



Selectivity control in one-pot myrtenol amination over Au/ZrO₂ by molecular hydrogen addition

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ABSTRACT

The one-pot myrtenol amination was studied over Au (3 wt.)/ZrO₂ catalyst under mixed N₂/H₂ atmosphere (9 bar). The effect of hydrogen addition was explored with the aim to increase selectivity to the target amines. Hydrogen addition timing depending on myrtenol conversion and hydrogenation temperature affected selectivity to the reaction products. Hydrogen addition (1 bar) after almost complete myrtenol conversion at 100 °C increased the yield to amine up to 68% preserving C=C bond in the initial myrtenol structure. Hydrogen addition at 180 °C irrespective of the myrtenol conversion level provoked reduction of both C=C and C=N bonds with formation of two diastereomers (yield up to 93%), with *trans*-isomer formation being preferred when hydrogen was added at almost complete myrtenol conversion. It was shown, that in the presence of a gold catalyst controlled hydrogenation of competitive C=C and C=N groups can be performed during one-pot alcohol amination by regulation of the reaction conditions.

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1. Introduction

Amines are important chemicals *per se* and as building blocks for the production of valuable compounds in a number of industries. Bio-derived natural extractives such as terpenes due to their molecular structure represent very attractive starting materials for producing fine and specialty chemicals [1,2]. Utilization as platform molecules of natural terpenoids, which often possess biological activities, can provide new opportunities for the synthesis of efficient chemicals for human disease prevention and therapy. In particular, terpene amines, synthesized from renewable raw materials, were shown to exhibit specific physiological properties and can be used as intermediates of potential drugs for neurological diseases [3–6]. On the other hand, terpenoids are highly reactive. There is a variety of different transformations such as, for example, iso-

merization that can occur along with the target reaction resulting in selectivity decrease [7–14]. Thus, selective synthesis of terpenoid amines is a challenging task.

One-pot alcohol amination is considered as an effective approach for C–N bond formation and for the synthesis of complicated amines [15]. The overall reaction generally proceeds through three consecutive steps: alcohol activation (dehydrogenation) to a more reactive carbonyl compound, which then reacts with an amine to form condensation products, and finally transfer of hydrogen subtracted from the alcohol during first step to the imine with the target amine formation. This approach in theory allows selective production of secondary amines without formation of a tertiary amine.

In our previous work interactions of widespread monoterpenoid myrtenol with aniline leading to formation of a corresponding amine were studied (Fig. 1). It was shown that gold catalysts exhibited promising catalytic activity along with a low impact of such side reactions as reduction of the reactive C=C group of myrtenol by hydrogen formed in the first step (Fig. 1) [16–18]. Basicity of catalyst support strongly affects effectivity of gold catalysts in alcohols activation [19]. Indeed, the catalytic performance in myrtenol ami-

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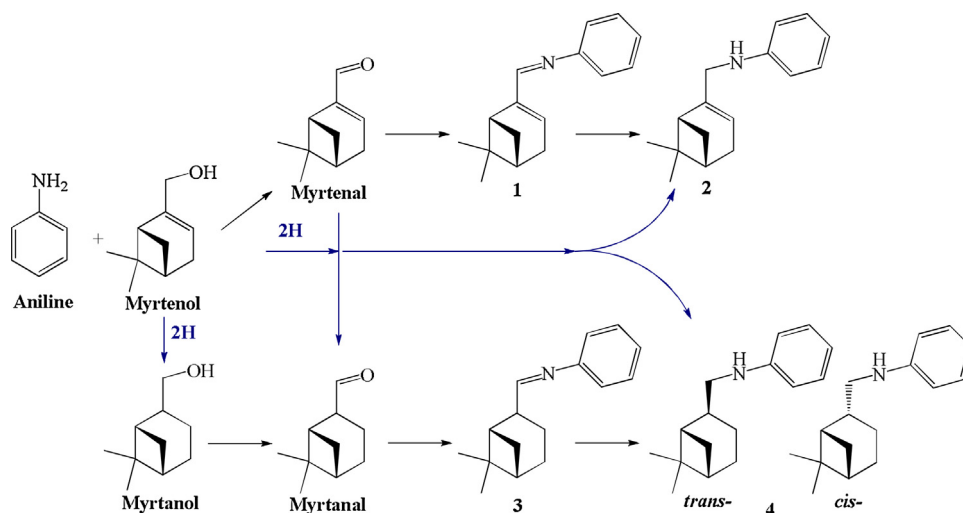


Fig. 1. Myrtenol amination with aniline over Au catalysts [16].

nation was shown to depend on acid–base properties of the selected catalyst supports [16] as well as on the catalyst redox pretreatment [18]. Based on these experimental data a detailed analysis of the reaction in terms of catalytic sites required for direct one-pot alcohol amination was performed. Among the catalysts tested in our studies Au/ZrO₂ pre-treated under oxidizing atmosphere was found to be optimal in terms of the target amine yield [16].

Based on kinetic data of myrtenol amination with aniline earlier published in [17] it can be tentatively proposed that hydrogenation of imine is somewhat slower than other steps, therefore debottlenecking of this step by introducing additional hydrogen is beneficial for the overall process. Such approach is of general interest for so-called hydrogen borrowing reactions, when hydrogen generated in a dehydrogenation step is transferred to an intermediate imine.

In the current study, therefore the effect of molecular hydrogen addition into the reaction system on the products selectivity was studied with the main aim to develop approaches for the direct terpene amines production minimizing influence of the side reactions.

2. Experimental/methodology

2.1. Catalysts preparation and characterization

The same sample of Au/ZrO₂ catalyst described well in our previous work was used [16]. Commercial monoclinic ZrO₂ (Alfa Aesar) with surface area 110 m²/g, pore volume 1.21 cm³/g and pore diameter 6.6 nm was selected as a support, which in the powder form with the particles size below 40 μm was used for catalyst preparation. Au/ZrO₂ catalyst (3 wt.% according to ICP) was synthesized by deposition-precipitation technique using HAuCl₄ (Alfa-Aesar) as a gold precursor and urea as a precipitating agent similar to the procedure described elsewhere [20]. In order to remove the excess of chloride after gold deposition, the sample was washed with a solution of NH₄OH (pH ca. 10), as in [21,22]. Thereafter the catalyst was washed with deionized water, filtered and dried at room temperature for 24 h. Before the catalytic tests, the sample was oxidized in air flow under a temperature increase to 350 °C with a ramp rate of 20 °C/min.

The prepared Au/ZrO₂ catalyst 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 °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 a mean diameter of Au nanoparticles more than 250 particles were counted. 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_α radiation (hν = 1486.58 eV) and fixed analyzer pass energy of 20 eV. All measured binding energies (BE) were referred to the C1s line of adventitious carbon at 284.8 eV. The spectra fitting was done using Shirley background estimation over the energy range of the fit.

2.2. Catalytic experiments

Liquid-phase (–)-myrtenol amination was performed in a stainless steel reactor, equipped with an electromagnetic stirrer (1100 rpm) and the sampling system. A mixture of (–)-myrtenol (1 mmol), aniline (1 mmol) and the catalyst (92 mg) in toluene (10 ml) was typically used. Generally two types of experiments were carried out depending on when addition of molecular hydrogen in the reaction system was performed, before or after initial (–)-myrtenol conversion. For the former case hydrogen being initially added to the system, the reaction was performed at 180 °C under N₂/H₂ atmosphere with H₂ partial pressure 1–2 bar and total pressure 9 bar. In the later case when hydrogen was introduced at almost complete (–)-myrtenol conversion hydrogen partial pressure was 1 bar (total N₂/H₂ 9 bar) and the temperature was 100 or 180 °C, while prior to hydrogen addition the reaction was carried out at 180 °C under N₂ atmosphere.

(–)-Myrtenol conversion was studied separately both in the presence or absence of molecular hydrogen. In a typical experiment, a mixture of (–)-myrtenol (1 mmol), Au/ZrO₂ catalyst (92 mg) in toluene (10 ml) was intensively stirred at

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