Preparation and Characterization of Small Silica-Supported Iridium Particles from Iridium Trisacetylacetonate Precursor

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This study treats the synthesis of silica-supported iridium metal particles by several different methods. Iridium trisacetylacetonate was first deposited on silica either by sublimation or by impregnation from a toluene solution. Infrared study showed no difference between the methods, each of which produced $Ir(acac)_3$ physisorbed at the surface. The physisorbed precursor was transformed by two methods and the reactions were followed by *in situ* infrared spectroscopy. In the first method, the solid was first heated under a flow of oxygen to produce surface iridium oxide, which was then reduced under hydrogen at different temperatures to provide iridium metal support particles. In the second method a physisorbed precursor was directly reduced under a hydrogen flow. Electron microscopy showed that both methods produced narrow distributions of metallic particle sizes between 1 and 5 nm, but for the first method very large metallic aggregates were also observed. The chemisorption of hydrogen, oxygen, and CO on the resultant supported metal materials at 25°C was investigated as a means of determining the dispersion of the samples. A discrepancy between the dispersions deduced from chemisorption of H_2, O_2, and CO and from electron microscopy on the resultant supported metal materials was tentatively interpreted as an indication that some very small Ir particles, present on the silica surface, were not detected. © 2000 Academic Press

Key Words: Ir/SiO_2; heterogeneous catalyst; small iridium metallic particles; H_2, O_2, and CO adsorption on Ir.

1. INTRODUCTION

It was recently reported that iridium particles could be active and selective catalysts for the hydrogenolysis of internal C–C bonds of cyclic molecules, but the preparation and the characterization of well-defined iridium metallic particles have not been fully studied.

Using $IrCl_3$ as a precursor and the incipient wetness technique or the urea method, Kip *et al.* (1, 2) prepared silica-supported and alumina-supported Ir particles. The size and the dispersion (number of surface metal atoms per total metal atoms, $D = Ir_s/Ir$) of the metallic particles were es-

timated from the coordination number of Ir atoms determined by EXAFS studies and the amount of hydrogen adsorbed was measured at 298 K. It was observed that the H/Ir values could not be directly correlated to the Ir_s/Ir values. H/Ir_s values greater than 2.6 were measured for smaller Ir particles, that is, for samples of a dispersion close to 0.9, and H/Ir_s values close to 2 were obtained on larger particles having a lower dispersion, close to 0.5. The authors concluded that hydrogen chemisorption cannot be directly used to determine particle sizes for highly dispersed metals. More recently, Gates *et al.* (3, 4) prepared alumina-supported iridium particles of various sizes by complete decomposition of $Ir_4(CO)_{12}$ and reported on the adsorption of H_2 on these materials. They observed that H/Ir values increased with the size of alumina-supported iridium particles. Using the same organometallic precursor, $Ir_4(CO)_{12}$, and CO as a molecular probe, Tanaka *et al.* (5) concluded that the iridium may be in the form of two-dimensional rafts on silica and alumina supports. The same conclusion was proposed by Guerra and Schulman (6) from TEM measurement and CO adsorption on silica-supported Ir. On alumina-supported Ir catalysts, CO/Ir ratios as high as 1.7 were observed by McVicker *et al.* (7) and from the absence of observed metallic particles by TEM, these authors concluded that Ir was possibly present as single metal atoms and crystallites less than 0.6 nm in diameter.

The main observation which can be draw from the previous works done on the silica- or alumina-supported iridium catalyst area is that the stoichiometry of CO and H_2 adsorption are greater than that expected. The precursors used in these works were carbonyl or chloride compounds. It is well known that CO is a poison to metallic surfaces and, in certain cases, can form carbonyl complexes with surface metallic atoms such as Ni catalysts (8). Chloride can remain on the support surface, leading to partial oxidation of the metal and thus to erroneous conclusions based on the chemisorption of molecular probes.

It is thus evident that further studies are necessary on the stoichiometry of hydrogen, oxygen, and CO adsorbed on supported iridium catalysts, prepared using a precursor without chloride, and that these results must be directly

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correlated to TEM observation. Iridium acetylacetonate could be a good precursor for this purpose.

When iridium trisacetylacetonate (Ir(AcAc)₃) is used as a precursor of iridium metallic particles, two main procedures are used to deposit the complexes on the silica surface. In the first, Ir(AcAc)₃ is sublimed onto the host surface without solvent. This procedure is very clean; the overall processes of deposition and decomposition of the complexes can be followed by infrared spectroscopy, but they cannot be applied at a large scale. In the second method, a solvent is used to carry the complexes to the silica surface. After the solvent is removed by filtration, the grafted complexes are decomposed. This route is more practical, but one cannot precisely follow the deposition reaction by, for example, infrared spectroscopy.

Once the Ir(AcAc)₃ complexes are deposited on the silica surface, two procedures are used to produce metallic iridium. The first is the progressive heating of the solid under oxygen to burn the organic compounds, followed by reduction under hydrogen to reduce the iridium oxide formed. The second procedure is direct decomposition of the organic groups by hydrogenolysis under hydrogen.

2. EXPERIMENTAL

The support used is a silica Aerosil from Degussa with a surface area of $200 \, m^2 \, g^{-1}$. Before each utilization the support is treated under flowing dry air at 520°C for 5 h.

Iridium trisacetylacetonate, Ir(AcAc)₃, was purchased from Strem Chemicals and used without further purification. The infrared spectra of pure Ir(AcAc)₃ are given in Fig. 1a.

The iridium loading of the samples was measured by elemental analysis.

Adsorption of H₂, CO, or O₂ is performed in a static volumetric apparatus as already described in (9). H₂, CO, and O₂ from Air Liquide are dried over molecular sieves (4 Å) before introduction into the volumetric apparatus.

The sublimation of Ir(acac)₃ was performed in sealed tube reactors pre-equipped with break-seal tubes for the introduction of nongaseous reactants and with CaF₂ windows to allow acquisition of infrared spectra, as described elsewhere (10).

Electron microscopy (CTEM) was performed by means of a JEOL 100CX electron microscope. Assuming spherical particles with diameter d_i, it is possible to determine the apparent average diameter d_{va} by

$$d_{va} = \sum n_i d_i^3 \Big/ \sum n_i d_i^2. \qquad [1]$$

From the apparent average diameter, it is possible to calculate the dispersion, D, which is the number of surface atoms divided by the total number of atoms, using the
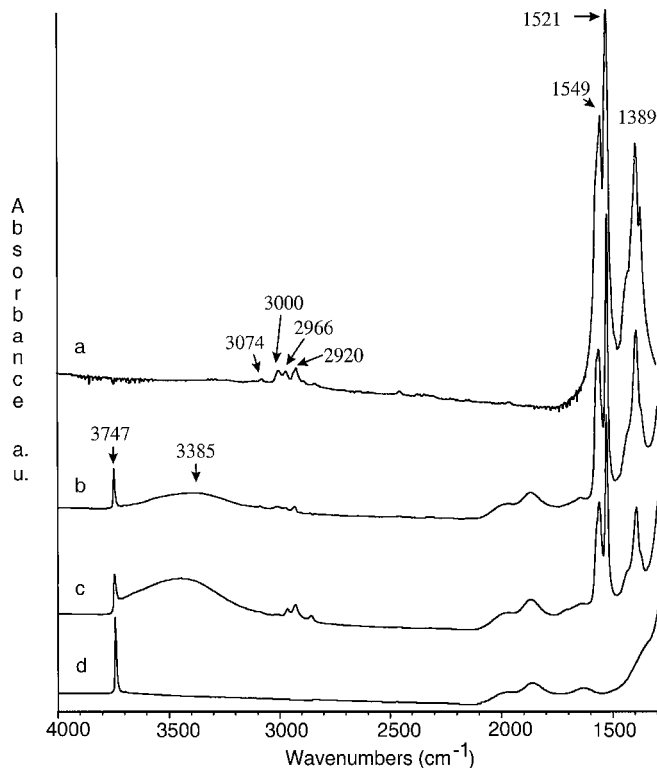

FIG. 1. Infrared spectra of (a) iridium trisacetylacetonate in KBr: Ir(acac)₃ + KBr (1/300), (b) Ir(acac)₃ deposited on SiO₂ by sublimation, and (c) Ir(acac)₃ deposited on SiO₂ by impregnation and (d) initial dehydroxylated silica.

formula

$$D = 6v_m/(a_m d_{va}), \qquad [2]$$

with, for Ir, $v_m = 14.24 \text{Å}^3$ and $a_m = 7.73 \text{ Å}^2$.

For cubooctahedral particles, if m is the number of atoms in a edge, the respective total (N_t) and surface (N_s) numbers of atoms are given by Eqs. [3] and [4]. For this particle, the apparent diameter (d_{app}) is calculated from the atomic diameter of the metal ($d_{at} = 0.271$) as in Eq. [3] and the dispersion is given by N_s/N_t:

$$N_t = 16m^3 - 33m^2 + 24m - 6, \qquad [3]$$

$$N_s = 30m^2 - 60m + 32, \qquad [4]$$

$$d_{app} = 1.105 \, d_{at} N_t^{1/3}. \qquad [5]$$

3. PREPARATION OF Ir/SiO₂

3.1. Impregnation of SiO₂ by Sublimation of Ir(AcAc)₃

The silica wafer is introduced into the infrared cell and treated under dynamic vacuum at 520°C. The initial dehydroxylated silica spectrum is presented in Fig. 1d. The iridium trisacetylacetonate was then sublimed onto the silica disk at room temperature. The white silica disk turned yellow and no gaseous products were observed (by infrared

and GC analysis). The spectrum of the product is represented in Fig. 1b, with the same scale used in Fig. 1d. The intensity of the peak at 3747 cm^{-1} decreases, indicating that some remaining silanols are involved in hydrogen bonds, and new bands appear: a broad band at 3385 cm^{-1} corresponding to hydrogen-bound νOH vibrations and sharp bands at 1568, 1524, and 1393 cm^{-1} characteristic of the acetylacetonatyl ligand. Notably, no acetyl acetone bands (expect those at 1708 and 1626 cm^{-1}) were observed (12) and so the hydrogen-bound νOH band is most likely due to silanols interacting with the organometallic precursor. Apparently, Ir(AcAc)$_3$ is physisorbed (by van der Waals bonds) on the surface of a dehydroxylated (520°C under vacuum) silica surface.

3.2. Impregnation of SiO$_2$ From a Solution of Ir(AcAc)$_3$ in Toluene

To carry out chemisorption measurements, larger amounts of catalyst are needed. Silica (10 g) was added to a solution of iridium acetylacetonate in toluene. The suspension was gently stirred for 72 h. The solid was then filtered and the iridium acetylacetonate in excess was removed by several washings with toluene. The yellow solid was dried at 70°C in an oven for 48 h and then under vacuum for 1 h. The infrared spectrum of this sample is reported in Fig. 1c and compared to the spectra of the sample obtained by sublimation (Fig. 1b). The same bands attributed to the adsorbed Ir(AcAc)$_3$ were observed, which suggests that Ir(AcAc)$_3$ is once again simply physisorbed on the silica surface. In this case, the silica was not treated under vacuum at 550°C before introduction of Ir(AcAc)$_3$, and so one observes a more important band in the hydrogen-bound silanols region (around 3500 cm^{-1}).

3.3. Decomposition of the Ir(AcAc)$_3$ Physisorbed on SiO$_2$

3.3.1. Decomposition under oxygen.
After impregnation of SiO$_2$ by sublimation and treatment of the sample under vacuum at room temperature, the infrared cell was filled with 400 mbar of oxygen and then the sample was treated with increasing temperature. Between 25 and 150°, there is no evolution of the infrared spectra. At 200°C, there was a drastic decrease of the bands corresponding to the acetylacetonate and a clear increase of the band corresponding to the free silanols (3747 cm^{-1}). Simultaneously, a band appeared at 2066 cm^{-1}, which can be attributed to adsorbed CO (6), and two small bands appeared at 1418 and 1374 cm^{-1}. At 200°C and above, carbon dioxide was observed in the gas phase (νCO: 2358 and 2343 cm^{-1}). Increasing the temperature to 250 and 300°C lead to the disappearance of the bands corresponding to acetylacetonate and adsorbed CO. After treatment of the solid at 300°C under vacuum, the two small bands remained in the infrared spectrum of the solid at 1418 and 1374 cm^{-1}. These bands could be attributed to carbonates adsorbed on the surface.

It seems that the decomposition under oxygen of the physisorbed Ir(AcAc)$_3$ occurs by complete oxidation of the acetylacetonate groups into CO, CO$_2$, CO$_3^{2-}$, and probably H$_2$O. The latter was observed in the gas phase (bands around 1700 and 3700 cm^{-1}), but not on the solid, apparently because it desorbs from the solid at 200°C and is condensed at a cold point of the infrared cell.

3.3.2. Decomposition under hydrogen.
An infrared cell which contained a sample obtained by sublimation of Ir(AcAc)$_3$ over a pre-dehydroxylated SiO$_2$ wafer was charged with 300 mbar of hydrogen at room temperature and then the sample was treated at increasing temperatures. Between 25 and 200°C, there was no evolution of the infrared spectra. At 200°C, there was a drastic decrease of the bands corresponding to the acetylacetonate, a clear increase of the band corresponding to the free silanols (3747 cm^{-1}), and the appearance of a band at 2066 cm^{-1} which can be attributed to adsorbed CO(6). Simultaneously, bands attributed to CO$_2$ (bands at 2329 and 2369 cm^{-1}) and water (broad bands at 1300–2000 and 3500–4000 cm^{-1}) appeared in the gas-phase spectrum. At 300°C, in the spectrum of the solid, the bands corresponding to the acetylacetonate and the adsorbed CO completely disappeared, and small bands at 1695 and 1560 cm^{-1} which could be attributed to acetylacetone were observed. In the same time, in the gas-phase spectrum, the doublet at 2358 and 2343 cm^{-1} associated to CO$_2$ increased and bands at 3017 and 2900–3000 cm^{-1} corresponding to alkane were observed. GC analysis of the gas phase showed the presence of methane, ethane, and propane. After treatment at 300°C under vacuum, there were no bands at 1418 and 1374 cm^{-1} previously attributed to carbonates adsorbed on silica, but it seems that some of the hydrocarbyl fragments remained on the surface. Apparently, the free silanols of the silica surface were almost completely recovered.

4. CHARACTERIZATION OF Ir/SiO$_2$

Three Ir/SiO$_2$ samples were prepared by impregnation of Ir(AcAc)$_3$ from a toluene solution (see Section 3). After drying in an oven at 70°C, one sample (Fl-Ir3) was treated under a flow of an O$_2$–N$_2$ mixture for 6 h at 350°C and then reduced at 350°C under a flow of hydrogen. The other two (Fl-Ir4 and Fl-Ir5) were treated under a flow of H$_2$ for 6 h at 350°C. The metal loading of each sample is reported in Table 1.

The metallic particle size distribution observed by electron microscopy (EM) is much more narrow in the case of samples directly treated under hydrogen (Fl-Ir4 and Fl-Ir5) than in the case of a calcinated sample (Fl-Ir3). Moreover, large aggregates of particles were observed in the case of the calcinated sample and not in the case of the directly reduced samples. For the Fl-Ir3 sample, the observed particle size ranged from 0.7 to 4 nm, with the most important

TABLE 1

Influence of the Method of Preparation on the Dispersion of the Various Ir/SiO₂ Catalysts

Preparation	Fl-Ir3 Oxid.–red.	Fl-Ir4 Red.	Fl-Ir5 Red.
Ir loading			
(w%)	0.97	0.58	0.64
(μmol/g)	50.5	30.2	33.3
d_{app} (nm)	>3.5	2.9	2.2
$D_{sph/cub}$(%)	<30/<30	38/41	50/41
n_{O2} (μmol/g of catal.)	9.5	8.4	9.0
n_{CO} (μmol/g of catal.)	20	16.5	18.0
$D_{(O2\ adsorption)}$ (%)	38	56	54
$D_{(CO\ adsorption)}$ (%)	40	55	54
$Ir_s{}^{a}$ (μmol/g of catal.)	20	16.9	18.0
n_{H2} (μmol/g of catal.)	14	16.6	20
$H/Ir_s{}^{b}$	1.4	1.9	2.2

[a] Number of surface iridium atoms, based on dispersion measured by O₂ and CO adsorption.

[b] Stoichiometry of the hydrogen adsorption, based on dispersion measured by O₂ and CO adsorption.

contributions around 1.8 nm. With Fl-Ir4 and Fl-Ir5, the size of the observed particles ranges from 0.7 to 3 nm, with a maximum around respectively 1.6 and 1.5 nm. From the metallic particle size distribution, it is possible to calculate the dispersion of the samples, assuming that the particles are spherical or cubooctahedral (see Experimental). The various values for the dispersion of Fl-Ir4 and Fl-Ir5 samples are reported in Table 1. The electron microscopic observation of the Fl-Ir3 sample shows the presence of large particles or/and large aggregates of particles that *were not* taken into account in the calculation of dispersion. Therefore, the dispersion of this sample measured by electron microscopy is by definition overestimated.

The infrared spectra of CO adsorbed on the Ir/SiO₂ (Fl-Ir3) sample shows only one band at 2060 cm^{-1} attributed to linearly adsorbed CO. The quantity of CO adsorbed on the silica and on the Ir/SiO₂ (Fl-Ir3) sample at various equilibrium pressures is reported in Fig. 2. There is a clear plateau for the adsorbed quantity of CO at equilibrium pressures above 100 mbar. The amount of CO adsorbed at 25°C and 100 mbar on Fl-Ir3, FL-Ir4, and Fl-Ir5 samples was respectively 20, 16.5, and 18 μmol/g. This value did not change upon the heating of the sample under 100 mbar of CO at 150°C for 1 h. This could suggest, as proposed by Gates *et al.* (3), that in the case of large iridium aggregates, CO adsorption is a surface phenomenon. Assuming a stoichiometry of 1 CO/Ir$_s$, the dispersion of the Fl-Ir3, Fl-Ir4, and Fl-Ir5 samples is respectively 40%, 55%, and 54%.

The quantity of O₂ adsorbed on the SiO₂ surface and on the Ir/SiO₂ (Fl-Ir3) sample at various equilibrium pressures is reported in Fig. 3 as a function of the time of adsorption.

At low pressure (15 mbar) and short adsorption time (5 min), the quantity of oxygen chemisorbed is close to
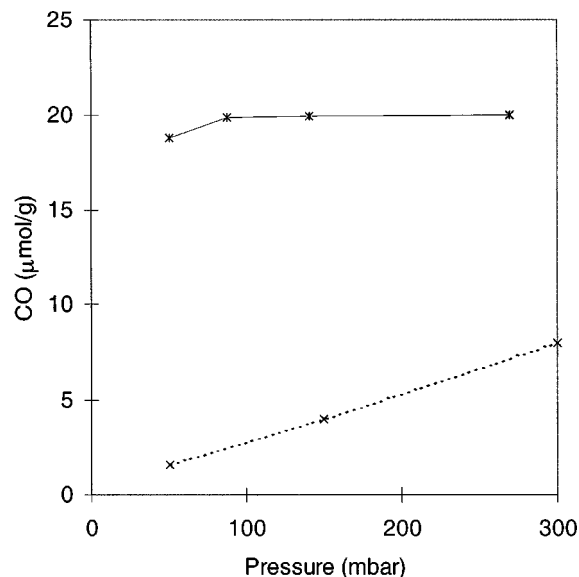
FIG. 2. Quantity of CO adsorbed on silica (dashed line) and FL-Ir3 catalyst (solid line, corrected for the adsorption on the support) after 30 min of reaction at 25°C as a function of the equilibrium pressure.

9.5 μmol/g, but the quantity of chemisorbed oxygen increased both with time of reaction and with increasing pressure. For equilibrium pressures higher than 100 mbar, the amount of oxygen adsorbed on the Fl-Ir3 sample was constant and close to 18 μmol/g.

Increasing the temperature of adsorption drastically increases the amount of oxygen adsorbed (Fig. 4). Under 150 mbar pressure, a stable value was obtained after the
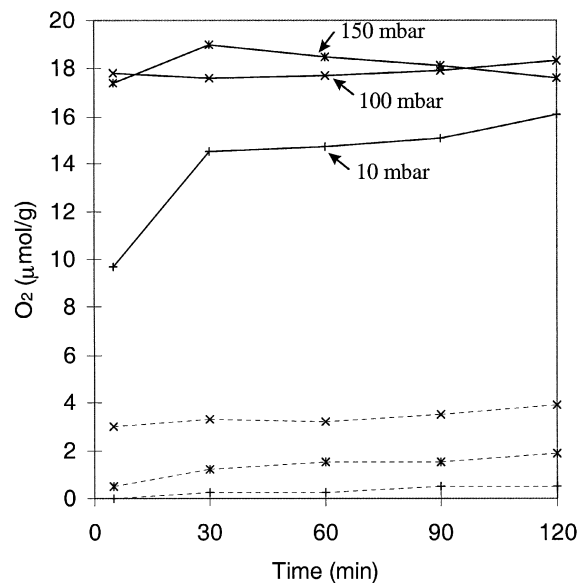
FIG. 3. Quantity of oxygen adsorbed at 25°C on silica (dashed line) and FL-Ir3 catalyst (solid line, corrected for the adsorption on the support) as a function of time and for various equilibrium pressures (+) 10 mbar, (∗) 100 mbar, and (×) 150 mbar.
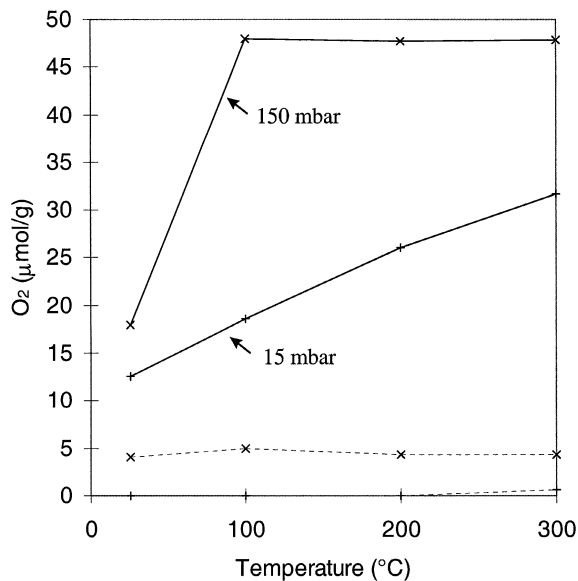
FIG. 4. Quantity of oxygen adsorbed on silica (dashed lines) and FL-Ir3 catalyst (solid lines, corrected for the adsorption on the support) after 30 min of reaction at various temperatures and under various equilibrium pressures (+) 15 mbar and (×) 150 mbar.
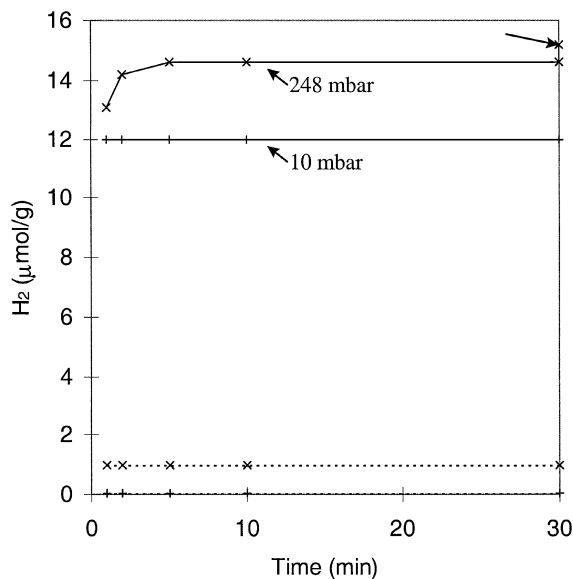

FIG. 5. Quantity of hydrogen adsorbed on silica (dashed lines) and FL-Ir3 catalyst (solid lines) at $25°C$ under (×) 10 mbar and (+) 248 mbar pressures, as functions of time. The point indicated by an arrow is the quantity obtained at $25°C$, after being heated at $300°C$ under 248 mbar pressure for 30 min.

sample was heated above $100°C$. The iridium loading of the sample was 0.97 wt% (51 μmol/g) and the total amount of adsorbed O_2 (at $300°C$ under 150 mbar pressure) was close to 48 μmol/g. Clearly, bulk IrO_2 has been formed under these conditions. At $25°C$, the quantity of oxygen chemisorbed increases with time. It seems that, at $25°C$, not only does the adsorption of oxygen proceed on the iridium surface but also that there is progressive migration of the oxygen atoms into the metallic particle, as previously observed in the case of Rh/SiO_2 catalysts (9). Nevertheless, for low pressures and low reaction times, the quantities of adsorbed oxygen on Fl-Ir3, Fl-Ir4, and Fl-Ir5 samples are respectively 9.5, 8.4, and 9.0 μmol/g. Assuming a stoichiometry of 1 O/Ir_s, the dispersions of the Fl-Ir3, Fl-Ir4, and Fl-Ir5 samples became respectively 38, 56, and 54%. These values are close to the values measured by CO adsorption (40%, 55%, and 54%). For the Fl-Ir4 and Fl-Ir5 samples, the dispersions measured by CO and O_2 chemisorption (close to 55%) are greater than the values estimated from the metallic particle size (respectively about 40% and 50%).

The quantity of H_2 adsorbed onto the SiO_2 surface and onto the Ir/SiO_2 samples at various equilibrium pressures is reported in Figs. 5 and 6. These values are stable with time and increase slightly by the samples being heated at $300°C$ under hydrogen (Fig. 5). The quantities of H_2 chemisorbed reached a plateau above 150 mbar at $25°C$ and can be fully removed from the catalyst surface by heating under vacuum at $300°C$. It is thus expected that hydrogen chemisorption is a surface phenomena. The quantities of H_2 chemisorbed in these conditions (150 mbar, $25°C$) on the Ir/SiO_2 sam-

ples are reported in Table 1. Using the values obtained by chemisorption of O_2 and CO for the dispersion of the samples, it is possible to calculate the stoichiometry, H/Ir_s of hydrogen adsorption at $25°C$ under 150 mbar pressure. The values reported in Table 1 for Fl-Ir3, Fl-Ir4, and Fl-Ir5 samples are respectively close to 1.4, 1.9, and 2.2 H/Ir_s. These
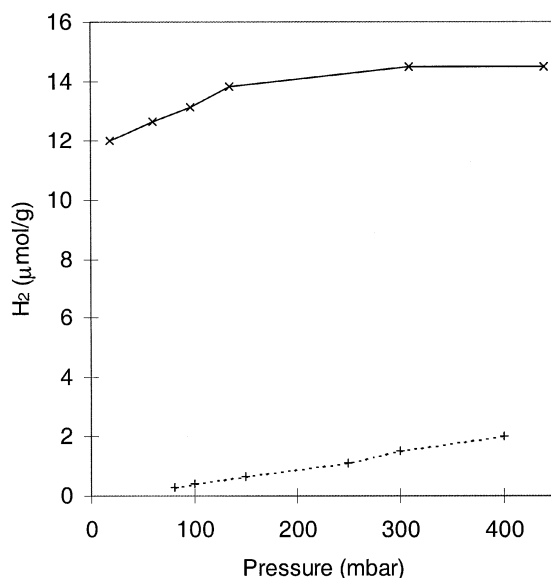

FIG. 6. Quantity of hydrogen adsorbed on silica (dashed line) and FL-Ir3 catalyst (solid line, corrected for the adsorption on the support) after 30 min of reaction at $25°C$ as a function of the equilibrium pressure.

values are lower than the values found by Kip *et al.* (1, 2) but are in the range of values previously proposed for H/Pt$_s$ (13).

5. DISCUSSION

After adsorption of Ir(AcAc)$_3$ on the silica surface, infrared spectra do not show any bands which could be attributed to acetylacetone; therefore, we can conclude that, at 25°C, iridium trisacetylacetonate is only physisorbed on the silica surface. Its decomposition either under oxygen or under hydrogen occurs at temperatures over 200°C and is complete at 300°C, leading to the formation of reduced metallic iridium particles under hydrogen and bulk IrO$_2$ under oxygen.

As the free silanols of the surface are almost completely recovered after decomposition at 300°C, it seems that little of the silica surface is in interaction with metallic particles.

It is evident that direct decomposition under hydrogen leads to much smaller metallic particles and a rather narrow distribution of metallic particle size around 1.5 nm. The larger metal particles and the formation of large aggregates observed after calcination could be ascribed to the volatility of IrO$_2$.

Only one infrared band is observed at 2061 cm^{-1} after CO adsorption at room temperature. This band corresponds to the formation of linear CO adsorbed onto one surface iridium atom (14). The amount of CO adsorbed at 25°C does not increase when the sample is heated to 150°C; therefore, there is apparently no formation of iridium carbonyl (Ir$_4$CO$_{12}$) or iridium gemdicarbonyl, as mentioned by McVicker *et al.* (7). If we assume a stoichiometry of 1 CO/Ir$_s$, the dispersion of the calcined and then reduced sample (FL-Ir3) is around 40% and the dispersion of the directly reduced samples (Fl-Ir4 and Fl-Ir5) is close to 55%.

Chemisorption of oxygen at 25°C is not suitable for metallic dispersion measurement because the formation of bulk IrO$_2$ occurs even at room temperature and is complete above 100°C. This result is in perfect agreement with the results of Gates *et al.* (15), who demonstrate by EXAFS that exposure of supported Ir clusters to air at 50°C results in almost total destruction of the metal frame and formation of IrO$_2$. As mentioned by Schmidt *et al.* (16, 17), among various noble-metal catalysts (Pt, Pd, Rh, Ir), Ir has the highest metal–oxygen bond energy and forms relatively stable surface oxides with various stoichiometries under fuel-lean conditions. Nevertheless, using a frontal method (18) to measure the amount of irreversibly adsorbed oxygen at room temperature on supported Ir catalysts, Guenin *et al.* (19) obtained a stoichiometry for O/Ir$_s$ close to 1. In the frontal method, the partial pressure of O$_2$ is never greater than 10 mbar and the time of adsorption is very low. In our case, at room temperature and under 10 mbar, the extrapolation to $t = 0$ gives a quantity of adsorbed oxygen which

corresponds, if we assume a stoichiometry of 1 O/Ir$_s$, to a dispersion close to 38% for the calcined and then reduced sample (FL-Ir3) and 55% for the directly reduced samples (Fl-Ir4 and Fl-Ir5). These values are very close to the values deduced from CO chemisorption.

For the three samples, the amount of chemisorbed H$_2$ at room temperature reaches a plateau for pressures greater than 150 mbar and does not increase when the sample is heated to 300°C. This means that our procedure allows one to measure the total amount of adsorbed hydrogen at room temperature without the need for preheating of the sample under hydrogen as mentioned by Kip *et al.* (2). This amount seems to be correlated to the number of surface iridium atoms. When the dispersion of the samples deduced from CO and O$_2$ chemisorption is taken into account, the stoichiometry of the chemisorbed hydrogen varies from 1.4 to 2.2 H/Ir$_s$. These values are lower than the values reported by Kip *et al.* (2), who found stoichiometries ranging from 2.5 H/Ir$_s$ for the low-dispersed sample to 3 H/Ir$_s$ for the almost fully dispersed catalysts, but are not far off the values obtained for H/Pt$_s$ in the case of silica-supported platinum particles of the same dispersion ($D = 60\%$, H/Pt$_s = 2$) (14). Nevertheless, if we take into account the dispersion of the Fl-Ir4 and Fl-Ir5 samples deduced from electron microscopy, the H/Ir$_s$ stoichiometries become respectively H/Ir$_s = 2.7$ and 2.4.

The values of the dispersion of the samples, deduced from CO, O$_2$, and H$_2$ chemisorption (assuming the following stoichiometry: CO/Ir$_s$ and O/Ir$_s = 1$, H/Ir$_s = 2$) are in rather good accordance, but they are clearly higher than the values expected from electron microscopic observation. It seems that the dispersion estimated from the size of the particle may be underestimated. The most probable explanation is that some very small particles (less than 0.7 nm in diameter) exist on the sample and are not counted (20).

6. CONCLUSION

Iridium particles supported on silica were prepared, starting with iridium trisacetylacetonate. At room temperature, Ir(acac)$_3$ is simply physisorbed onto the surface. The decomposition of the precursor under a flow of hydrogen at 300°C produced metallic particles with narrow distributions of sizes between 1 and 5 nm. The dispersions of the metallic particles deduced from electron microscopy observation is always lower than the dispersions calculated from chemisorption of H$_2$, O$_2$, and CO, assuming the following stoichiometry: CO/Ir$_s$ and O/Ir$_s = 1$, H/Ir$_s = 2$. It was proposed that the dispersion estimated from the size of the particle could be underestimated.

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