



Co-based heterogeneous catalysts from well-defined α -diimine complexes: Discussing the role of nitrogen



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ABSTRACT

Ar-BIANs and related α -diimine Co complexes were wet impregnated onto Vulcan[®] XC 72 R carbon black powder and used as precursors for the synthesis of heterogeneous supported nanoscale catalysts by pyrolysis under argon at 800 °C. The catalytic materials feature a core-shell structure composed of metallic Co and Co oxides decorated with nitrogen-doped graphitic layers (NGr). These catalysts display high activity in the liquid phase hydrogenation of aromatic nitro compounds (110 °C, 50 bar H₂) to give chemoselectively substituted aryl amines. The catalytic activity is closely related to the amount and type of nitrogen atoms in the final catalytic material, which suggests a heterolytic activation of dihydrogen.

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1. Introduction

Many of the industrially relevant catalytic processes in the fine chemical industry are still based on expensive and rare late transition metals such as Pd, Pt, Rh, Ru and Ir [1–5]. Although these metals exhibit very good catalytic performance for advanced organic substrates, the decreasing availability of these elements requires the development of efficient alternative metal-based catalysts [6]. In this regard, the design of catalytic systems based on abundant and biocompatible metals is an important goal for the implementation and progress of green and sustainable chemistry. Hence, transition metals such as Fe, Co and Cu are ideal candidates, which meet these requirements [7–10]. As a matter of fact, these elements are among the most abundant metals in the Earth's upper crust, thus being readily accessible [11]. Recently, heteroatom-doped carbon materials attracted major interest in the field of metal supported heterogeneous catalysts for both chemical synthesis [12–14] and/or energy-relevant transformations [15,16]. Indeed, doping graphene with heteroatoms such as N, B, P, or S leads to a radical modification of the electronic properties of both

the support and the supported metal [17–19]. Consequently, it is possible to modify the activity and adjust the selectivity of the final catalytic material toward the desired transformation. Among the various dopants, nitrogen attracted most interest [15,20–22] and applications of transition metal/N-doped graphene (NGr) based catalytic systems ranges from oxygen reduction reactions (ORR) [23–26], hydrogen evolving reactions (HER) [27,28], photocatalysis [29,30], oxidation [31–38], and reduction [39–44] reactions of organic molecules, C–C bond formation [45] to many others [46–51]. Hence, merging rationally-designed suitable modified supports with cheap transition metals permits access to the design of active, selective and cheap catalytic materials thus allowing to match or to outperform noble-metal-based catalysts. During the last three years, some of us reported the preparation of active and selective NGr-decorated Co-based catalysts from the pyrolysis of in situ generated 1,10-phenanthroline (Phen) metal complexes using Vulcan[®] XC 72 R carbon [52–60], ceria [61] or α -alumina as supports [62]. Some of the obtained nanoscale catalysts exhibit a core-shell architecture in which a Co metallic core is enveloped by an oxidic sheath composed of Co₃O₄. In addition, this oxidic shell is augmented by layers of NGr derived from the thermal decomposition of the Phen ligand. Nevertheless, from an economical point of view, phenanthroline is expensive and its functionalization requires multistep fair-yielding transformation procedures. Thus, we were interested in using other, more easily tunable, nitrogen compounds. In this respect, chelating

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α -diimines, especially Ar-BIAN ligands, are widely used in transition-metal catalyzed reactions [63]. As the starting materials are inexpensive (acenaphthenequinone and a variety of aromatic or aliphatic amines), it is possible to prepare a large number of ligands with different electronic and steric properties. This allows for the synthesis of tailor-made transition-metal based catalysts. Nevertheless, apart from a traditional immobilized complexes [64], to the best of our knowledge, no examples of their use as heterogeneous catalysts precursors are known. Herein, we report for the first time that Ar-BIANs and related ligands are able to generate efficient Co/NGr catalysts for the hydrogenation of aromatic nitro compounds.

2. Experimental

2.1. Synthesis of the ligands

Concerning the synthesis of the ligands, all the reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. All glassware and magnetic stirring bars were kept in an oven at 120 °C for at least two hours and were cooled to room temperature under vacuum prior to use. CDCl_3 used for the NMR experiments was filtered on basic alumina and stored under nitrogen over 4 Å molecular sieves. Chemicals and solvents were purchased from Sigma-Aldrich, Alfa Aesar or Tokyo Chemical Industry. Seven different ligands were prepared (**L1**–**L7**) following protocols previously reported by some of us (for the preparation of **L1**, **L2**, **L4**, **L5** see [Supporting Information](#)) [65]. Ligand **L3** has been known for more than one century [66] and its synthesis was performed adapting a procedure previously described in the literature [67]. Concerning the preparation of ligand **L6**, its synthesis was adapted from that previously reported by some of us [68]. Finally, **L7** was synthesized adapting a procedure reported many years ago [66]. The detailed protocols for the preparation of the seven ligands are reported in the [Supporting Information](#).

2.2. General analysis and characterization methods

TEM measurements were performed at 200 kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope is equipped with a JED-2300 (JEOL) energy-dispersive X-ray spectrometer (EDXS) for chemical analysis. The sample was deposited without any pre-treatment on a holey carbon supported Cu-grid (mesh 300) and transferred to the microscope. The High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF) images were recorded with a spot size of approximately 0.1 nm, a probe current of 120 pA and a convergence angle of 30–36°. The collection semi-angles for HAADF and ABF were 70–170 mrad and 11–22 mrad, respectively.

XPS data were obtained with a VG ESCALAB220iXL (Thermo Scientific) with monochromatic Al K α (1486.6 eV) radiation. The electron binding (EB) energies were obtained without charge compensation. For quantitative analysis, the peaks were deconvoluted with Gaussian-Lorentzian curves, and the peak area was divided by a sensitivity factor obtained from the element specific Scofield factor and the transmission function of the spectrometer.

XRD patterns of the materials were recorded on a Panalytical X'Pert Pro diffractometer in reflection mode with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a silicon strip detector (X'Celerator).

NMR spectra of ligands and isolated anilines were recorded on a Bruker Avance DRX 300 or on a Bruker Avance DRX 400 operating at 300 and 400 MHz, respectively.

CHN analyses were performed using a Leco Microanalyser TruSpec or a PerkinElmer 2400 CHN. Metal content of the catalysts was determined by atom absorption spectroscopy using a

PerkinElmer AAS Analyst 300 after fusion melts and acidic dissolving of the sample.

TPR- H_2 measurements were conducted using a Micrometrics Autochem II 2920 instrument equipped with a TCD detector. The experiment run was carried out from 36 °C to 700 °C in a 5% H_2/Ar flow ($20 \text{ cm}^3 \text{ min}^{-1}$) with a heating rate of 10 K min^{-1} .

2.3. Catalyst preparation

The procedure was adapted from that reported for the synthesis of Co/Phen based catalysts [58] (see [Fig. 1](#)). Cobalt(II) acetate tetrahydrate was added to absolute ethanol (40 mL of EtOH for 1 mmol of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) and stirred until complete solubilization (10 min., formation of a clear purple solution). Then the ligand (2 mmol) was added (color change to deep red) and the resulting solution was stirred at 60 °C for 2 h. Owing to their scarce solubility in EtOH, ligands **L2** and **L7** were initially solubilized in the minimum amount of inhibitor-free THF and then dropwise added to a solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in EtOH. After that, VULCAN XC 72R[®] (1.392 g for 1 mmol of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) was portionwise added during about 30 min and the suspension was stirred at 25 °C for 18 h. Then, the solvent was removed and the obtained solid was dried for 4 h under vacuum, grinded to a very fine powder and finally transferred into a ceramic crucible, equipped with a lid, and placed in the pyrolysis oven. The oven was evacuated to ca. 5 mbar and then flushed with argon. Afterward, it was heated to 800 °C at a rate of 25 °C per minute and held at 800 °C for 2 h under Ar atmosphere. Finally, heating was stopped and the oven was cooled down to room temperature. During the whole process, a constant flux of argon through the oven was maintained. The elemental analyses of the prepared materials are reported in the [Supporting Information](#).

2.4. General methods for catalytic reactions in the autoclave

In an 8 mL glass vial fitted with a magnetic stirring bar and a septum cap, the catalyst (the amount depends on the catalyst) was added followed by the nitroarene (0.5 mmol), the internal standard (hexadecane, 20 mg) and the solvent (2 mL). A needle was inserted in the septum cap, which allows dihydrogen to enter. The vials (up to 7) were placed into a 300 mL steel Parr autoclave which was flushed twice with dihydrogen at 20 bar and then pressurized to 50 bar. Then the autoclave was placed into an aluminum block pre-heated at 110 °C. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, diluted with a suitable solvent, filtered using a Pasteur pipette filled with Celite[®] (6 cm pad) and analyzed by GC using *n*-hexadecane as an internal standard. Control experiments showed that the position of the vial inside the autoclave is not influential. The same outcome was obtained when the reaction was repeated by moving a vial from a peripheral to a central position.

2.5. Procedure for quantitative determination of the reaction products

All nitroarenes employed and all anilines reported in [Fig. 8](#) are commercially available compounds. Their amount was determined by GC analysis (HP 6890 series GC system) using *n*-hexadecane as internal standard and calibrating the response factor by using pure compounds (Aldrich, Alfa-Aesar, Tokyo Chemical Industry). For product **2aa**, at the end of the reaction the catalyst was separated using a Pasteur pipette filled with Celite[®] and the Celite[®] pad was washed with EtOH. The solvent was evaporated and the desired product isolated using column chromatography (AcOEt:heptane = 1:1). The product was obtained as a light brown solid. Regarding product **2ab**, after the reaction was complete, the cata-

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