



Gold catalyzed one-pot myrtenol amination: Effect of catalyst redox activation



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ABSTRACT

The effect of the gold catalysts redox treatment on the formation of active catalysts for one-pot myrtenol amination with aniline was studied. A series of nanosized gold catalysts over metal oxides such as ZrO₂, CeO₂, La₂O₃ different in their basicity were synthesized by the deposition–precipitation method and characterized using TEM, XPS and TPR-, TPO-MS. One-pot myrtenol amination was carried out in a batch reactor at 180 °C under nitrogen pressure 9 bar. The catalytic activity and selectivity were shown to depend on the catalyst redox treatment. Pre-reduced gold catalysts supported on zirconium or cerium oxides were shown to be more effective in alcohol activation while once pre-oxidized catalysts promoted formation of the target amine with high selectivity. It was shown that thermal activation of catalysts in oxygen resulted in higher efficiency of ammonia removal compared to treatment in hydrogen. Difference in activity and selectivity for pre-reduced and pre-oxidized catalysts was proposed to be mainly related to the different degree of the support basic properties modification by residual ammonia.

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1. Introduction

This work continues a series of investigations devoted to one-pot amination of terpene alcohol, myrtenol [1,2], to produce complicated amines, that are of a great interest for the development of new pharmaceuticals for neurological diseases [3–6]. The one-pot alcohol amination (Fig. 1) generally proceeds through three consecutive steps: i) dehydrogenation of an alcohol to a reactive aldehyde, ii) interactions of the formed aldehyde with an amine to produce a corresponding imine and iii) the hydrogen transfer from the alcohol to the imine with the amine formation [7]. The results of our previous work [1,2] have shown that gold catalysts are active in one-pot myrtenol amination and resulted in predominant hydrogenation of C=N bond in the last step instead of hydrogenation

of a more reactive C=C group of myrtenol (Fig. 2). Therefore, the supported gold catalysts, which inspired much interest due to their specific activity and selectivity in many types of catalytic reactions, were shown to be perspective for their further application in one-pot amination of alcohols, namely terpene alcohols with a complicated structure.

In general, the regularities of one-pot alcohol amination have been actively studied resulting in a plausible reaction mechanism based on the obtained data (Fig. 1) [1,8–10]. The first step of alcohol deprotonation is promoted on the support basic sites giving an alkoxide intermediate on the support surface with a consecutive β-hydride elimination catalyzed by the active metal to form a carbonyl compound. The adsorbed aldehyde and amine interact to form hemiaminal, which then undergoes an attack by the hydride ion stabilized on active metal nanoparticles and the proton from the support surface resulting in production of the final product. Hence, both the support nature, namely its acid–base properties, and the chemical state of the gold species formed on the catalyst surface could affect alcohol conversion and selectivity to the target amine.

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The significant effect of support nature on alcohol conversion and amine yield was clearly demonstrated for myrtenol as well as for benzyl alcohol amination [1,8,10]. In our previous work a series of nanosized gold catalysts over ZrO_2 , Al_2O_3 , CeO_2 and La_2O_3 were tested to explore the role of the support. In both cases the correlation between the electronegativity of metal ions in metal oxide supports and the alcohol conversion as well as selectivity to secondary amine for myrtenol amination was obtained. It is known that the electronegativity of metal element or metal ion in the metal oxide support determines the acid–base properties of metal oxides and an increase in electronegativity leads to the increase an acidity of the metal oxide surface. Thus, the electronegativity was used as parameter for estimation of acid–base properties of the metal oxides used as supports. Finally, it was found that catalytic performance in each step strongly depends on support acid–base properties and a certain balance between *acid and base sites* is required for the efficient alcohol amination that was in a good agreement with data on the plausible reaction mechanism. Among the catalysts tested in the reaction a zirconia-supported gold catalyst with both acidic and basic surface sites was observed to promote an optimum consecutive myrtenol transformation resulting in the total conversion of myrtenol and selectivity to the target amine of about 53%. As it was mentioned above, the basic sites on metal oxide surfaces are required for the initial alcohol activation, while the availability of protonic groups was suggested to be important for the target amine formation [1]. On the other hand, catalyst pre-treatment may also affect both the support acidity and active Au species taking part in the reaction mechanism. Controlled regulation of catalytic activity through the catalyst modification is one of the key issues to improve the process efficiency.

The aim of the present work was to evaluate the effect of the gold catalysts redox pre-treatment on the catalytic activity and selectivity in the myrtenol amination. To explore effect of redox thermal treatment on the myrtenol amination the gold catalysts supported on zirconia, ceria and lanfana differing in their acidity were selected for the current investigation.

2. Experimental methodology

2.1. Preparation of catalysts

Catalysts with 3%wt. Au supported on commercial CeO_2 , La_2O_3 or ZrO_2 (Alfa Aesar) were synthesized by deposition–precipitation technique using $H AuCl_4$ (Alfa–Aesar) as a gold precursor and urea as

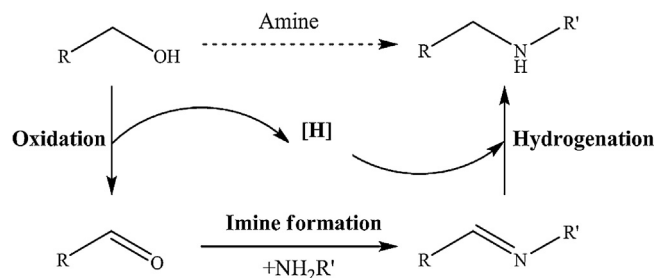


Fig. 1. General scheme of the one-pot alcohols amination.

a precipitating agent similar to the procedure described elsewhere [1,11]. The detailed characteristics of oxides are presented in [1]. In order to remove the excess of chloride after gold deposition, the samples were washed with a 25 M solution of NH_4OH (pH ca. 10), as in [12,13]. Thereafter the samples were washed with deionized water, filtered and dried at room temperature for 24 h. To study effect of redox pre-treatments the dried samples were reduced in hydrogen or oxidized in oxygen flow under a temperature increase to $350^\circ C$ with a ramp rate of $20^\circ C/min$.

2.2. Characterization of supports and catalysts

The gold content in synthesized catalysts was analyzed with an inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Varian Liberty 110 ICP Emission Spectrometer.

Specific surface area and pores of the samples were determined with the BET method by physisorption of nitrogen in a Tristar II 3020 Micromeritics equipment. Prior to measurements, the samples were treated in vacuum (0.05 mbar) at $350^\circ C$ for 12 h.

Transmission electron microscopy (TEM) was performed with a JEOL 2010 microscope. Before TEM measurements the samples were dispersed in isopropanol and dropped on a copper grid coated with a carbon film. To estimate the value of mean diameter of Au nanoparticles more than 250 particles were chosen. The mean diameter (d_m) of particles was calculated using the following equation: $d_m = \frac{\sum_i (x_i d_i)}{\sum_i x_i}$, where x_i is the number of particles with diameter d_i .

The electronic state of gold species was studied by X-ray photoelectron spectroscopy (XPS) with Kratos AXIS 165 photoelectron spectrometer using monochromatic $AlK\alpha$ radiation ($h\nu = 1486.58 eV$) and fixed analyzer pass energy of 20 eV. All mea-

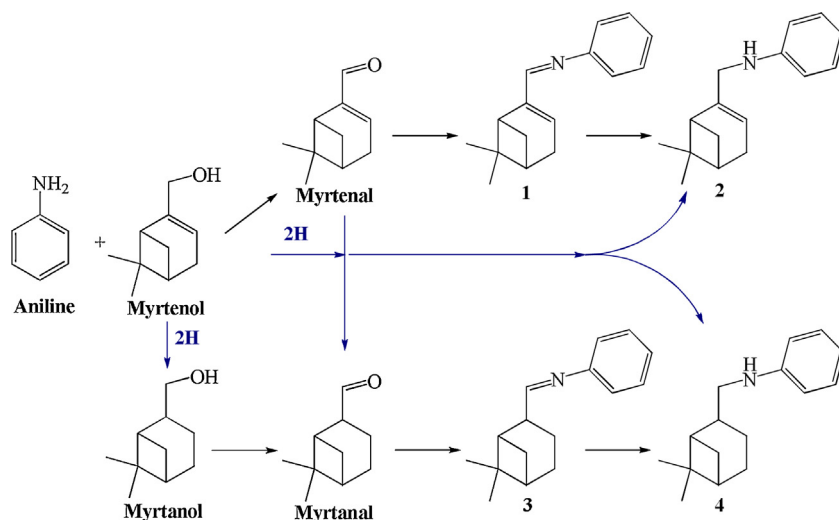


Fig. 2. Myrtenol amination with aniline over Au catalysts.

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