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Selective carvone hydrogenation to dihydrocarvone over titania supported gold catalyst

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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/TiO_2 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 C_1—C_3 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.

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 $Bu_3SnH/Pd(PPh_3)_4$ in the presence of protic or Lewis acids [8], metals hydrides [9,10], zinc powder in the presence of $NiCl_2$ [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/Al_2O_3, PtSn/Al_2O_3, PtGe/Al_2O_3, 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 SiO_2 [19], Pd, Rh, or Ru supported on Al_2O_3 in supercritical CO_2 [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

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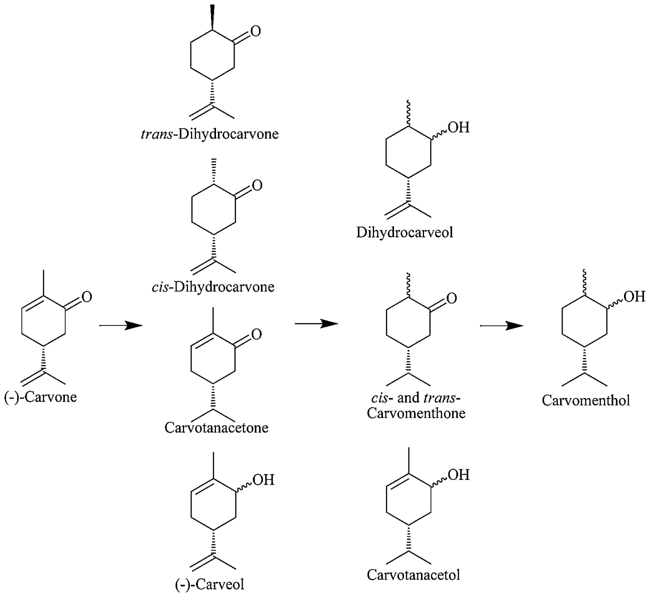

Scheme 1. Reaction pathways of carvone hydrogenation.

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 TiO_2 or Au/TiO_2, Au 0.3 mol % to substrate) was intensively stirred at 100 °C under H_2 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 $CDCl_3$ 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/TiO_2 catalyst was prepared from a $HAuCl_4$ aqueous solution (5×10^{-4} M) by deposition–precipitation with urea (DPU) at 81 °C for 24 h using as a support TiO_2 (Degussa AG, Aerolyst 7708, anatase >70%, $S_{BET} = 45\ m^2/g$). In order to remove an excess of chloride after the gold deposition, the obtained slurry was washed with NH_4OH 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/TiO_2 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 $Au^{\delta-}$ 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/TiO_2 catalyst in methanol is $2.7 \times 10^{-5}\ mol\ l^{-1}\ s^{-1}$. The total selectivity to

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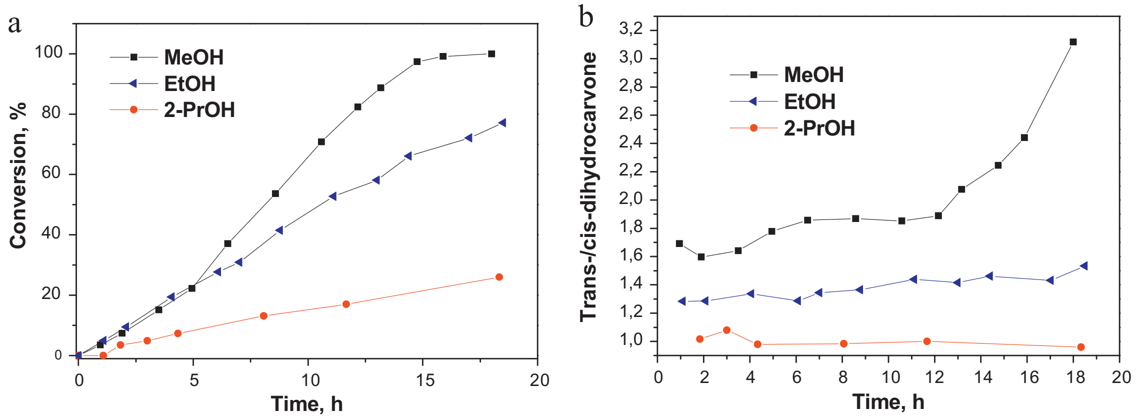

Fig. 1. Solvent effect on carvone conversion and *trans-/cis*-dihydrocarvone ratio over Au/TiO_2 catalyst. The reaction conditions: $T = 100\,°C$, $p(H_2) = 9$ bar, (−)-carvone (10 mmol), solvent (36 ml), Au catalyst (336 mg, Au 0.3 mol% to substrate).

dihydrocarvone of 62% was achieved at a nearly complete carvone conversion (90%) after 13 h (Fig. 2).

Carvone hydrogenation was further accompanied by increasing the *trans-/cis*-dihydrocarvone ratio along with an increasing impact of the side reactions, such as consecutive dihydrocarvone hydrogenation with carvomenthone formation as well as formation of small amounts of the isomers of the former (Scheme 1). An increase of the *trans-/cis-* ratio can be explained by two phenomena. The first one is a predominant hydrogenation of *cis*-isomer to carvomenthone while the second one is related to isomerization of *cis*-dihydrocarvone to *trans*-dihydrocarvone. Activity of gold catalysts in *cis–trans* isomerization was recently demonstrated for azobenzene [38]. In general epimerization of cyclohexane derivatives is well known [39–42]. In order to explain this observation as well as clarify the reaction scheme dihydrocarvone hydrogenation was performed over Au/TiO_2 under the same reaction conditions. As a result the same changes in the ratio between *trans-* and *cis*-dihydrocarvone for the same reaction time were obtained with formation of small carvomenthone amounts (Fig. 3). Therefore, it can be supposed that the thermodynamically controlled isomerization of *cis-* to *trans*-dihydrocarvone is likely to occur with the further transformation of both isomers to carvomenthone. It is important to note that TiO_2 per se was not active in both carvone hydrogenation and dihydrocarvone isomerization.

Measurements of catalytic activity were performed in the kinetic region. An impact of internal diffusion was determined through an estimation of the Weisz–Prater criterion (Φ) [43]. The value of this criterion ($\Phi = 4 \times 10^{-5}$) calculated for the maximal initial carvone hydrogenation rate (2.7×10^{-5} mol l^{-1} s^{-1}) with Au/TiO_2 in methanol indicated that the substrate diffusion inside the catalyst pores does not limit the reaction rate. At the same time the impact of external diffusion was avoided by conducting experiments with the stirring speed of 1100 rpm, which was proved to be efficient enough to avoid external mass transfer limitations.

Influence of the solvent nature on catalytic performance in hydrogenation of α,β-unsaturated carbonyl compounds was studied in detail [44–50]. Recently a systematic investigation of the solvent effect on the catalytic activity in the liquid-phase hydrogenation of acetophenone was reported [47]. In general the solvent effect can be related mainly to specificity of the solvent interactions with the reactants and the catalysts. Differences in carvone hydrogenation in various solvents could not be attributed to hydrogen solubility in the liquid phase similar to observations in [47]. According to the literature data [47] hydrogen solubility changes follow the pattern 2-PrOH < MeOH < EtOH, while in the current work activity and selectivity follow the order 2-PrOH < EtOH < MeOH.

At the same time based on the transition state theory and the Kirkwood treatment [51], which considers a reaction between ions and dipolar molecules, or between two dipolar molecules, it is

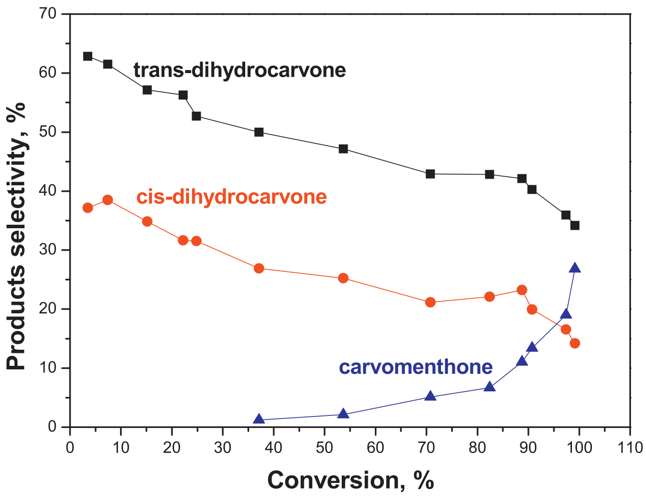

Fig. 2. Distribution of the main reaction products for carvone hydrogenation over Au/TiO_2 catalyst. The reaction conditions: $T = 100\,°C$, $p(H_2) = 9$ bar, (−)-carvone (10 mmol), methanol (36 ml), Au catalyst (336 mg, Au 0.3 mol% to substrate).

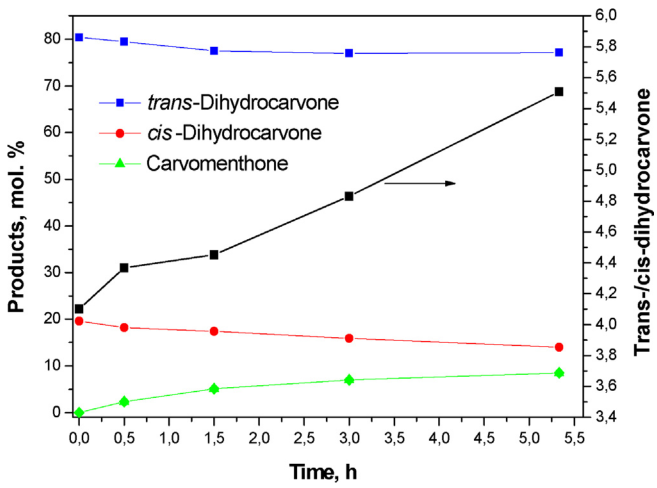

Fig. 3. Dihydrocarvone hydrogenation over Au/TiO_2 catalyst. The reaction conditions: $T = 100\,°C$, $p(H_2) = 9$ bar, dihydrocarvone (10 mmol), methanol (36 ml), Au catalyst (336 mg, Au 0.3 mol% to substrate).

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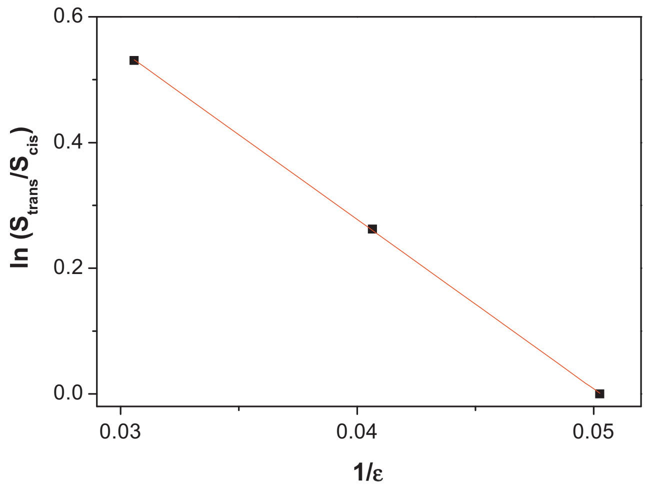


Fig. 4. Dependence of the ratio between selectivity (S) to *trans*- and *cis*-dihydrocarvone on dielectric constants. Experimental data: square symbols; calculations: solid line.

possible to account for solvent effect on the reaction. The reaction rate (k) proportional to $e^{-\Delta^{\neq}G^0/kT}$ for the case when the reactant and the transition state are not charged is defined by

$$\ln k = \ln k_0 - k'\frac{(\mu^{\neq})^2-(\mu_A)^2}{\varepsilon} \qquad (1)$$

where ε is the dielectric constant, μ denotes the dipole moment of the activated complex ($\mu^{\neq}$) and the reactant (μ_A) respectively, k' is the temperature dependent constant.

Eq. (1) is useful in predicting the influence of solvent polarity on kinetics. This approach was successfully applied recently for investigation of the solvent effect in the enantioselective hydrogenation of 1-phenyl-1,2-propanedione [50] and ethyl benzoylformate [52]. The rate constant can be expressed in the following way:

$$k = k_0 e^{\alpha/\varepsilon} \qquad (2)$$

where α is a constant.

Therefore, the ratio between selectivity (S) to *trans*- and *cis*-dihydrocarvone can be written in the case of the same reaction orders for formation of *trans*- and *cis*-dihydrocarvone as

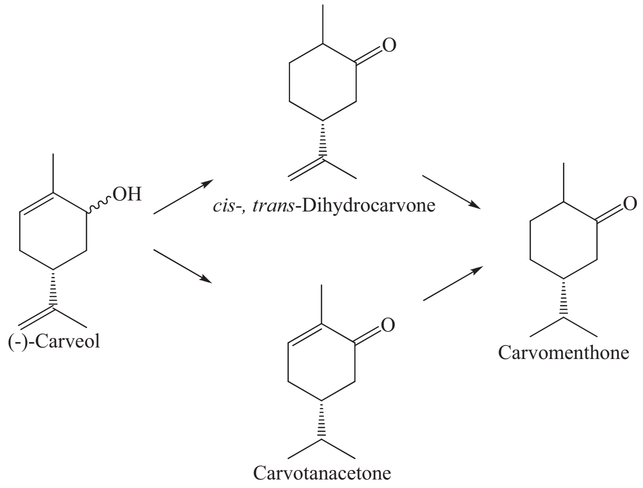
$$\ln\frac{S_{trans}}{S_{cis}} = \ln\frac{k_{trans}}{k_{cis}} = \frac{{k_0}^{trans}}{{k_0}^{cis}} + \Delta\alpha\frac{1}{\varepsilon} \qquad (3)$$

where $\Delta\alpha$ is the difference between constants for *trans*- and *cis*-isomers, ${k_0}^{trans}$ and ${k_0}^{cis}$ are the solvent independent parts of the rate constants.

Eq. (3) was applied to describe the dependence of the ratio between dihydrocarvone isomers on dielectric constants. The values of the dielectric constants are 32.7, 24.6, 19.9 for MeOH, EtOH, 2-PrOH, respectively. An adequate description was obtained as shown in Fig. 4. The following values of parameters were found $\Delta\alpha = -26.9$ and ${k_0}^{trans}/{k_0}^{cis} = 1.3$. The reaction rate of *trans*-isomer formation as well as the total rate increases with an increasing solvent dielectric constant and hydrogen donor ability. The developed correlation was able to describe the behavior of the system as a function of the solvent dielectric constant.

Thus, gold nanoparticles supported on titania were found to promote stereo- and chemoselective carvone hydrogenation to dihydrocarvone with predominant formation of *trans*-isomer.

Hydrogenation of carveol (Scheme 2) and limonene (Scheme 3) with a similar structure as carvone but with different functional groups was also performed over Au/TiO$_2$ catalyst at the same reaction conditions as for carvone hydrogenation.

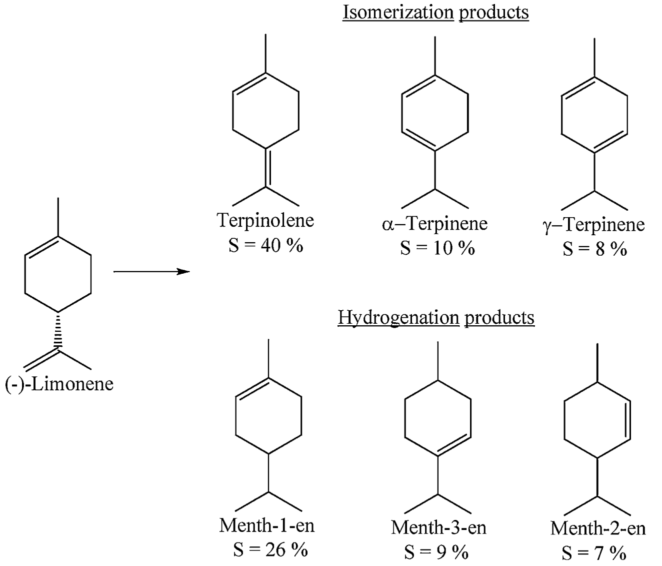


Scheme 2. Reaction pathways of carveol hydrogenation over Au/TiO$_2$ catalyst.

In our investigation carveol, which contains both *cis*- and *trans*-isomers in nearly equal amounts (*cis*-/*trans*- = 54:46), was utilized. The isomerization products, such as dihydrocarvone, carvotanacetone, as well as carvomenthone (Fig. 5), were mainly obtained.

In the case of carveol the replacement of C=O group by C—OH led to a significant decrease in Au/TiO$_2$ catalytic activity in exocyclic C=C bond hydrogenation. It is worth to note that two carveol isomers had different reactivities and only *trans*-carveol conversion was observed, while the *cis*-isomers concentration was approximately constant during the reaction. *Trans*-carveol conversion after 21 h was about 33% in sharp contrast to the *cis*-isomer (3%). Note, that the ratio between dihydrocarvone isomers was similar to the one for carvone hydrogenation.

The lowest catalytic activity in the corresponding C=C group hydrogenation was obtained in the case of limonene, which is a hydrocarbon and does not possess any oxygen containing groups (Scheme 3). Limonene conversion after 21 h was about 14% with its isomers being the main products. The limonene isomers, such as terpinolene, α-terpinene, γ-terpinene, were formed with the combined selectivity of about 58%. Among the hydrogenation products



Scheme 3. Limonene hydrogenation over Au/TiO$_2$ catalyst. The reaction conditions: T = 100 °C, $p(H_2)$ = 9 bar, (−)-limonene (10 mmol), methanol (36 ml), Au catalyst (336 mg, Au 0.3 mol % to substrate), 21 h. The products selectivity (S) is presented for 14% limonene conversion.

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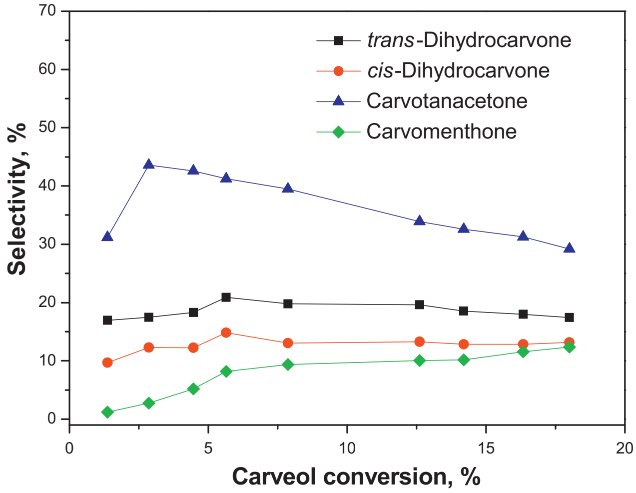

Fig. 5. Products distribution for carveol hydrogenation over Au/TiO_2 catalyst. The reaction conditions: $T = 100\,°C$, $p(H_2) = 9$ bar, (−)-carveol (10 mmol), methanol (36 ml), Au catalyst (336 mg, Au 0.3 mol% to substrate), 21 h.

menth-1-ene with an exocyclic C=C double bond was mainly observed with selectivity 26%.

Based on the results above it can be stated that the conjugation with C=O is important for selective C=C hydrogenation promoting C=C activation as well as influencing adsorption on the catalyst surface. According to the results reported previously the adsorption mode of the substrate is a key parameter, determining selectivity toward the product formation [53,54]. There are many different possible adsorption modes of unsaturated carbonyl compounds including participation of either a C=C group or a C=O group or both of them. Therefore, for hydrogenation of a particular group its specific adsorption mode is needed. In the present case selective dihydrocarvone formation with a hydrogenated C=C double bond implies adsorption of the corresponding C=C moiety. Based on these results the reaction mechanism for the conjugated C=C double bond hydrogenation can be envisaged as presented in Fig. 6.

The predominant formation of *trans*-isomer can be explained by the specificity of carvone adsorption on the catalyst surface. As it can be seen the carvone conformation resulting in *trans*-dihydrocarvone contains an equatorially oriented isopropylene group, whereas to form *cis*-dihydrocarvone a less favorable axial position of the isopropylene group is required.

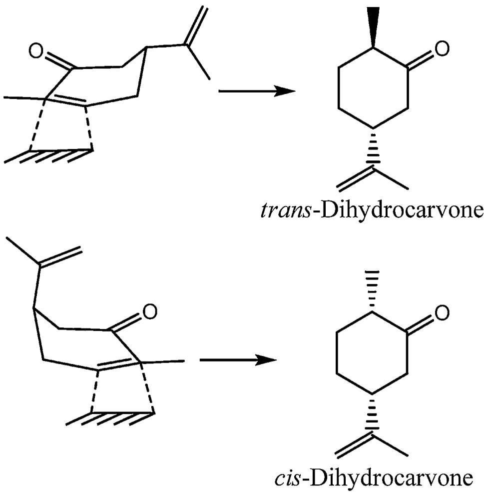

Fig. 6. A schematic mechanism for conjugated C=C double bond hydrogenation in carvone over Au/TiO_2 catalyst.

4. Conclusions

In summary carvone hydrogenation was studied over 1.9 wt.% Au/TiO_2 catalyst. The gold catalyst was found to promote stereo- and chemoselective carvone hydrogenation to dihydrocarvone with predominant formation of the *trans*-isomer. This can be considered as a novel synthetic method for an industrially valuable dihydrocarvone. Moreover, the obtained results demonstrate a possibility of gold catalysts utilization for preferential hydrogenation of a C=C bond conjugated with a carbonyl group even when another C=C group is present in the substrate. The solvent effect on the catalytic activity as well as on the ratio between *trans*- and *cis*-dihydrocarvone was observed. A range of C_1–C_3 alcohol solvents was applied for carvone hydrogenation and the highest yield of dihydrocarvone was achieved in the case of methanol. Based on the transition state theory a quantitative description of the *trans*-/*cis*-dihydrocarvone ratio variations in different solvents was made.

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