Catalysis Letters, Vol. 114, Nos. 3–4, April 2007 (© 2007)
DOI: 10.1007/s10562-007-9051-7

Supported iridium catalysts prepared by atomic layer deposition: effect of reduction and calcination on activity in toluene hydrogenation

R. J. Silvennoinen,[a,b,*] O. J. T. Jylhä,[a,d] M. Lindblad,[c] H. Österholm,[c] and A. O. I. Krause[a]

[a] *Laboratory of Industrial Chemistry, Helsinki University of Technology, P.O. Box 6100, FI-02015 Helsinki, Finland*
[b] *Laboratory of Optics and Molecular Materials and Center for New Materials, Helsinki University of Technology, P.O. Box 2200, FI-02015 Helsinki, Finland*
[c] *Neste Oil Corporation, P.O. Box 310, FI-06101 Porvoo, Finland*
[d] *Planar Systems, Inc., Olarinluoma 9, P.O. Box 46, FI-02201 Espoo, Finland*

Received 22 November 2006; accepted 12 January 2007

Ligand removal from supported iridium catalysts prepared by atomic layer deposition from $Ir(acac)_3$ was studied by direct reduction in hydrogen flow and by calcination in oxygen flow followed by reduction in hydrogen flow, as well as by thermogravimetric analysis. Thermal decomposition of acac ligand residuals required high temperatures, and in samples containing no iridium the removal of carbonaceous species was not complete. Metallic iridium particles less than 2 nm in size were formed during direct reduction and larger particles upon calcination followed by reduction. The activity of the catalysts in toluene hydrogenation in most cases depended on particle size.

KEY WORDS: iridium catalysts; toluene hydrogenation; reduction; calcination; atomic layer deposition; ALD.

1. Introduction

Atomic layer deposition (ALD), which relies on self-terminating gas–solid reactions, is a useful method for the preparation of noble metal catalysts [1,2]. We have described the deposition of iridium from iridium(III) acetylacetonate, $Ir(acac)_3$, on alumina, silica, and silica–alumina supports [3]. After deposition of the metal compound, the catalyst is commonly activated through removal of the ligands in treatments with hydrogen (reduction) or oxygen (calcination). The effect of the activation procedure on iridium catalyst has earlier been studied by Lai *et al.* [4] and Cunha *et al.* [5]. Lai *et al.* [4] showed that, at 250 °C, oxygen causes oxidation and fragmentation of Ir_4 clusters prepared from $Ir_4(CO)_{12}$. After exposure of the oxidized and fragmented Ir_4 clusters to hydrogen at 300 °C, the original Ir_4 clusters are reconstructed with a minor degree of aggregation [4]. Cunha *et al.* [5] showed that, iridium on alumina exhibits larger particle sizes after reduction at 400 °C than after calcination followed by reduction at 400 or 500 °C. This observation concerning the tendency of iridium oxide to form aggregates [6] is of some interest. However, the catalysts of Cunha *et al.* [5] were prepared from H_2IrCl_6 and the chlorine residuals may have affected the particle size.

Temperature programmed desorption (TPD) and thermogravimetric (TG) studies in nitrogen have been used to clarify the mechanism of thermal ligand decomposition of supported β-diketonates (e.g. $M(acac)_3$). Until now, TPD or TG analyses have not been reported for supported $Ir(acac)_3$. The following results have been obtained for chromium(III) acetylacetonate, $Cr(acac)_3$, a compound proposed to behave similarly to $Ir(acac)_3$ in ALD reactions [3], and for acetylacetonate (2,4-pentanedione), H-acac. The main thermal desorption products for silica-supported $Cr(acac)_3$ and alumina-supported H-acac were acetone (at 250–400 °C) and CO_2 (at 300–450 °C) [7,8]. Acetone is formed in the reaction of M-acac$_x$ (M = Cr or Al) species with OH groups on the surface or with water released from the support upon heating. The mass loss in thermogravimetric analysis of silica-supported $Cr(acac)_3$ samples with a maximum at 290–310 °C has been attributed to the decomposition of hydrogen bonded acac ligands in associatively adsorbed $Cr(acac)_3$ [7,9–11]. The stability of surface Cr complexes increases when there is no hydrogen bond between acac ligands and the silica surface and when acac ligands decompose to acetate. The more stable Cr complexes are responsible for the second maximum, at 440 °C, in TG analysis. Temperature programmed reduction (TPR) has been used to study the reduction properties of metal catalysts [12].

Iridium catalysts have been used in toluene hydrogenation [5,13–15], naphthenic ring opening reactions [16], and selective reduction of nitrogen oxide (NO) [17,18]. In this work, the activity of iridium catalysts was tested in toluene hydrogenation reaction. Although toluene hydrogenation is known to be a structure insensitive reaction [19], earlier studies [5, 13–15] have

---

*To whom correspondence should be addressed.
E-mail: Riitta.Silvennoinen@tkk.fi

1011-372X/07/0400–0135/0

indicated that it requires iridium particles at least 1–3 nm in diameter for this structure insensitive behavior. Zhao *et al.* [13] and Xu *et al.* [15] suggested that as the particle size decreases, the increasing effect of the support, like ligand bonded to iridium, makes the iridium particles more non-metallic-like. The effect of the support on the particle size appears to be different on silica and alumina surfaces. The iridium particle size increases more as a function of iridium loading on silica than on alumina [5]. According to Cunha *et al.* [5], the explanation of the different aggregation tendencies is that, on alumina, strong Ir–Al_2O_3 interaction counteracts sintering of Ir particles.

Cunha *et al.* [5] report that alumina supported iridium catalysts prepared from H_2IrCl_6, calcined and thereafter reduced at 400–500 °C have turnover frequency (TOF) values in toluene hydrogenation at 60 °C of $1.6–1.9 \times 10^{-3}$ s^{-1}. After direct reduction at 400 °C the same catalysts have TOF values about five times as large. For Ir/Al_2O_3 catalysts prepared from $Ir_4(CO)_{12}$ and reduced directly at 200–400 °C, Alexeev *et al.* [14] measured TOF values at 60 °C of $17.2–55.3 \times 10^{-3}$ s^{-1}. After calcination at 300 °C followed by reduction at 400 °C TOF values for the same catalyst were about eight times as large. Although Cunha *et al.* [5] obtained better TOF values after direct reduction and Alexeev *et al.* [14] after calcination followed by reduction, both state that the catalyst activity increases as the particle size increases for particles under 2–3 nm. Also Zhao *et al.* [13] report that the activity of Ir_6 clusters on alumina in toluene hydrogenation is lower (per total iridium atom) than the activity of small aggregates of iridium (about 50 atoms each) on alumina.

The iridium catalysts used in this study were prepared by atomic layer deposition [3]. The mechanism for the reaction of $Ir(acac)_3$ in gas phase on alumina, silica–alumina, and silica supports was investigated earlier [3]. The main reaction mechanism on all supports is ligand exchange reaction with OH groups and the formation of Ir-$acac_x$ surface species. On alumina and silica–alumina, steric effects of acac ligand limit the amount of iridium deposited on the surface. Thus, H-acac was used to block some of the active sites and reduce the iridium content. H-acac reacts with alumina-type surface species forming Al-$acac_x$, as well as some Al-acetates, but it does not react with silica-type surface species [3,7,20]. Here, the blocking reduced the iridium content on alumina by more than 90%, but on silica–alumina by only 30–50%; on silica the blocking had almost no effect [3]. Al-$acac_x$ and Al-acetates were also observed after the reaction of $Ir(acac)_3$ on non-blocked alumina and silica–alumina. All ligand residues need to be effectively removed in the activation of both non-blocked and blocked iridium catalysts.

In this study we wished to clarify the mechanisms involved in the removal of ligands from ALD-prepared samples as a means of achieving active iridium catalysts. The activation of iridium catalysts, prepared by impregnation, has been studied earlier [4,5], but since the mechanism of iridium catalyst preparation is different when done by ALD and impregnation, the behavior in activation may well differ too. The activation of $Cr(acac)_3$ has been studied earlier [8–12], but as the noble nature affects the preparation process [3], the behavior of iridium in activation can be expected to be different from that of chromium. Catalytic activity of the iridium catalysts was tested in toluene hydrogenation and the results were compared with earlier results [5,13–15]. We studied the effect of reduction and of calcination followed by reduction on alumina and silica–alumina supported iridium catalysts prepared from iridium(III) acetylacetonate ($Ir(acac)_3$) by atomic layer deposition [3]. (The catalysts were characterized after direct reduction and after calcination followed by reduction and were tested in toluene hydrogenation.) Impregnated alumina catalyst was prepared from $IrCl_3$ and tested in toluene hydrogenation as a reference. Ligand removal mechanisms were studied by TG and TPR.

2. Experimental

Iridium(III)acetylacetonate, $Ir(acac)_3$, (Volatec Oy, Finland, purity 99.9%) was used as metal precursor and H-acetylacetone, H-acac, (Merck, purity >99%) as blocking agent. Support materials were γ-alumina (Akzo 001-1.5E) and two amorphous silica–aluminas (Nikki Chemical N-631-HN and N-632-HN). The silica–alumina samples had identical Al_2O_3 contents of 25.1 wt% (Si/Al = 2.54). The BET surface areas and pore volumes of the support materials after calcination in ambient air at 400 °C were 255 m^2/g and 0.72 cm^3/g for alumina, and 382 m^2/g and 0.55 cm^3/g (N-631-HN) and 470 m^2/g and 0.73 cm^3/g (N-632-HN) for the silica–alumina samples. These values were obtained with a Coulter Omnisorp 100CX apparatus.

The atomic layer depositions (ALD) were carried out in a commercial flow-type F-120 ALD reactor (Microchemistry Ltd., Finland) usually at 5–10 kPa. The reactions of $Ir(acac)_3$ and H-acac with the support were carried out at 200 or 250 °C. The ligands were removed by direct reduction or by calcination followed by reduction, as described below. Preparation of the catalysts by ALD is described in detail elsewhere [3].

Impregnated alumina-supported iridium catalyst was prepared as a reference sample for toluene hydrogenation studies. The aqueous impregnation was carried out at room temperature using $IrCl_3 \times 3H_2O$. Because of the low solubility of $IrCl_3 \times 3H_2O$ in water, the sample was prepared by wet impregnation. The sample was dried at 110 °C overnight. The iridium content after impregnation was 3.8 wt%.

The samples are named according to the preparation procedure. Samples with $Ir(acac)_3$ reacted with alumina and silica–alumina are denoted as IrA and IrSA, respectively, while samples with H-acac reacted with alumina and silica–alumina are denoted as BA and BSA, (B referring to the blocked support). When both precursors, $Ir(acac)_3$ and H-acac, were reacted with the support the notations are IrBA and IrBSA. The reaction temperatures are indicated at the end of the abbreviations (e.g. IrA200). The impregnated alumina-supported iridium catalyst is denoted as IrAimp.

The carbon contents of the samples were measured with a Leco SC-444 analyzer by combustion at 1350 °C in oxygen. Thermogravimetric analyses were performed with a Mettler TGA 850 instrument, with 15 mg samples in nitrogen atmosphere. The weight change was recorded as a function of temperature between 25 and 700 °C. The heating rate was 10 °C/min. Temperature programmed reduction (TPR) measurements were carried out with an Altamira Instruments AMI-100 catalyst characterization system. The samples (about 20 mg) were pretreated at 50 °C in argon flow. In the reduction procedure, samples were heated at 10 °C/min from 50 to 500 °C with 10% hydrogen–argon mixture flowing through the bed. Isothermal periods of 30 min were used at the beginning and end of the reduction measurements. The consumption of hydrogen was monitored with a thermal conductivity detector (TCD). Quantitation was made by pulse calibration, recorded as the average area of 10 pulses of 94 μL 10% hydrogen–argon mixtures.

Hydrogen uptake values of iridium were measured in a Coulter Omnisorp 100CX apparatus using static volumetric method with pure hydrogen at room temperature. Before the measurement, the sample (150 mg) was outgassed inside the apparatus at room temperature to a pressure of $670*10^{-6}$ Pa or better. It was then further pretreated in the apparatus by first purging with helium at 150 °C for 30 min. The effect of the activation procedure on hydrogen uptake and the efficiency of ligand removal was studied by reducing directly (direct reduction) or by first removing the ligands with oxygen and then reducing the metal oxide (calcination followed by reduction). In direct reduction the sample was reduced in pure hydrogen flow at the selected temperature for 2 h and then evacuated at 25 °C above the reduction temperature for 2 h. Calcination was done in a flow of 20% oxygen–helium mixture at the selected temperature for 2 h, followed by evacuation for 2 h. Calcination was followed by similar reduction steps as in direct reduction. Finally, the sample was cooled to room temperature for the adsorption measurement. The adsorption isotherm was measured twice with one hour evacuation between the measurements, thus giving both total and reversible adsorption isotherms. Particle sizes were calculated from the irreversible adsorption assuming spherical particles and using 22.65 g/m^3 for the density of iridium [21]. Hydrogen to metal stoichiometry of 1 was used.

The crystal structure of the iridium species was determined by X-ray diffraction (XRD) with a Siemens D500 apparatus equipped with a Cu anode and a curved graphite monochromator in the reflected beam. Crystal phases were identified with International Centre for Diffraction Data-Powder Diffraction Files (ICDD-PDF) reference library. Crystallite size was determined from the full width at half maximum (FWHM) of XRD reflections using the fundamental parameters program or Scherrer's equation. The [111] peak at 40° 2θ for Ir^0 and the [101] peak at 35° 2θ for IrO_2 were used for determinations of crystallite size. Both reduced and calcined samples were studied.

Catalyst activity was tested in toluene hydrogenation reaction. The reaction was carried out in a continuous tubular reactor (Altamira Instruments AMI-100) and gases were analyzed with a mass spectrometer (Balzers MSC200 MS-Cube). The sample was pretreated in the reactor using 20% oxygen–helium mixture for calcination and hydrogen for reduction. The mass spectrometer was calibrated with toluene (Riedel–de Haën 99.7%, Sigma–Aldrich) and methylcyclohexane (Aldrich 99%), while zero gas (background) calibration was done with 5% oxygen–helium mixture. In toluene hydrogenation reaction, 10% hydrogen–argon carrier gas was bubbled through 0 °C toluene. The input included 8900 ppm toluene calculated from vapor pressure. The sample was heated at 5 °C/min to 200 °C two or three times, and in between, it was cooled in a flow of 10% hydrogen in argon. Methylcyclohexane (MCH) was the only product observed (no cracking took place). Peaks of methylcyclohexane, toluene, argon, and hydrogen were followed with the mass spectrometer. The hydrogenation procedure was repeated two to three times, but only the first ramps are compared since deactivation changes the catalysts (not discussed here). Conversion was calculated by the formula: IN–OUT/IN, where IN was calculated as the sum of molar flows of methylcyclohexane and toluene out of the reactor and OUT was the molar flow of toluene out of the reactor. Turnover frequency (TOF) at 60 °C was calculated as molar flow (MCH_{out})/(hydrogen uptake × mass of catalyst).

All gases used in the analysis and measurements were at least 99.99% pure and purchased from AGA.

3. Results

3.1. Ligand removal

Ligands were removed under different treatments in Altamira Instruments AMI-100: by direct reduction with hydrogen at 275, 350, 400 and 450 °C, by calcination at 350 °C followed by reduction at 275 °C, or by calcination at 400 °C followed by reduction at 400 °C.

Table 1
Ligand removal treatments and carbon content before and after treatment

Sample (wt-% Ir)	Treatment	Carbon content % before treatment	Carbon content % after treatment
IrA200 (5.4%)	R350	4.6	0.4
	R400	4.6	0.4
	R450	4.2	0.3
	C350R275	4.6	0.3
	C400R400	4.6	0.2
IrA250 (6.1%)	C350R275	4.5	0.2
IrBA200 (0.14%)	R275	4.2	2.9
	C350R275	4.2	0.3
IrBA250 (0.45%)	R275	4.5	3.3
	R350	4.5	1.3
	R400	4.5	0.8
	C350R275	4.5	0.2
IrSA200 (7.2%)	R275	5.5	0.6
	R350	5.6	0.5
	R400	5.4	0.3
	C350R275	5.4	0.1
IrBSA200 (4.6%)	R275	7.6	1.2
	R350	7.6	0.9
	R400	7.6	0.7
	C350R275	7.6	0.3

Iridium contents are given in parenthesis after sample abbreviation. R indicates reduction, C indicates calcination and the numbers show the temperature of the treatment. For sample identification, see text.

The carbon contents of the samples before and after the various activation procedures are shown in table 1.

Higher reduction temperatures were required to remove the carbon from the blocked samples. Calcination at 350 °C followed by reduction at 275 °C appeared to be effective treatment for all samples since it decreased the carbon content below 0.5% in all cases.

Thermogravimetric analysis (TG) was performed on as-prepared ALD samples to determine at what temperatures ligands are released from or decomposed on the catalyst surface in nitrogen atmosphere. Since the support was calcined at 400 °C, the peaks above 400 °C may be partly due to the release of water through dehydroxylation of the support OH groups.

As shown in figure 1 after reaction of Ir(acac)$_3$ with alumina (IrA200), a weight loss maximum occurred at about 330 °C, but the width of the peak suggests that also another maximum may be present at around 400 °C. Blocked alumina with (IrBA250) and without iridium (BA250) exhibited a single weight loss maximum at about 420 °C. After reaction of Ir(acac)$_3$ with silica–alumina, (IrSA250), TG showed weight loss maximum at around 320 °C. Similar behavior was observed for iridium treated blocked silica–alumina (IrBSA250), where a single maximum is seen at about 330 °C, but the peak is wider than with IrSA250 suggesting that also another peak may be present. Blocked silica–alumina, (BSA250), exhibited a weight loss maximum at about 390 °C.

Previous results obtained by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy [3] showed the presence of Ir-acac$_x$ species on all samples containing iridium except IrBSA250. No peaks of Ir-acac were seen for IrBSA250 despite the relatively high iridium content of the sample (7.1 wt% Ir). This result was proposed to be due to covering the peaks of Ir-acac$_x$ by the strong Al-acac peaks. The presence of Al-acac$_x$ species was seen with DRIFT, most clearly in the blocked samples, and to some extent in the non-blocked samples.

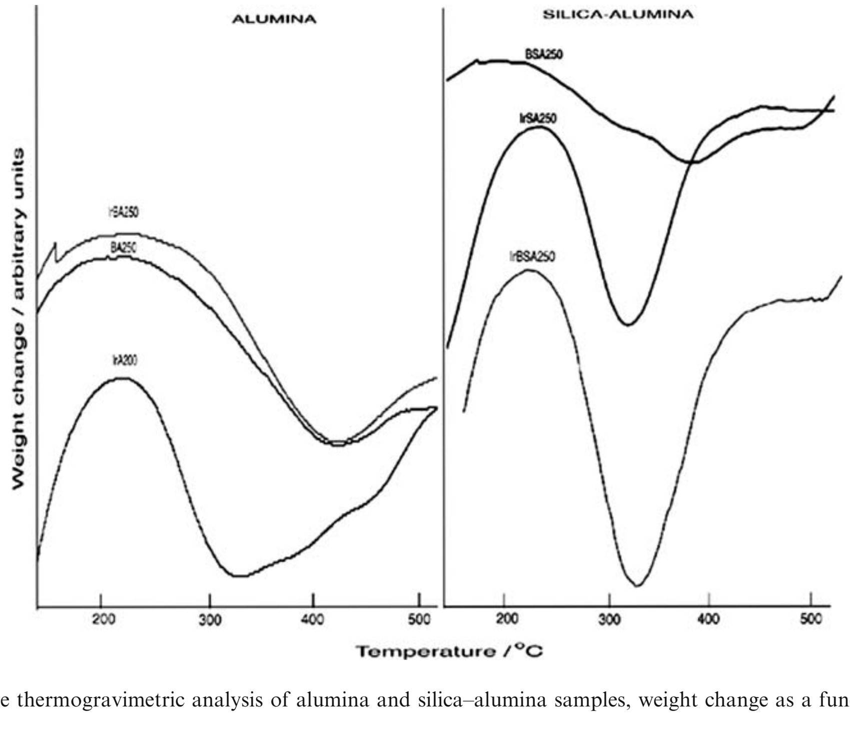

Figure 1. Derivative thermogravimetric analysis of alumina and silica–alumina samples, weight change as a function of temperature.

Since most acac ligands in IrA200 are bonded to iridium [3], the weight loss at 330 °C must be related to acac ligands in Ir-acac$_x$ species: their release as H-acac or their decomposition. Similarly, the weight loss at 420 °C on alumina may be related to the release or decomposition of acac ligands in Al-acac$_x$ species, for blocked samples as well as for IrA200, where also Al-acac$_x$ species are present [3,7]. The similar behavior of IrBA250 and BA250 can be explained by the very low iridium content of 0.45% in IrBA250. However, since the mass loss at 420 °C on blocked samples is less than the amount of carbon in the sample, evidently some carbonaceous species are not removed below 500 °C in N_2 atmosphere.

As on alumina, the weight loss on silica–alumina at the lower temperatures of 320–330 °C is related to Ir-acac$_x$ species, and at the higher temperature of 390 °C to Al-acac$_x$ species. The blocking did not reduce the iridium content to such a high degree on silica–alumina as on alumina and now the iridium containing samples, IrBSA250 and IrSA250, behaved similarly. The broadening of the peaks at 320–330 °C for the iridium containing samples towards higher temperature, especially for the blocked sample, indicates the presence of Al-acac$_x$ species.

Temperature programmed reduction was used to determine what temperature is needed to remove ligands with hydrogen from the catalyst surface.

After reaction between Ir(acac)$_3$ and alumina (IrA250, figure 2), the maximum hydrogen consumption was detected at 410 °C; no hydrogen consumption was detected on blocked alumina (BA250). Total hydrogen consumption of the IrA250 sample was 3300 μmol/g.

One silica sample containing 7 wt% of iridium was measured by TPR as a reference (figures 1 and 2). The maximum was detected at 380 °C and shoulder at 315 °C. Total hydrogen consumption was 1900 μmol/g.

Ir(acac)$_3$ deposited on non-blocked silica–alumina (IrSA250, figure 3) shows hydrogen consumption with maximum at 390 °C and shoulders at 330 and 450 °C. After reaction of Ir(acac)$_3$ with blocked silica–alumina (IrBSA250), the hydrogen consumption has a maximum at 420 °C and shoulder at 350 °C. Total hydrogen consumptions were >3000 μmol/g on both IrSA250 and IrBSA250. Almost no hydrogen consumption was detected on blocked silica–alumina (BSA250), only a slight increase around 340 °C. After calcination of IrSA250 at 350 °C, hydrogen consumption maxima appeared at 207 and 307 °C. The H_2 consumption at 207 °C corresponds to 800 μmol/g and that at 307 °C to 685 μmol/g. The Ir content was 530 μmol/g, which means that 1060 μmol H_2/g would be needed for full reduction of IrO_2 to Ir^0.

3.2. H_2 uptake

Hydrogen uptake as a function of activation treatment of iridium supported on alumina and silica–alumina is shown in figures 4 and 5. Hydrogen uptake per gram of iridium is used to measure the amount of active sites on catalyst.

On non-blocked alumina sample (IrA200), hydrogen uptake was highest after reduction at 400 °C, whereas on blocked alumina sample (IrBA250) hydrogen uptakes were highest after calcination at 350 °C followed by reduction at 275 °C. The IrBA250 with high hydrogen uptake values after calcination followed by reduction had very low iridium content, 0.45%. On silica–alumina, hydrogen uptake values were highest after reduction at 400 °C for both

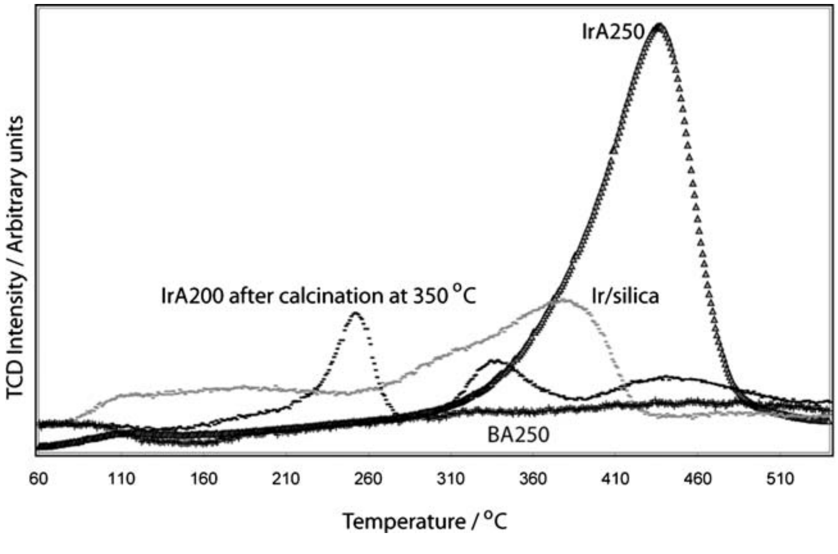

Figure 2. Temperature programmed reduction of alumina catalysts after blocking (BA250), after reaction with Ir(acac)$_3$ (IrA250) and of IrA200 after calcination at 350 °C. Iridium deposited on silica at 250 °C is shown as a reference.

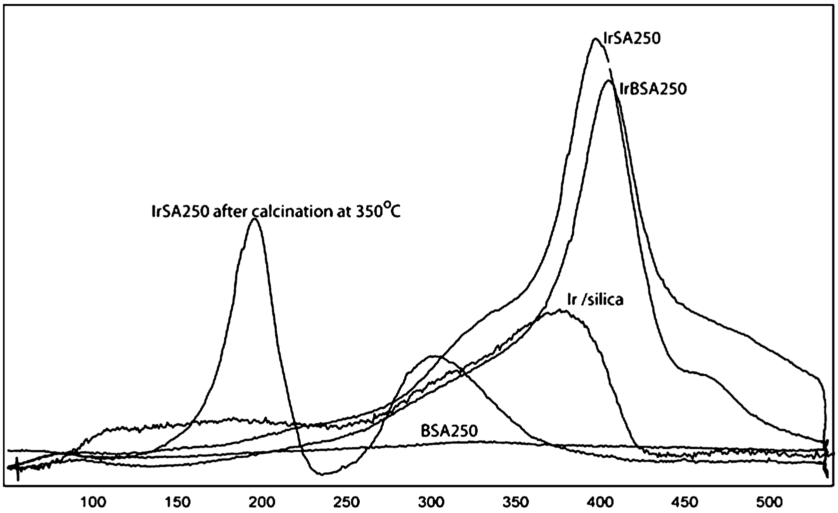

Figure 3. Temperature programmed reduction of silica–alumina after blocking (BSA250) and after reaction with Ir(acac)$_3$ (IrSA250); of blocked silica–alumina surface after reaction with Ir(acac)$_3$ (IrBSA250); and of IrSA250 after calcination at 350 °C. Iridium deposited on silica at 250 °C is shown as a reference.

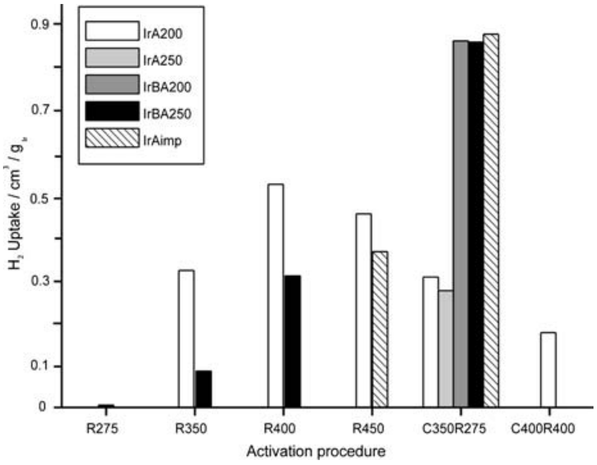

Figure 4. Hydrogen uptake as a function of activation procedure for alumina supported samples. All activation procedures were not carried for samples IrBA250 and IrAimp.

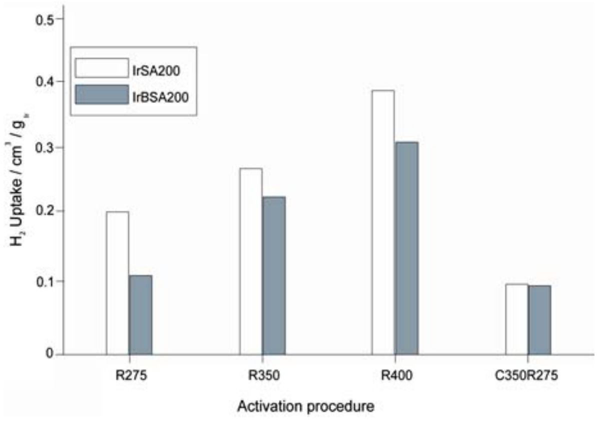

Figure 5. Hydrogen uptake as a function of activation procedure for silica–alumina supported samples IrSA250 and IrBSA250.

blocked and non-blocked sample. Iridium content was more than 4% in all samples. When reduction was done at low temperatures, especially with blocked samples, the carbon residuals were not all removed and lower hydrogen uptake values were observed (see Table 1).

The hydrogen-to-metal stoichiometry has been under debate in the literature and it has been proposed that the stoichiometry varies from 0.5 to 2.5 depending on the metal particle size and metal–metal coordination number [19,22,23]. Because of this variation, we do not convert hydrogen uptakes to dispersion values. Dispersion calculations normally assume hydrogen-to-metal stoichiometry of one. If this assumption is made here, the highest hydrogen uptake values in figure 4 coincide with dispersion values over 100% indicating that a hydrogen-to-metal stoichiometry greater than 1 should be used.

3.3. Crystalline state of iridium particles

X-ray diffraction (XRD) was used to determine the crystallite size of iridium after reduction and calcination treatments. After direct reduction of alumina and silica–alumina supported iridium catalysts (350–400 °C), no metallic iridium (Ir^0) was observed by XRD, indicating the presence of very small metal crystallites (under 2 nm). In calcination of silica–alumina supported iridium, IrO$_2$ with average crystallite size of 4.5 nm was formed. When the sample was reduced after calcination, metallic iridium with crystallite size of 3.4 nm was formed. Similar results were obtained for the alumina samples. The tendency of IrO$_2$ to sinter is related to the larger crystallite sizes obtained after calcination.

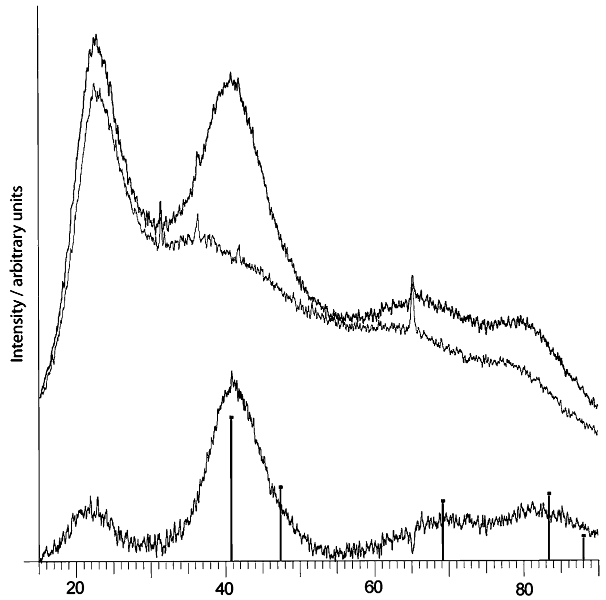

Figure 6. XRD patterns of iridium supported on silica, after exposure to argon at 320 °C (top), after ALD with $Ir(acac)_3$ (middle) and the differential pattern to which ICDD-PDF pattern 6-598 for metallic iridium is added.

Influence of inert heat treatment with argon at 320 °C on iridium supported on amorphous silica was tested. This support has no interfering XRD reflections with iridium compounds, subsequently the subtraction of the silica pattern from the pattern of the heat-treated sample can be made quantitatively. The residual XRD pattern clearly indicated that iridium was present in the metallic state and the crystallite size was less than 3 nm (figure 6).

3.4. Results of activity tests

Catalyst activity was measured in toluene hydrogenation reaction. Turnover frequencies as a function of hydrogen uptake are shown in figure 7. If H/Ir stoichiometry of one is assumed, the hydrogen uptakes in figure 7 correspond to particle sizes from 6.4 to 0.7 nm. In a structure insensitive reaction the TOF values would show no response to particle size. In our case, TOF values appear to increase as the particle size increases despite a change in the H/Ir stoichiometry from 0.5 to 2.5.

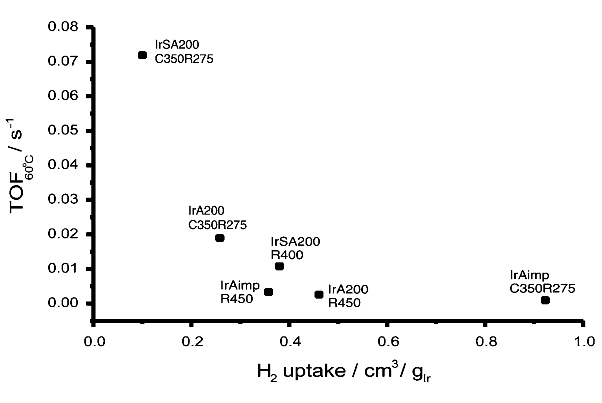

Figure 7. Turnover frequency (TOF) at 60 °C in toluene hydrogenation reaction as a function of hydrogen uptake of iridium samples.

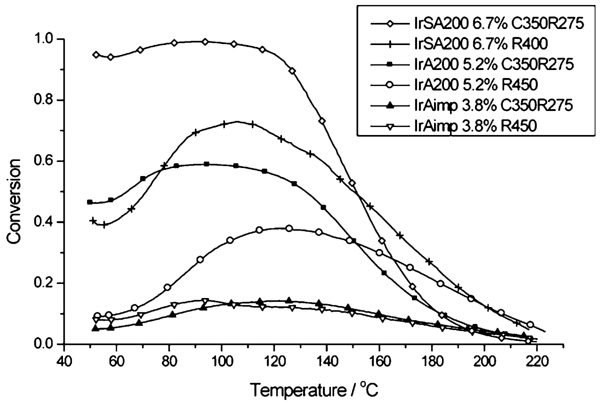

Figure 8. Conversions of iridium catalysts in toluene hydrogenation reaction as a function of temperature.

Conversions as a function of temperature are shown in figure 8. The best conversions are observed for silica–alumina samples. Conversion depended on iridium loading: the higher the iridium content of the sample the higher the conversion. (Also,) for the ALD catalysts, conversions after calcination followed by reduction were better than conversions after direct reduction. The conversions of impregnated catalysts were independent of activation.

4. Discussion

4.1. Ligand removal

TG and TPR results provide some indications for the decomposition mechanism of acac ligands in Ir-acac$_x$ and Al-acac$_x$ species. According to the TG measurements, thermal decomposition of acac ligands in Ir-acac$_x$ species took place at temperatures around 320–330 °C, but those in Al-acac$_x$ species not until 390–420 °C. In addition, for blocked samples without iridium, thermal treatments did not remove all decomposition products of Al-acac$_x$ from the surface at temperatures below 500 °C.

The TPR results showed that relatively high temperatures are needed for reductive decomposition of acac residues in alumina and silica–alumina supported iridium catalysts, the main maxima being observed at 410 °C for IrA250, 390 °C for IrSA250 and 420 °C for IrBSA250. Practically no hydrogen consumption was detected on blocked alumina (BA) or silica–alumina (BSA) samples. This was also the case when iridium content was below 0,5% as in IrBA, giving similar TPR behavior for BA250 and IrBA250.

Since H-acac does not react with silica surface [3,7,20], the maximum at 380 °C with a shoulder at 315 °C observed in TPR of silica-supported iridium catalyst must be related to reductive decomposition of Ir-acac$_x$ species. Similarly, on alumina and silica–alumina, the hydrogen consumption at or below 380 °C must be related to Ir-acac$_x$ species. Hydrogen consumption above 400 °C is then related to the reductive decomposition of Al-acac$_x$ species found on alumina and silica–alumina surfaces [3]. The exact position of the main maximum in TPR depends on the relative contribution of these decompositions in each sample. Comparison of the TPR and TG results suggests that some ligands bound to iridium could be thermally decomposed (TG maximum at 320–330 °C) before reductive decomposition commences (TPR maximum at 380 °C).

The TPR measurements also showed that the reductive decomposition of acetylacetonate species requires the presence of iridium. To possess hydrogenation activity, iridium must be in the metallic state. Since no separate TPR maximum assignable to the reduction of iridium was observed, and iridium is not in metallic state after preparation (see XPS results in Ref. 3), we propose that iridium is partly reduced to the metallic state during some initial thermal decomposition, as was shown on silica supported iridium treated in argon at 320 °C (figure 6).

However, the mechanism of thermal decomposition of Ir-acac$_x$ species to metallic iridium particles in nitrogen is not yet fully understood. The gradual decomposition of acac-ligands during heating in nitrogen has been studied for alumina-supported H-acac and silica-supported Cr(acac)$_3$ by analyzing the decomposition products released into the gas phase [7,8]. On the basis of these TPD results, thermal decomposition has been proposed to begin with the reaction of acac-ligand residues with surface OH groups or water, releasing acetone into gas phase and leaving acetate species on the surface. During further increase in temperature, CO_2 is released from the surface species. In our previous work, the formation of Al-acetate species was observed by DRIFT spectroscopy immediately after the reaction of H-acac or Ir(acac)$_3$ with alumina or silica–alumina [3]. A similar thermal decomposition route can be suggested for Ir-acac$_x$ and Cr-acac$_x$, but iridium, as a noble metal, is probably easily reduced by the decomposition products to metallic state, whereas chromium forms CrO_x surface species. Further support for the formation of metallic iridium Ir^0 during thermal decomposition is obtained from the preparation of alumina and silica supported palladium catalysts by ALD using a β-diketonate complex as precursor [24]. It was shown that metallic palladium is formed during the reaction of the β-diketonate complex with the support surfaces at 180 °C in nitrogen atmosphere.

The carbon analysis of iridium catalysts clearly showed the high efficiency of ligand removal by calcination followed by reduction. In calcination, acac ligand residues were burned off from Ir-acac$_x$ species forming iridium oxide (XRD). Much lower reduction temperatures were needed than for directly reduced samples, as shown by the TPR maxima of calcined IrSA250 at 207 and 307 °C. The maximum at 207 °C may be associated with the reduction of iridium oxide ($IrO_2 + 2H_2 \rightarrow Ir^0 + 2H_2O$). Similar reduction of iridium oxide at 200 °C was detected by Foger and Jaeger [25]. The hydrogen consumption at 207 °C (800 μmol/g) was lower than the theoretical amount (1060 μmol/g) needed to reduce IrO_2, assuming that all iridium was converted to the oxide form. Since the maximum at 307 °C corresponds to the shoulders at 315–350 °C observed for directly reduced IrSA250, IrBSA250 and silica samples, it is likewise assigned to the reduction of residual Ir-acac$_x$ species by metallic iridium. The incomplete oxidation of acac ligands might be due to the oxidation conditions used in the TPR measurement.

The hydrogen uptake values varied with the activation procedure and reduction temperature. For directly reduced ALD catalysts containing more than 4 wt% iridium, the hydrogen uptake value increased with the reduction temperature up to 400 °C. In addition, lower hydrogen uptake values were obtained for blocked iridium catalysts than for the corresponding non-blocked catalysts. The low hydrogen uptake values are most probably due to the limited ability of metallic iridium to adsorb and dissociate hydrogen – either because carbonaceous species on the support partially shade the metal particles or because ligand decomposition products adsorb on the metal particles. The lower hydrogen uptake values when carbon is totally removed may be related to the larger metal particle sizes.

For ALD catalysts containing more than 4 wt% iridium, hydrogen uptake values were lower for samples that were activated in the reduction preceded by calcination than for the directly reduced samples. Calcination led to the formation of IrO_2, which is known to easily sinter into larger particles. The unexpectedly high hydrogen uptake values obtained for iridium on blocked alumina are most probably related to the very low iridium concentrations (<0.5 wt%), which hinder sintering of these samples.

In contrast to the behavior of our ALD catalysts, the impregnated catalyst showed higher hydrogen uptake values after calcination followed by reduction treatment than after direct reduction at 450 °C. This is in accord with the findings of Cunha *et al.* [5]. The reason for the different behavior of impregnated catalysts is not yet known but the effect of chlorine residuals could be important.

In summary, direct reduction of alumina and silica–alumina supported iridium catalysts prepared from Ir(acac)$_3$ in most cases resulted in higher hydrogen uptake values than the activation procedure where the catalysts were calcined before reduction. A drawback in direct reduction was the removal of acac ligands from Al-acac$_x$ species on the support surfaces. Al-acac$_x$ surface species are formed when the blocking agent H-acac is used to reduce the iridium content of the catalyst, but also to a minor extent during the reaction of Ir(acac)$_3$. The thermal decomposition of Al-acac$_x$ species required high temperatures and, in samples containing no iridium, the removal of carbonaceous species was not complete. The presence of iridium enhanced the removal of acac ligands from Al-acac$_x$ species by reductive decomposition.

4.2. *Catalytic activity*

The activity of the catalysts in toluene hydrogenation reaction was dependent on hydrogen uptake. The most active catalyst, measured as TOF at 60 °C, was the silica–alumina catalyst activated by calcination followed by reduction. The reasons for the high activity of IrSA200 may be the higher acidity of the support, which can enhance hydrogenation reaction [26] and the relatively lower hydrogen uptake values, indicating also larger particle sizes than for alumina. Although the exact values of particle size cannot be calculated from hydrogen uptake because of uncertainty about the H/Ir stoichiometry, it is clear that, independent of the stoichiometry between 0.5 and 2.5, TOF values increase as the particle size increases. Thus, we conclude that the main factor influencing catalytic activity in toluene hydrogenation is particle size. Relevant to the larger particle size on silica–alumina is an observation that Cunha *et al.* [5] made in regard to silica and alumina surfaces: iridium particles more easily form aggregates on silica than on alumina surface. On alumina, our TOF values at 60 °C after calcination and subsequent reduction were slightly higher than those Cunha *et al.* [5] reported, whereas after direct reduction our values were slightly lower. Alexeev *et al.* [14] obtained higher TOF values at 60 °C with all possible treatments. Our results are in good agreement with the results in the literature indicating that the particle size affects the activity [5,13–15]. The impregnated catalysts showed low activity in toluene hydrogenation, perhaps because of the small particle size or impurities from the preparation.

Since the location of the conversion maximum varied with different catalyst, it is clear that the support material has an effect. All the catalysts had different activation energies and the optimal conditions varied therefore. The catalyst on silica–alumina activated by calcination followed by reduction was the most efficient of our catalysts in toluene hydrogenation.

5. Conclusions

Study was made of the activation of iridium catalysts supported on alumina and silica–alumina by ligand removal. The ligands from Ir-acac$_x$ species were removed at about 380 °C, but the removal of Al-acac$_x$ and its decomposition products from the support surface was difficult in absence of metallic iridium and hydrogen. Since some chemical reactions are structure sensitive and the activation procedure may affect particle size, choice of the activation procedure may be relevant to the activity of the catalyst. In this study, catalytic activity in toluene hydrogenation increased with particle size. Reduction with hydrogen led to small well-dispersed iridium particles, whereas calcination led to bigger particles. The results of this study should help in choosing the correct activation procedure for iridium catalysts.

Acknowledgments

We thank Ms. Mirja Rissanen, Ms. Riitta Vuorenmaa and Ms. Helena Leuku at the Analytical Department of Neste Oil Corporation for TG, TPR and XRD measurements. We are grateful to Ms. Heli Vuori for helping us with the toluene hydrogenation experiments. Financial support for R.J.S. was provided by the Finnish Cultural Foundation. R.J.S. thanks the Laboratory of Optics and Molecular Materials at Helsinki University of Technology and the Center for New Materials for allocating funds sufficient for preparing the manuscript.

References

[1] R.L. Puurunen, J. Appl. Phys. 97 (2005) 121301.
[2] E.-L. Lakomaa, Appl. Surf. Sci. 75 (1994) 185.
[3] R.J. Silvennoinen, O.J.T. Jylhä, M. Lindblad, J.P. Sainio, R.L. Puurunen and A.O.I. Krause, submitted to Appl. Surf. Sci. (2006).
[4] F.S. Lai and B.C. Gates, Nano Lett. 1 (2001) 583.
[5] D.S. Cunha and G.M. Cruz, Appl. Catal. A 236 (2002) 55.
[6] F. Locatelli, B. Didillon, D. Uzio, G. Niccolai, J.P. Candy and J.M. Basset, J. Catal. 193 (2000) 154.
[7] A. Kytökivi, A. Rautiainen and A. Root, J. Chem. Soc., Faraday Trans. 93 (1997) 4079.
[8] A. Hakuli and A. Kytökivi, Phys. Chem. Chem. Phys. 1 (1999) 1607.
[9] J.C. Kenvin, M.G. White and M.B. Mitchell, Langmuir 7(1991) (1999) 1198.
[10] I.V. Babich, Yu.V. Plyuto, P. Van Der Voort and E.F. Vansant, J. Colloid Interface Sci. 189 (1997) 144.
[11] P. Van Der Voort, M.B. Mitchell, E.F. Vansant and M.G. White, Interface Sci. 5 (1997) 169.
[12] Y.-J. Huang, J. Xue and J.A. Schwarz, J. Catal. 111 (1998) 59.
[13] A. Zhao and B.C. Gates, J. Am. Chem. Soc. 118 (1996) 2458.
[14] O. Alexeev and B.C. Gates, J. Catal. 176 (1998) 310.
[15] Z. Xu, F.-S. Xiao, S.K. Purnell, O. Alexeev, S. Kawi, S.E. Deutsch and B.C. Gates, Nature 372 (1994) 346.
[16] U. Nylén, J. Frontela Delgado, S. Järås and M. Boutonnet, Appl. Catal. A 262 (2004) 189.
[17] M. Nawdali, E. Iojoiu, P. Gélin, H. Praliaud and M. Primet, Appl. Catal. A 220 (2001) 129.
[18] M.D. Amiridis, C. Mihut, M. Maciejewski and A. Baiker, Top. Catal. 28 (2004) 141.

[19] M. Boudart and G. Djéga-Mariadassou, *Kinetics of Heterogeneous Catalytic Reactions* (Princeton University Press, 1984).

[20] A. Rautiainen, M. Lindblad, L. Backman and R.L. Puurunen, Phys. Chem. Chem. Phys. 4 (2002) 2466.

[21] Gmelin Handbuch, *Der anorganischen Chemie* (Berlin, Heidelberg, New York, 1978).

[22] B.J. Kip, F.B.M. Duivenvoorden, D.C. Koningsberger and R. Prins, J. Am. Chem. Soc. 108 (1986) 5633.

[23] J.M. Guil, A. Pérez Masiá, A. Ruiz Paniego and J.M. Trejo Menayo, Thermochim. Acta 312 (1998) 115.

[24] M. Lashdaf, T. Hatanpää, A.O.I. Krause, J. Lahtinen, M. Lindblad and M. Tiitta, Appl. Catal. A 241 (2003) 51.

[25] K. Foger and H. Jaeger, J. Catal. 67 (1981) 252.

[26] B.L. Mojet, J.T. Miller, D.E. Ramaker and D.C. Koningsberger, J. Catal. 186 (1999) 373.