



# Structure-activity relationships of carbon-supported platinum-bismuth and platinum-antimony oxidation catalysts



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## ABSTRACT

Compositional and morphological studies on supported platinum are important for the improvement and expanded use of catalysts for oxidative coupling reactions. Nanocomposites consisting of 5% Pt supported on activated carbon and promoted with 5% Bi or Sb were prepared by electroless deposition and microwave-assisted (MW) methods. Addition of promoters significantly increases the dispersion of Pt. Bismuth reacts with residual phosphorus of the support to form various phases of BiPO<sub>4</sub>, while Sb cannot be detected by XRD. However, samples prepared by the MW method are unique in that they contain crystalline PtBi or PtSb alloys as part of the phase matrix. The thermal stability of the samples in air and the TOFs for the oxidation of 2-methyl-1-naphthol correlate with the metal dispersion. Since the oxidation reaction is understood to take place on the surface of metals with high standard electrode potentials, sufficient Pt exposure is one of the key performance parameters.

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## 1. Introduction

The IUPAC nomenclature [1] distinguishes between *amorphous carbon* (no long-range crystalline order), *non-graphitic carbon* (two-dimensional long-range order of the carbon atoms in planar hexagonal networks), and *graphitic carbon* (three-dimensional hexagonal crystalline long-range order). In principal, activated carbon (AC) consists of non-graphitic carbon, as any tarry and amorphous carbon is removed during the manufacturing (activation) process, and graphite is normally absent [2,3]. AC has a highly porous texture and is characterized by high thermal stability (in the absence of air), a large surface area, and phenomenal adsorptive properties [2]. AC can intercalate metal nanoparticles (NPs) to form composite materials that are useful in water purification, fuel cells and general catalysis [3–6]. AC has the added advantage of supporting the product life cycle: carbon burns readily when heated in air, allowing supported metals to be easily recovered and recycled [3].

Metal/AC composites can be prepared with the help of chemical and physical methods. Chemical methods include impregnation

and electroless (reductive) deposition (ED). Physical methods make use of lasers, sonication, microwave (MW) and UV irradiation, as well as plasma technology and supercritical fluids [7]. The method of preparation has a decisive influence on the structure and morphology of the final product [8]. Depending on the synthesis conditions, different metal and oxide phases can be generated, which allows tuning of the sample properties to the requirements of the envisaged application. The shape and size distribution of NPs are also important, e.g. in catalysis the particle size has often a crucial influence on catalyst activity and selectivity [9,10]. Precipitation of metals onto supports by deposition methods results frequently in an extended particle-size distribution (PSD), accompanied by agglomeration [7]. In contrast, use of MW irradiation during synthesis can be expected to create homogeneous nucleation sites, resulting in a narrow PSD with a high metal dispersion and uniform particle shapes [10,11]. In addition, MW irradiation offers shorter reaction times and reduced energy consumption [10,12]. In combination with ethylene glycol it is a very convenient, fast and efficient method of metal deposition onto supports [13], as glycol can act both as the solvent and as the reducing agent for metal precursors [14].

Pt-Bi and Pt-Sb composites have applications in thermoelectronics and batteries [15–17]. Carbon-supported Pt-Sb is a promising material for direct formic-acid and methanol fuel cells

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[6,17,18]. Pt-Bi<sub>2</sub>O<sub>3</sub> was found by Moniz et al. [19] to facilitate the photolysis of water, which neither Pt nor Bi<sub>2</sub>O<sub>3</sub> can accomplish on their own. Pt-Bi/AC is a commercially available catalyst for electrocatalysis and selective oxidation reactions. With respect to the latter application, it is speculated that Bi exerts a geometric blocking effect on Pt, thus decreasing the active site ensembles of Pt. These minimized sites still allow for the desired chemical reaction to proceed, but they are inactive for unwanted side reactions [20–23].

In our previous studies, 5%Pt-5%Bi/AC was used for the oxidation and oxidative coupling of 1-naphthols [24,25], while 5%Pt-5%Sb/AC was shown to have superior selectivity for the oxidation of cinnamyl alcohol to cinnamaldehyde in comparison with corresponding Bi-containing catalysts [26]. In the present study, the properties of 5%Pt-5%Bi/AC and 5%Pt-5%Sb/AC composite materials prepared by ED, including MW-assisted glycol reduction, are described. The different nanofeatures obtained under varying synthesis conditions have an influence on the autocatalytic oxidation of the composite materials. In addition, they have an impact on the catalytic activities and selectivities of chemical oxidation reactions; this is demonstrated by example of the oxidative coupling of 2-methyl-1-naphthol (Scheme 1).

The oxidative coupling of naphthols is an important method for the formation of new C–C bonds [27,28]. Apart from other reaction parameters, the outcome depends on the composition and the properties of the catalyst, as well as on the electronic and steric nature of the substrate. The formation of coupled products occurs often concurrently with the formation of mono-quinones. Only a limited amount of work described in the literature is dedicated to the heterogeneous catalytic oxidation of 2-methyl-1-naphthol (Scheme 1). Most of these studies are aimed at the conversion of **1** to menadione (**4**), and the coupled products (**2** and **3**) are considered to be by-products [29–32]. Menadione is a blood coagulating agent (vitamin K<sub>3</sub>) [33]. The development of a viable and environmentally sustainable catalytic route to this molecule is of great commercial interest. High yields of **4** can be obtained over oxide catalysts in combination with hydrogen peroxide, e.g. Ti-MMM-2 (mesoporous titanium-silicate): 78% [34], Nb<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub>: 42% [35], Ti-SBA-15: 93% [31], Nb-SBA-15: 97% [32]. However, isolated yields were not reported, and the mass of the catalyst in relation to the mass of the starting material (SM) is always high (SM/cat. = 0.9–2.0 m/m). In contrast to oxides, metallic-state catalysts favor the formation of coupled products [24,25]. Depending on the reaction conditions and the solvent used, **2** or **3** can be obtained in high yields over Pt supported on AC (96–97%, SM/cat. = 25 m/m). Previously, Kral and Laatsch obtained **3** with a yield of 72% by the coupling of **1** with stoichiometric amounts of AgO as the oxidant [36]. The maximum menadione yield obtained over Pt is 30.5% [25].

## 2. Experimental

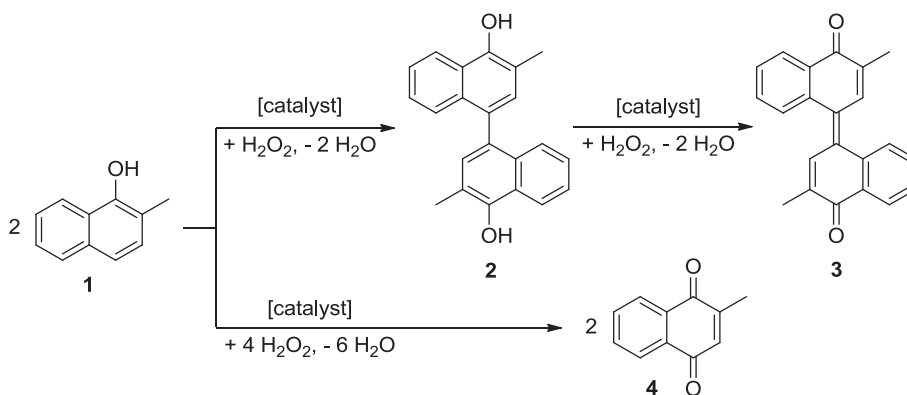
### 2.1. Materials

Activated carbon (Darko KB-G 174), bismuth(III) nitrate pentahydrate (98%), antimony chloride (99%), hydrazine monohydrate (98%), nitromethane (95%) and silica gel for column chromatography (pore size 60 Å, 70–230 mesh) were purchased from Sigma-Aldrich. Hexachloroplatinic acid (metal content 40.31%) was bought from SA Precious Metals. Hydrogen peroxide (30%), dichloromethane (99.5%), ethyl acetate (99%), methanol (99.5%) and petroleum ether (90%) were obtained from SMM Instruments, ethylene glycol (99.5%) from Promark Chemicals, and Triton X-100 (98–102%) from BDH. 2-Methyl-1-naphthol was prepared as described previously [24].

### 2.2. Synthesis of nanocomposites

Electroless deposition (ED): for the preparation of 5%Pt-5%Bi on AC, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (0.1328 g, 0.2564 mmol Pt) and Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.1162 g, 0.2396 mmol Bi) were dissolved in 50% H<sub>2</sub>O/50% CH<sub>3</sub>OH (v/v, 100 ml). Triton X-100 (3 ml) was added, and the mixture was placed in an ultrasonic bath for 2 h to completely dissolve the bismuth nitrate. After addition of the AC support (0.9005 g), the mixture was stirred using a magnetic stirrer. After 10 min a 98% aqueous solution of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (0.2 ml, 4.041 mmol) was added dropwise with a syringe to reduce the metal ions. Stirring continued for 28 h. Each sample was filtered and washed with deionized water to pH 7, and finally washed with CH<sub>3</sub>OH. By testing with AgNO<sub>3</sub>, the final aqueous filtrate was found to be free of chloride. Samples were dried under different conditions, i.e. at room temperature (r.t.) under vacuum for 4 h (VD), or in an oven at 140 °C for 24 h (OD). The same procedure was used to prepare VD 5%Pt/AC, as well as VD and OD 5%Pt-5%Sb/AC; SbCl<sub>3</sub> (0.1228 g, 0.4108 mmol) was the precursor for Sb.

Microwave-assisted loading (MW): for the preparation of MW 5%Pt-5%Bi/AC, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (0.1328 g, 0.2564 mmol) and Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.1161 g, 0.2393 mmol) were transferred into a 100 mL beaker containing ethylene glycol (20 mL), followed by ultrasonication for 10 min to completely dissolve the salts. To this mixture, AC (0.9001 g) was added, followed by ultrasonication for 1 h prior to MW irradiation. The MW-assisted metal loading was conducted in a Mars Xpress MW system at 600 W and 190 °C in a closed Teflon vessel. The time to reach the final temperature was set at 5 min, and irradiation continued for 10 min at 190 °C to allow for the complete reduction of Pt(IV) to Pt(0). Samples were centrifuged, washed with deionized water, and left to air-dry (AD) for 24 h. The same method was followed to prepare



**Scheme 1.** Oxidation and oxidative coupling of 2-methyl-1-naphthol (**1**) using H<sub>2</sub>O<sub>2</sub> as the oxidant.

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