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Dense and narrowly distributed silica-supported rhodium and iridium nanoparticles: Preparation via surface organometallic chemistry and chemisorption stoichiometry

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ABSTRACT

Silica supported iridium and rhodium nanoparticles were prepared via surface organometallic chemistry (SOMC). Following the synthesis and characterization of organometallic molecular precursors $[(COD)MOSiOR]_2$ (M = Ir or Rh; R = Me or $Si(OtBu)_3$), their controlled grafting on partially dehydroxylated silica yields isolated dinuclear surface species, as determined by ^1H and ^{13}C solid state NMR as well as infrared transmission spectroscopies and elemental analysis. The decomposition under hydrogen of the well-defined surface species affords a narrow size distribution and a homogeneous spatial repartition of small M(0) particles despite a high metal density (1.2 ± 0.3 nm and 1.4 ± 0.3 nm for Ir and Rh, respectively). A combination of transmission electronic microscopy and gas chemisorption provides the H_2 and CO adsorption stoichiometries on the metal surface, which are highly dependent on the precursor and the preparation route, indicating the necessity to control each step and the danger to determine particle size solely from chemisorption studies for small iridium and rhodium supported particles.

1. Introduction

Supported nanoparticles play a key role in catalysis, where the control of their characteristics (size, shape, composition) is key for the understanding of their properties and the improvement of their performance [1]. Most of the supported metallic nanoparticles are prepared by homogeneous deposition-precipitation or by impregnation of a metal precursor on a support, followed by post-thermal/chemical treatments. The impregnation approach is broadly used for the preparation of supported iridium and rhodium nanoparticles, which are used in catalytic conversion processes, such as the hydrogenolysis of hydrocarbons or deNOx processes. Of various precursors, metal chlorides, nitrates and acetylacetonates (acac) are widely used. For instance, $Ir(acac)_3$ dispersed on silica leads to the formation of Ir particles with size ranging between 1 and 5 nm after treatment under H_2 [2–4]. For Rh, surface ion exchange using $RhCl_3$ in the presence of ammonia allows for a homogeneous distribution of $[RhCl(NH_3)_5]^{2+}$ at the surface through a strong interaction of this cationic species with the negatively charged silica surface, thus leading to the formation of particles with a size ranging between 1 and 2 nm after decomposition [5]. However, a common issue resulting from impregnation techniques with some inorganic derivatives is the formation of particle aggregates and broad particle size distribution. In addition, the decomposition of the metal precursor (its ligands) can not only lead to the uncontrolled growth of nanoparticles, but also to the pollution of the metal surface by the presence of residual ligands, which cannot be readily detected by transmission electron microscopy. Such pollution has important consequences on the chemisorption of probe molecules such as H_2 and CO, which are often used to evaluate the particle size (when the probe molecule surface stoichiometry is known). It may thus not be too surprising that to date there is no consensus concerning H_2 or CO adsorption stoichiometry for some metals like iridium and rhodium, while it is now well-established for other metals such as ruthenium [6], osmium [7], nickel [8,9], and platinum [10]. In fact, the H/M_{surf} ratio has been reported in a range from 0.8 to 2.8 in the case of iridium [3,11,12] and from 1.2 to 2.0 for rhodium [11–13]. In view of the importance of Rh and Ir in catalyis, it is important to develop more controlled methods to obtain small supported Rh and Ir nanoparticles with a narrow distribution, a high particle density on the

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support with a clean surface and to establish the adsorption stoichiometry.

One possible and alternative approach to prepare supported nanoparticles is to use surface organometallic chemistry [14–22], which relies on the controlled grafting of molecular precursor, typically on the hydroxyl surface functionalities of an oxide support. This process yields well-defined surface complexes, whose metal density is mainly controlled by the initial OH density, which can be controlled by the pre-treatment temperature of the support [23]. Upon post-treatment, typically under H_2, this approach allows for the controlled growth of nanoparticles with small sizes with a narrow distribution and a homogeneous spatial distribution combined with a high metal surface density. This concept, already proposed by Ermakov in the early 1980s [15], has been used more recently for preparing silica-supported Au [24] and Pt nanoparticles with narrow size distribution and controlled interfaces [10,25,26]. In the context of Rh and Ir, the decomposition of iridium and rhodium allyl complexes was also studied on various supports, and leads to metal nanoparticles with diameters ranging between 1 and 3 nm [27–29]. In a more recent study, $[Ir(COD)Cl]_2$ was used to prepare 2.7 nm iridium particles on alumina [30–32]. Other alternative approaches have used small rhodium and iridium clusters as metal source [33,34].

Here, we focus our study on the controlled growth of silica-supported Rh and Ir nanoparticles, starting from well-defined and readily prepared cyclooctadiene M(I) precursors, [M(COD)(X)], with X = Cl, OMe and $OSi(OtBu)_3$. We investigate the effect of the nature of the anionic ligand X on the final supported nanoparticles, in particular with respect to the size, the density and the hydrogen and CO chemisorption stoichiometry.

2. Experimental section

2.1. General procedures

All experiments were conducted under argon atmosphere using Schlenk or glove-box techniques. Hydrated iridium trichloride, hydrated rhodium trichloride, (acetylacetonato)(1,5-cyclooctadiene)iridium(I) and hydrated rhodium nitrate were purchased from Strem. $[(COD)IrCl]_2$ [35], $[(COD)RhCl]_2$ [36], $[(COD)IrOMe]_2$ [37], $[(COD)RhOMe)]_2$ [37] and $[(COD)RhOSi(OtBu)_3]_2$ [38] were prepared according to published procedures. Tris(tert-butoxy)silanol 99.999% ($HOSi(OtBu)_3$) was purchased from Sigma–Aldrich and used as received. Pentane, diethyl ether and dichloromethane were dried using an MBraun solvent purification system, and then contacted with 4 Å molecular sieves (MS) and degassed under vacuum. Benzene was dried over Na/K/benzophenone and distilled. Dihydrogen was purified over R3-11 BASF catalyst/MS 4 Å prior to use. Gas phase analyses were performed on an Agilent Technologies 7890 A Gas Chromatography apparatus equipped with a flame ionization detector (FID) and a KCl/Al_2O_3 column (50 m × 0.32 mm). Elemental analyses were performed at "Mikroanalytisches Labor Pascher" in Germany.

2.2. Characterization methods

2.2.1. FTIR spectroscopy

Infrared spectra were recorded on a Bruker Alfa-T spectrometer (inside a glove-box under argon atmosphere) using Opus software. Samples were pressed into a thin pellet using a 7 mm die set. Typically 24 scans were accumulated for each spectrum at a resolution of $4\ cm^{-1}$.

2.2.2. Nuclear magnetic resonance (NMR) spectroscopy

^1H magic angle spinning (MAS) and ^{13}C cross polarization (CP)-MAS solid-state NMR spectra were recorded on Bruker Avance 400 and 700 MHz spectrometers with a conventional double resonance 4 mm CP-MAS probe. The samples were introduced under Ar in a zirconia rotor, which was then tightly closed. In all experiments, the rotation frequency was set to 10 kHz unless otherwise noted. Chemical shifts are given with respect to tetramethylsilane as the external reference for both ^1H and ^{13}C NMR. ^1H and ^{13}C liquid-state NMR spectra were recorded on Bruker DRX 200, 250 and 300 and 400 MHz spectrometers. The spectra were recorded at room temperature. Chemical shifts are given with respect to the residual solvent peak chemical shift.

2.2.3. X-ray crystallography

The crystals were placed in paratone and mounted in the beam under a flow of nitrogen at 100 K on a Bruker SMART APEX II diffractometer equipped with a CCD area detector using Mo Kα radiation. Empirical absorption correction was performed with SADABS-2008/1 (Bruker). The structures were solved by direct methods (SHELXS-97) followed by least-square refinement (SHELXL-97) using WinGX suite of programs and OLEX2-1.1. The non-hydrogen atoms were refined anisotropically. For $\mathbf{Rh_{OSi(OtBu)3}}$, the hydrogen atoms were refined anisotropically while they were placed at calculated positions for other complexes. Projected surface areas were calculated with ChemAxon MarvinSketch software using structures obtained by single crystal XRD.

CCDC 969418 ($[(COD)Ir(OSi(OtBu)]_2$), CCDC 969419 ($[(COD)IrOMe]_2$), and CCDC 969420 ($[(COD)Rh(OSi(OtBu)]_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Figure Graphics are generated using MERCURY 3.1 supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2001–2012.

2.2.4. Computational details

Optimizations carried out using density functional theory (DFT) calculations were performed with Gaussian 03 [39], using the hybrid functional B3LYP [40–42] with SDD basis set. Geometry optimizations were achieved either with or without symmetry restriction.

2.2.5. Transmission electron microscopy (TEM)

Transmission Electron Micrographs were obtained on a Tecnai F30 ST with 300 kV acceleration voltage and High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) was performed on a Hitachi HD2700CS with 200 kV acceleration voltage, in mode resulting in atomic number contrast (Z contrast). Lacey carbon grids were prepared by directly "dipping" the grid into the silica powder (displacement of NPs was observed in case of preparation of the grid by sonication of the grid in suspension of the particles in ethanol). The particle size distribution was estimated by statistical analysis of *ca.* 300 particles. Metal dispersion, defined as the ratio between surface and total metal atoms, was calculated back from particle size distribution. A simple average of a particle size distribution is not representative of the sample dispersion, as a large particle will carry much more weight than a small one on the final $M_{surface}/M_{total}$ ratio. In fact, for instance iridium particles of 1 nm are made of roughly 38 atoms, while those of 1.7 nm contain 201 atoms. Hence, a more representative estimation of metal dispersion was calculated using the truncated cubic octahedron model to sum the surface and bulk metal atoms of all individual particles counted from TEM pictures.

2.2.6. Chemisorption of H_2 and CO

Chemisorption experiments were carried out on a Belsorb-Max device from BEL Japan. In a measuring cell, *ca.* 100 mg of catalyst were treated at 10^{-6} mbar at 623 K for 3 h using a ramp of $1\ K\ min^{-1}$. Adsorption isotherm measurements performed at 298 K after this