



Selective carvone hydrogenation to dihydrocarvone over titania supported gold catalyst

Yu.S. Demidova^a, E.V. Suslov^b, O.A. Simakova^{c,d}, I.L. Simakova^{a,*}, K.P. Volcho^b, N.F. Salakhutdinov^b, D.Yu. Murzin^c

^a Borekov Institute of Catalysis, 630090, pr. Lavrentieva, 5, Novosibirsk, Russia

^b Novosibirsk Institute of Organic Chemistry, 630090, pr. Lavrentieva, 9, Novosibirsk, Russia

^c Process Chemistry Centre, Åbo Akademi University, FI-20500 Turku/Åbo, Finland

^d School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 30332-0100 Atlanta, GA, USA

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ABSTRACT

Selective hydrogenation of natural carvone to industrially valuable dihydrocarvone was carried out at 100 °C under hydrogen pressure over a 1.9 wt.% Au/TiO₂ catalyst. The gold catalyst has demonstrated high activity as well as stereo- and chemoselectivity in conjugated C=C double bond hydrogenation with predominant formation of *trans*-dihydrocarvone. The catalytic activity and *trans*- to *cis*-isomers ratio were shown to strongly depend on the solvent. In a range of C₁–C₃ alcohol solvents both catalytic activity and *trans*- to *cis*-dihydrocarvone ratio increased following the order: 2-propanol < ethanol < methanol. The total selectivity to dihydrocarvone 62% was achieved at a nearly complete carvone conversion (90%) after 13 h in the case of methanol, with the *trans*- to *cis*-dihydrocarvone ratio being about 1.8. Based on the transition state theory a quantitative description of *trans*- to *cis*-dihydrocarvone ratio variations in different solvents was made.

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1. Introduction

Carvone is one of the most widespread natural monoterpenoids [1], which is widely used in food and perfumery industry [2] as well as in the synthesis of fine chemicals [3–6]. Carvone hydrogenation is of great practical interest in synthesis of a range of valuable products, including dihydrocarvone (Scheme 1). The latter is formed as a mixture of two stereoisomers, has a spearmint-like odor and is used as a food flavoring additive [2,7]. At the same time carvone is an interesting substrate to explore catalytic activity in stereo- and chemoselective hydrogenation, since it contains an asymmetric center with a specific configuration as well as three types of functional groups, which can be hydrogenated: C=O, a conjugated C=C and an isolated C=C groups. In general, selective hydrogenation of multifunctional organic molecules is one of the main challenges in catalytic fine organics synthesis.

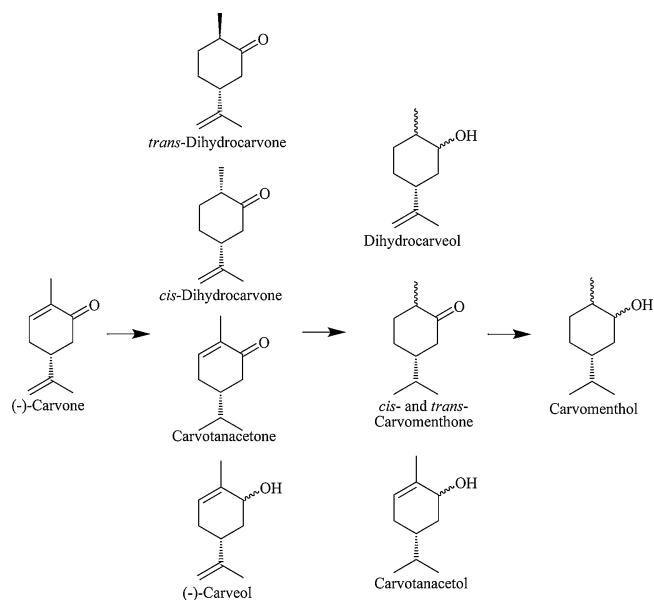
Carvone can be hydrogenated to dihydrocarvone by using Bu₃SnH/Pd(PPh₃)₄ in the presence of protic or Lewis acids [8], metals hydrides [9,10], zinc powder in the presence of NiCl₂ [11] and an alkali solution in alcohols [6], Me(EtO)₂SiH in the presence of

various complexes of copper and palladium [12], sodium dithionite [13] and finally applying enzymes [14]. At the same time carvone hydrogenation by molecular hydrogen in the presence of heterogeneous catalysts is a more efficient approach in terms of both practical and ecological considerations. The main advantages of heterogeneous catalysts are an easy and efficient separation of high value products from the catalyst as well as significantly lower amounts of wastewater containing harmful pollutants. There are many examples of carvone hydrogenation over different heterogeneous catalysts, including Pt/Al₂O₃, PtSn/Al₂O₃, PtGe/Al₂O₃, Pt/C and PtSn/C [15], Pd/Y exchanged zeolites [16], β-cyclodextrin immobilized on Pd nanoparticles [17], Cu/MCM-41 [18], Pd–Cu on SiO₂ [19], Pd, Rh, or Ru supported on Al₂O₃ in supercritical CO₂ [20], a supported rhodium complex [21], Raney nickel [22], Pd-black, Pt-black and Pd/C, Pt/C [23]. However, in the presence of these catalysts dihydrocarvone was not found at all or was formed in a relatively small yield up to 30% as a part of a complex mixture, containing carvomenthone, carvotanacetone, carvacrol and dihydrocarveol [22,23]. To the best of our knowledge, there is no heterogeneous catalyst reported which allows formation of dihydrocarvone via carvone hydrogenation with high selectivity.

A growing interest in application of gold in catalysis is related to unique catalytic activity of gold in a number of reactions. Gold

* Corresponding author. Tel.: +7 3833269531; fax: +7 3833308056.

E-mail address: simakova@catalysis.ru (I.L. Simakova).



Scheme 1. Reaction pathways of carvone hydrogenation.

has been identified as a promising catalyst in hydrogenation reactions especially where selectivity is an issue. For a long time a significant attention was given to chemoselective hydrogenation of unsaturated carbonyl compounds to the corresponding unsaturated alcohols over gold catalysts [24–34]. An advantage of using Au catalysts is in the ability to selectively hydrogenate the C=O group in the presence of a C=C group, while the latter hydrogenation is kinetically and thermodynamically favored. At the same time, in the case of carbonyl compounds containing different conjugated and isolated C=C double bonds, predominant conjugated C=C double bond hydrogenation was observed over the gold catalysts, for example in the case of citral [35]. Additionally in ketones with a more sterically unhindered C=O group compared to aldehydes, the C=C double bond was predominantly hydrogenated [27]. Therefore, utilization of gold catalysts for carvone hydrogenation to a valuable product – dihydrocarvone can be promising.

In this work the aim was, therefore, to study carvone hydrogenation regularities over a gold catalyst with a general idea to investigate both activity in competitive hydrogenation of different functional groups and to develop an approach to the synthesis of valuable carvone derivatives such as dihydrocarvone.

2. Experimental

2.1. Catalytic experiment

The reactions were carried out in a stainless steel reactor (150 ml) equipped with an electromagnetic stirrer (1100 rpm) and the sampling system. In a typical experiment, a mixture of the substrate (10 mmol), solvent (36 ml) and the solid catalyst (336 mg of TiO₂ or Au/TiO₂, Au 0.3 mol % to substrate) was intensively stirred at 100 °C under H₂ atmosphere (9 bar). (-)-Carvone, *D*(+)-dihydrocarvone (mixture *cis*- and *trans*-isomers, *cis*-/*trans*- = 20:80), *L*(-)-carveol (mixture *cis*- and *trans*-isomers, *cis*-/*trans*- = 54:46) and (-)-limonene were used as substrates, while methanol, ethanol and 2-propanol were applied as solvents. Reagents and solvents were purchased from commercial suppliers and used as received except for the solvents, which were dried prior to experiments.

At appropriate time intervals aliquots were taken and analyzed by gas chromatography (Tzvet-500) using a Carbowax-20

M column (length 50 m, inner diameter 0.2 mm and film thickness 0.5 μm) at 160 °C and a flame ionization detector operating at 250 °C. Additionally the product structures were confirmed by analysis with a gas chromatograph–mass spectrometer (Agilent Technologies 7000 GC/MS Triple Quad, HP-5MS column) as well as by nuclear magnetic resonance (NMR) spectroscopy. The chemical shifts of the *cis*- and *trans*-dihydrocarvones were determined in accordance with [36]. ¹H NMR spectra were recorded by Bruker AV-400 spectrometer (400.13 MHz (¹H)) in the CDCl₃ solutions of the reaction mixture. To estimate reproducibility of GC analysis of the reaction mixture some withdrawn samples were analyzed twice both by GC/MS and NMR in a parallel way. To judge reproducibility of the catalytic data some experiments were carried out three times. As a result, the measurement errors calculated for carvone hydrogenation, e.g., in methanol at 100 °C after 1 h were found to be 4.7 ± 2.1% and 1.7 ± 0.1 for carvone conversion and the *trans*- to *cis*-dihydrocarvone ratio, respectively.

2.2. Catalyst preparation

The 1.9 wt.% Au/TiO₂ catalyst was prepared from a HAuCl₄ aqueous solution (5 × 10⁻⁴ M) by deposition–precipitation with urea (DPU) at 81 °C for 24 h using as a support TiO₂ (Degussa AG, Aerolyst 7708, anatase >70%, S_{BET} = 45 m²/g). In order to remove an excess of chloride after the gold deposition, the obtained slurry was washed with NH₄OH aqueous solution (4 M). Thereafter, the catalyst was thoroughly washed with deionized water, dried at 60 °C for 12 h and calcined at 300 °C for 4 h. The catalyst was characterized by a variety of state of the art physical methods described in detail in [37]. The gold particle size was determined by using transition electron microscopy (TEM). A histogram of the particle size distribution was obtained by counting at least 100 gold particles on micrographs. The obtained gold catalyst was chemically analyzed with an inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Varian Liberty 110 ICP Emission Spectrometer. The surface analysis of the catalysts by X-ray photoelectron spectroscopy (XPS) was used to clarify the chemical state of the gold species formed on the catalyst surface.

3. Results

Carvone hydrogenation was performed in different solvents over 1.9 wt.% Au/TiO₂ catalyst with the Au particle size of 1.9 ± 1.0 nm. According to XPS analysis the catalyst was mainly characterized by the presence of metallic gold species with the binding energy values at 87.8 and 84.1 eV corresponding to Au 4f_{5/2} and 4f_{7/2} components respectively. At the same time a shift of binding energy by 0.9 eV was attributed to the presence of Au^{δ-} species, probably located in the gold-support interface as discussed in [37].

A series of protic solvents including methanol (MeOH), ethanol (EtOH) and 2-propanol (2-PrOH), which can also act as hydrogen donor, were used. The catalytic activity was shown to be strongly dependent on the solvent. Results of the catalytic experiments are presented in Fig. 1a. The carvone hydrogenation resulted mainly in *cis*- and *trans*-dihydrocarvone formation with the *trans*-isomer being the main product in most cases. Moreover, the solvent nature profoundly affected the *trans*-/*cis*-isomers ratio (Fig. 1b). According to the obtained data both catalytic activity and the *trans*-/*cis*-dihydrocarvone ratio increased in the following order of solvents: 2-propanol < ethanol < methanol. Thus, the highest activity as well as the *trans*-/*cis*-isomers ratio among the solvents applied for carvone hydrogenation was observed in the case of methanol. The initial carvone hydrogenation rate obtained for the Au/TiO₂ catalyst in methanol is 2.7 × 10⁻⁵ mol l⁻¹ s⁻¹. The total selectivity to

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