Preparation and characterization of very highly dispersed iridium on Al2O3 and SiO2

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PREPARATION AND CHARACTERIZATION OF VERY HIGHLY DISPERSED IRIDIUM ON Al2O3 AND SiO2

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ABSTRACT

To obtain highly dispersed alumina- and silica-supported iridium catalysts, two preparation methods, the incipient wetness method and the urea technique, were investigated. Hydrogen and carbon monoxide chemisorption clearly showed that on γ-Al2O3 the incipient wetness method resulted in catalysts with a very high iridium dispersion (H/Ir > 2.0 for loadings < 2.5 wt% Ir and H/Ir > 1.0 up to 6.0 wt% Ir), in contrast with the catalysts made by this technique on SiO2 (H/Ir < 1.0 for Ir loadings between 0.4 and 7.0 wt% Ir). Temperature programmed reduction, desorption and oxidation studies supported this conclusion. The behaviour of these systems in oxygen at elevated temperature also demonstrates a stronger interaction between iridium and alumina. The difference between the alumina- and silica-supported systems is caused by differences in adsorption processes during the impregnation. Using the urea technique, highly dispersed Ir/SiO2 and Ir/Al2O3 catalysts were obtained (H/Ir = 1.6 for 1.5 wt% Ir/SiO2, and H/Ir = 1.2 for 5.5 wt% Ir/SiO2, H/Ir = 2.5 for 1.5 wt% Ir/Al2O3, and H/Ir = 1.6 for 5.7 wt% Ir/Al2O3). Thus, the incipient wetness method proved successful for Al2O3, whereas the urea technique resulted in highly dispersed iridium catalysts on both supports.

INTRODUCTION

As a result of many industrial applications, e.g. the purification of automobile exhaust gas, the reforming of petroleum naphthas and the hydroformylation of olefins, group VIII metals are studied extensively. Also in the hydrogenation of carbon monoxide to hydrocarbons and oxygenated products, group VIII metals are very important. Rhodium was found to be considerably selective for the production of oxygenated products [1-5]. Since in the periodic table iridium is placed below rhodium and to the left of platinum (which produces mainly methanol [6]), the catalytic behaviour of iridium is of interest. Recently, we reported that the major products of the reaction of synthesis gas over alumina and silica supported iridium catalysts were methane, methanol and dimethylether [7].

Preparation and characterization of supported iridium catalysts starting from the Ir4(CO)12 complex were reported by Anderson et al. [8-11], Tanaka et al. [12] and Ichikawa et al. [13]. The dispersion of these systems was comparable to that of systems prepared by ordinary impregnation of the support with a solution.
of IrCl₃. McVicker et al. [14] reported the chemisorption properties of alumina-supported iridium catalysts prepared by incipient wetting γ-Al₂O₃ with an aqueous solution of chloro-iridic acid. They found that for 0.3 to 1.0 wt% Ir/Al₂O₃ catalysts H/Ir and CO/Ir ratios were close to two and that the particles could not be detected by high-resolution TEM, indicating that the particles were smaller than 6 Å. Their conclusion was that isolated iridium atoms can adsorb up to two hydrogen atoms, while iridium clusters (d > 6 Å) adsorb a single hydrogen atom per exposed metal atom. Krishnamurthy et al. [15], using temperature programmed desorption to characterize Ir/Al₂O₃ systems, also found that up to two atoms of hydrogen were chemisorbed per iridium atom. These results indicate that highly dispersed alumina-supported iridium catalysts can be prepared by the incipient wetness method. McVicker and Krishnamurthy both only used the relatively strongly bonded hydrogen (irreversibly adsorbed hydrogen) to calculate the H/Ir ratios. When the total amount of adsorbed hydrogen is taken into account, they both measured H/Ir values exceeding two (H/Ir = 2.5 for 0.5 wt% Ir/Al₂O₃).

Studies in our laboratory have shown that in the case of rhodium the incipient wetness method resulted in well dispersed alumina-supported systems [16] but less well dispersed silica-supported systems [17]. Geus et al. [18-20] showed that using the urea technique highly dispersed silica-supported nickel and copper catalysts could be prepared. In this method the pH of a suspension of SiO₂ and metal ions in water is increased slowly by means of the decomposition of urea. This leads to the formation of a homogeneously and well dispersed layer of Ni or Cu on the surface of the support. Until now, this method has not been used for the preparation of supported iridium catalysts.

Vis et al. [16,21] showed that chemisorption measurements and temperature programmed reduction (TPR) and oxidation (TPO) are very powerful techniques in characterization of supported noble metal catalysts. Using TPR and TPO, the state of an impregnated, reduced or oxidized catalyst could be studied successfully. Clearly, TPR/TPO as a characterization technique has proven useful in a variety of fields in catalysis, e.g. Rh/Al₂O₃, Rh/Al₂O₃ and bimetallic catalysts like Co-Rh/Al₂O₃ [22] and Pt-Ir/Al₂O₃ [23-26]. In this paper, Al₂O₃- and SiO₂-supported iridium catalysts prepared via the incipient wetness method and the urea technique are discussed and it will be shown that these methods lead to very highly dispersed systems. Hydrogen and carbon monoxide chemisorption and temperature programmed reduction and oxidation are used to characterize the various catalysts.

**EXPERIMENTAL**

**Preparation of the catalysts**

Ir/Al₂O₃ and Ir/SiO₂ catalysts were prepared via the incipient wetness method and via the urea technique [18-20]. γ-Al₂O₃ was supplied by Ketjen (000-1.5E, surface area 200 m² g⁻¹, pore volume 0.6 ml g⁻¹, granulates with particle size 0.25-0.40 mm), SiO₂ by Grace (S.D. 2-324.382, surface area 290 m²...
Sk pore volume 1.2 ml g\(^{-1}\), granulates with particle size 0.10-0.20 mm) and IrCl\(_3\)-xH\(_2\)O by Drijfhout (50.9 wt% Ir). The supports were used without thermal treatment. After incipient wetting the support with an aqueous solution of IrCl\(_3\), the resulting catalysts were dried in air at 395 K for 16 h (heating rate 2 K min\(^{-1}\)). To prepare catalysts by the urea technique, a solution of IrCl\(_3\)-xH\(_2\)O in water was added to a vigorously stirred and heated (365 K) aqueous suspension of the support and urea (Merck, p.a., ten-fold excess of urea based on iridium) adjusted to pH=2.5 by addition of HCl. The reaction was allowed to proceed for 10 h, after which time the suspension was filtered, the residue washed with distilled water and dried at 395 K for 16 h (heating rate 2 K min\(^{-1}\)). Part of the dried catalyst was prereduced in flowing hydrogen at 773 K for 1 h (heating rate 5 K min\(^{-1}\)). Prior to removing the catalysts from the reduction reactor, they were passivated at room temperature by replacing the hydrogen-flow by nitrogen and subsequently slowly adding oxygen up to 20%. The dried, reduced and passivated catalysts were stored in a dessicator for further use. XPS studies have shown that in the case of 1.5 wt% Rh/Al\(_2\)O\(_3\) a considerable amount of chlorine remained on the support after reduction (Cl/Rh\(_{\text{surface}}\)= 1.7), while in the case of 1.5 wt% Rh/SiO\(_2\) almost no chlorine was present in the reduced samples (Cl/Rh\(_{\text{surface}}\)= 0.1) [7].

Characterization techniques

Chemisorption measurements. Volumetric hydrogen and carbon monoxide chemisorption measurements were performed in a conventional glass system at 298 K. The catalyst sample (typically 0.5 g) was placed in a quartz reactor attached to the chemisorption apparatus using greased quick fit glass joints. Hydrogen was purified by passing through a palladium diffusion cell, carbon monoxide (researchgrade) was used without further purification. Before measuring the H\(_2\) and CO chemisorption the catalysts were reduced at 773 K (heating rate 8 K min\(^{-1}\)) for 1 h and evacuated at 773 K for 0.5 h resulting in an ultimate vacuum of 10\(^{-2}\) Pa at the catalyst sample. After hydrogen admission at 473 K or carbon monoxide admission at 293 K desorption isotherms were measured at room temperature. The total amount of chemisorbed H atoms or CO molecules was obtained by extrapolating the linear high pressure part (20 kPa < P < 80 kPa) of the isotherm to zero pressure and by correcting for the extrapolated value of the bare support [27,28].

Hydrogen is admitted at 473 K because hydrogen adsorption at room temperature is a slow process. The H/Ir values obtained by admission at 473 K are somewhat higher than the H/Ir values obtained by admission at room temperature and waiting for 3 h, as was measured for 0.81 wt% Ir/Al\(_2\)O\(_3\) (H/Ir(473 K)= 2.68, H/Ir(298 K)=2.49).

In literature, often a distinction is made between reversibly and irreversibly adsorbed hydrogen [14,15]. We think that this is not correct because the amount of reversibly adsorbed hydrogen is dependent on the apparatus and pump used. The question of reversibly and irreversibly adsorbed hydrogen is extensively discussed
by Crucq et al. [27]. However, to get an idea of the amount of relatively weakly bonded hydrogen in our case, we have measured it for the 0.81 wt% Ir/Al₂O₃ catalyst. After 20 minutes of pumping, 23% of the originally adsorbed hydrogen could be readorsorbed (H/Ir_{rev} = 2.07, H/Ir_{rev}=0.61).

Temperature programmed reduction, desorption and oxidation. TPR, TPD and TPO experiments were carried out in 4% H₂ in Ar, 100% Ar and 4% O₂ in He, respectively, with 200-400 mg catalyst in an apparatus as described by Boer et al. [29]. H₂, Ar and He were purified over molecular sieves (Union Carbide, 5A) for the removal of water and over a BTS column for the removal of traces of oxygen. O₂ was purified over molecular sieves. A Thermal Conductivity Detector (TCD) of the diffusion type, is used to detect the difference of hydrogen or oxygen concentration of the mixture entering and leaving the reactor. The TCD signal monitored as a function of temperature, yields the TPR, TPD or TPO profile. The heating rate during all temperature programmed measurements was 10 K min⁻¹ and the gas flow rate 5 ml min⁻¹. The temperature ramp started at 223 K and ended at 873 K. Since water is formed during reduction of the supported oxides, the reactor effluent is dried by molecular sieves before entering the thermal conductivity cell. We have already described the sequence of experiments used during temperature programmed reaction elsewhere [16,21,30]. In a standard experiment a TPR is done on a dried catalyst, followed by a TPD (of the now reduced catalyst covered with hydrogen), followed by a TPO (of the reduced catalyst without adsorbed hydrogen), followed by a TPR (of the now oxidized catalyst). The amount of gas consumed (TPR, TPO) or produced (TPD) is expressed per total amount of metal (H₂/Ir, O₂/Ir and H/Ir respectively).

Ultraviolet/visible spectroscopy. In order to get more insight in the adsorption processes during impregnation UV/VIS-spectroscopy was used. Spectra were recorded by means of a Hitachi 150-20 Spectrophotometer equipped with an integrating sphere reflection unit. The samples were grounded and supported on a pellet by means of double sided adhesive tape. The scan speed was 200 nm min⁻¹.

RESULTS

A. Incipient wetness method catalysts

Hydrogen and carbon monoxide chemisorption. The hydrogen and carbon monoxide chemisorption results for the Ir/γ-Al₂O₃ and Ir/SiO₂ catalysts prepared by the incipient wetness method are represented graphically in Figure 1. For all Ir/Al₂O₃ catalysts, H/Ir is above 1.0, for the catalysts with metal loadings less than 2.5 wt%, H/Ir is even above 2.0. The H/Ir values for Ir/SiO₂ are below 1.0 for all metal loadings, indicating a lower dispersion for these systems. The CO-chemisorption measurements support this conclusion, CO/Ir for alumina supported iridium catalysts is higher than CO/Ir for silica supported systems. CO/Ir values were corrected for adsorption on alumina (20 μmol CO g⁻¹), SiO₂ did not adsorb CO.
Temperature programmed desorption. In figure 2, the TPD profiles of some of the hydrogen covered catalysts are presented. These TPD profiles were measured subsequent to the first TPR measurements so hydrogen admission took place at 873 K. Note that for TPD the heating rate of 10 K min\(^{-1}\) is low so that readsoption of hydrogen will take place and no kinetic parameters for hydrogen desorption can be determined. Nevertheless, the results can be used to obtain information about dispersion and differences in strength of hydrogen adsorption. The TPD profile of 0.4 wt% Ir/Si\(_2\)O\(_2\) is characterized by one broad peak around 473 K. Ir/Si\(_2\)O\(_2\) catalysts with higher loadings show a second maximum in hydrogen desorption at lower temperatures (273-323 K) indicating weaker bonded hydrogen. The TPD profile of 0.4 wt% Ir/Al\(_2\)O\(_3\) has a peak at 523 K, at somewhat higher temperature than the TPD peak of 0.4 wt% Ir/Si\(_2\)O\(_2\) and a small peak around 823 K. For the higher loaded Ir/Al\(_2\)O\(_3\) systems a third desorption area around 323 K is measured.

Although the hydrogen pressure range for the TPD measurements (0-5 kPa) differed from the hydrogen chemisorption measurements (20-80 kPa) and the temperature at which hydrogen was adsorbed is different, the H/Ir values obtained from the TPD experiments are in good agreement with the H/Ir values obtained from hydrogen chemisorption measurements for Ir/Al\(_2\)O\(_3\) and Ir/Si\(_2\)O\(_2\) systems (correlation coefficient \(R = 0.996\), slope = 0.993, intercept = 0.023).

Temperature programmed reduction and oxidation. The temperature programmed reduction profiles of the impregnated and dried Ir/Si\(_2\)O\(_2\) catalysts are all similar. The TPR of 2.3 wt% Ir/Si\(_2\)O\(_2\) is shown in Figure 3a. All Ir/Si\(_2\)O\(_2\) catalysts start to reduce at 323 K, show a maximum in hydrogen consumption at 473-483 K and have a weak tail up to 673 K. The hydrogen consumption around 1.5 H\(_2\)/Ir is in agreement with the theoretical value for the reduction of Ir\(^{3+}\) to metallic Ir. The dried and impregnated Ir/Al\(_2\)O\(_3\) systems (Figure 3b,c) start to reduce at 323 K, have a maximum in hydrogen consumption at 413 K and a shoulder at 443 K. Between 493 and 593 K desorption of hydrogen, adsorbed during the reduction, occurs. The net hydrogen consumption during the whole TPR run amounted to 1.4-1.7 H\(_2\)/Ir, indicating that the degree of reduction of iridium after a TPR run is 100 % (± 5%). The TPR profile of 6.8 wt% Ir/Al\(_2\)O\(_3\) (Figure 3d) shows a main peak around 420 K and a second peak around 480 K. Although the experiments indicate that crystalline IrCl\(_3\) is not present in Ir/Al\(_2\)O\(_3\), nor in Ir/Si\(_2\)O\(_2\) (crystalline IrCl\(_3\) has a maximum in hydrogen consumption at 503 K, Figure 3e), the reduction behaviour of Ir/Si\(_2\)O\(_2\) resembles that of crystalline IrCl\(_3\) most.

Figure 3f and g show the TPR profile of a passivated Ir/Al\(_2\)O\(_3\) and Ir/Si\(_2\)O\(_2\) catalyst. All passivated catalysts show a hydrogen consumption maximum around 373 K followed by a hydrogen desorption. The net hydrogen consumption per iridium is dependent on the metal loading and the support. For Ir/Al\(_2\)O\(_3\) H\(_2\)/Ir varied between 1.0 (high metal loading) and 1.3 (low loading), for Ir/Si\(_2\)O\(_2\) H\(_2\)/Ir varied between 0.6 (high loading) and 1.1 (low loading). For highly dispersed Rh/Al\(_2\)O\(_3\) Vis et al. [16] found that during passivation rhodium was almost completely oxidized. The
FIGURE 1 Hydrogen and carbon monoxide chemisorption of catalysts prepared by the incipient wetness method:

- o: H/Ir for Ir/Al$_2$O$_3$
- x: H/Ir for Ir/SiO$_2$
- □: CO/Ir for Ir/Al$_2$O$_3$
- +: CO/Ir for Ir/SiO$_2$

FIGURE 2 Temperature programmed desorption profiles of Ir/Al$_2$O$_3$ and Ir/SiO$_2$ catalysts prepared via the incipient wetness method:  

- a. 0.4 wt% Ir/SiO$_2$
- b. 2.3 wt% Ir/SiO$_2$
- c. 7.0 wt% Ir/SiO$_2$
- d. 0.4 wt% Ir/Al$_2$O$_3$
- e. 2.6 wt% Ir/Al$_2$O$_3$
- f. 6.8 wt% Ir/Al$_2$O$_3$
FIGURE 3  Temperature programmed reduction profiles of:
- impregnated and dried 2.3 wt% Ir/SiO$_2$ (a), 0.8 wt% Ir/Al$_2$O$_3$ (b), 2.6 wt% Ir/Al$_2$O$_3$ (c) and 6.8 wt% Ir/Al$_2$O$_3$ (d) catalysts
- IrCl$_3$.xH$_2$O (e)
- reduced and passivated 3.8 wt% Ir/Al$_2$O$_3$ (f) and 3.7 wt% Ir/SiO$_2$ (g) catalysts.
FIGURE 4 Temperature programmed oxidation profiles of reduced Ir/SiO$_2$ and Ir/Al$_2$O$_3$.

FIGURE 5 The influence of the oxidation temperature on the H/Ir for 2.3 wt% Ir/SiO$_2$ and 1.0 wt% Ir/Al$_2$O$_3$.
present results show that for highly dispersed iridium systems this is not the case.

The TPO profiles of the Ir/Al₂O₃ and Ir/SiO₂ catalysts are shown in Figure 4. For all Ir/SiO₂ systems, oxygen consumption starts at 223 K. Furthermore, the oxygen consumption rises again at the beginning of the temperature ramp. Besides a broad oxygen consumption area around 325-373 K, two maxima around 573 and 773 K are visible. The third area around 773 K is becoming more important at higher metal loadings. For all catalysts the oxygen consumption per iridium is around 1.0, indicating the formation of IrO₂. The TPO's of the low loaded Ir/Al₂O₃ systems (< 3 wt%) showed some oxygen consumption at 223 K, a rise of O₂-consumption at the beginning of the temperature ramp and a maximum at 373-473 K. The TPO profiles of the reduced Ir/Al₂O₃ catalysts with higher loadings also showed oxidation around 773 K. The total oxygen consumption for all catalysts amounted to 1.0, indicating the formation of IrO₂.

The TPR profiles of the oxidized Ir/SiO₂ and Ir/Al₂O₃ systems were all the same, a very sharp reduction peak at about 493 K with a hydrogen consumption of H₂/Ir = 1.9-2.1 in agreement with the theoretical value of 2.0 for the reduction of IrO₂. The reduction peak was rather sharp (width at half height is 30 K, while for the impregnated and dried systems this is 50-100 K) and no desorption was seen after the reduction peak (for Rh/Al₂O₃ and Rh/SiO₂ systems such desorption has been observed in the TPR of the oxidized systems [16]).

In literature several authors [23,35] reported that the dispersion of supported iridium systems is badly influenced by oxygen at elevated temperature. We have studied this effect for the Ir/Al₂O₃ and Ir/SiO₂ catalysts prepared by the incipient wetness method. In Figure 5, the relative dispersion for a 2.3 wt% Ir/SiO₂ (H/Ir = 0.75) and a 1.0 wt% Ir/Al₂O₃ (H/Ir = 1.9) catalyst is shown as a function of the oxidation temperature (oxidized in 5 % O₂ in N₂, starting temperature 298 K, heating rate 5 K min⁻¹, final temperature Tox maintained for 1 h). The dispersion of the Ir/SiO₂ system starts to decrease after an oxidation for 1 h at 473 K and is very small (H/Ir < 0.1) after oxidation above 773 K. Ir/Al₂O₃ behaves similar although the decrease in dispersion is at a somewhat higher oxidation temperature (573 K), indicating a higher interaction between iridium oxide and the support in the latter case. TPR profiles of 1.0 wt% Ir/Al₂O₃ oxidized at different temperatures (the reduced and passivated system was oxidized in 4 % O₂ in He, Tstart =298 K, heating rate 5 K min⁻¹, 1 h at Tox) are shown in Figure 6. After oxidation at higher temperature a reduction peak at 493 K becomes visible. Oxidation at 773 K results in one sharp peak at 493 K and the disappearance of hydrogen desorption.

UV/VIS-spectroscopy. In order to obtain more information about the adsorption processes during the incipient wetness method, UV/Vis spectroscopy was used. In Figure 7, the spectra for 3.8 wt% Ir/Al₂O₃, 3.7 wt% Ir/SiO₂ and physically mixed IrCl₃ and SiO₂ are presented. The adsorption spectrum of 3.7 wt% Ir/SiO₂ (Figure 7b) resembles that of physically mixed IrCl₃-SiO₂, an absorption peak at 300 nm and
FIGURE 6 TPR profiles of 1.0 wt% Ir/Al₂O₃ oxidized at different temperatures after reduction.

FIGURE 7 UV/Vis spectra of 3.8 wt% IrCl₃/Al₂O₃ (a), 3.7 wt% IrCl₃/SiO₂ (b) and IrCl₃-SiO₂, physically mixed (c).
a shoulder at 390-400 nm. The spectrum of 3.8 wt% Ir/Al₂O₃ is quite different, it shows an absorption peak at 570 nm and one at 300 nm.

B. Catalysts prepared by the urea technique

Hydrogen chemisorption. The hydrogen chemisorption data for the Ir/Al₂O₃ and Ir/SiO₂ catalysts prepared by the urea technique are presented in Table 1. The H/Ir values of the Ir/Al₂O₃ catalysts prepared by this method are comparable to those of Ir/Al₂O₃ systems prepared with the incipient wetness method, while the H/Ir values for the Ir/SiO₂ systems prepared by the urea method are by a factor 2-3 higher than those of the incipient wetness method, indicating that the urea technique produces highly dispersed iridium on both supports.

TABLE 1
Hydrogen chemisorption measurements of Ir/Al₂O₃ and Ir/SiO₂ catalysts prepared by the urea technique.

<table>
<thead>
<tr>
<th>system</th>
<th>H/Ir</th>
<th>system</th>
<th>H/Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 wt% Ir/Al₂O₃</td>
<td>2.45</td>
<td>1.5 wt% Ir/SiO₂</td>
<td>1.65</td>
</tr>
<tr>
<td>5.7 wt% Ir/Al₂O₃</td>
<td>1.62</td>
<td>5.3 wt% Ir/SiO₂</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Temperature programmed reduction, desorption and oxidation. The TPR, TPD and TPO profiles of the catalysts prepared by the urea method are presented in Figure 8. The profiles of the alumina and silica supported systems are similar. The reduction of the dried samples starts at 373 K and proceeds up to 773 K. The H₂/Ir values are rather high (1.6-2.8), indicating that not only Ir³⁺ (H₂/Ir = 1.5) has been reduced. Elemental analysis, using a Perkin Elmer Element Analyzer Model 240, shows that nitrogenous decomposition products of the urea are deposited on the catalyst (5.7 wt% Ir/Al₂O₃ : 0.14 wt% N, 5.3 wt% Ir/SiO₂ : 0.62 wt% N), no carbonaceous decomposition products were found. Hydrogenation of these nitrogenous deposits results in an increased hydrogen consumption. The hydrogen desorbed per iridium during the TPD is in agreement with the hydrogen chemisorption results (see Figure 8B). The TPD profiles of the Ir/SiO₂ and Ir/Al₂O₃ systems prepared by the urea technique resemble the TPD profiles of the Ir/Al₂O₃ systems prepared by the incipient wetness method, except for the desorption peak at high temperature which is only present in the TPD profiles of the Ir/Al₂O₃ systems. The TPO profiles of the reduced systems show a broad oxygen consumption area, already starting at 298 K. The high temperature oxygen consumption (around 773 K), measured for the Ir/SiO₂ systems and higher loaded Ir/Al₂O₃ systems prepared by the incipient wetness method, is absent.
FIGURE 8 TPR, TPD and TPO profiles of Ir/Al$_2$O$_3$ and Ir/SiO$_2$ catalysts prepared by the urea technique:

- a: TPR of dried catalysts
- b: TPD of reduced and hydrogen covered catalysts
- c: TPO of reduced catalyst
DISCUSSION

Hydrogen chemisorption has been used through the years by many workers to characterize metal surfaces [1,23,31-35]. When attempts were made to calculate metal surface areas from hydrogen chemisorption data, a hydrogen to metal stoichiometry of one has been used. Recently several authors published H/M and also CO/M values exceeding unity. Wanke and Dougharty [31] reported the adsorption of more than one hydrogen atom per surface rhodium atom for Rh/Al₂O₃ catalysts, Vis et al. [16,21] reported H/Rh = 1.53 for 2.3 wt% Rh/Al₂O₃, Krishnamurthy et al. [15] showed that Ir/Al₂O₃ (0.2-1.0 wt%) chemisorbed up to two hydrogen atoms and carbon monoxide molecules per iridium atom using only the strongly bonded hydrogen. McVicker et al. [14] found the same upper limit of 2.0 adatoms per Ir. Taking into account the total amount of adsorbed hydrogen, McVicker and Krishnamurthy reported H/Ir values up to 2.5 for 0.5 wt% Ir/Al₂O₃. Crucq et al. [27] reported H/Pt = 1.32 for 5.7 wt% Pt/SiO₂. Recently Sato [36] described a Pt/TiO₂ system made by photoimpregnation of hexachloroplatinic acid with H/Pt = 2.5.

First of all, we want to exclude several trivial effects which could explain the high H/M values:
- unreduced Ir³⁺ was not present, as can be concluded from the TPR experiments. Within the experimental error (5%), all Ir was reduced to Ir⁰.
- contamination of the catalyst with carbon did not occur. Elemental analysis (using Perkin Elmer Element Analyzer Model 240) showed that no carbon residues existed initially on the catalyst. Carbon residues could be produced by grease or oil vapours during evacuation. However, the TPD measurements are absolutely grease and oil vapour free, and resulted in similarly high H/Ir values.
- partial reoxidation during outgassing at high temperature, mentioned by Martin et al. for Fe [37] and Ni [38], can be excluded because oxygen consumption during oxidation at 773 K after reduction and evacuation at 773 K was measured to be 1.96 O/Ir for 1.5 wt% Ir/Al₂O₃ (H/Ir = 2.4). IrO₂ is the most stable oxide of iridium, so this result shows that reoxidation can only account for an increase in hydrogen chemisorption of 0.08, proving that H/Ir values in excess of 1.0 are not caused by reoxidation of the metal during outgassing.

The high hydrogen chemisorption data are often explained by hydrogen spillover on the support. Although we cannot completely exclude this, we think that the H/Ir values (up to H/Ir = 3.0) presented here are real and that the chemisorbed hydrogen is all bound to the metal. Modeling calculations of the area around a small particle on a support confirm the idea that more than one hydrogen atom can be adsorbed per metal atom. A computer programme was made to determine the area available for chemisorption around a supported small metal particle. In the spirit of Wynblatt and Gjeststein [39] the shape of the metal particle was calculated as a function of the relative magnitude of the metal-metal and metal-support interaction energy by minimizing the total energy. We assumed the support to consist of a flat (111) layer of oxygen anions, the size of which was taken equal to that of the
metal atoms. The metal atoms were assumed to be fcc packed, and thus to fit epitaxially on the support surface. The shape of a metal particle with \( n + 1 \) atoms was obtained from that of the particle with \( n \) atoms by putting the extra metal atom at the position of minimum energy. Such calculations were carried out over a whole range of \( \alpha \) values, with \( \alpha \) being the ratio of the metal atom-oxygen anion interaction \( E(M-O^{2-}) \) and the metal atom-metal atom interaction \( E(M-M) \).

To obtain an estimate of the number of hydrogen atoms that can be placed around such a metal particle, we assumed that the hydrogen atoms will occupy the free fcc positions around the metal particle and that only one hydrogen atom per vacant fcc position is allowed. Although X-ray diffraction results for metal hydride complexes point to a hydrogen atom radius which is much smaller than that of the Ir atoms [40], the same results also point out that H-H distances smaller than M-M distances are rarely observed. Our assumptions therefore seem very reasonable.

**TABLE 2: Results of computer calculation on small metal particles.**

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>( \alpha = 0.5^a )</th>
<th>( \alpha = 2.0^a )</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
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<tr>
<td>1 metal neighbour</td>
<td>9 15 16 19 36</td>
<td>11 13 14 14 29</td>
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<tr>
<td>5</td>
<td>0 0 2 2 15</td>
<td>0 0 0 0 18</td>
</tr>
<tr>
<td>Dispersion</td>
<td>1.0 1.0 0.80 0.62 0.36</td>
<td>1.0 1.0 0.80 0.60 0.35</td>
</tr>
<tr>
<td>H/Ir (c)</td>
<td>4.5 3.0 1.8 1.0 0.46</td>
<td>4.5 2.9 1.7 1.0 0.45</td>
</tr>
<tr>
<td>H/Ir (d)</td>
<td>2.3 1.5 1.2 0.85 0.42</td>
<td>1.8 1.6 1.2 0.85 0.41</td>
</tr>
<tr>
<td>D (Å)</td>
<td>5.6 9.0 12 19 35</td>
<td>7.6 10 14 20 38</td>
</tr>
</tbody>
</table>

a) \( \alpha = E(M-S)/E(M-M) \).
b) empty f.c.c. positions around the metal particle that have at least one metal neighbour, which can be occupied by H atoms.
c) assuming that all f.c.c. positions around the particle with at least one metal neighbour, are filled by hydrogen.
d) assuming that only positions with more than one metal neighbour are filled by hydrogen.

Table 2 summarizes the results of the calculations for two situations, one in which the interaction between metal and oxygen is half that of the metal-metal interaction, \( E(M-O^{2-}) = 0.5 \ E(M-M) \), which results in spherical particles, and one in which \( E(M-O^{2-}) = 2 \ E(M-M) \), resulting in raft-like particles. Dispersions
(defined as the fraction exposed metal atoms), diameters of the particles and H/M values are presented as a function of the number of atoms per particle. The H/M values were calculated on the basis of two assumptions. Very high H/M values (up to 4.5) were obtained if hydrogen was allowed to occupy all free fcc positions, even those where hydrogen is bonded to only one metal atom. If only free positions, where the hydrogen atom is bonded to at least two metal atoms were considered, still a H/M value of 2.3 could be obtained.

On the basis of these calculations, one can conclude that geometrically very high H/M values can be obtained for fcc packed metals. For Ir, high H/M values are actually measured. For Rh and Pt, H/M values are not exceeding two. In a recent paper we studied metal particle sizes in Ir, Pt and Rh catalysts using hydrogen chemisorption and EXAFS [41]. The metal-metal coordination number N, which gives information about the metal particle size, versus H/M relationship could be described by a single straight line for each metal. Differences in adsorption stoichiometries between the metals were explained using electronic reasons. The order of H/M_surface stoichiometries for Pt, Rh and Ir was found to be analogous to the order of stability of the corresponding metal polyhydride complexes. This study also demonstrated that the high H/M stoichiometries cannot be a result of hydrogen spillover to the support.

The CO/Ir values also exceed unity. The measured values had to be corrected for adsorption on the support in the case of Al2O3. Krishnamurthy et al. [15] also noted the adsorption of CO on Al2O3, while McVicker [14] did not mention this effect.

As a consequence of the variability of the hydrogen-metal and carbon monoxide-metal stoichiometry, it is impossible to calculate particle sizes from chemisorption data for the highly dispersed systems. Nevertheless, the chemisorption data can be used to compare dispersions of different systems, taking into account the linear relationship between the metal-metal coordination number N and the measured H/Ir values [41].

The chemisorption measurements presented in this paper clearly show that using the incipient wetness method, well dispersed Ir/SiO2 catalysts and very highly dispersed Ir/Al2O3 catalysts can be obtained. For both systems, a systematic decrease of the relative amount of adsorbed hydrogen (or carbon monoxide) with increasing iridium content is observed, reflecting a decrease in dispersion at higher metal loadings.

Temperature programmed desorption measurements support this conclusion. The amount of desorbed hydrogen per iridium atom agrees with the H/Ir values observed in the hydrogen chemisorption measurements. The TPD profiles (Figure 2) also show that in the case of high H/Ir values the hydrogen is adsorbed more strongly on the metal surface (desorbing at higher temperature). For the Ir/Al2O3 systems, three species were detected during desorption, similar to the desorption spectra reported in literature for supported Ir and Pt catalysts [42,43]. Candy et al. [39] detected
two species desorbing at 223-323 K ($\beta_1$) and at 373-673 K ($\beta_2$) for supported Pt catalysts. The formation of $\beta_2$ is reported to be activated, with an activation energy of $5 \pm 2$ kcal mol$^{-1}$. From Figure 2, one can conclude that the higher loaded catalysts desorbed more hydrogen at low temperature, the $\beta_1$ type. For the alumina supported systems a third desorption area around 823 K is observed. Candy et al. also reported this high temperature desorption peak ($\beta_3$), when hydrogen was admitted at high temperature (900 K) as also was done in our experiment (873 K). They interpreted this species as H atoms in bridged position between metal and support. However, Escard et al. [43] reported desorption of hydrogen around 800 K for a 36 % Ir/Al$_2$O$_3$ catalyst and for unsupported Ir. We therefore believe that the hydrogen desorbing at high temperatures is not linked to the support or support-iridium interface, but is really bonded to the metal.

Hydrogen on Ir/Al$_2$O$_3$ desorbs at a higher temperature than on Ir/SiO$_2$ and desorption of hydrogen adsorbed on samples with a high iridium loading occurs at a lower temperature, so hydrogen bond strength increases with decreasing particle size, as is expected if stronger bonding is associated with metal atoms of lower coordination number such as edge and corner sites [44]. In a recent study of the heat of adsorption on Pt catalysts, Vannice et al. [45] reported an opposite trend, a decrease in heat of adsorption with decreasing particle size. Thus, our hydrogen chemisorption and TPD experiments indicate very clearly that our Ir/Al$_2$O$_3$ catalysts are indeed highly dispersed.

The TPR profile of the dried IrCl$_3$/SiO$_2$ catalysts almost resembles the profile of pure IrCl$_3$.H$_2$O, whereas the dried IrCl$_3$/Al$_2$O$_3$ catalysts reduce at much lower temperature. Hydrogen consumption during the TPR profile showed that within the uncertainty of the method complete reduction to metallic iridium occurred in both cases ($H_2/Ir = 1.5$).

The difference between the silica and alumina supported systems must be due to the adsorption properties of the supports. When an excess of IrCl$_3$ solution was added to alumina and silica in an adsorption experiment (2 h), a 3.8 wt% Ir/Al$_2$O$_3$ and a 0.01 wt% Ir/SiO$_2$ catalyst was obtained (when all metal salt would have been adsorbed, a 4.6 wt% Ir catalyst would have resulted in both cases). We also noticed that the pH of the IrCl$_3$ solution increased during the adsorption in the case of alumina. Thus the pH of the starting IrCl$_3$ solution was 1.9, the pH of the solution after adsorption on alumina was 4.9, while the pH of the solution in the case of adsorption on silica remained 1.9. We think that alumina OH groups are protonated during adsorption, forming adsorption sites for anionic iridium complexes in solution, probably [IrCl$_3$(H$_2$O)$_2$(OH)]$^-$. The UV/Vis-spectra supported this idea. The reflection spectrum of the impregnated IrCl$_3$/SiO$_2$ system resembled that of physically mixed IrCl$_3$ and SiO$_2$, while the spectrum of the impregnated IrCl$_3$/Al$_2$O$_3$ system was completely different. The OH-groups of the silica can not be protonated in the pH-region used and therefore no adsorption sites are available for the negatively charged iridium complexes in the solution. Thus, during the incipient wet-
ness method, the IrCl₃ adsorbs on alumina and a high dispersion is obtained. On the contrary, on SiO₂ no adsorption occurs (no sites available) and during the drying process the IrCl₃ is deposited as crystallites on the surface of the support. Now we can understand the different TPR profiles of the impregnated and dried samples. The reduction profile of IrCl₃/SiO₂ resembles that of IrCl₃ because on silica crystallites of IrCl₃ are formed during the drying process. In case of alumina, with low metal loading, IrCl₃ is adsorbed as a complex on the surface and therefore its reduction behaviour is influenced by the support. Apparently single [IrCl₃(H₂O)₂]⁺ species are more easy to reduce than crystallites of IrCl₃·xH₂O. In the case of the 6.8 wt% Ir/Al₂O₃ catalyst, the iridium loading is above the loading that can maximally be obtained by adsorption (3.8 wt%), so only part of the IrCl₃ is adsorbed during the impregnation, the rest is deposited as larger particles during the drying of the catalyst, resulting in a bimodal particle size distribution. The first part reduces easily, like Ir/Al₂O₃ with a low metal loading, the latter part reduces at a higher temperature, like an Ir/SiO₂ catalyst. Summarizing the above mentioned results, the chemisorption and TPR measurements of the dried systems clearly show that the incipient wetness method provides very highly dispersed Ir/Al₂O₃ catalysts and reasonably dispersed Ir/SiO₂ catalysts.

The TPR profiles of the passivated catalysts (Figure 3f,g) show that during passivation no complete oxidation to IrO₂ has occurred (0.6 < H₂/Ir < 1.3). This is in contrast to the results published by Vis et al. [16,21] for the passivation of well dispersed Rh/Al₂O₃ systems. Two explanations for this effect can be given:
- during passivation the iridium particles are covered only by a layer of chemisorbed oxygen and real oxidation does not occur at all
- during passivation a protective oxide skin is formed, preventing further oxidation at room temperature.

The amount of hydrogen used per iridium during the reduction of the passivated systems decreases with increasing metal loading and is higher for the Ir/Al₂O₃ systems than for the Ir/SiO₂ systems. Thus the higher dispersed systems more oxygen molecules have adsorbed/reacted per iridium atom during passivation.

During TPO, oxygen consumption per iridium atom was close to 1.0, indicating the formation of the thermodynamically most stable IrO₂ phase. The TPO profiles of Ir/SiO₂ show three areas of oxygen consumption. The exact assignment of processes responsible for the oxygen consumption in these three areas is difficult since literature does not provide much information about the mechanisms of oxidation of supported metal catalysts. However, the theory of metal oxidation, dealing with bulk materials, does provide three phenomena as separated stages in oxidation processes, as we described before [16,21]. The first stage of oxidation is chemisorption, which is known to occur at clean surfaces [46] at low temperatures. Formation of an oxide film, the second stage, occurs at temperatures typically up to 573-673 K, following a logarithmic rate equation and leading to an oxide film [47-49]. Finally Wagner's oxidation theory [50] describes the third stage, the oxi-
dation process of the bulk, rate controlled by volume diffusion of the reacting ions and/or electrons through the growing oxide scale, leading to parabolic rate equations. We suppose that analogous models can describe the oxidation processes in supported metal particles, dependent on their sizes. We think that the three processes mentioned, oxygen chemisorption, oxidation of the skin and thorough oxidation are related to the three observed oxygen consumption areas. The first two stages of oxygen consumption are visible for all catalysts. The third stage, the thorough oxidation, however, is absent for the low loaded Ir/Al₂O₃ samples, and increases for both Ir/Al₂O₃ and Ir/SiO₂ with metal loading. Since dispersions, as measured with H₂ and CO chemisorption, decrease with metal loading, there is clearly a relation between particle size and the high temperature oxygen consumption. For the very highly dispersed low loading Ir/Al₂O₃ catalysts thorough oxidation is absent, indicating that the particles are very small indeed. As the dispersion, related to the fraction of surface metal atoms, decreases, the particle size and the size of the metallic (bulk like) kernel will increase, accompanied with a higher oxygen consumption at high temperatures, as can be seen in Figure 4. The oxygen consumption during the first and second peak can also be used to determine the dispersion, since during these processes only the surface is oxidized. However, the third peak is badly separated from the first and second peak so no quantification can be made. Qualitatively, we observe a correlation between the H/Ir and CO/Ir values and the amount of oxygen consumed during the first and second peak in the TPO. Note, that for 6.8 wt% Ir/Al₂O₃ (with H/Ir > 1), thorough oxidation is visible (high temperature oxidation peak), indicating that some of the metal particles have a (bulk like) kernel, as we also concluded from the TPR profile of the dried 6.8 wt% Ir/Al₂O₃ catalyst (Figure 3d). Thus, the TPO profiles support the conclusion of the chemisorption, TPD and TPR results that the Ir/Al₂O₃ catalysts are highly dispersed and the Ir/SiO₂ catalysts less well dispersed.

The TPR profiles of the oxidized samples show one very sharp reduction peak without any noticeable hydrogen desorption. This indicates the formation of large IrO₂ particles during the preceding TPO. Studies on the effect of the oxidation temperature on the dispersion of Ir/Al₂O₃ and Ir/SiO₂ confirm this. Oxidation at various temperatures followed by TPR clearly shows the formation of a distinct IrO₂ phase during oxidation, reducing in a very narrow temperature region (Figure 6). Several authors have described the loss of dispersion of supported iridium catalysts in oxygen atmosphere at elevated temperature. Wanke et al. [35] showed the loss of dispersion for Ir/Al₂O₃ systems, Foger et al. [23,51,52] for Pt-Ir/Al₂O₃, Pt-Ir/SiO₂ and Ir/TiO₂ systems. The latter authors concluded that if T₀ < 573 K, a surface oxide Ir₂O₃ is formed, but that if T₀ > 573 K, IrO₂ grows out from metal particles as thin blades or sheets due to the fact that IrO₂ is volatile. The reduction of the iridium oxide is autocatalytic, once metal particles have been nucleated, atomic hydrogen is produced which nucleates further metal particles on the adjacent oxide. It is likely that the surfaces of the large IrO₂ particles are
well defined. Thus, as all surfaces are very similar, reduction will start for all particles at about the same temperature. Since this first reduction is rate determining, this will result in a very sharp hydrogen consumption peak in TPR. We also see that the loss of dispersity due to the formation of large IrO₂ particles occurs at a lower temperature for Ir/SiO₂ (Figure 5), indicating an interaction between IrO₂ and alumina that prevents sintering of the iridium oxide at lower temperature.

From the results described above, we can conclude that IrCl₂, Ir and IrO₂ are very well dispersed on alumina, thus having an intimate contact with the support, while Ir, IrCl₃ and IrO₂ on SiO₂ are less well dispersed. Recent results of an EXAFS study of these catalysts [41,53] support these conclusions.

In order to get highly dispersed Ir/SiO₂ systems, the urea technique was used. H/Ir values exceeding unity and the absence of the high temperature oxidation area in the TPO's for the catalysts obtained by this method show that the urea technique is very well suited to prepare highly dispersed Ir/SiO₂ and Ir/Al₂O₃ catalysts. Two explanations can be given for these results:

- during the decomposition of urea the pH is smoothly increasing, causing the formation of insoluble iridium hydroxide. The hydroxide will deposit on the support in the form of tiny crystallites.
- during the decomposition of urea iridium forms complexes with NH₃, the SiO₂ surface will slowly be deprotonated because of the increase of pH and adsorption of Ir complexes on the support will be possible.

Adsorption of the [Ir(NH₃)₅Cl]Cl₂ complex on silica at pH = 10 resulted in a catalyst with a loading of only 0.2 wt% Ir (when all the available complex would have been adsorbed, a 2.5 wt% Ir catalyst would have resulted). This disfavours the second explanation, so we think that the high dispersion in the case of the urea technique is a result of the formation of tiny crystallites of insoluble iridium hydroxide. The urea technique enables one to make very dispersive Ir/SiO₂ catalysts, much better than with the incipient wetness method.

CONCLUSIONS

With a limited number of techniques, chemisorption measurements and temperature programmed reduction, desorption and oxidation, we have obtained a good insight into the state a catalysts can be brought in by impregnation and reduction/oxidation. Hydrogen and carbon monoxide chemisorption and TPR/TPD clearly showed the difference between Ir/SiO₂ and Ir/Al₂O₃ prepared by the incipient wetness impregnation. On alumina H/Ir was above 2.0 up to an iridium loading of 2.5 wt% and still above 1.0 for 6.8 wt% Ir, whilst in the case of Ir/SiO₂ H/Ir was below 1.0 even for an iridium loading of 0.4 wt%. Temperature programmed desorption experiments gave the same results. Reduction behaviour of the dried systems, oxidation behaviour of the reduced systems and the loss of dispersity as a function of oxidation temperature support this conclusion. The difference in dispersion is caused by the
absence of adsorption sites on the SiO₂ support during the incipient wetness impregnation. Thus, no mononuclear iridium species are adsorbed on this support and large salt crystallites are formed during the drying process. The urea method proved successful for both supports. During the decomposition of the urea (363 K), the pH of the solution increased slowly and small metal hydroxide particles were deposited on the carrier resulting in H/Ir = 1.6 for 1.5 wt% Ir/SiO₂ and H/Ir = 1.2 for 5.5 wt% Ir/SiO₂. The results for the alumina supported systems prepared via the urea method were comparable with those for the systems prepared via the incipient wetness method. Thus with these two methods we are able to prepare highly dispersed Ir/Al₂O₃ and Ir/SiO₂ systems.

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REFERENCES