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# Water-soluble single source precursors for homo- and hetero-metallic nanoparticle catalysts supported on nanocarbons

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## ABSTRACT

Homo- and hetero-metallic catalysts were prepared in water from a single metal source and in a single step, and were tested in cinnamaldehyde selective hydrogenation. Two new water-soluble clusters, namely  $[\text{Ru}_5\text{C}(\text{CO})_{14}(\text{TPPTS})_1]$  and  $[\text{Ru}_5\text{PtC}(\text{CO})_{15}(\text{TPPTS})_1]$ , were synthesized by the addition of phosphine TPPTS to starting homo- and hetero-metallic clusters soluble in organic solvents. They were then impregnated onto nanocarbons (CNF and CNT) in water at different pH values. Cluster deposition occurred via two adsorption modes and was the most successful when attractive electrostatic interactions took place. Thermal activation of these samples led to heterogeneous catalysts with a small mean particle size between 2 and 4 nm. The homemade catalysts showed increased conversions and selectivities (up to 73%) towards the thermodynamically unfavored product cinnamyl alcohol compared to a commercial catalyst. The selectivity was in general higher with CNF support, with less oxygenated function and with bigger particles. The selectivity increased slightly with the addition of platinum to ruthenium but the activity was enhanced tremendously (up to 57% at  $t = 30$  min).

## 1. Introduction

The selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes is of great importance in the industry as unsaturated alcohols are widely used in pharmaceuticals, cosmetics or food additives and are highly valuable [1,2]. To obtain such alcohols is not an easy task as  $\alpha,\beta$ -unsaturated aldehydes present two hydrogenable sites. Hydrogenation of the olefin bond leads to the saturated aldehyde, which is the thermodynamically (stronger negative free reaction enthalpy of  $35 \text{ kJ mol}^{-1}$ ) and kinetically favored path over aldehyde hydrogenation leading to the alcohol [1,3,4]. Selective hydrogenation can be achieved by using reducing agents in stoichiometric amounts or via catalytic Meerwein-Ponndorf reduction in homogeneous conditions, but both result in a high amount of waste [1,5–7]. Much research has thus been focused on environmentally friendlier processes and heterogeneous catalysts have been considered as a valuable option [8]. Hydrogenation of unsaturated aldehydes has also been chosen as a model reaction to study relations between catalyst structure and activity/selectivity.

In this work, cinnamaldehyde (abbreviated as CAL) was chosen as a benchmark substrate. Its hydrogenation can lead to cinnamyl alcohol (unsaturated alcohol, COL), hydrocinnamaldehyde (saturated aldehyde, HCAL) or hydrocinnamyl alcohol (saturated alcohol, HCOL), as shown in Fig. 1. COL is a valuable product used in perfumery and in

deodorant for its aroma as well as for its fixation properties. HCAL, although easier to obtain, is also a product of interest as it was recently reported as drug synthesis intermediate for the treatment of HIV [9,10]. A great number of catalytic factors can influence the chemoselectivity of this particular reaction, such as the metal nature, the support, particle sizes, the metal precursor, the catalyst preparation, the activation procedure, the presence of a second metal, the solvent or the reaction conditions [1,4,11,12]. Concerning the metal nature, Ru and Pt show a moderate selectivity towards COL that can be easily modulated by associating another metal. This and their appreciable activity are the reason why these two metals are exceedingly used in this reaction [13–19]. The association of Ru and Pt in particular has driven much attention because of strong synergistic effect [8,16,20–24]. This effect is mainly explained by an electron transfer from Ru to Pt that leads to an electrophilic activation of the C=O bond by this more electropositive Ru. The more electronegative Pt is also believed to inhibit adsorption via the C=C bond [1,22]. Regarding the support, ordered carbons, like carbon nanotubes (CNT), carbon nanofibers (CNF) or graphene, seem to be more selective towards COL than non-graphitic carbons, like activated carbons. This observation is attributed to a better electron mobility between the support and the metal particle [24,25]. Charge transfer from the electron-rich  $\pi$ -system of carbonaceous surfaces influences the supported metal entities. The graphene sheets that are part of the ordered carbons are also susceptible

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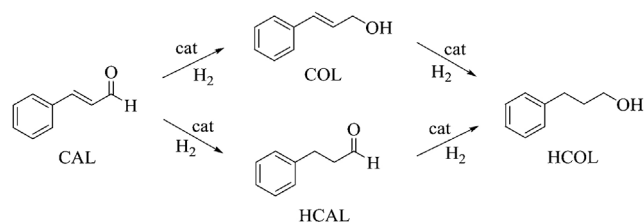


Fig. 1. Selective hydrogenation of cinnamaldehyde.

to make  $\pi$ - $\pi$  interactions with the phenyl ring of CAL, orienting the C=O groups toward the metal particle [22]. Another advantage of CNF is that it is a mesoporous support, hence avoiding mass transfer limitations. The CNFs are known to allow easy diffusion of reactant and products through the internal cavity and between the entangled fibers, which do not aggregate as bundles.

The vast majority of hetero-metallic heterogeneous catalysts are obtained from homo-metallic precursors, usually salts, where a close contact between both metals in the final nanoparticle is not guaranteed. On the contrary, the use of molecular clusters (i.e. molecular species comprising at least three metal atoms in their core bound by minimum two metal-metal bonds and stabilized by a ligand shell, following the organometallic definition) allows a better control on the particle chemical composition [26]. Indeed if a bimetallic cluster is deposited and then activated onto a support, both metals should be present in the final nanoparticles with the same molar ratio as in the starting cluster. When using clusters, the activation step is defined as the heating step to remove all the organic ligands surrounding the metallic core with concomitant formation of 'naked' nanoparticles by limited aggregation of metal atoms. The true hetero-metallic nature of nanoparticles obtained from cluster precursors was indeed confirmed many times by EXAFS and the resulting catalysts usually present increased catalytic performances in comparison with catalysts arising from homo-metallic counterparts [27–31].

The present work deals with the preparation of ruthenium-based homo- and hetero-metallic supported nanoparticles in water from hydrosoluble single source cluster precursors. The synthetic strategy involves studying the aqueous impregnation of water-soluble clusters onto nanocarbons at different pH values, in order to maximize the cluster-support interactions. First, new water-soluble Ru and Ru-Pt clusters will be prepared by incorporating a water-soluble phosphine within the coordination sphere of renowned carbonyl clusters that are initially soluble in organic solvents. The feasibility of this synthesis strategy has been proven with several phosphine-cluster pairs [32–37]. The phosphine ligand selected here is TPPTS (triphenylphosphine trisulfonate trisodium salt), which has been often successfully used to produce various metallic complexes or clusters that are highly soluble in water [38–41]. Second these water-soluble clusters will be impregnated onto nanocarbons (CNF and CNT) at different pH values. We have recently demonstrated that cluster impregnation onto nanocarbons occurs via two adsorption mechanisms in water [42]. We postulated that the first adsorption mode is either  $\pi$ -bonds coordination between a triangular face of the cluster and the carbon aromatics or reaction with edges and point defects at the carbon surface, occurring at all pH values. This was suggested by the specific reactivity of molecular clusters with soluble carbon allotropes such as fullerenes [43–49]. The second adsorption mode occurs through electrostatic interactions that can be of attractive or repulsive nature and increase or decrease the loading, respectively. These electrostatic interactions are made possible by the presence of oxygenated surface functions onto carbonaceous materials, that can be charged in water depending on the pH [50]. In other words, carbonaceous supports possess a PZC (Point of Zero Charge), i.e. a specific pH value where the surface is globally neutral. At a pH value below this PZC, the surface becomes positively charged and can attract negatively charged precursors, and vice versa. This

coulombic viewpoint has been extensively exploited to produce heterogeneous catalysts onto carbon or inorganic oxide supports using mononuclear complexes, and was coined SEA for 'Strong Electrostatic Absorption' by J. Regalbuto et al. [51–54]. We noted that these electrostatic interactions lead in the case of clusters to bigger particles after thermal activation than when 'other' interactions ( $\pi$ -bonds and defects interactions as described above) take place. The present work will therefore also investigate the thermal activation of these water-impregnated samples and test the obtained heterogeneous catalysts in cinnamaldehyde hydrogenation to observe the effects of metal nature, support and synthetic route. In particular, hetero-metallic effects will be given particular emphasis. To the best of our knowledge, this is the first time that catalysts are prepared using a single source hetero-metallic precursor in water.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. General

All manipulations were carried out under argon atmosphere using Schlenk techniques and the samples were stored under argon, unless otherwise stated. Dichloromethane was dried and distilled over calcium hydride prior to use and stored under argon on molecular sieves. Methanol and demineralized water were degassed prior to use and stored under argon. All commercially available products were used without further purification. Triruthenium dodecacarbonyl ( $[\text{Ru}_3(\text{CO})_{12}]$ , 99%), bis(triphenylphosphoranylidene)ammonium chloride (PPNCl, 97%), dodecane (ReagentPlus,  $\geq 99\%$ ), cinnamaldehyde (99%), cinnamyl alcohol (98%), hydrocinnamyl alcohol (98%) and hydrogen peroxide solution (35% in  $\text{H}_2\text{O}$ ) were supplied by Sigma Aldrich. Oleum (20–30%) and hydrocinnamaldehyde (95%) were supplied by Acros. Triphenylphosphine (TPP,  $\geq 98.5\%$ ) was supplied by Fluka. Dichloro(1,5-cyclooctadiene)platinum(II) ( $\text{Pt}(\text{COD})\text{Cl}_2$ ) was supplied by TCI. Reference catalyst Ru/AC (activated carbon) with 5 wt.% Ru was supplied by Alfa Aesar.  $\text{DMSO-}d_6$  and  $\text{D}_2\text{O}$  were supplied by Euriso-top. Nanofibers Pyrograf III PR-24-XT-LHT and Pyrograf III PR-24-XT-LHT-OX were supplied by Applied Sciences, Inc. and abbreviated as LHT and LHT-OX, respectively. Thin multi-wall carbon nanotubes were supplied by Nanocyl (NC3100, 95 + % Carbon purity) and abbreviated as CNT.

#### 2.1.2. Cluster synthesis

TPPTS **1** was synthesized following a reported procedure from the reaction of TPP in oleum that allowed the NMR monitoring of the reaction [55]. After purification, the pure product contains 4.5% of phosphine oxide. Yield: 42%. IR ( $\nu_{\text{CO}}$   $\text{cm}^{-1}$  in KBr): 1466(m), 1402(m), 1210(s).  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.46–7.58 (m, 6H), 7.82 (dd, 6H,  $^3J = 18$  Hz,  $^4J = 9$  Hz).  $^{31}\text{P}$  NMR (121 MHz,  $\text{D}_2\text{O}$ )  $\delta$  -5.3, 35.05 (4.5%, phosphine oxide).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.09–7.14 (m, 3H), 7.35–7.40 (m, 3H), 7.61–7.64 (m, 6H).  $^{31}\text{P}$  NMR (121 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -4.55, 26.25 (4.5%, phosphine oxide). The deliberate oxidation of ligand TPPTS **1** was performed according to [56] in a  $\text{H}_2\text{O}_2$  solution. Yield: quant.  $^{31}\text{P}$  NMR (121 MHz,  $\text{D}_2\text{O}$ )  $\delta$  35.08.

$[\text{Ru}_5\text{C}(\text{CO})_{15}]$  **2**, the first starting cluster, was prepared according to a previously reported procedure [57].  $[\text{Ru}_3(\text{CO})_{12}]$  is dimerized into  $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ , that is in turn used to form the purple solid  $[\text{Ru}_5\text{C}(\text{CO})_{15}]$  **2**. Overall yield: 66%. IR ( $\nu_{\text{CO}}$   $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ): 2067(s), 2034(s), 2017(sh).

$[\text{Ru}_5\text{PtC}(\text{CO})_{16}]$  **3**, the second starting cluster, was prepared following modified literature procedures [58] and [59]. First,  $[\text{Ru}_5\text{C}(\text{CO})_{15}]$ , previously prepared as described above, was used to form  $[\text{PPN}]_2[\text{Ru}_5\text{C}(\text{CO})_{14}]$ , according to [58]. Then 200 mg of  $[\text{PPN}]_2[\text{Ru}_5\text{C}(\text{CO})_{14}]$  (0.100 mmol) and 38 mg of  $\text{Pt}(\text{COD})\text{Cl}_2$  (0.102 mmol, 1.01 equiv.) were dissolved in 30 mL of  $\text{CH}_2\text{Cl}_2$  with 10 spatula tips of silica in a funnel equipped three-necked Schlenk flask.

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