Journal of Molecular Catalysis A: Chemical 420 (2016) 142–148

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Selective one-pot carvone oxime hydrogenation over titania supported gold catalyst as a novel approach for dihydrocarvone synthesis

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ARTICLE INFO

Article history:
Received 10 November 2015
Received in revised form 14 April 2016
Accepted 15 April 2016
Available online 19 April 2016

Keywords:
Gold catalyst
Chemoselective hydrogenation
Carvone oxime
Dihydrocarvone
Stereoselectivity

ABSTRACT

It was shown for the first time that dihydrocarvone can be selectively produced by gold-catalyzed one-pot transformation of carvone oxime. This reaction was carried out at 100 °C under hydrogen pressure of 9 bar over 1.9 wt.% Au/TiO_2 catalyst using methanol as a solvent. Dihydrocarvone synthesis was shown to occur via carvone formation with the subsequent hydrogenation of its conjugated C═C double bond. Application of Au/TiO_2 catalyst for both deoximation and selective hydrogenation of olefinic C═C functional group is reported for the first time. The combination of these steps provides optimization of the synthetic method for dihydrocarvone production from carvone oxime which is a key intermediate in carvone synthesis from limonene. Despite a lower reaction rate than in the case of carvone, a significant increase in the stereoselectivity towards *trans*-dihydrocarvone was observed in the case of carvone oxime hydrogenation. The ratio between *trans*- and *cis*-dihydrocarvone was close to 4.0 compared to 1.8 achieved in the case of carvone hydrogenation.

1. Introduction

Dihydrocarvone is a valuable product that has a spearmint-like odor and is used as a flavoring additive in food industry. It is typically formed as a mixture of two stereoisomers and may be obtained starting from biomass derived carvone hydrogenation using molecular hydrogen over Ni, Pt, Pd, Rh, Ru catalysts [1–8]. This reaction path requires hydrogenation of conjugated C═C double bond in the presence of other unsaturated functional groups, such as C═O and an isolated C═C bonds. Application of the above mentioned catalysts typically favors hydrogenation of other unsaturated functional groups, resulting in formation of a complex mixture, with the target dihydrocarvone yield being less than 30%. In our previous work stereo- and chemoselective carvone hydrogenation to dihydrocarvone catalyzed by Au/TiO_2 catalyst with predominant formation of the *trans*-isomer was reported for the first time [9]. This novel approach is of significant interest in terms of a possibility to obtain industrially valuable dihydrocarvone via direct carvone hydrogenation. The highest total selectivity to dihydrocarvone (62%) was achieved at a nearly complete carvone conversion (90%) after 13 h, with the *trans*-to-*cis*-dihydrocarvone ratio being about 1.8.

Despite that (+)- and (−)-carvones can be isolated by fractional distillation of caraway and spearmint oils, respectively, currently carvones are mainly produced semi-synthetically starting from (+)- and (−)-limonenes through intermediate formation of carvone oxime (Scheme 1) [10,11]. Acid hydrolysis of the oxime group in the presence of a hydroxylamine acceptor, such as acetone, yields the target compound-carvone. From the viewpoint of improving the chemical synthesis efficiency, a one-pot multistep carvone oxime transformation to dihydrocarvone can be a promising approach.

According to the literature data there are a few examples of direct carvone oxime conversion into dihydrocarvone including attempts of consecutive reduction via a corresponding ketone using $LiAlH_4$ in hexamethylphosphoramide (HMPA) [12] or by application of cell suspension cultures of *Nicotiana tabacum*, which promoted a slow formation of the target dihydrocarvone in a relatively low yield as a part of a complex mixture [13]. Despite a higher

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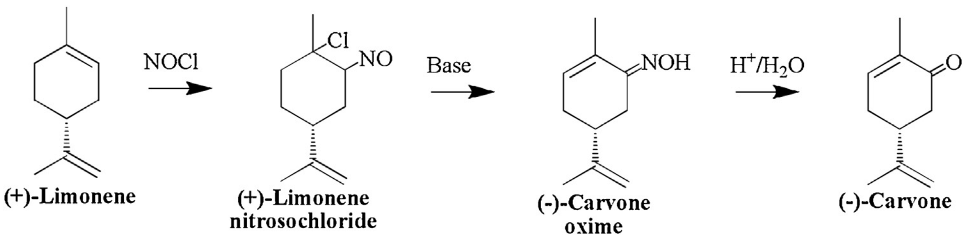
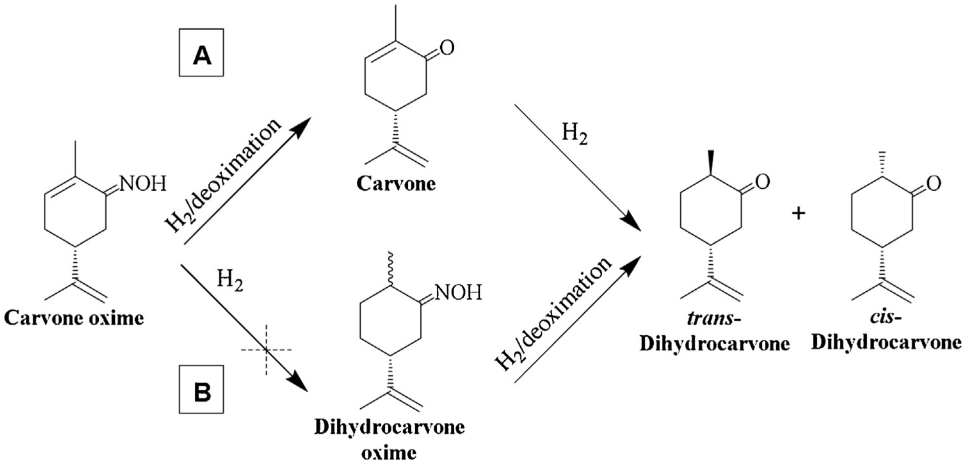
http://dx.doi.org/10.1016/j.molcata.2016.04.013



Scheme 1. Industrial method of carvone synthesis [10,11].



Scheme 2. Possible reaction pathways for carvone formation from carvone oxime over Au/TiO_2.

dihydrocarvone yield achieved by using the $LiAlH_4$/HMPA system, the method has significant disadvantages in terms of practical and ecological considerations.

As it is well known, oximes possess a relatively high hydrolytic stability compared to imines [14]. According to the literature oximes can be also catalytically hydrogenated to produce imines or other nitrogen-containing derivatives followed by their further hydrolysis to form ketones [15–17]. Recently gold nanoparticles supported on TiO_2 or Fe_2O_3 were shown by Corma and co-workers to be highly active in chemoselective hydrogenation of *a* nitro-group in the presence of other reducible functional groups [18–21]. Furthermore, highly catalytically active yolk–shell Au-CeO_2@ZrO_2 nanoreactors were applied recently for the 4-nitrophenol selective reduction to 4-aminophenol [22]. More conventional platinum group metal catalysts along with the nitro-group hydrogenation can also activate olefinic or carbonyl groups due to stronger interactions with other functional groups [19,21,23–25]. Noteworthy is also, that application of more inexpensive metal as an active component, such as copper-containing catalysts, results in a preferable hydrogenation of a carbonyl group into hydroxyl group [26]. In this connection application of gold catalysts for oxime consecutive transformations to dihydrocarvone may be of high relevance.

As it was mentioned above an outstanding activity of Au/TiO_2 catalyst in carvone hydrogenation to valuable dihydrocarvone was previously demonstrated in our work. As a next step this study is focused on one-pot process consisting of sequential transformations of carvone oxime which is a key intermediate in carvone synthesis from limonene to dihydrocarvone. The combination of these steps can provide optimization of the synthetic method for dihydrocarvone production and moreover will exclude acid hydrolysis in an aqueous medium making dihydrocarvone synthesis more efficient in line with the guidelines of green chemistry. To the best of our knowledge there were no reports in the open literature on heterogeneous catalysts for both deoximation and selective hydrogenation of olefinic C=C functional group.

Thus the goal of this work was to study regularities of carvone oxime transformation over Au/TiO_2 catalyst with the main aim to explore feasibility of the one-pot synthesis of dihydrocarvone starting from carvone oxime.

2. Experimental

2.1. Starting materials

(−)-Carvone (Aldrich, ≥97%), (5*R*)-dihydrocarvone (SAFC, ≥97%, mixture of *trans*- and *cis*-isomers 4:1) and methanol (J.T. Baker, ≥99.8%) were purchased from commercial suppliers and used as received. (−)-Carvone oxime and (2*R*,5*R*,*E*)-dihydrocarvone oxime were synthesized according to the methods presented below. ^1H NMR and ^{13}C NMR spectra of the compounds were recorded by *Bruker AV-400* spectrometer (400.13 MHz (^1H), 100.61 MHz (^{13}C)) in the $CDCl_3$ solutions.

2.2. Synthesis of (−)-carvone oxime and (2R,5R,E)-dihydrocarvone oxime

First to obtain (−)-carvone oxime a 100-ml round-bottom flask was charged with hydroxylamine hydrochloride (13.4 mmol, 0.93 g), sodium acetate (13.4 mmol, 1.10 g), (−)-carvone (6.67 mmol, 1.00 g, $[\alpha]_D^{20} = -58$ (c = neat)), methanol (20 ml) and water (17 ml). The solution was stirred for 4 days at r.t. and then water (100 ml) was added. The reaction mixture was extracted with ethyl acetate (EtOAc) (3 × 50 ml). The combined organic phase was washed with saturated sodium bicarbonate (2 × 25 ml), brine (2 × 25 ml) and then dried (Na_2SO_4). As a result, (−)-carvone oxime (0.83 g (75%)) was obtained. The synthesized (−)-carvone oxime was characterized by ^{13}C and ^1H NMR (supplementary data,

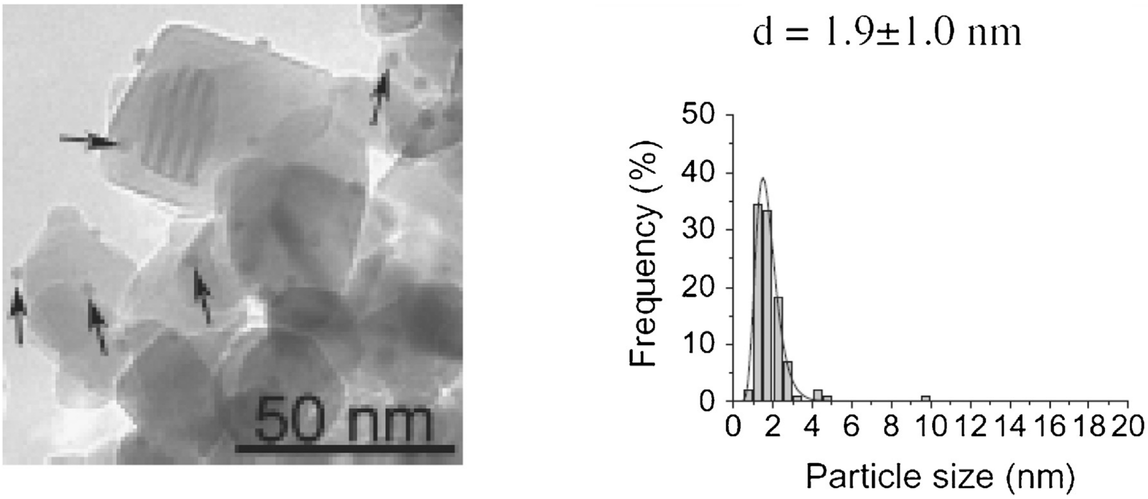


Fig. 1. TEM micrographs (left) and histogram of particles size distribution (right) of Au/TiO_2 catalyst.

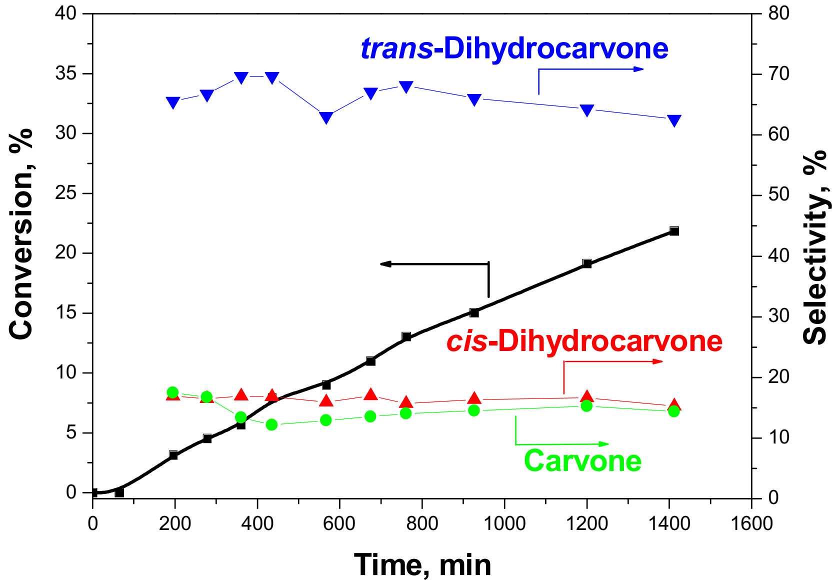


Fig. 2. Carvone oxime hydrogenation over Au/TiO_2. Conversion of carvone oxime (■) and selectivity towards carvone (●), *trans*- (▼) and *cis*-dihydrocarvone (▲). Reaction conditions: T = 373 K, p (H_2) = 9 bar, carvone oxime (5 mmol), methanol (15 ml), Au/TiO_2 (140 mg).

Figs. S1 and S2 , respectively). The ^{13}C NMR spectral characteristics of (−)-carvone oxime corresponded to those described in the literature [27].

(2*R*,5*R*,*E*)-Dihydrocarvone oxime was synthesized starting from a mixture of *trans*- and *cis*-dihydrocarvone. 500-ml flask was charged with hydroxylamine hydrochloride (67.4 mmol, 4.65 g), sodium acetate (67.7 mmol, 5.53 g), (5*R*)-dihydrocarvone (33.2 mmol, 5.05 g, a mixture of *trans*- and *cis*-dihydrocarvone (4:1)), methanol (100 ml) and water (85 ml). The solution was stirred for 4 days at r.t. The precipitate formed was filtered and dissolved in diethyl ether (Et_2O). The diethyl ether phase was dried over Na_2SO_4, the drying agent was filtered off and washed with Et_2O, and then the solvent was removed. As a result, (2*R*,5*R*,*E*)-dihydrocarvone oxime (3.07 g (55%)) was obtained. Moreover, the mixture of (2*R*,5*R*,*E*)-, (2*S*,5*R*,*E*)- and (2*S*,5*R*,*Z*)-isomers of dihydrocarvone oxime (2.36 g, 43%; 4.4:2.1:1) was obtained from the mother liquor by extraction with EtOAc (4 × 70 ml). ^{1}H NMR spectrum of (2*R*,5*R*,*E*)-dihydrocarvone oxime is presented in Fig. S3 (supplementary data). The ^{1}H NMR spectral characteristics of dihydrocarvone oximes corresponded to those described in the literature [28].

2.3. Catalytic experiments

(−)-Carvone, (−)-carvone oxime and (2*R*,5*R*,*E*)-dihydrocarvone oxime were used as substrates, while methanol was applied as a solvent. The reactions were carried out in a stainless steel reactor equipped with an electromagnetic stirrer (1100 rpm) and the sampling system. In a typical experiment, a mixture of the substrate (5 mmol), solvent (15 ml) and 1.9 wt.% Au/TiO_2 catalyst (140 mg) was intensively stirred at 100 °C under H_2 or N_2 atmosphere (9 bar).

At regular time intervals, the samples were withdrawn and analyzed by gas chromatography (Tsvet-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 structure of reaction products was confirmed by analysis with a gas chromatography-mass spectrometer (Agilent Technologies 7000 GC/MS Triple Quad, HP-5MS column) as well as by NMR spectroscopy. The chemical shifts of the *cis*- and *trans*-dihydrocarvones were determined in accordance with [29]. ^{1}H NMR spectra were recorded by Bruker AV-400 spectrometer (400.13 MHz (^{1}H)) in the $CDCl_3$ solutions of the reaction mixture.

2.4. Catalyst preparation

The 1.9 wt.% Au/TiO_2 catalyst was prepared from $HAuCl_4$ aqueous solution (5×10^{-4} M) by deposition-precipitation method with urea at 81 °C during 24 h over TiO_2 (Degussa AG, Aerolyst 7708, anatase >70%, $S_{BET} = 45\ m^2/g$) [30]. The obtained slurry was washed with NH_4OH aqueous solution (4 M) and deionized water. Thereafter, the catalyst was dried at 60 °C for 12 h and calcined at 300 °C for 4 h. The obtained catalyst was characterized by a variety of state of the art physical methods described in detail elsewhere [30].

Electron microphotographs of the samples were taken by LEO 912 OMEGA energy-filtered transmission electron microscope by using 120 kV acceleration voltage. 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 PerkinElmer, Optima 5300DV spectrometer. The surface analysis of the catalysts was performed by X-ray photoelectron spectroscopy (XPS) in a PHI Quantum 2000 Scanning ESCA Microprobe spectrometer with Al anode to clarify the chemical state of the gold species formed on the catalyst surface.

3. Results

Carvone oxime hydrogenation was studied in the presence of Au/TiO_2 catalyst synthesized by the deposition-precipitation method. The Au content in the synthesized catalyst determined by ICP-AES was 1.9 ± 0.2 wt.%. The TEM micrograph and histogram of the particle size distribution are presented in Fig. 1. According to TEM the mean diameter of gold nanoparticles was 1.9 nm. According to XPS analysis the catalyst was mainly characterized by the presence of metallic gold species with the corresponding binding energy values for Au $4f_{5/2}$ and $4f_{7/2}$ components at 87.8 and 84.1 eV, respectively. A shift of binding energy by 0.9 eV can be attributed to the presence of $Au^{\delta-}$ species, probably located in the gold-support interface discussed earlier [30].

The catalytic experiments were performed at 100 °C under hydrogen pressure 9 bar in the kinetic regime, which was established according to the previously described procedure [9]. Moreover, in our previous work [9] the effect of solvent on the catalytic performance in carvone hydrogenation to dihydrocarvone was studied in detail. Both catalytic activity and *trans*- to *cis*-dihydrocarvone ratio were shown to strongly depend on the solvent and increase in the following order: 2-propanol < ethanol < methanol. Such behavior was quantitatively described based on the transition state theory and the Kirkwood treatment [9]. Therefore, in the current work, methanol was used as an optimal solvent providing the highest yield of dihydrocarvone starting from carvone as well as higher stereoselectivity to the *trans*-isomer among other alcohols.

As a result, carvone oxime transformation under hydrogen atmosphere catalyzed by Au/TiO_2 was found to result in formation of carvone and *trans*-, *cis*-dihydrocarvones (Scheme 2). Concomitant with a lower initial reaction rate of carvone oxime transformation (3.3×10^{-3} mol/h) in comparison to that of carvone hydrogenation (2.4×10^{-2} mol/h) [9], the increase in the stereoselectivity towards *trans*-dihydrocarvone was observed (Fig. 2). In the case of carvone oxime, the ratio between *trans*- and *cis*-dihydrocarvone was ca. two fold compared to carvone hydrogenation (Fig. 3). Thus the use of carvone oxime as a starting material for dihydrocarvone preparation led to an increase of the synthesis efficiency in terms of stereoselectivity to the *trans*-isomer as well as a possibility to have an one-pot multistep process.

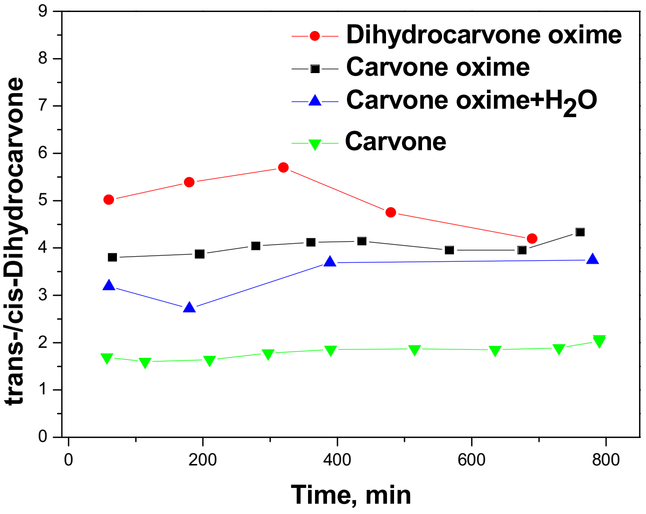


Fig. 3. Effect of substrate structure and water addition (0.15 ml) on *trans*-/*cis*-dihydrocarvone ratio. Reaction conditions: T = 373 K, p (H_2) = 9 bar, carvone or carvone oxime or dihydrocarvone oxime (5 mmol), methanol (15 ml), Au/TiO_2 (140 mg).

The recycling experiments were performed in order to study the catalyst stability. The catalyst after the first reaction run was filtered, washed with ethanol and dried at 373 K before reusing. The second reaction run was performed at the same reaction conditions keeping the ratio between substrates, the solvent and the catalyst constant. During the second reaction run the catalyst exhibited carvone oxime conversion 20% and total selectivity to dihydrocarvone 75% with *trans*-/*cis*-dihydrocarvone = 4 after 23 h indicating its stable performance and absence of significant deactivation during the reaction.

To study whether the reaction can occur non-catalytically or can be promoted by the support *per se*, TiO_2 was examined for carvone oxime hydrogenation at the same reaction conditions. As a result the support *per se* did not promote any carvone oxime transformation demonstrating that carvone formation from oxime occurs only in the presence of Au/TiO_2. In addition TiO_2 as such was also shown to be inactive in both carvone hydrogenation and dihydrocarvone isomerization [9]. Thus, both steps of carvone formation from carvone oxime and its subsequent hydrogenation a require presence of the gold catalyst.

Since carvone accumulation was observed during the reaction, carvone oxime hydrogenation was proposed to occur first via carvone formation with the subsequent hydrogenation of its conjugated C═C double bond (route A, Scheme 2). At the same time a parallel route B in Scheme 2 proceeding via dihydrocarvone oxime formation should be taken into account as a possible route resulting in dihydrocarvone. To improve understanding of gold-catalyzed carvone oxime transformation and to clarify the reaction scheme, hydrogenation of dihydrocarvone oxime was also studied over Au/TiO_2 catalyst at the same reaction conditions as for carvone oxime (Scheme 2). As a result, the reaction rate of dihydrocarvone oxime conversion to dihydrocarvone was lower compared to carvone oxime transformation (Fig. 4), while the ratio between *trans*- and *cis*-dihydrocarvone slightly increased (Fig. 3). To sum up absence of dihydrocarvone oxime in the reaction mixture along with a lower rate of dihydrocarvone formation from dihydrocarvone oxime with the saturated endocyclic C═C bond was observed. These results excluded C═C bond hydrogenation in carvone oxime prior to ketone formation and confirmed dominance of the route A (Scheme 2).

Note that previously the C═C bond conjugation with C═O in carvone was shown to be important for the initial C═C activation and

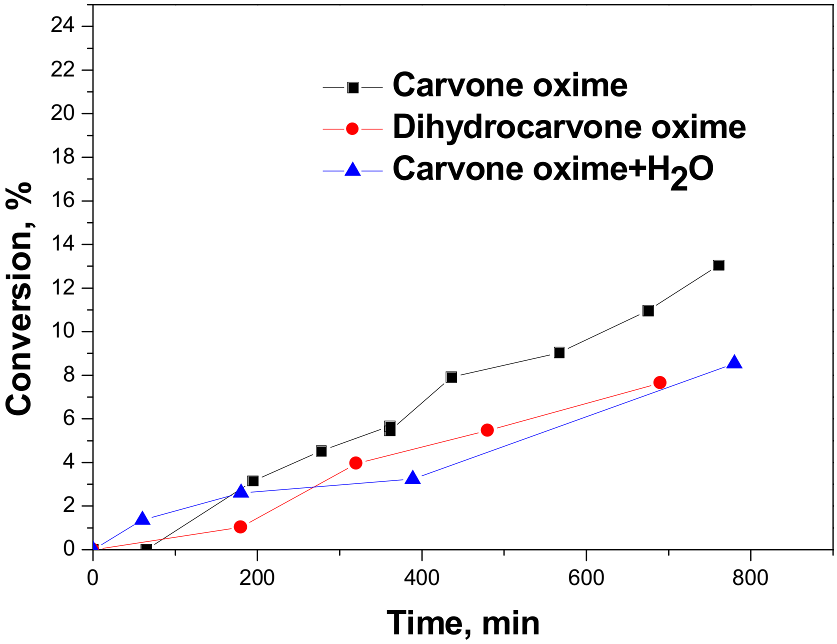


Fig. 4. Effect of substrate structure and water addition (0.15 ml) on conversion. Reaction conditions: T = 373 K, p (H_2) = 9 bar, carvone or carvone oxime or dihydrocarvone oxime (5 mmol), methanol (15 ml), Au/TiO_2 (140 mg).

substrate adsorption on the catalyst surface resulting in selective dihydrocarvone formation [9]. The results obtained for dihydrocarvone oxime additionally confirmed an influence of double bonds conjugation on the initial molecule activation on the catalyst surface probably due to a stronger adsorption through both groups with, however, a more favorable initial activation of the C=N group followed by C=C bond hydrogenation. Nevertheless, to clarify the reaction mechanism in terms of molecular interactions on the surface resulting in chemo- as well as stereo selective hydrogenation of carvone oxime over Au/TiO_2 catalyst a theoretical adsorption study is still required.

Taking into account the obtained data the next logical step was to explore in detail a possible mechanism of carvone formation from carvone oxime, while carvone hydrogenation to dihydrocarvone was mainly investigated earlier [9]. In this connection a series of experiments was performed. In fact, theoretically there are several transformations including hydrogenation and hydrolysis that can occur in different sequences resulting in ketone formation from oxime. Acid-catalyzed hydrolysis usually is applied for obtaining ketones from corresponding oximes. At the same time some other approaches are well known such as biotransformations or oxidative deoximation [31] as well as reductive deoximation [15,32,33]. To the best of our knowledge, Au catalysts have never been applied before for reductive deoximation. According to the literature data in the case of gold catalyzed hydrogenation of C=N group to produce imines or other nitrogen-derivatives followed by its further hydrolysis to form ketone seems to be more feasible [15–17].

Nevertheless, to determine an impact of the direct carvone oxime hydrolysis as an initial reaction step, conversion of carvone oxime was studied under nitrogen instead of hydrogen keeping the other conditions constant. As a result, no carvone oxime transformation was observed under nitrogen atmosphere. Even water addition (0.15 ml, 1 vol.%) under nitrogen atmosphere did not lead to carvone formation as well as in general did not promote any carvone oxime hydrolysis.

At the same time water addition to the reaction mixture (0.15 ml to 15 ml of methanol, 1 vol.%) under hydrogen atmosphere increased selectivity to carvone (Fig. 5), concomitant with a decrease in the reaction rate (Figs. 4 and 5) and selectivity to dihydrocarvone. The ratio between *trans*- and *cis*-dihydrocarvone was not significantly affected by water addition (Fig. 3).

Sensitivity of the catalytic performance to water in the case of gold catalysts was actively studied, especially for oxidation reactions [34–38]. Catalytic activity of Au/TiO_2 catalyst in CO [34–37] and alcohols [38] oxidation was shown to be promoted significantly by water due to oxygen activation and/or beneficial role of surface OH groups, originating from water. At the same time water addition to the gas feed during propylene oxidation over Au/TiO_2 caused decrease in catalytic activity because of competitive adsorption of water and propylene oxide [38]. In the case of carvone oxime transformation water addition most likely leads to partial active catalyst sites blocking through competitive water adsorption preventing carvone oxime adsorption and suppressing its hydrogenation, favouring, however, further hydrolysis to form carvone from intermediate nitrogen containing derivatives.

Summarizing it can be proposed that, carvone oxime hydrogenation appeared to be the first step initializing the overall one-pot consecutive transformations catalyzed by Au/TiO_2. Note that no intermediate products were observed during carvone oxime transformations to carvone that can be related to trace amounts of these compounds in the reaction mixture or to a more complicated reaction mechanism over Au/TiO_2 catalyst via a simultaneous oxime protonation followed by an intramolecular rearrangement. Analysis of the reaction mixture by ^{13}C NMR did not allow any additional reaction products determination.

Finally, it is known that both molecular hydrogen and methanol used as a solvent can act as hydrogen donors during hydrogenation. A possibility of conjugated C=C double bond reduction in carvone by hydrogen transfer from alcohol in the presence of alumina as a catalyst was demonstrated recently [39]. To elucidate the role of hydrogen, taking part in hydrogenation of each substrate, transformations of the corresponding substrates were studied under nitrogen pressure instead of hydrogen. First, as it was mentioned above, no carvone oxime hydrogenation occurred without hydrogen presence. As for carvone, maintaining it under nitrogen pressure at 100 °C for 6 h did not result in any transforma-

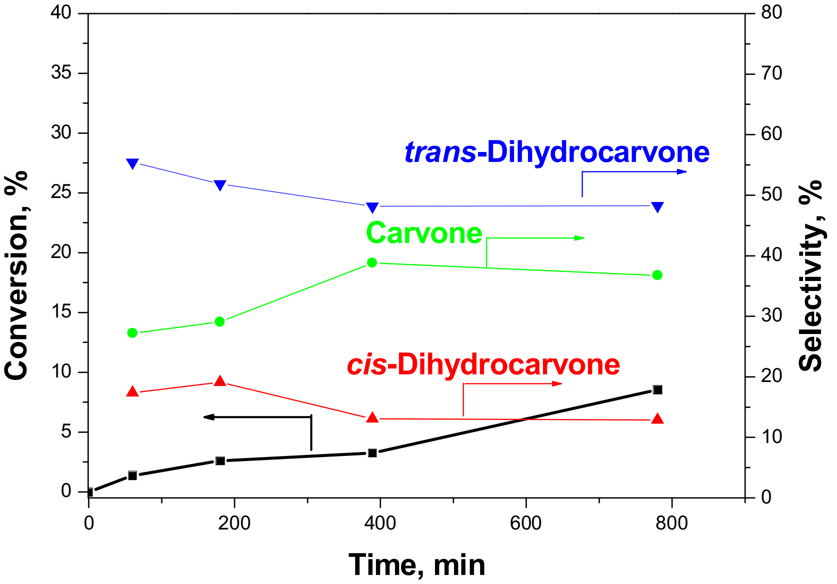


Fig. 5. Effect of water addition on oxime hydrogenation over Au/TiO_2. Conversion of carvone oxime (■) and selectivity towards carvone (●), *trans*- (▼) and *cis*-dihydrocarvone (▲). Reaction conditions: T = 373 K, p (H_2) = 9 bar, carvone oxime (5 mmol), methanol (15 ml), water (0.15 ml), Au/TiO_2 (140 mg).

tion also, whereas subsequent nitrogen replacement by hydrogen led to 26% of carvone conversion after 4 h. A higher carvone conversion compared to the previously obtained value (17% after 4 h [9]) was achieved probably due to preliminary substrate activation on the catalyst surface. Nevertheless these results demonstrated that both reduction steps required the presence of molecular hydrogen.

The results obtained in the present work showed for the first time that dihydrocarvone can be selectively produced by gold-catalyzed one-pot transformation of carvone oxime. This method has a significant advantage in terms of stereoselectivity, since more than two fold *trans*- to *cis*-dihydrocarvone ratio was achieved compared to direct carvone hydrogenation.

4. Conclusions

Gold nanoparticles supported on TiO_2 were shown to catalyze selective carvone oxime transformation to dihydrocarvone. The process was proposed to occur via catalytic carvone formation followed by its hydrogenation to the target product. A possible mechanism of carvone oxime conversion to dihydrocarvone over Au/TiO_2 catalyst was discussed. Application of Au/TiO_2 catalyst for both deoximation and selective hydrogenation of olefinic C═C functional group is reported for the first time. Utilization of carvone oxime as a starting material allowed increasing of stereoselectivity to *trans*-dihydrocarvone up to *trans*-/*cis*-dihydrocarvone = 4.0. At the same time, the reaction rate was lower compared to carvone hydrogenation and after 23 h carvone oxime conversion was 22% contrary to total conversion after 18 h in the case of carvone. Nevertheless, application of the gold catalyst for dihydrocarvone synthesis from carvone oxime in particular and in general to control consecutive chemoselective hydrogenation of different functional groups seems to be promising due to high selectivity. Moreover, catalytic one-pot mode dihydrocarvone synthesis from carvone oxime which is a key intermediate in carvone synthesis from limonene provides optimization of the synthetic method.

Acknowledgement

The work was partly supported by RFBR (Russia) through grant No. 15-33-20198.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.04.013.

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