



# Monoterpenoid Oximes Hydrogenation Over Platinum Catalysts

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## Abstract

Platinum nanoparticles supported on MgO, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> were utilized for monoterpenoid oximes hydrogenation. Monocyclic menthone and carvone oximes synthesized from bio-derived monoterpenoids with a different structure were used to explore the effect of substrate structure on the reaction regularities. The oximes hydrogenation was carried out under hydrogen atmosphere at 100 °C using methanol as a solvent. Platinum catalysts were prepared by the impregnation methods. The catalysts were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray fluorescence spectroscopy, nitrogen physisorption. Hydrogenation of carvone oxime containing a conjugated oxime group and several reducible functional groups resulted in both hydrogenation and deoxygenation giving 5-isopropyl-2-methylcyclohexanamine and carvomenthone over Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/ZrO<sub>2</sub> catalysts. Menthone oxime hydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with an average particle size of 0.8 nm provided the desired menthylamine formation with the selectivity of 90% at complete oxime conversion. Platinum catalysts based on MgO, ZrO<sub>2</sub> and TiO<sub>2</sub> enhanced menthone oxime deoxygenation to menthone.

**Keywords** Hydrogenation · Carvone oxime · Menthone oxime · Menthylamine · Platinum catalyst · Terpene

## 1 Introduction

Widespread monoterpenoids form the largest group of natural compounds and are extensively applied as platform molecules in food, pharmaceutical and perfumery industries [1]. Complicated structures of monoterpenoids with several functional groups and asymmetric centers allow synthesis of a broad range of the products. On the other hand, development of selective catalytic processes for monoterpenoids transformations is a challenging task because of their high

reactivity. Hydrogenation of monoterpene oximes is one of the key steps in the synthesis of valuable compounds, including those with carbonyl and amino groups.

Previously it has been found in our work that Au/TiO<sub>2</sub> catalyst promoted an one-pot synthesis of dihydrocarvone comprising sequential transformations of carvone oxime to dihydrocarvone [2], which is a novel approach to obtain a valuable additive in food industry [3]. Application of Au/TiO<sub>2</sub> catalyst with a low hydrogenation activity provided carvone oxime deoxygenation followed by selective hydrogenation of the conjugated C=C bond. At the same time carvylamine, which can be formed as a result of oxime group hydrogenation [4], has not been detected in the reaction mixture in the presence of Au/TiO<sub>2</sub> catalyst. Such amines are, however, of interest for the synthesis of biologically active compounds [5, 6] and molecularly imprinted polymers [7].

Reduction of menthone oxime with a simpler structure leads to formation of menthylamine [4], which is of great practical interest due to its wide application in asymmetric catalysis [8–10] and synthesis of biologically active compounds [11, 12]. The methods for menthylamine synthesis, both synthetic and catalytic ones provided the desired product yield not exceeding 40–60% [4, 13, 14]. Only platinum black in glacial acetic acid and Raney nickel in methanol

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were proposed as catalysts for menthone oxime reduction. Generally, Pt catalysts exhibited rather high activity in cyclohexanone oxime hydrogenation to the amine compared to Pd, Ru and Rh catalysts [15]. Recently heterogeneous Pd complexes were shown to be highly active for the hydrogenations of oximes to primary amines under hydrogen atmosphere [16].

In the current study Pt catalysts were selected aiming at the development of direct approaches for monoterpene amines synthesis via oximes hydrogenation, being important step in fine organic synthesis. Monocyclic monoterpene oximes, carvone and menthone oxime, obtained from corresponding natural terpenoids were used to reveal fundamentals of the hydrogenation of oximes over Pt catalysts.

## 2 Experimental

### 2.1 Preparation of Catalysts

Platinum catalysts supporting on commercial powdered metal oxides, including TiO<sub>2</sub> (Degussa AG, Aerolyst 7708), ZrO<sub>2</sub> (Alfa-Aesar), Al<sub>2</sub>O<sub>3</sub> (Sasol), MgO (Vekton), were prepared by the impregnation methods using an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> (0.1 M) (Krastsvetmet, Russia). The measured BET surface areas of the supports are presented in Table 1. After impregnation procedure the samples were dried at 110 °C for 12 h. Before the catalytic tests, the samples were reduced in hydrogen flow increasing temperature to 350 °C with a temperature ramp of 2 °C/min during 3 h to remove the excess of chloride.

### 2.2 Characterization of Supports and Catalysts

The texture of metal oxides was evaluated by N<sub>2</sub> adsorption in a Micromeritics TriStar II-3020 device (Micromeritics Instrument Corp., USA). The samples were degassed in vacuum at 300 °C for 4 h using a Micromeritics VacPrep 061-Sample degas system (Micromeritics Instrument Corp., USA).

The platinum content in the catalysts was determined by X-ray fluorescence spectroscopy (XRF) with the powder

pellet method using an ARL PERFORM'X spectrometer equipped with a rhodium anode X-ray tube (Thermo Fisher Scientific, USA).

The average size of platinum nanoparticles was analyzed by TEM using JEM-2010 microscope (JEOL, Japan) with a lattice resolution of 0.14 nm at an accelerating voltage of 200 kV. More than 150 particles were measured to provide reliable metal particles size distribution.

X-ray photoelectron spectra of the fresh catalysts were recorded using a SPECS Surface Nano Analysis GmbH (Germany) equipped with PHOIBOS-150 hemispherical electron energy analyzer, FOCUS-500 X-ray monochromator, and XR-50 M X-ray source with double Al/Ag anode. Monochromatic Al K $\alpha$  radiation ( $h\nu = 1486.74$  eV) and energy of fixed analyzer pass of 20 eV under ultra-high-vacuum conditions were used to obtain the core-level spectra. The binding energy of peaks was calibrated by setting the Ti2p<sub>3/2</sub> peak at 459.0 eV, the Al2p peak at 74.5 eV, the Zr3d<sub>5/2</sub> peak at 182.5 eV and the Mg2p peak at 50.1 eV for titania-, alumina-, zirconia- and magnesia-based catalysts, respectively. The Shirley method was applied for the spectra fitting after the background subtraction using CasaXPS software.

### 2.3 Catalytic Experiments

Methanol (JT Baker,  $\geq 99.8\%$ ), (–)-carvone (Aldrich,  $\geq 97\%$ ), *L*-menthone (SAFC, *trans*-/*cis*-isomer = 85/15) were purchased from commercial suppliers and used as received. (–)-Carvone oxime was synthesized starting from (–)-carvone according to the method presented in [2]. (–)-Menthone oxime was obtained according to the method presented below.

In a typical experiment, a mixture of oxime (1 mmol), methanol (10 ml) and the catalyst (< 63  $\mu$ m, 0.150 g, the active metal to substrate = 1.5 mol%) was intensively stirred (1100 rpm) at 100 °C under H<sub>2</sub> atmosphere (7.5 bar) in a batch reactor. Based on our previous estimation of the Weisz-Prater criterion the experiments were performed in the kinetic regime [2]. During the reaction the samples with the volume of *ca.* 0.1–0.2 ml were withdrawn and analyzed by gas chromatography using HP-5 column (length 30 m, inner diameter 0.25 mm and film thickness 0.25  $\mu$ m) and flame ionization detector operating at 300 °C, helium carrier gas (flow rate 2 mL/min, split ratio 5:1), temperature range from 120 to 280 °C, heating 20 °C/min. The products were confirmed by gas chromatography-mass spectrometry (Agilent Tech. 7890 A gas chromatograph with an Agilent 5975C quadrupole mass spectrometer, HP-5MS column, length 30 m, inner diameter 0.25 mm and film thickness 0.25  $\mu$ m, helium carrier gas, flow rate 1 mL/min, split ratio 10:1, temperature range from 50 to 280 °C, heating 15 °C/min). <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded

**Table 1** Characterization of 2 wt% Pt catalysts and the corresponding supports

Support	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)	Pt particle size (nm)
MgO	33	0.2	22.6	2.2
Al <sub>2</sub> O <sub>3</sub>	204	0.5	10.3	0.8
ZrO <sub>2</sub>	103	0.3	10.8	0.9
TiO <sub>2</sub>	45	0.2	7.6	2.0

using a *Bruker DRX-500* spectrometer 500.13 MHz ( $^1\text{H}$ ) and 125.76 MHz ( $^{13}\text{C}$ ) in  $\text{CDCl}_3$  and *Bruker AV-400* spectrometer 400.13 MHz ( $^1\text{H}$ ) and 100.61 MHz ( $^{13}\text{C}$ ) in  $\text{CDCl}_3$ .

TOF was calculated as a number of converted oxime moles per mole of exposed catalytic site per unit time during the first hour of the reaction corresponding to the linear part of the kinetic curves according to the following equation:  $\text{TOF} = (n^0 - n)/n_{\text{Me}} \cdot D \cdot t$ , where  $n^0$  and  $n$  are the initial and after 1 h molar amounts of oxime,  $n_{\text{Me}}$  (mol) is the active metal amount in the catalyst,  $D$  is the metal dispersion assuming their spherical shape and  $t = 1$  h is the reaction time.

## 2.4 Synthesis of (2*S*,5*R*)-2-Isopropyl-5-Methylcyclohexanone Oxime (Menthone Oxime)

To the solution of *L*-menthone (9.99 g, 64.8 mmol) in ethanol (40 ml), hydroxylammonium chloride (5.99 g, 86.2 mmol), sodium carbonate (8.93 g, 84.3 mmol) and water (40 ml) were added. The obtained mixture was stirred at room temperature for 5 days. Then ethanol was distilled off, the mixture was diluted with water (40 ml) and extracted by hexane (50 ml) three times. The combined organic layer was washed with brine (30 ml), dried over sodium sulfate and evaporated. The synthesized menthone oxime was purified by column chromatography ( $\text{SiO}_2$  60–230  $\mu$  (Macherey–Nagel), the eluent was EtOAc/hexane (0–3%) yielding 6.68 g (39.4 mmol, 61%) of menthone oxime as the single *trans*-stereoisomer. NMR  $^1\text{H}$  and  $^{13}\text{C}$  spectra are presented in Supplementary Materials.

## 3 Results and Discussion

### 3.1 Catalysts Characterization

The Pt content in the synthesized catalysts determined by XRF was close to the theoretical one (2 wt%). TEM micrographs and histograms of the particle size distribution are presented in Fig. 1. According to TEM data Pt nanoparticles were characterized with a uniform distribution of spherical metal nanoparticles. Pt average nanoparticles size seems to depend on the support nature and its textural properties. Thus, titania and magnesia with a lower BET surface area compared to alumina and zirconia were characterized with Pt nanoparticles with the average size of 2.0 and 2.2 nm, respectively (Table 1, Fig. 1). The average particle sizes of Pt nanoparticles were 0.8 and 0.9 nm for Pt/ $\text{Al}_2\text{O}_3$  and Pt/ $\text{ZrO}_2$  catalysts, respectively (Table 1, Fig. 1).

The chemical state of platinum was studied by the XPS. The Pt4*f* core-level spectra are shown in Fig. 2. Typically,

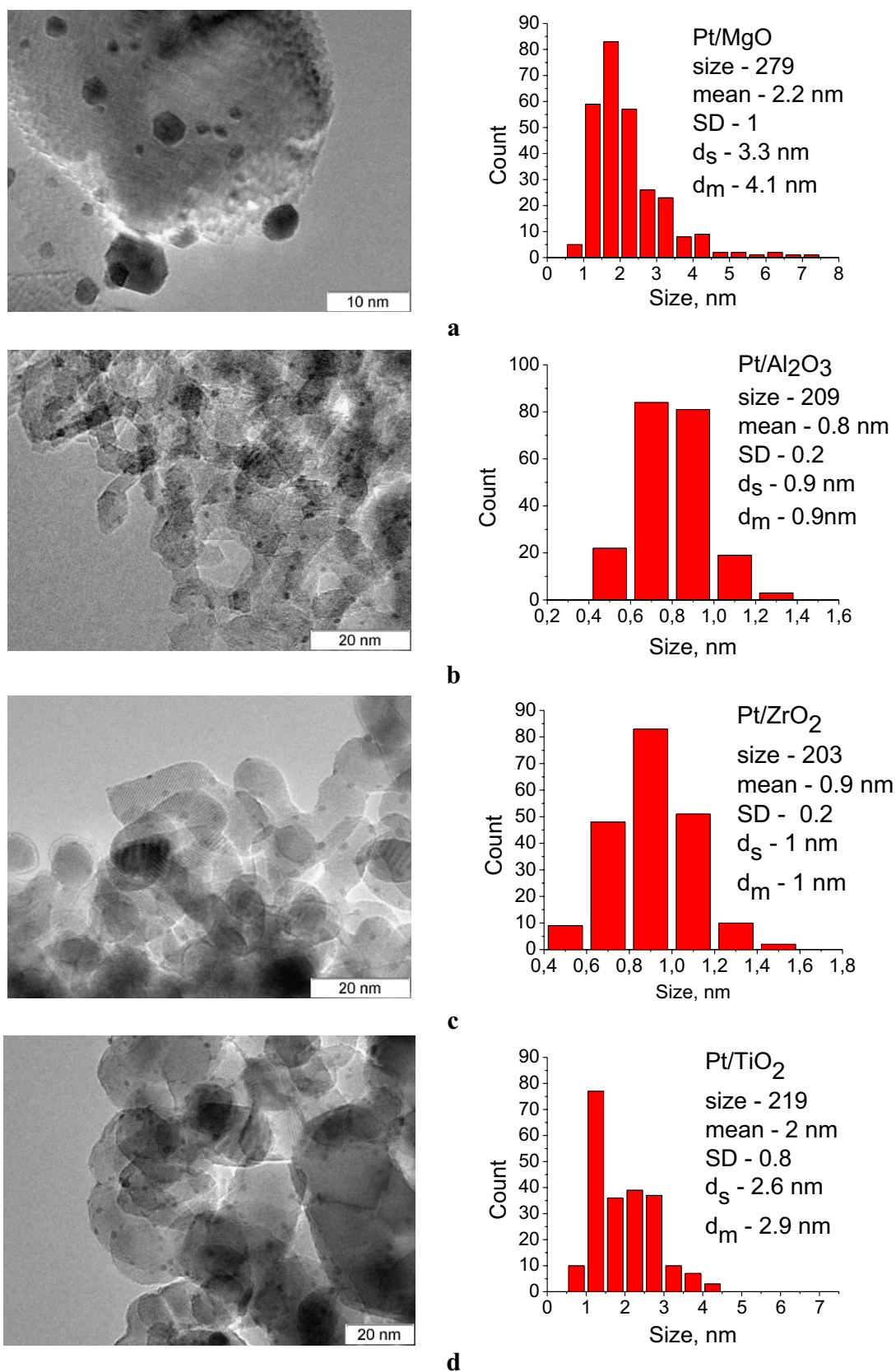
Pt4*f* spectra were characterized by Pt4*f*<sub>7/2</sub>–Pt4*f*<sub>5/2</sub> doublet, where the spin–orbit splitting is 3.33 eV. The XP spectra of Pt/MgO, Pt/ $\text{Al}_2\text{O}_3$  and Pt/ $\text{ZrO}_2$  catalysts were approximated by one Pt4*f*<sub>7/2</sub>–Pt4*f*<sub>7/2</sub> doublet with the binding energy values for Pt4*f*<sub>7/2</sub> at 72.6–72.9 eV, which can be assigned to Pt<sup>2+</sup> species [17–20]. The latter seems to be present on MgO,  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  surfaces in the form of PtO, being caused by covering of small Pt nanoparticles with the oxide layer [21, 22]. At the same time Pt/ $\text{TiO}_2$  catalyst was characterized by one asymmetric doublet with the binding energy values for Pt4*f*<sub>7/2</sub> at 70.7 eV. A low value of the binding energy as well as peak asymmetry is a feature of platinum in the metallic state [23, 24]. In the case of titania Pt nanoparticles decoration by the support ( $\text{TiO}_x$  fragments) can stabilize the metallic state [25, 26].

### 3.2 Catalytic Results

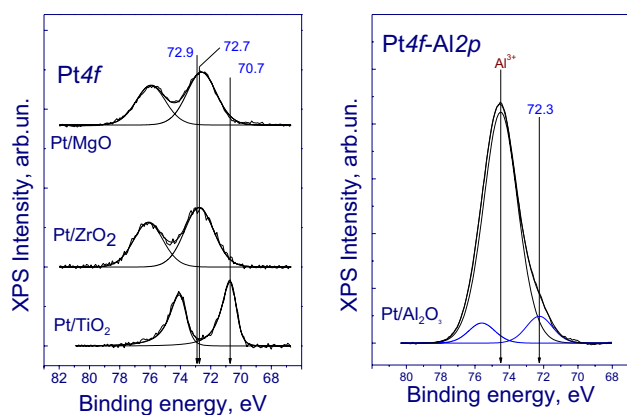
First platinum catalysts supported over the metal oxides ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ , MgO) were used for menthone oxime hydrogenation. The main idea was to explore feasibility of Pt catalysts application for monoterpene oxime hydrogenation to amine and to determine fundamental regularities for hydrogenation of monoterpene oxime with a simpler structure in terms of functional groups capable of competitive hydrogenation. During the reaction the desired menthylamine as well as *trans*- and *cis*-menthone were detected in the reaction mixture (Fig. 3). The menthylamine has several stereocenters resulting in diastereoisomers formation. Based on NMR analysis it was observed that two of the three stereocenters were involved in catalytic processes resulting in four diastereoisomers—neomenthylamine, menthylamine, isomenthylamine, neoisomenthylamine (Fig. 3). In the current study, the overall selectivity to menthylamine was mainly determined, while a detailed investigation of the reaction kinetics will be reported separately. Nevertheless, stereoselectivity for both menthone and menthylamine seems to be determined by thermodynamics.

Note that the metal oxides per se catalyzed only menthone oxime deoxygenation to *trans*- and *cis*-menthone with small to moderate conversion (Table 2). The catalytic activity was noticeably lower compared to the corresponding Pt catalysts and no menthylamine was observed.

In the case of supported Pt nanoparticles, the catalytic activity and selectivity depended significantly on the metal oxide type (Table 2). Platinum supported on magnesia promoted menthone oxime hydrogenation with a higher activity and predominant formation of the desired menthylamine (Table 2). At the same time slightly less active alumina supported platinum catalyst provided more selective menthylamine formation due to absence of side transformation. Platinum nanoparticles on  $\text{TiO}_2$  and  $\text{ZrO}_2$ , having an average particle size (2.0 and 0.9 nm) similar to MgO and  $\text{Al}_2\text{O}_3$  (2.2



**Fig. 1** TEM micrographs and histograms of synthesized Pt catalysts: **a** Pt/MgO, **b** Pt/Al<sub>2</sub>O<sub>3</sub>, **c** Pt/ZrO<sub>2</sub>, **d** Pt/TiO<sub>2</sub>



**Fig. 2** Pt4f core-level XPS spectra of Pt catalysts (symbols—experimental data, curves—fitting)

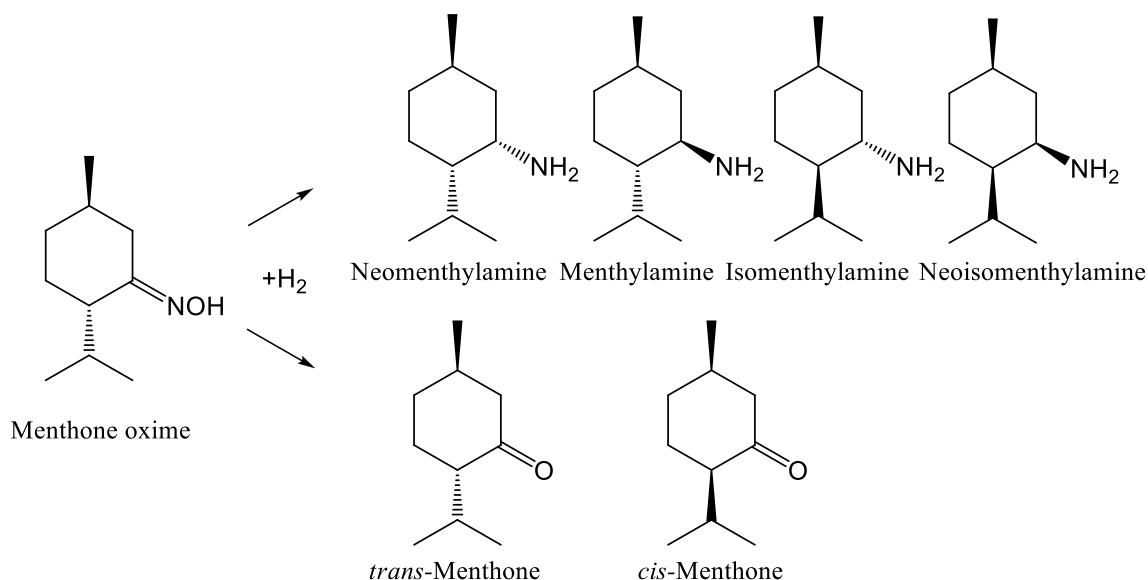
and 0.8 nm), respectively, demonstrated completely different activity and selectivity, producing menthone in a quite high yield. Pt/ZrO<sub>2</sub> catalyzed menthone oxime transformation with a significantly lower activity and produced menthylamine with a slightly higher selectivity compared to menthone. The substrate deoxygenation to menthone dominated over Pt/TiO<sub>2</sub> catalysts. Probably, menthone oxime hydrolysis via hydroxyl species transfer from the support can lead to menthone formation. Interestingly, no deoxygenation over Pt/TiO<sub>2</sub> and TiO<sub>2</sub> proceeded without hydrogen.

In our previous study on one-pot catalytic transformation of carvone oxime to dihydrocarvone via formation of carvone as an intermediate, it was demonstrated that deoxygenation of the oxime requires both the presence of the gold catalyst and molecular hydrogen [2]. At the same time water

addition to the reaction mixture (1 vol%) under hydrogen atmosphere increased selectivity to the corresponding ketone, concomitant with a decrease in the reaction rate and selectivity to dihydrocarvone. Based on the obtained results and the recent publication [16] it can be tentatively proposed, that the oxime hydrogenation proceeds via imine formation followed by its further hydrogenation or hydrolysis depending on the nature of the catalyst.

According to the literature, no structure sensitivity was observed for hydrogenation of a nitro group over Pt [27, 28]. Hydrogenation of nitrocompounds to amines was shown to proceed via an intermediate hydroxylamine derivative formation, while Corma et al. obtained oxime from  $\alpha,\beta$ -unsaturated nitrocompounds with H<sub>2</sub> using a gold catalyst [29, 30]. Thus, there could be some common features in the reduction of nitrocompounds and oximes, particularly, in the substrate activation on the catalyst surface. At the same time, in several studies hydrogenation of acetonitrile and imines over Pt catalysts [31] was demonstrated to be structure sensitive. In this work completely different catalytic activity was observed for Pt/TiO<sub>2</sub> and Pt/MgO as well as Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/ZrO<sub>2</sub> catalysts with almost the same average particle size in hydrogenation of the C=N bond in menthone oxime. In the case of competitive hydrogenation, it was demonstrated by Corma et al. that chemoselectivity over Pt catalysts can be regulated by controlling the metal particles morphology [27, 28], while the support also affected significantly the catalytic activity. The latter seems to be associated with the support influence on Pt rather than the support acidity/basicity.

On the other hand, the metal-support effects for Pt catalyzed hydrogenation of crotonaldehyde [32] and amides [33] were discussed in terms of the functional groups activation



**Fig. 3** Scheme of platinum-catalyzed transformation of menthone oxime under hydrogen atmosphere

**Table 2** The catalytic properties of Pt catalysts in menthone oxime hydrogenation after 7 h

Sample	TOF <sup>a</sup> (h <sup>-1</sup> )	Conversion (%)	Selectivity (%)		<i>trans</i> -/ <i>cis</i> - Menthone
			Men- thyl- amines	Menthones	
TiO <sub>2</sub>	–	14	0	82	3.9
ZrO <sub>2</sub>	–	20	0	100	3.0
Al <sub>2</sub> O <sub>3</sub>	–	38	0	92	4.0
MgO	–	22	0	90	3.0
Pt/TiO <sub>2</sub>	9	67	2	70	3.7
		80 <sup>b</sup>	11	62	2.6
Pt/ZrO <sub>2</sub>	8	46	47	34	2.8
		52 <sup>b</sup>	44	40	3.0
Pt/Al <sub>2</sub> O <sub>3</sub>	32	100	90	2	1.0
Pt/MgO	56	98	72	13	1.6

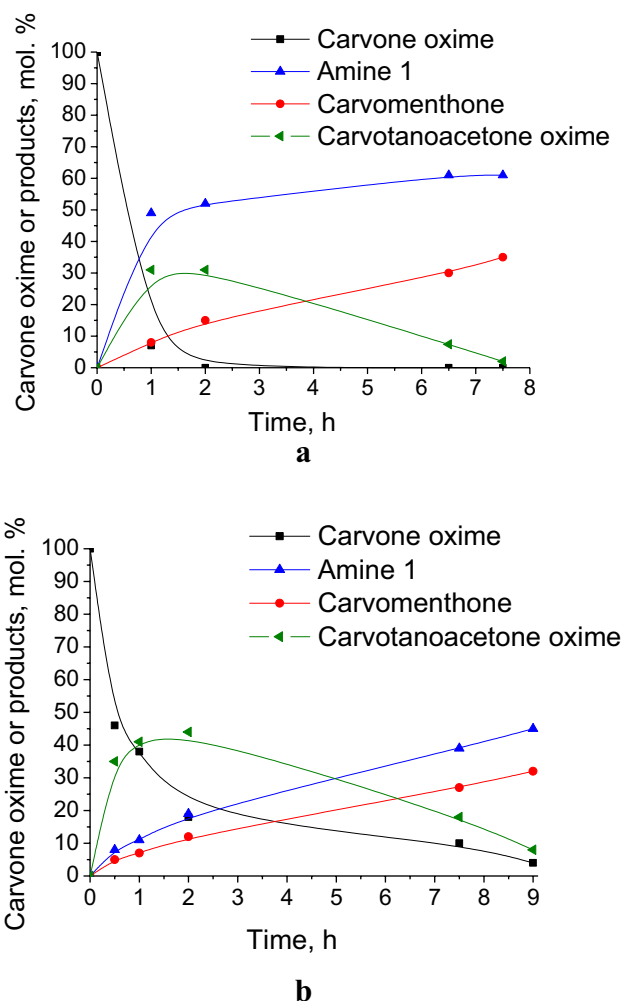
The reaction conditions: T=100 °C, p (H<sub>2</sub>)=7.5 bar, menthone oxime 1 mmol, methanol 10 ml, catalyst 150 mg (Me/menthone oxime = 1.5 mol%)

<sup>a</sup>Turnover-frequency was calculated after 1 h;

<sup>b</sup>Catalytic activity after 9 h

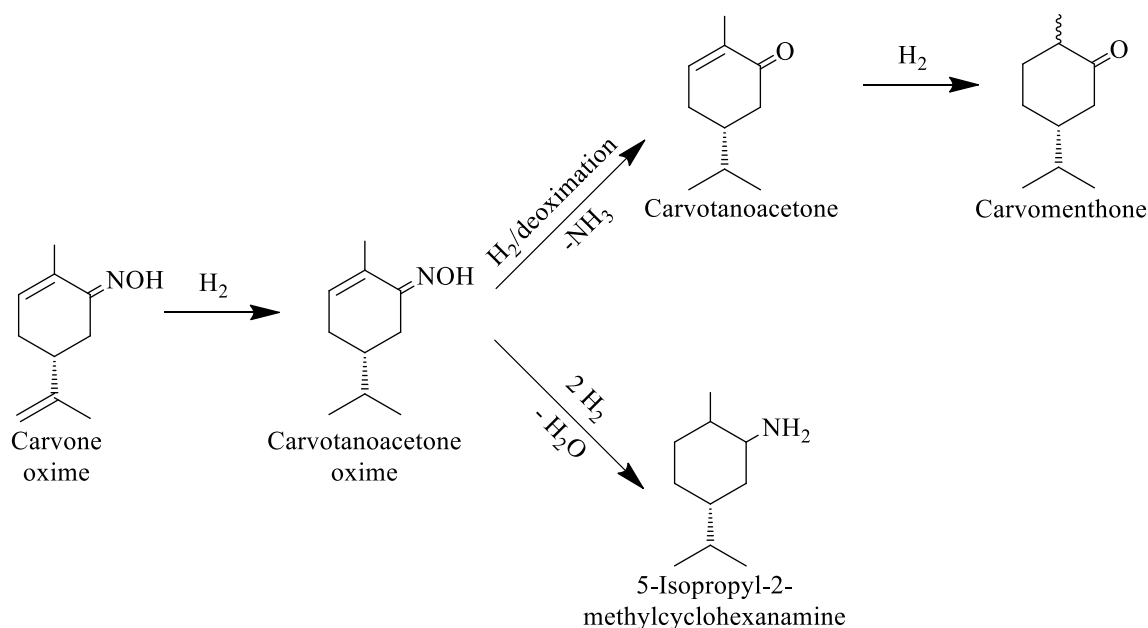
on the support surface. Thus, the strength of the C=O bond activation on the support surface affected both the catalyst activity and selectivity. Efficient activation of the functional group resulted in a direct hydrogen transfer from Pt nanoparticles. Among different Pt catalysts on metal oxide, including alumina and zirconia, those which are supported on titania were recognized to provide quite strong interactions with the carbonyl oxygen atom of an amide or an aldehyde. In this work, Pt/TiO<sub>2</sub> transformed menthone oxime selectively to menthone under hydrogen atmosphere contrary to other catalysts that also gave menthylamine. Probably stronger interactions of Pt/TiO<sub>2</sub> catalyst with the oxime group can change the reaction pathway. In addition, as proposed above, menthone formation can be a result of the oxime hydrolysis via hydroxyl species transfer from the support. Pt catalysts based on alumina with a more acidic character provided higher selectivity to menthylamine, whereas Pt nanoparticles on MgO, ZrO<sub>2</sub> and TiO<sub>2</sub> enhanced menthone formation.

As a next step synthesized Pt catalysts were used for carvone oxime hydrogenation aiming at synthesis of carvylamine. Contrary to menthone oxime, carvone oxime has a double bond conjugated with the oxime group and an isolated C=C bond, which does not have a steric hindrance from the oxime group. In the presence of platinum catalysts supported on Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> non-selective hydrogenation of carvone oxime was observed resulting in predominant 5-isopropyl-2-methylcyclohexanamine (amine 1) formation (Fig. 4). The reaction proceeded through first hydrogenation of the C=C bond in isopropyl substituent of carvone oxime (Fig. 5). Subsequent hydrogenation and deoxygenation



**Fig. 4** Catalytic activity of Pt/Al<sub>2</sub>O<sub>3</sub> (a) and Pt/ZrO<sub>2</sub> (b) catalysts in carvone oxime hydrogenation. The reaction conditions: T=100 °C, p (H<sub>2</sub>)=7.5 bar, carvone oxime 1 mmol, methanol 10 ml, catalyst 150 mg (Me/menthone oxime = 1.5 mol%). Amine 1—5-Isopropyl-2-methylcyclohexanamines

of carvotanoacetone oxime gave amine 1 as well as carvotanoacetone and carvomenthones, respectively, with the former being the main product. Note that formation of 5-isopropyl-2-methylcyclohexanamines (four diastereoisomers) was observed by NMR [32]. A higher catalytic activity and overall selectivity to amines 1 was observed in the presence of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (Table 3). Similar to menthone oxime platinum supported on MgO, ZrO<sub>2</sub> and TiO<sub>2</sub> enhanced deoxygenation. Pt/TiO<sub>2</sub> and Pt/MgO catalysts initially promoted hydrogenation of carvone oxime to carvotanoacetone oxime, followed by mainly deoxygenation (Table 3). As mentioned above, deoxygenation most likely proceeds via transfer of the hydroxyl species from the support. Contrary to other Pt catalysts the one with magnesia as a support was characterized by noticeable side transformations resulting in a complex mixture of ketones and dimers with a minor contribution of



**Fig. 5** Scheme of platinum-catalyzed transformation of carvone oxime under hydrogen atmosphere

**Table 3** The catalytic properties of Pt catalysts in carvone oxime hydrogenation after 7 h

Sample	TOF <sup>a</sup> (h <sup>-1</sup> )	Conversion (%)	Selectivity (%)		
			5-Isopropyl-2-methylcyclohexanamines	Carvomenthones	Carvotanoacetone oxime
Pt/TiO <sub>2</sub>	6	46	0	28	33
Pt/ZrO <sub>2</sub>	16	90	41	29	23
		98 <sup>b</sup>	45	33	8
Pt/Al <sub>2</sub> O <sub>3</sub>	34	100	61	35	2
Pt/MgO	21	100	8	15	20

The reaction conditions: T = 100 °C, p (H<sub>2</sub>) = 7.5 bar, carvone oxime 1 mmol, methanol 10 ml, catalyst 150 mg (Me/oxime = 1.5 mol%)

<sup>a</sup>Turnover-frequency was calculated after 1 h

<sup>b</sup>Catalytic activity after 9 h

amines 1 (Table 3). In the case of carvone oxime transformations over Pt/TiO<sub>2</sub> only different ketones were formed, being in a good agreement with the results on menthone oxime hydrogenation. No amines 1 were detected during the reaction.

Compared to Au/TiO<sub>2</sub> catalyst there was both hydrogenation of all reducible functional groups as well as deoxygenation in the presence of Pt catalysts, with activation of isopropyl fragment being preferred. The current results revealed that Pt catalysts are suitable for only 5-isopropyl-2-methylcyclohexanamine synthesis from carvone oxime via catalytic hydrogenation by molecular hydrogen. Gold nanoparticles supported on the same TiO<sub>2</sub> were less active but provided selective carvone oxime deoxygenation to

carvone followed by conjugated C=C bond hydrogenation leading to dihydrocarvone, whereas no carvylamine was also obtained during the transformation [2]. Worth to note that gold was almost not active in activation of C=C bond in isopropyl fragment. Obviously, carvone oxime is activated in a different way over the platinum catalysts compared to the gold ones. Particularly, earlier Corma et al. also recognized that the catalytic behavior of Pt is different compared to Au catalysts in hydrogenation of nitroaromatics [27, 28, 34, 35]. As mentioned above, hydrogenation of nitrocompounds was proposed to proceed via an intermediate hydroxylamine derivative formation. Corma et al. obtained oxime from α,β-unsaturated nitrocompounds as a final product [27, 28]. Typically, Pt interacts very strongly

with different functional groups making the catalysts on the one hand highly active and on the other hand not chemoselective in hydrogenation of compounds with several unsaturations.

Thus, in the current work carvone oxime, containing several reducible functional groups and a conjugated oxime group, seems to be activated over Pt catalysts in the way leading to non-selective hydrogenation. Pt catalysts based on metal oxides were successfully applied for menthone oxime hydrogenation into valuable menthylamine. In particular, Pt/Al<sub>2</sub>O<sub>3</sub> provided higher activity and selectivity to the desired amine.

## 4 Conclusions

In the current work Pt catalysts over metal oxides such as magnesia, titania, zirconia and alumina were used for monoterpene oximes hydrogenation to amines by molecular hydrogen. Monocyclic carvone and menthone oximes synthesized from natural monoterpenoids were utilized to explore the role of the substrate structure on the reaction regularities. Both hydrogenation of all reducible functional groups in carvone oxime and deoxygenation were observed over Pt catalysts on zirconia and alumina. Pt catalysts were shown to be suitable for only 5-isopropyl-2-methylcyclohexanamine synthesis from carvone oxime. Higher yield of 5-isopropyl-2-methylcyclohexanamine was achieved in the presence of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Platinum catalysts on ZrO<sub>2</sub>, MgO and TiO<sub>2</sub> enhanced deoxygenation. Hydrogenation of menthone oxime over Pt catalysts led to the desired menthylamine formation. The catalytic behavior was noticeably influenced by the support nature. Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/MgO catalysts with the average particle size of 0.8 and 2.2 nm, respectively, exhibited higher activity in menthone oxime hydrogenation to menthylamine, with the former being more selective to the desired amine. Pt/ZrO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts with the average particle size of 0.9 and 2.0 nm, respectively, showed significantly lower selectivity to menthylamine at the expense of deoxygenation resulting in menthone formation.

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## Compliance with Ethical Standards

**Research Involving Human and Animal Participants** No research involving Human Participants and/or Animals was performed. In the current study accepted principles of ethical and professional conduct have been followed.

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