Effective gold catalysts for one-pot amination of myrtenol
(natural terpene alcohol)

Yu.S. Demidova1, I.L. Simakov1, M. Estrada3, E.V. Suslov1, K.P. Volcho1,
N.F. Salakhutdinov2, D.Yu. Murzin3, S. Beloshapkin1 and A. Simakov2,∗
1Borovsk Institute of Catalysis, 630090, Novosibirsk, pr. Lavrentieva, 5 (Russia)
2Postgraduate in Física de Materiales, CICESE, 22860, Ensenada, B.C.(México)
3Novosibirsk Institute of Organic Chemistry, 630090, Novosibirsk, pr. Lavrentieva, 9 (Russia)
∗Process Chemistry Centre, Åbo Akademi University, FI-20500, Turku/Åbo (Finland)
1Materials and Surface Science Institute, University of Limerick, Limerick (Ireland)
2Centro de Nanociencias y Nanotecnología, UNAM, 22860, Ensenada, B.C.(México)
*andrey@cnyn.unam.mx

Introduction
A large number of medicinally and biologically important compounds owe their
activity to the presence of amino groups. Particularly complicated terpene amines, synthesized
from renewable raw materials, were also recently shown to exhibit specific physiological
properties and can be used as intermediates of potential drugs for neurological diseases [1].
One of the challenges in catalytic fine organic chemistry is to develop selective amination of
alcohols to yield amines with of an adequate structure having specific physiological properties.
A perspective environmentally-benign approach to the synthesis of complicated amines is the
one-pot amination in the presence of heterogeneous catalysts [2], which consists of
three consecutive steps: i) the dehydrogenation of alcohol to aldehyde, ii) the condensation
of aldehyde with amine to form imine and iii) the hydrogen transfer to produce secondary amine.

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\begin{align*}
\text{Oxidation} & \quad \text{O} \quad \text{H} \quad \text{H}_2 \quad \text{H}_2 \text{O} \quad \text{H} \quad \text{N} \quad \text{H} \\
\text{Hydrogenation} & \quad \text{H} \quad \text{H}_2 \quad \text{H}_2 \quad \text{O} \quad \text{H} \quad \text{N} \quad \text{H} \\
\text{Imine Formation} & \quad \text{N} \quad \text{H} \quad \text{R} \quad \text{H} \quad \text{N} \quad \text{H} \\
\end{align*}
\]

The main idea of this work is to study one-pot amination of myrtenol (natural terpene alcohol with primary –OH group) with aniline to corresponding amines.

Materials and Methods
The gold (3wt.%) on different metal oxides (ZrO2, MgO, Al2O3, CeO2, La2O3) were
supported as a gold hydroxide by deposition-precipitation method using HAuCl4 as a gold
precursor and urea as a precipitation agent. After drying samples of catalysts were pretreated
in oxygen or in hydrogen at 350°C. Prepared catalysts have been characterized with XRD, TEM,
XPS and MASS-UV-Vis in situ. The activity and selectivity of the catalysts in the myrtenol
amination with aniline were tested in the liquid-phase at 5-9 bar nitrogen pressure within 100-
180°C temperature interval. The initial reagents and obtained products were identified by GC-
MS.

Results and Discussion
Catalytic activity and product distribution are shown to be strongly dependent on the support
nature, which seems to be connected with the acid-base properties of the metal oxides (Fig.1,
left). The increase in acidity results in relatively lower alcohol conversion which confirms
initial alcohol activation on the basic sites of metal oxide surfaces. At the same time the
availability of protonic groups on the support surface was suggested to be important for the
target amine formation.

The other hand type of sample pretreatment affect electronic state of gold changing relative
contribution of metallic and cationic species (Fig.1, right) and, as a consequence, catalytic
activity.

The highest activity among the tested catalysts was obtained over preoxidized Au/ZrO2 with
both acidic and basic surface sites.

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