



# Covalently and non-covalently immobilized clusters onto nanocarbons as catalysts precursors for cinnamaldehyde selective hydrogenation



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## ABSTRACT

Ru-based nanoparticles were deposited on carbon nanotubes and graphene via an organometallic approach involving mixed-metal clusters modified with appropriate ligands. These ligands allowed either covalent or non-covalent  $\pi$ - $\pi$  interactions with the carbonaceous surfaces. The immobilized clusters were then coalesced at different temperatures to give carbon-supported nanoparticles of different sizes. The obtained catalysts were tested in the selective hydrogenation of cinnamaldehyde. It was found that the nature of the metal(s), support nature, incorporation method and activation temperature all had a profound influence on activity and selectivity. Interestingly, the selectivity could be shifted from cinnamyl alcohol (COL) to hydrocinnamaldehyde (HCAL) by changing the reaction solvent. The best catalysts gave a very high selectivity in cinnamyl alcohol, which is not the more thermodynamically favored product, and could be reused several times without loss of activity or selectivity.

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## 1. Introduction

Supported catalysts to be competitive should simultaneously fulfill the following criteria: a high activity and selectivity coupled to stability and ease of recovery over time [1]. The chemoselective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes has been often selected to evaluate the above-mentioned criteria [1–5]. These compounds present two hydrogenable sites which means that two competitive reaction pathways can be followed: the selective transformation of the aldehyde into the corresponding unsaturated alcohol or the thermodynamically more favoured reduction of the olefin bond. These reactions pathways determine the chemoselectivity of the transformation and can be moreover complicated by side reactions occurring either on the metal active phase or on the support [3]. The Meerwein–Ponndorf–Verley reaction applied to these aldehydes in homogeneous catalysis allows to selectively obtain the unsaturated alcohol with a high conversion but a large amount of waste: This methodology is therefore prescribed for

costly chemicals [2,6,7]. The development of heterogeneous catalysts on various supports, environmentally friendlier and able to selectively hydrogenate both functions separately was thus considered as a valuable option by many authors [1–3,5,8–17].

Since the transformation in the two hydrogenated products, that is hydrocinnamaldehyde and cinnamyl alcohol, is of chemical interest, cinnamaldehyde was chosen as benchmark substrate. The abbreviations used, namely cinnamaldehyde (CAL), hydrocinnamaldehyde (HCAL), cinnamyl alcohol (COL) and hydrocinnamyl alcohol (HCOL), as well as the structure of the molecules, are shown in Fig. 1. COL is generally described as the most challenging product to obtain and is moreover the most valuable: It is a critical intermediate in the production of chemicals such as flavors, pharmaceuticals and perfumes [1,18]. Nevertheless C=C double bond hydrogenation to obtain HCAL as a product was recently reported as intermediate in the synthesis of medicines for the treatment of HIV, which makes it also a challenging product [19].

The chemoselectivity toward both products is affected by a considerable number of parameters such as particles metal(s) nature and type of faces exposed, steric and electronic effects, catalyst preparation, activation procedure, selected support or even reaction conditions [1,2,7,21]. A comprehensive review written by Gallezot et al. deals with this topic [2]. Among these parameters, the most explored is undoubtedly the metal nature. Studies

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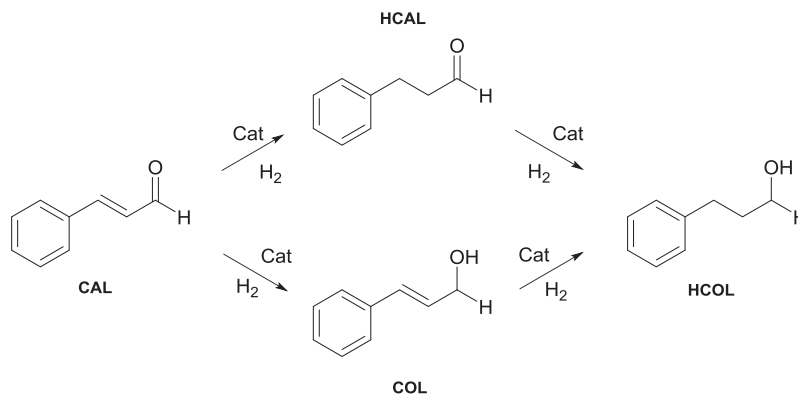


Fig. 1. The structure and conversion routes of  $\alpha,\beta$ -cinnamaldehyde.

conducted on metals deposited on carbon supports revealed that Pt and Ru, because of their acceptable activity, selectivity and stability, feature among the best considered metals to obtain the desired unsaturated alcohol [21]. In addition, a combination of several metals can greatly improve the selectivity toward the desired product [12,18,20,22,23]: Pt–Ru bimetallic catalysts gave impressive activity and selectivity [1,24–27]. This activity/selectivity enhancement is a result of synergism effect [28] which can be explained mainly by electronic and geometric effects: The former is due to an alloy formation or intimate contacts between metals [29] while the latter comes from effects such as a modification of the metal dispersion [30,31] or a surface enrichment [32–34]. In general, both effects go hand in hand. Synthetic routes to obtain supported bimetallic nanoparticles are well documented and range from simple to more sophisticated methods such as ion exchange, impregnations methods, homogeneous deposition precipitation or even colloidal microwave process [22,35]. In almost all cases, these multi-metallic nanoparticles arise from separate monometallic precursors. The different metals are thus not necessarily in a close contact which is assumed to be of importance for catalysis [3]. The use of clusters [36] as nanoparticles precursors can *de facto* circumvent this problem. Relatively few studies deal with their use as single precursors for high performance nanocatalysts [37–42].

The catalyst support, whose main task consists in dispersing the metal on its surface, displays also a significant and sometimes critical role on both the activity and the selectivity in the targeted selective hydrogenation [3,4]. Oxides, such as silica and alumina, and carbon based supports including activated carbon, carbon nanofibers, carbon nanotubes (CNTs) and recently graphene

oxide/reduced graphene oxide (GO/rGO) are the most commonly used supports [1–3,5,8–17,43]. Among them, nanocarbons (CNTs, GO, rGO) have been selected for this work. It seems interesting to evaluate in terms of activity and selectivity the possible difference between these supports arising from metal dispersion and electronic effects. Indeed, graphene is a 2D system compared to the 1D CNTs [2]. Moreover, oxygenated functions, present in high amounts in GO (and rGO on a smaller scale), could also be of importance for the selectivity [44,45].

The present work reports an unconventional methodology to covalently and non-covalently anchor Ru-based mono- and Ru–Pt, Ru–Au and Ru–Pt–Au multi-metallic precursors onto nanocarbons. The undertaken route is depicted in Fig. 2, which shows schematically the successive steps envisaged. To this end, multi-walled carbon nanotubes (MWNTs) and graphene were selected as supports. Two pathways were attempted to obtain the target materials: a non-covalent and a covalent methodology. When the covalent pathway was undertaken, a pre-functionalization step is required (I): Acyl chloride functions were formed on GO or MWNTs on oxygenated functions located at defects- and end-sites. A recently reported radical approach involving xanthate chemistry applied to MWNTs was also selected to pre-functionalize nanocarbons [46]. In the next step, mono- and multi-metallic clusters were selected as single source metal precursors and immobilized onto nanocarbons by a covalent or a non-covalent strategy (II). In the latter case, a polar solvent and polyaromatics, that is pyrenes moieties, are required to perform this non-covalent immobilization involving  $\pi$ – $\pi$  stacking [47]. All these catalysts, once thermally activated at different temperatures

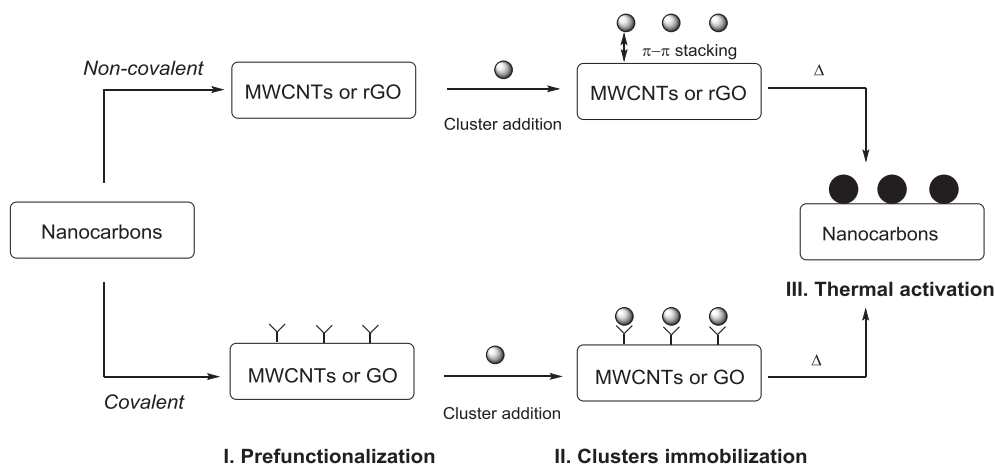


Fig. 2. General methodology to obtain mono- or multi-metallic nanoparticles arising from a single source metal precursor.

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