic materials. In spite of its limited application, due mainly to experimental problems caused by the short-lived ^{193}Os Mössbauer source, the technique has been applied with success to the study of the two main groups of iridium-containing catalytic materials, i.e., the Pt-Ir catalysts for the catalytic reforming of naphthas and the Fe-Ir catalysts for the synthesis of methanol.

The main results of these investigations have shown that this technique can be of great help at several levels of the research. In the first place, it permits the study of the chemical state of the precursors, giving direct information on their behaviour upon adsorption on a support. Moreover, in the case of multimetallic systems, ^{193}Ir Mössbauer spectroscopy allows the estimation of the composition of the Ir-containing alloys that are possibly formed during the activation treatments. Such valuable properties, which can be hardly obtained by other techniques, are of great interest in catalyst design, where it is necessary to correlate the physico-chemical properties of a material with its catalytic properties.

Further important development of the technique may regard a more comprehensive study of the quantum-size effect, i.e., the development of special electronic properties observed in the case of small metallic clusters, the study of surface segregation in multimetallic systems and the study of the strength of the interaction with the support. For all these developments, however, measurements at variable temperature are necessary, which would require further experimental developments.

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References

1. *Mössbauer Effect Reference and Data Journal* (J. G. Stevens Ed.) Mössbauer Effect Data Center, Asheville, North Carolina (1990).
2. G. C. Bond. Acc. Chem. Res. **26**, 490 (1993).
3. *Chemical Applications of Mössbauer Spectroscopy* (V. I. Goldanskii, and R. H. Herber Eds.) Academic Press, New York (1968).
4. N. N. Greenwood, and T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall Ltd, London (1971).
5. *Mössbauer Effect Methodology* (I. J. Gruverman Ed.) vol. 1–9, Academic Press, New York (1965–1974).
6. *Mössbauer Spectroscopy* (U. Gonser Ed.) Springer-Verlag, Berlin (1975).
7. P. Gütlich, R. Link and A. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry*, Springer-Verlag, Berlin (1978).
8. *Mössbauer Isomer Shifts* (G. K. Shenoy, and F. E. Wagner Eds.) North-Holland, Amsterdam (1978).
9. H. Topsoe, J. A. Dumesic, and S. Mørup, in *Applications of Mössbauer Spectroscopy* (R. L. Cohen Ed.) Academic Press, New York (1980) p. 55.
10. F. J. Berry, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry* (G. J. Long Ed.) Plenum Press, New York (1984) p. 391.
11. L. Guczi, Stud. Surf. Sci. Catal., **29**, 221 (1986).
12. J.W. Niemantsverdriet, *Spectroscopy in Catalysis*, VCH, Weinheim (1995) p. 111.
13. K. Nakagawa, K. Anzai, N. Matsui, N. Ikenaga, T. Suzuki, Y. Yeng, T. Kobayashi, and M. Haruta, Catal. Lett., **51**, 163 (1998).
14. A. Erdohelyi, K. Fodor, and G. Suru, *Appl. Catal. A: General*, **139**, 131 (1996).
15. E.J. Ditzel, J. G. Sunley, R.J. Watt U.S. Pat. 5877347 (1999).

16. V.I. Savchenko, I. A. Makaryan and V. G. Dorokhov, Platinum Metals Rev. **41**, 176 (1997).
17. J. H. Sinfelt, U.S. Patent, 3,953,368 (1976).
18. T. Fukushima, Y. Ishii, Y. Onda, and M. Ichikawa, J. Chem. Soc. Chem. Comm., 1752 (1985).
19. D. C. Konigsberger, C. P. J. H. Borgmans, A. M. J. van Elderen, B. J. Kip, and J. W. Niemantsvedriet, J. Chem. Soc. Chem. Comm., 892 (1987).
20. A. Fukuoka, T. Kimura, N. Kosugi, H. Kuroda, Y. Minai, Y. Sakai, T. Tominaga, and M. Ichikawa, J. Catal., **126**, 434 (1990).
21. R. Psaro, C. Dossi, R. Della Pergola, L. Garlaschelli, S. Calmotti, S. Marengo, M. Bellatreccia, and R. Zanoni, Appl. Catal. A: General, **121**, *L19* (1995).
22. S. Marengo, R. Psaro, C. Dossi, S. Calmotti, and R. Della Pergola, Stud. Surf. Sci. Catal., **101**, 1411 (1996).
23. L. M. P. van Gruijthuijsen, S. P. A. Louwers, R. A. van Santen, and J. W. Niemantsvedriet, Catal. Lett., **43**, 45 (1997).
24. L. M. P. van Gruijthuijsen, G. J. Howsmon, W. N. Delgass, D. C. Konigsberger, R. A. van Santen, and J.W. Niemantsvedriet, J. Catal., **170**, 331 (1997).
25. S. Marengo, R. De Castro, R. Psaro, C. Dossi, R. Della Pergola, and L. Stievano, Stud. Surf. Sci. Catal., **119**, 503 (1998).
26. F. E. Wagner, and U. Wagner, in *Mössbauer Isomer Shift* (G. K. Shenoy, and F. E. Wagner Eds.) North-Holland, Amsterdam (1978) p. 431.
27. F.E. Wagner, and U. Zahn, Z. Physik, **233**, 1 (1970).
28. A. Maddock, *Mössbauer Spectroscopy Principles and Applications*, Horwood Publishing, Chichester (1997) pp. 239–242.
29. J. A. Sawicki, F. E. Wagner, and J. H. Rolston, Mat. Res. Soc. Symp. Proc. vol. 111, North-Holland, Amsterdam (1988) p. 219.
30. F. E. Wagner, J. A. Sawicki, and J. H. Rolston, Hyperfine Interact., **41**, 733 (1988).
31. H. von Brandis, F. E. Wagner, J. A. Sawicki, and J. H. Rolston, Hyperfine Interact., **46**, 575 (1989).
32. J. A. Sawicki, T. Tyliszczak, F. E. Wagner, J. H. Rolston, A. P. Hitchcock, and D. E. Clegg, Physica B, **158**, 203 (1989).
33. H. von Brandis, F. E. Wagner, J. A. Sawicki, K. Marcinkowska, and J. H. Rolston, Hyperfine Interact., **57**, 2127 (1990).
34. F. Y. Fradin, B. D. Dunlap, G. K. Shenoy, and C. W. Kimball, Intern. J. Magnetism, **2**, 415 (1971).
35. E. Raub, and W. Plate, Z. Metallkunde, **47**, 688 (1956).
36. Y. Minai, T. Fukushima, M. Ichikawa, and T. Tominaga, J. Radioanal. Nucl. Chem. Lett., **87**, 189 (1984).
37. J. W. Niemantsvedriet, J. A. C. van Kaam, C. F. J. Flipse, and A. M. van der Kraan, J. Catal., **96**, 58 (1985).
38. F.J. Berry, X. Changai, and S. Jobson, J. Chem. Soc. Faraday Trans., **86**, 165 (1990).
39. J. W. Cobes III, and J. Phillips, J. Phys. Chem., **95**, 5545 (1991).
40. R. L. Mössbauer, M. Lengsfeld, W. von Lieres, W. Potzel, P. Teschner, F. E. Wagner, and G. Kaindl, Z. Naturforsch., **26a**, 343 (1971).
41. F.J. Berry, and S. Jobson, Hyperfine Interact., **41**, 613 (1988).
42. F.J. Berry, and S. Jobson, Hyperfine Interact., **46**, 559 (1988).
43. L. Stievano, Ph.D. Thesis, University of Ferrara (Italy, 1999).
44. R. Della Pergola, L. Garlaschelli, F. Demartin, M. Manassero, N. Masciocchi, and M. Sansoni, J. Chem. Soc. Dalton Trans., 127 (1990).
45. L. Stievano, S. Calogero, R. Psaro, M. Guidotti, R. Della Pergola, and F. E. Wagner, J. Cluster Sci., accepted for publication (2000).

46. M. Ichikawa, in *Chemisorption and Reactivity on Supported Clusters and Thin Films* (R. M. Lambert, and G. Pacchioni Eds.) Kluwer Academic Pub., Dordrecht (1997) pp. 153–192.
47. M. Hayashi, E. Gerkema, A.M. van der Kraan, and I. Tamura, Phys. Rev. B, **42**, 9771 (1990).
48. L. Stievano, S. Santucci, L. Lozzi, S. Calogero, and F. E. Wagner, *J. Non-Crystal. Sol.*, **232–234**, 644 (1998).