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Glycerol to lactic acid conversion by NHC-stabilized iridium nanoparticles

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Hydrogen reduction of an Ir(I) complex featured by a bulky N-heterocyclic carbene (NHC) ligand in dichloromethane gave small-sized (1.8 nm) Ir nanoparticles (NPs) decorated with NHC ligands (IrNHNC). 1,4-Dioxane solutions of the latter particles were successfully applied to convert glycerol into lactic acid in the presence of NaOH (i.e., 1 mol equivalent with respect to glycerol). IrNHNC showed an atom-related TOF value of almost 10^4 h⁻¹, an almost exclusive formation of liquid reaction products, a high selectivity for lactic acid (93.0%) and a complete recyclability in air atmosphere. Attempts to synthesize analogous NHC-stabilized Ir NPs on a high surface area carbon support (C₆) by reducing the same Ir(I) precursor, supported onto C₆, prior to the hydrogen reduction in water, gave almost naked C₆-supported Ir NPs (1.4 nm). Their catalytic activity tested for the same reaction in water as reaction medium, exhibited much lower catalytic activity (4 × 10³ h⁻¹), a lower percentage of liquid reaction products (i.e., 27.0% of the converted glycerol) and a lower selectivity for lactic acid compared to IrNHNC.

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1. Introduction

Lactic acid (LA) is an important organic platform molecule used to be converted to lactate ester, propylene glycol, 2,3-pentanediol, propanoic acid, acrylic acid, acrolein, acetaldehyde and lactide [1]. The latter mainly used for the synthesis of poly(lactic acid), an important bioplastic material [1,2]. One pot catalytic syntheses of LA from glycerol (GLY) (i.e., obtained from biodiesel production [3]) give hydrogen as reaction product, obtained under acceptorless dehydrogenation reaction conditions [4–8]. Highly active Ru-[9] and Ir-based [10,11] molecular catalysts were employed to convert GLY to LA under acceptorless catalytic conditions, obtaining a LA selectivity of 96%. All successfully employed molecular Ir(I) catalysts are stabilized by N-heterocyclic carbene (NHC)-ligands, which are known to be suitable ligands for transition metals occurring in different oxidation states. Their suitability as ligands is due to: (i) their electron donor property, leading hence to strong metal-ligand bonds; (ii) their steric properties, which can be simply modified by substituting the nitrogen atoms in 1,3-positions of the imidazol-based ring with the desired substituent and (iii) their stability under oxidizing reaction conditions [12,13]. In addition, the variable bulkiness of the NHC-ligands has found to be exploitable for the stabilization of metal-nanoparticles (NPs) of different size. As a result, an increasing steric bulk of the NHC ligand leads to the stabilization of small NPs [14–19]. NHC-decorated metal NPs have been synthesized by either ligand exchange reactions (i.e., ligand-stabilized metal NP reacts with the desired in situ generated NHC ligand) [14,20] or by decomposition of an NHC-containing organometallic species [15–17,21,22]. An IrN₇-polyhydride cluster containing NHC-ligands (i.e., NHC = 1,3-dimethylimidazol-2-ylidine) has been obtained and isolated from a catalytic GLY to LA conversion, proving the decomposition of Ir(I)-NHC organometallic species under real catalytic conditions [23]. Similar observations were made with Ir(I)-mono NHC complexes used for the hydrogen-transfer reactions of GLY bringing about the formation of Ir NPs [24].

Recently, Tu immobilized an Ir(I)-NHC species by a supramolecular assembly approach, obtaining a highly efficient (LA selectivity up to 98%) and recyclable catalyst (up to 30 times) [25]. Heterogeneous catalysts employed for the GLY to LA conversion are metal nanoparticle (NP)-based [26] and GLY conversions under acidic
Herein we report for the first time the synthesis of unsupported Ir NPs, stabilized by a bulky NHC ligand through a controlled decomposition of an Ir(I)-NHC precursor under a hydrogen atmosphere. In order to prove, if the same type of Ir NPs could be obtained on a support by hydrogen reduction of the same supported Ir(I)-NHC precursor, we have chosen a carbon support characterized by a high surface area (1400 m²/g) in order to avoid crystallization of the organometallic compound during the deposition step [39] upon maximizing the dispersion of the supported Ir(I)-NHC compound on the support prior to reduction with hydrogen. The obtained Ir NPs were then tested as catalyst for the conversion of GLY to LA under basic reactions conditions.

2. Experimental section

2.1. Materials

Glycerol (GLY), 1,2-propanediol (1,2-PD), [IrCl(COD)]₂ (COD = 1,5-cyclooctadiene), 1,4-dioxane and NaOH were purchased from Aldrich and used as received. Water was distilled. Ketjenblack EC-600D (C⁰) (1400 m⁡²/g) [39] was purchased from Cabot Corp. USA. [IrCl(COD)(L⁰NHC)] with L⁰NHC = 1,3-bis((2,6-di-isopropyl)phenyl)imidazol-2-ylidene was synthesized according to a reported procedure [40]. Dichloromethane was obtained over CaH₂ in a nitrogen atmosphere. CDC₁₃ used for NMR characterization was purchased from Aldrich and used without further treatment.

2.2. Catalysts' synthesis

2.2.1. Unsupported Ir NPs (Ir⁰NHC and Irblack)

A deaerated CH₂Cl₂ solution (30.0 mL) of [IrCl(COD)(L⁰NHC)] (60.0 mg) was transferred under a nitrogen atmosphere into an evacuated teflonated stainless steel autoclave by suction. Afterwards the autoclave was pressurized (150 psi) with hydrogen, followed by heating the autoclave to 373 K and adjusting the hydrogen pressure to 435 psi. The autoclave was continued to heat by means of an oil bath for three hours. The autoclave was then cooled to 283 K, the hydrogen gas carefully vented off and the clear brown solution transferred into a Schlenk tube under nitrogen atmosphere. The obtained solution was analyzed by GC–MS and the solvent evaporated by means of a vacuum pump. A portion of the obtained brown powder (Ir⁰NHC) was dissolved in CDC₁₃, followed by the acquisition of ¹H and ¹³C{¹H} NMR spectra of room temperature, while the other portion was used for powder X-ray analysis. The same synthesis protocol was applied when [IrCl(COD)]₂ was used as Ir(I) precursor. The obtained black precipitate (Irblack) was separated from solution by decantation, dried under vacuum and used to acquire a powder X-ray spectrum.

2.2.2. Carbon-supported Ir NPs (Ir¹⁰@C⁰ and Ir²@C⁰)

Ketjenblack (C⁰) (1.70 g) was suspended in distilled CH₂Cl₂ (200.0 mL) upon magnetic stirring for one hour at room temperature in a nitrogen atmosphere. Then a solution of [IrCl(COD)(L⁰NHC)] (70.8 mg, 97.79 μmol) in CH₂Cl₂ (20.0 mL) was added to the black C⁰-suspension, which was continued to stir for 3 h at room temperature in a nitrogen atmosphere. The solvent was then completely removed and the black residue dried at 100 °C [32] with the main drawback that the reaction has to be conducted at lower pressure (72.5 psi) and a high NaOH/GLY molar ratio of 4. The same applies to Au@CeO₂ [35] and Au-Pt@TiO₂ [31]. In this context iridium-based NPs are efficiently also in the absence of an hydrogen acceptor and do not require an excess of inorganic base [34].
XPS signal. The relative quantity of Ir amounted to about 0.07–0.13%. This low amount of Ir did not permit to detect the N 1s signal (originating from the NHC-ligand) because of the low sensitivity factor of N 1s (i.e. relative sensitivity factor for N 1s is about 7 times lower than that for C 1s) [46]. The O 1s peak is ascribable to oxygen stemming from water and oxygen containing functional groups present on C K support [39].

The iridium metal loading of the C K-supported Ir NPs were determined by ICP-OES (ICAP6300 Duo, purchased from Thermo Fisher Scientific) applying an external calibration methodology. The samples (10.0 mg) were microwave digested (5.0 mL HCl 37% + H2O2 30%) and diluted with highly deionized (Milli-Q Academic, Millipore) to a final weight of 10.0 g. Iridium leaching was measured with the same procedure starting from 100.0 mg of reaction solution (after catalysis), which was filtered (0.2 μm) at the end of catalytic reaction. ICP-OES analyses carried out on isolated Ir1@C2K and Ir2@C2K revealed an Ir content of 0.77 and 0.94 wt%, respectively.

2.4. Catalytic performance test

2.4.1. Catalytic reactions in 1,4-dioxane

Catalytic reactions with IrNHC in 1,4-dioxane were carried out as follows: GLY (14.34 g, 156.0 mmol) and NaOH (6.24 g, 156.0 mmol) were placed in a stainless steel autoclave (320.0 mL), which was sealed and evacuated. Then a solution of IrNHC (Ir, 5.65 μmol) in deaerated 1,4-dioxane (30.0 mL) was added by suction. The autoclave was then heated under vigorous mechanically stirring at 418 K for the desired reaction time, followed by cooling to 283 K by means of an ice water mixture. Then the gas was formed was released and collected in a burette for GC-analysis, whereas the 1,4-dioxane solution was decanted and the highly viscous residue solubilized in water. The water phase was acidified to pH = 7 by adding H2SO4. The 1,4-dioxane and acidified water solutions were subjected to HPLC analysis. Recycling experiments were performed by using the recovered 1,4-dioxane solution and a new portion of GLY.

2.4.2. Catalytic reactions in water

Catalytic reactions with Ir1@C2K and Ir2@C2K in water were carried out as follows: The solid catalysts (Ir, 5.65 μmol) were placed in a stainless steel autoclave (320.0 mL), which was sealed and evacuated. Then a deaerated water solution (30.0 mL) of GLY (14.34 g, 156.0 mmol) and NaOH (6.24 g, 156.0 mmol) was introduced in the autoclave by suction, which was then heated to 418 K and mechanically stirred (900 rpm) for the desired reaction time. The autoclave was then cooled to 283 K by means of a water ice bath, the gas formed collected in a burette and the suspension centrifuged. The recovered catalyst was washed several times (pH = 7) and then dried in a vacuum oven at 323 K to constant weight. The water solution was cooled to 283 K, acidified with sulfuric acid to pH = 1 and analyzed by HPLC. Recycling experiments with recovered Ir1@C2K and Ir2@C2K were performed following the above described experimental procedure.

2.5. Analysis of the reaction products

2.5.1. Analysis of the liquid reaction products

The acidified catalytic water solutions (pH = 1) were filtered by a paper filter in order to remove precipitated Na2SO4, while 1,4-dioxane solutions were analyzed without further treatment. Both solutions (1,4-dioxane and water) were analyzed by HPLC using a Shimadzu-UFLC apparatus, equipped with a RID detector and a Alltech OA-1000 organic acid column of 300 mm (length) and a 6.5 mm (i.d.): 0.01 N H2SO4 was used as eluent with a flow rate of 0.4 mL/min at 338 K. The percentage of GLY conversion, the surface-related TOF values and the percentage of the selectivity of the liquid reaction products were calculated as follows:

GLY conversion (%) = 100 × [mmol(GLY initial) – mmol(GLY converted)]/[mmol(GLY initial)]

TOF = mmol(GLY converted)/[mmol(Ir surface)×t]; mmol(Ir surface) = 2.91 × 10⁻³[IrNHC]; 3.64 × 10⁻³[Ir1@C2K] and 3.75 × 10⁻³[Ir2@C2K].

Selectivity (liquid prod.) (%) = 100 × mmol(prod)/[mmol(LA) + mmol(1,2PD) + mmol(FA) + mmol(EG)]; lactic acid(LA), 1,2-propandiol(1,2PD), formic acid(FA) and ethylene glycol(EG).

2.5.2. Analysis of the gaseous reaction products

After the catalytic reactions, the autoclave was cooled to 283 K and the gas phase analyzed off-line using a gas tight syringe. The GC was used a Shimadzu GC 2010 apparatus, equipped with a TCD and a fused silica capillary column (Supelco Carboxen 1010 PLOT (30.0 mm × 0.32 mm). Helium was used as carrier gas and the following temperature program was utilized for the analysis: 413 K for 9 min followed by a heating ramp of 30 K per minute up to 498 K and lasting this latter temperature for 30 min.

3. Results and discussion

3.1. Catalysts’ synthesis

We synthesized unsupported Ir NPs reduction of [IrCl(COD)(LNC)] [40] and [IrCl(COD)2] in CH2Cl2 at 373 K in the presence of hydrogen pressure (435 psi) (Scheme 1).

As a result, a clear brown dichloromethane solution of IrNHC was obtained when [IrCl(COD)(LNC)] was used as Ir(1) precursor, whereas the reduction of [IrCl(COD)2] under identical experimental conditions gave a black precipitate (Irblack) and a clear supernatant.

GC–MS analyses of both dichloromethane reaction solutions revealed the presence of cyclo-octane in solution, indicating that the hydrogenation of the COD ligand is mandatory for the Ir(1) reduction.

Ketjenblack (C5); surface area of 1400 m2/g)-supported Ir NPs were generated by evaporation of dichloromethane solutions of [IrCl(COD)(LNC)] and [IrCl(COD)2] in the presence of C K (i.e. impregnation method). As a result, the isolated Ir(1)-supported compounds [IrCl(COD)(LNC)]@Irblack and [IrCl(COD)2]@Irblack were then suspended in water (i.e. water avoids lacking of the organometallic compound from the support) during the reduction step conducted at 418 K in the presence of hydrogen pressure (769 psi) (Scheme 1). After reduction, the black solids (Ir1@C2K and Ir2@C2K) were separated from water solution by centrifugation and dried under vacuum at 323 K. The high surface area carbon support was chosen in order to avoid crystallization of the organometallic Ir(1) species on the support [39] and to prevent undesired interactions between

![Scheme 1. Syntheses of Ir NPs upon reduction of Ir complexes.](image-url)
the functional groups of the support with the Ir(I) metal centre. In this context, carbon is much more suitable than an inorganic oxide as support.

3.2. Catalysts’ characterization

A PXRD spectrum of isolated IrNHC exhibited a broad Bragg reflex centered at 7.5° (2θ), which originated from the NHC ligand, whereas the corresponding spectrum of Irblack showed the typical Bragg reflexes of fcc-iridium (Fig. 1, trace b). A Debye-Scherrer analysis of particle size, based on the Ir (1 1 1) Bragg reflex gave an average NPs’ size of 2.5 nm.

HAADF-STEM and high resolution HR-TEM analysis of Ir NHC (Fig. 2) clearly confirmed the presence of isolated and homogeneously dispersed Ir NPs featured by a mean diameter (d_m) of 1.8 nm. The efficient separation of the NPs from each other is due to the steric repulsion of NHC ligands located on different Ir NPs’ surfaces [47,48].

IrNHC is completely soluble in most organic solvent, due to the high affinity of the NHC ligand with the latter solvents. Hence, 1H and 13C(1H) NMR spectra of IrNHC were acquired in CDCl3 (Figs. S1 and S2) showing broad NMR peaks in the chemical shift range expected for the carbene ligand. Particularly, the 1H NMR signals assigned to the iso-propyl units of the NHC ligand were subject to broadening [49,50]. This spectroscopic result is the consequence of the close localization of the aromatic rings of the on the Ir NPs’ surface (i.e. interaction of the NPs’ surface and the aromatic rings [51]), bringing about a line broadening in the NMR spectra due to spin-spin relaxation and chemical shifts distribution originating from different binding sites on the metal NPs [52].

PXRD spectra of [IrCl(COD)(LNHC)]@CK and [IrCl(COD)]2@CK are identical, showing hence only the typical large Bragg reflexes for CK (Fig. S3) indicating hence the complete amorphous structure of the supported organometallic species deposited onto CK [39]. In order to prove the in-alteration of [IrCl(COD)(LNHC)] upon impregnation with CK, [IrCl(COD)(LNHC)]@CK was treated with CDCl3 in order to extract the organometallic compound from support. As a result, the corresponding 1H NMR spectrum showed the same NMR pattern as the as-synthesized Ir(I) compound (Fig. S4), confirming the stability of the complex during the impregnation procedure. The PXRD spectra of Ir1@CK and Ir2@CK showed only the pattern of CK, indicating the small size of the Ir NPs obtained (Fig. S3).

HR-TEM micrographs of Ir1@CK and Ir2@CK revealed well-dispersed Ir NPs’ characterized by an average size of 1.4 and 1.2 nm, respectively (Fig. 3). Irrespective of the organometallic...
compound used to generate Ir NPs, the obtained supported Ir NPs’ are of spherical shape.

ICP-OES analyses of the C K-supported Ir NPs revealed an Ir content of 0.77 wt% and 0.94 wt% for Ir 1@CK and Ir 2@CK, respectively.

XPS analyses carried out on Ir 1/2@CK confirmed the presence of Ir(0) (B.E. (4f 7/2) 60.8 eV, (Ir 1/2@CK)), and Ir(IV) (B.E. (4f 7/2) 61.8 eV (Ir 1/2@CK)) (Fig. 4). The relative high abundance of metallic phase was reported in the literature for 2 nm sized Ir NPs on graphite nano-fibers [53] or for an Ir monolayer protected cluster [54]. The metallic state is dominant also in Pd and Pd-Ir nanoparticles [55]. The amount of metallic phase in Ir 1/2@CK (i.e. 73 ± 3% (Ir 1@CK) and 60 ± 3% (Ir 2@CK)). The presence of Ir(IV) is due to the partial oxidation of the small Ir NPs in air atmosphere forming IrO 2 [44,56]. The survey spectrum for Ir 1@CK did not show the presence of nitrogen (N 1s), which we expected for the NPs’ coordinating NHC ligand. Unfortunately, the very low amount of coordinated NHC ligand and the much lower (almost one eight) sensitivity factor of N 1s compared to Ir 4f did not allow to detect the presence of nitrogen originating from NHC ligand.

3.3. Catalysts’ performance

Ir NHC and Ir 1/2@CK were employed to catalyze the conversion of GLY into lactic acid (major product) in an autoclave under a nitrogen atmosphere using equimolar amounts of GLY and NaOH (i.e. one mol equivalent of base is required for a quantitative intramolecular Cannizzaro reaction to occur, step C in Scheme 2). Ir NHC, which was not soluble in water due to the hydrophobicity of the NHC ligand, was tested in 1,4-dioxane as reaction medium. The advantages in using 1,4-dioxane as solvent for Ir NHC catalyzed GLY to LA conversions consist in: (i) the complete solubility of the catalyst in the reaction medium; (ii) the formation of a two phase system between 1,4-dioxane and GLY at room temperature, while upon heating one phase is formed; (iii) the insolubility of sodium lactate (NaL, main reaction product) in 1,4-dioxane. As a consequence, the separation of the catalytic 1,4-dioxane solution from NaL and excess GLY consisted in a simple decantation step.

The organic reaction products formed during the Ir NHC and Ir 1/2@CK-mediated GLY conversion in 1,4-dioxane and water, respectively, were LA (major product), 1,2-propanediol (1,2-PD), ethylene glycol (EG) and formic acid (FA) (Scheme 2). The results of the catalytic reactions are compiled in Table 1 and the reported TOF values are surface atom-related.

Fig. 3. Representative HR-TEM micrographs and relative histograms for as-synthesized Ir 1@CK (A) and Ir 2@CK (B).

Fig. 4. Ir 4f XPS spectra of Ir 1@CK (below) and Ir 2@CK (above).
reaction products formed (Table 1, entry 1). Almost complete GLY conversion was achieved after lasting the reaction for 8 h (98.0% GLY conversion) along with a small drop of LA selectivity to 91.0% (Table 1, entry 2), which is mainly due to an increased formation of 1,2-PD (i.e. an increase of the hydrogen pressure inside the autoclave fosters reaction step E, Scheme 2).

The catalytic performance of Ir NHC was maintained during three consecutive catalytic reactions (Table 1, entry 1 vs 3 and 4). In addition, Ir NHC led to an almost quantitative conversion of GLY to LA, avoiding almost complete formation of CO2 (i.e. CO2 is entrapped as carbonate during the catalytic reaction) which originated from metal-catalyzed C-C splitting reactions. The recovering of the catalyst consisted in decantation of the 1,4-dioxane solution of Ir NHC in water mixture, which gave significantly lower GLY conversion, i.e., reducing hence the concentration of base in solution and as consequence the overall catalytic activity. Only 27.0% of the converted GLY were liquid reaction products (Table). In addition, Ir NHC exhibited higher hydrogenation activity for the tautomer of pyruvaldehyde (Scheme 2, step E), compared to Ir NHC. Although, Ir NHC and Ir OC exhibited comparable selectivity, which is indicating that catalytic active sites are of the same nature. In addition, Ir OC showed a higher activity compared to Ir NHC (Table 1, entries 6/7 vs 8/9) and could hence be recycled without a significant decay of the catalytic performance.

A mass balance of 98% and 88–90% was found for Ir NHC and Ir OC, respectively.

Table 1

<table>
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<th>Entry a</th>
<th>Catalyst</th>
<th>t (h)</th>
<th>Conv. GLY (%)</th>
<th>TOF (h−1)b</th>
<th>Liquid prod. (%)</th>
<th>Sel. liquid prod. (%)c</th>
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a Catalytic conditions: catalyst (Ir, 5.6 \times 10^{-3} \text{ mmol}), GLY (156.0 \text{ mmol}), NaOH (156.0 \text{ mmol}), T 418 K, solvent (30.0 \text{ mL}).

b Surface atom-related TOF (h−1).

c Selectivity of liquid products (%).

d 1st recycle.

e 3rd recycle.

f 1:2 (v:v) 1,4-dioxane water mixture.
The high selectivity of Ir\textsuperscript{NHC} in 1,4-dioxane for liquid reaction products is mainly due to the steric blocking of the NPs’ surface, favoring the metal-catalyzed dehydrogenation of a terminal OH group of GLY, which requires only the interaction of a terminal OH group of GLY with the NPs’ surface. In contrast, metal-catalyzed C–C bond scission reactions need the interaction of C–C bonds with NPs’ surface, which is sterically more demanding, and thus more favored on naked Ir NPs. In the absence of water the Ir\textsuperscript{NHC} catalytic system showed good stability under strong reducing conditions (i.e. presence of hydrogen) \cite{60}.

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Appendix A. Supplementary material
Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2018.10.024.

References

4. Conclusion
In conclusion, we found that [IrCl(COD)(L\textsuperscript{NHC})] with L\textsuperscript{NHC} = 1,3-bis(2,6-di-isopropyl)phenylimidazol-2-ylidene was suitable to generate small Ir NPs (1.8 nm) decorated with L\textsuperscript{NHC} (Ir\textsuperscript{NHC}) by using CH\textsubscript{3}Cl\textsubscript{2} as solvent and hydrogen pressure as reducing agent. Attempts to synthesize the same type of NHC-stabilized Ir NPs’ on a high surface area carbon support (C\textsuperscript{0}) using water as reaction medium and hydrogen as reducing agent failed and gave almost naked Ir NPs (Ir\textsuperscript{0}) of 1.4 nm in size were obtained.

1,4-Dioxane solutions of Ir\textsuperscript{NHC} in the presence of glycerol (GLY) and NaOH in an 1:1 M ratio gave almost 98.0% liquid reaction products, of which lactic acid (LA) was formed with a selectivity of 93.0%. The catalytic activity of Ir\textsuperscript{NHC} (i.e. surface-atom-related TOF value of 10\textsuperscript{4} h\textsuperscript{-1}) combined with the high selectivity for LA and easy recyclability (i.e. separation of the catalytic 1,4-dioxane solution from sodium lactate and excess GLY by simple decantation in air atmosphere) makes this catalytic system superior to the best known homogeneous catalysts of comparable LA selectivity \cite{10,11}.

Scheme 3. Reaction sequence for the Ir\textsuperscript{NHC}-catalyzed conversion of GLY to glyceraldehyde.


