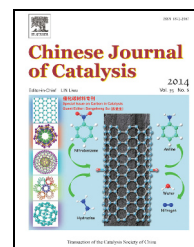


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## Fragrances by selective oxidation of long-chain alcohols

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### ABSTRACT

The activity and the selectivity of Ru and Pt based carbon catalysts in the selective oxidation of long-chain aliphatic alcohols (C8, C10, C12) have been investigated. Ru/AC and Pt/AC always showed good initial activity, however deactivation phenomena rapidly depressed the catalytic performance of the catalysts. These phenomena can be limited by modification of Ru/AC and Pt/AC with Au improving the durability of the catalyst. Ru/AC and AuRu/AC showed good selectivity to the corresponding aldehyde (>95%) making these catalysts promising for fragrances manufacturing. The advantage in using Au modified catalyst lies on the easier regeneration procedure compared to the one necessary for Ru/AC. Pt/AC and AuPt/AC showed a lower selectivity to aldehyde promoting the formation of the acid and the ester formation respectively. The addition of water in the solvent system speeds up the reaction rate but drastically decreased the selectivity to aldehyde especially in the case of Pt based catalysts.

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### 1. Introduction

Aldehydes with a linear aliphatic carbon chain have desirable olfactory properties and they found several industrial applications in the production of perfumes and essences [1–4]. For example, *n*-octanal (present in lemon oil), *n*-capraldehyde (C10) (present in sweet orange, lemongrass, coriander), and *n*-dodecanal (present in oils and lemon) are so effective that they markedly affect the feature of the perfume to which they are incorporated [5]. These aldehydes can be found in natural products such as essential oils and fruits of plants, but the growing market demand has made the synthetic route increasingly attractive. The selective oxidation of the corresponding long chain alcohols constitutes a highly convenient alternative [5]. For environmental and economic reasons, replacing stoichiometric oxidants with heterogeneous catalysts and molecu-

lar oxygen, as a green and selective oxidant, is very desirable [1–4]. Many heterogeneous catalytic systems have been reported for the selective oxidation of aliphatic alcohols. However, the most part of the catalysts, in particular those based on Au [6–9], Pt [10–13], Pd [11,14], and Ru [15–19] have been only tested in the base free oxidation of 1-octanol, as representative of the non-activated long chain aliphatic primary alcohol.

Ru based catalysts seem to be the most promising for the typical high selectivity to carbonyl compounds instead of carboxylic ones. Different groups showed, for example, that Ru nanoparticles supported on hydroxyapatite [15,16] or graphene nanosheets [19] are very efficient in the 1-octanol oxidation with a selectivity to aldehyde of >95%. We recently showed that it is possible to enhance the catalytic performance of Ru catalysts by alloying Au nanoparticles, maintaining a high

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selectivity to octanal (>99%) [18].

Conversely, only a few examples of selective catalytic oxidation concerning long aliphatic chain alcohol (>C10) have been reported [5], and very low yields to the desired aldehyde are usually achieved. For example, a 10% commercial Ru/AC catalyst was able to convert 1-decanol using toluene/H<sub>2</sub>O as solvent (90 °C, 1 atm O<sub>2</sub>) with decanoic acid as main product (59%) [20]. Musawir et al. [21] reported the oxidation of 1 dodecanol in toluene at 100 °C using a Ru-Co binary oxide with the addition of 2,6-di-tert-butyl-p-cresol, yielding to a maximum conversion of 52% with a selectivity of 83% to aldehyde. Mori et al. [22] reported the oxidation of 1-dodecanol to 1-dodecanoic acid without any formation of the corresponding aldehyde using RuHAP- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and toluene as solvent (90 °C, O<sub>2</sub> flow). Therefore, it appears clear that the development of an efficient catalytic system able to oxidize long chain aliphatic alcohols to the corresponding aldehyde is still challenging.

In this paper, different aliphatic alcohols (1-octanol, 1-decanol, and 1-dodecanol) have been considered with the aim to correlate the length of the chain to the activity, selectivity and stability in the oxidation reaction. The effect of the nature of the metal (Ru and Pt) as well as the beneficial effect of Au addition, already evidenced in the 1-octanol and glycerol oxidation, have been investigated. The effect of solvent was also studied. Indeed, it has been recently shown that the presence of water is particularly beneficial and is able to speed up the reaction up in the case of Pt/AC in the selective oxidation of 1-octanol [13].

## 2. Experimental

### 2.1. Materials

NaAuCl<sub>4</sub>·2H<sub>2</sub>O and K<sub>2</sub>PtCl<sub>4</sub> were obtained from Aldrich (99.99% purity), NaBH<sub>4</sub> of purity >96% from Fluka and polyvinylalcohol (PVA) ( $M_w = 13000$ – $23000$ , 87%–89% hydrolyzed) from Aldrich were used. Gaseous oxygen and hydrogen from SIAD was 99.99% pure. Stock aqueous solutions of PVA (1%, wt/wt) and NaBH<sub>4</sub> (0.1 mol/L) were prepared. 1-octanol, 1-decanol and 1-dodecanol (99.5%) and all the intermediates were from sigma Aldrich. Commercial Ru/AC (Escat 40, 5%wt) was from Engelhard.

### 2.2. Catalyst preparation

#### 2.2.1. Monometallic catalyst

Au/AC: solid NaAuCl<sub>4</sub>·2H<sub>2</sub>O (0.051 mmol) and PVA (Au/PVA = 1:1 wt/wt) solution were added to 100 mL of H<sub>2</sub>O. The solution was stirred for 3 min, 0.1 mol/L NaBH<sub>4</sub> (Au/NaBH<sub>4</sub> = 1:4 mol/mol) solution was added to the yellow solution under vigorous magnetic stirring. A ruby red Au(0) sol was immediately formed. Within few minutes from their generation, the colloids (acidified at pH 2, by sulphuric acid) were immobilized by adding the support under vigorous stirring. The amount of support was calculated as having a gold loading of 1 wt%. The catalysts were filtered, thoroughly with distilled water (neutral mother liquors) and dried at 80 °C for 4h.

Pt/AC: K<sub>2</sub>PtCl<sub>4</sub> (Au:0.051 mmol) was dissolved in 100 mL of H<sub>2</sub>O, and PVA was added (Pt/PVA = 1:1 wt/wt). The solution was stirred for 3 min, after which 0.1 mol/L NaBH<sub>4</sub> (Pt/NaBH<sub>4</sub> = 1:16 mol/mol) was added under vigorous magnetic stirring. The light-grey Pt(0) sol was formed after 30 min. Within 1h of sol generation, the Pt sol was immobilized by adding the support (acidified to pH 2 by sulphuric acid) under vigorous stirring. The amount of support was calculated as having a Pt loading of 1 wt%. After 2 h, the slurry was filtered and the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 80 °C for 4h.

#### 2.2.2. Bimetallic catalyst

AuRu/AC: Bimetallic system was prepared as reported in [18], immobilizing PVA stabilized AuNPs on commercial Ru/AC (i.e. AuRu/AC). Preparation of PVA stabilized AuNPs: solid NaAuCl<sub>4</sub>·2H<sub>2</sub>O (0.051 mmol) and PVA (Au/PVA = 1:1 wt/wt) solution were added to 100 mL of H<sub>2</sub>O. After 3 min, 0.1M NaBH<sub>4</sub> (Au/NaBH<sub>4</sub> = 1:4 mol/mol) solution was added to the yellow solution under vigorous magnetic stirring. A ruby red Au(0) sol was immediately formed. Within few minutes from their generation, the colloid (acidified at pH 2, by sulphuric acid) was immobilized by adding the Ru/AC under vigorous stirring. The amount of support was calculated in order to obtain a final metal loading of 1 wt% (on the basis of quantitative loading of the metal on the support) and Au/Ru ratio of 1/10 mol/mol. The catalyst was filtered, washed on the filter and dried at 80 °C for 4 h.

AuPt/AC: NaAuCl<sub>4</sub>·2H<sub>2</sub>O (Au: 0.031 mmol) was dissolved in 60 mL of H<sub>2</sub>O, and PVA (1 wt%) was added (Au/PVA = 1:1 wt/wt). The yellow solution was stirred for 3 min, after which 0.1 mol/L NaBH<sub>4</sub> (Au/NaBH<sub>4</sub> = 1:4 mol/mol) was added under vigorous magnetic stirring. The ruby-red Au(0) sol was formed immediately. Within a few minutes of sol generation, the gold sol was immobilized by adding the support (acidified to pH = 2 by sulphuric acid) under vigorous stirring. The amount of support was calculated as having a gold loading of 0.60 wt%. After 2 h, the slurry was filtered and the catalyst washed thoroughly with distilled water (neutral mother liquors). The Au/support was dispersed in 40 mL of water, with K<sub>2</sub>PtCl<sub>4</sub> (Pt: 0.02 mmol) and PVA solution (Pt/PVA = 1:1 wt/wt) added. H<sub>2</sub> was bubbled (50 mL/min) under atmospheric pressure and room temperature for 2 h. After an additional 18 h, the slurry was filtered and the catalyst washed thoroughly with distilled water, and dried at 80 °C for 4h. The total metal loading was 1 wt%.

### 2.3. Characterisation

The Au@(Ru/AC) catalyst was examined in a FEI Titan 80-300 electron microscope equipped with CEOS image spherical aberration corrector, Fischione model 3000 HAADF STEM detector and EDAX SUTW EDX detector. The microscope was operated at an accelerating voltage of 300 kV in TEM mode for HRTEM and in STEM mode for STEM and EDX spectrum imaging. The Pt@(Au/AC) catalyst was examined in a Philips CM200 FEG microscope equipped with an EDAX DX4 analyzer for EDX spectra acquisition. The electron microscope was operated at

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