Original paper

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Catalytic myrtenol amination over gold, supported on alumina doped with ceria and zirconia

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Abstract: In the current work gold catalysts supported on both commercial oxides and oxides synthesized by the sol-gel method were used for the one-pot alcohol amination of myrtenol. In general, utilization of metal oxides synthesized by the sol-gel method as the gold catalyst support enhanced the knowledge regarding key parameters determining catalytic behavior. Synthesized alumina was characterized by stronger acid sites favoring primary amine accumulation on the catalyst surface, as compared to the commercial oxide. Utilization of mixed metal oxides synthesized by the sol-gel method resulted in the non-additive behavior of different oxides enhancing the catalytic activity. Introduction of ceria into alumina modified the support basicity resulting in more efficient alcohol activation.

Keywords: one-pot alcohol amination, gold, mixed oxides, ceria-alumina, ceria-alumina-zirconia, alumina, terpene alcohol

1 Introduction

Amines are important chemicals, both intrinsically, and as building blocks in the production of valuable compounds

for several applications. Due to their molecular structure, bio-derived natural extractives such as terpenes represent very attractive starting materials for fine and functional chemicals for human disease prevention and therapy [1]. Complicated amines based on natural monoterpene alcohols are of high practical interest for the development of new pharmaceuticals. In particular complicated terpene amines, synthesized from renewable raw materials, exhibit specific physiological properties, such as antiparkinsonian, anxiolytic, and antiepileptic activities, and can be used as intermediates of potential drugs for neurological diseases [2-5]. One-pot alcohol amination is considered as an effective and sustainable approach for C-N bond formation and for the synthesis of complicated amines, and consists of three consecutive steps. The reaction proceeds via dehydrogenation of the alcohol used as a starting material to the carbonyl compound, a further reaction with amine is then followed by C=N bond hydrogenation using the hydrogen generated in the first step (Fig. 1). The process complexity provides higher efficiency, and at the same time requires precise control over the main and side reactions. Typically, the natural terpenoids have a reactive structure and the side transformations can affect the target product selectivity. The results of our previous work have shown that gold catalysts are rather active in the one-pot amination of the natural terpene alcohol myrtenol leading to the predominant hydrogenation of the C=N bond in the final step instead of the side transformation of the more reactive C=C group of myrtenol (Fig. 1) [6, 7].

Recent studies [6, 7, 8] have also shown that the catalytic performance and the product distribution are sensitive to the acid-base properties of the support. According to the plausible reaction mechanism [6] basic sites on the metal oxide surface are required for the initial alcohol activation to give an alkoxide intermediate, while availability of protonic groups is important for the primary amine accumulation on the surface and the target product formation. At the same time the gold species plays an essential role during the hydrogen transfer. Despite the

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Fig. 1. One-pot myrtenol amination over Au catalysts [6].

initial alcohol activation on the basic sites of the support, the alcohol dehydrogenation proceeds only on the support active sites leading to an inability to produce enough hydrogen species for further hydrogenation [6, 9, 10]. The current study was performed to expand the understanding of reaction regularities and the nature of the active sites, aiming at catalyst optimization and the overall synthesis of terpene amines and similar compounds and the minimization of side reactions. A series of gold catalysts supported over metal oxides, including mixed oxides such as Ce–Al–O and Ce–Zr–Al–O, synthesized by the sol-gel method were used. The catalytic activity was compared with that of gold supported on commercial metal oxides examined earlier in our work [6, 8]. Utilization of mixed metal oxides is expected to result in active site modification and the enhancing of catalytic activity that has been previously demonstrated for several reactions [11–13]. Furthermore, modification of the support properties as well as variation of the active site composition revealed important aspects of the reaction mechanism.

2 Experimental/methodology

2.1 Catalysts preparation and characterization

The same gold catalysts based on nanostructured alumina and mixed oxides described earlier in [14] were used in the current work. Briefly, alumina and mixed oxides Ce–Al–O with the ceria content 10 and 30 wt.% (denoted further as $\text{Ce}_{0.1}\text{Al}_{0.9}$ and $\text{Ce}_{0.3}\text{Al}_{0.7}$, respectively)

and Ce–Zr–Al–O with the content of ceria:zirconia of 15:15 wt.% (denoted further as $(\text{CeZr})_{0.3}\text{Al}_{0.7}$) were prepared by the sol-gel method from organo-metallic precursors following a procedure reported previously [15]. A solution of cerium (III) 2,4-pentanedionate hydrate (Alfa-Aesar) and/or zirconium (IV) 2,4-pentanedionate (Alfa-Aesar) in ethanol under moderate agitation was added to a mixture of aluminum sec-butoxide (Alfa-Aesar) in 2-methyl-2,4-pentanediol (Alfa-Aesar), and refluxed with moderate agitation at 90°C for 3 h. Hydrolysis was initiated by the addition of deionized water. The obtained gel was aged for 10 h. The samples were dried under vacuum at 100°C for 12 h and then heated in an N_2 atmosphere up to 450°C and maintained for 12 h, with a subsequent treatment in O_2 at 650°C for 4 h for the decomposition of organic precursors.

The catalytic performance of gold supported on mixed oxides was compared with gold supported on individual commercial oxides. The same gold catalysts based on commercial single oxides (ZrO_2 , Al_2O_3 and CeO_2) described earlier in [6] were used in the current work.

In all cases gold (3 wt.%) was supported on the nanostructured oxides by a deposition-precipitation technique using HAuCl_4 (Alfa-Aesar) as a gold precursor and urea as a precipitating agent similar to the procedure described elsewhere [16]. In order to remove the excess of chloride after gold deposition, the sample was washed with NH_4OH solution (pH ca. 10) [17, 18]. Thereafter, the catalyst was washed with deionized water, filtered and dried at room temperature for 24 h. Before catalytic testing the samples were treated in hydrogen or air flow at 350°C with a ramp rate of 20°C/min.

The characterization of gold catalysts is described

in detail in [18, 14, 19]. The prepared gold catalysts were analyzed with an inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Varian Liberty 110 ICP Emission Spectrometer. Specific surface area and pore volume of the samples was determined with the BET method by physisorption of nitrogen in a Tristar II 3020 Micromeritics instrument. Prior to measurement, the samples were treated in vacuum (0.05 mbar) at 350°C for 12 hours. Transmission electron microscopy (TEM) was performed with a JEOL 2010 microscope. The electronic state of the gold species was studied by X-ray photoelectron spectroscopy (XPS) with a Kratos AXIS 165 photoelectron spectrometer using monochromatic AlK_{α} radiation ($h\nu = 1486.58$ eV) and a fixed analyzer pass energy of 20 eV. All measured binding energies (BE) were referenced to the C1s line of adventitious carbon at 284.8 eV. The spectra fitting was performed using the Shirley background estimation

over the energy range of the fit. The qualitative and quantitative analysis of the acid sites of the supports was performed with Fourier transform infrared spectroscopy (FTIR) using pyridine as a probe molecule [19]. Spectral bands at 1545 cm^{-1} and 1450 cm^{-1} corresponding to Brønsted (BAS) and Lewis (LAS) acid sites respectively, were analyzed. The characteristic features of the catalysts are collected in Table 1 and Table 2.

2.2 Catalytic experiments

The liquid-phase (-)-myrtenol amination was performed in a stainless steel reactor, equipped with an electromagnetic stirrer (1100 rpm) and the sampling system. Typically a mixture of (-)-myrtenol (1 mmol), aniline (1 mmol) and the catalyst (92 mg, 1.4 mol. % Au) in toluene (10 ml) was used.

Table 1. BET surface area, pore diameter and concentration of surface Lewis acid sites (LAS) on the supports [19].

Support	BET surface area, m ² /g	Pore diameter, nm	LAS, μmol/g		
			Weak	Medium	Strong
Supports synthesized by sol-gel method					
Al ₂ O ₃	210	9.0	0	0	20
Ce _{0.1} Al _{0.9}	340	12.0	10	10	0
Ce _{0.3} Al _{0.7}	270	7.0	10	10	0
(CeZr) _{0.3} Al _{0.7}	270	-	10	15	0
Commercial supports (Alfa-Aesar)					
ZrO ₂	90	6.6	10	0	0
Al ₂ O ₃	110	5.4	15	10	0
CeO ₂	20	6.0	0	10	0

Table 2. Average diameter of Au nanoparticles according to TEM and XPS data for gold samples supported on oxides, depending on the type of the catalysts pre-treatment [14, 18].

Support	Type of the pre-treatment	Au NPs size, nm	Type and relative content of Au species, %
Supports synthesized by sol-gel method			
Al_2O_3	TPO	3.9	Au^0 100.0
	TPR	2.0	Au^0 100.0
	TPR	3.8	Au^0 100.0
$Ce_{0.1}Al_{0.9}$	TPR	3.7	Au^0 100.0
$Ce_{0.3}Al_{0.7}$	TPR	3.7	Au^0 100.0
$(CeZr)_{0.3}Al_{0.7}$	TPR	1.7	Au^0 100.0
Commercial supports (Alfa-Aesar)			
ZrO_2	TPO	2.5	Au^0 76.1; Au^+ 23.9
	TPR	1.8	Au^0 86.3; Au^+ 13.7
Al_2O_3	TPO	2.6	Au^0 93.4; Au^+ 6.6
	TPR	2.4	Au^0 100.0
CeO_2	TPO	2.4	Au^0 78.3; Au^+ 21.7
	TPR	2.2	Au^0 76.7; Au^+ 23.3

The measurement of catalytic activity was performed in the kinetic regime. The impact of internal diffusion was determined through the estimation of the Weisz-Prater criterion. The impact of external diffusion resistance was suppressed by conducting experiments at the stirring speed of 1100 rpm, which is proven to be sufficient to avoid external mass transfer limitations.

Aliquots were withdrawn from the reactor at appropriate time intervals and analyzed by gas chromatography using an SLB-5ms column (length 30 m, inner diameter 0.25 mm and film thickness 0.25 μm , gas carrier He, 40 ml/min) and a flame ionization detector operating at 300°C. Additionally the product structure was confirmed by analysis with a gas chromatograph-mass spectrometer (Agilent 7000 GC/MS Triple Quad, HP-5MS column). The product structures were determined earlier by ^1H - and ^{13}C -NMR [6].

Selectivity for a particular product was calculated based on the following equation: selectivity = yield of the product/total yield of all products.

TOF was calculated as a number of converted myrtenol 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 curve according to the following equation: $\text{TOF} = \frac{n_{\text{myrtenol}}^0 - n_{\text{myrtenol}}}{n_{\text{Au}} \cdot D_{\text{Au}} \cdot t}$, where n_{myrtenol}^0 and n_{myrtenol} are the initial amount of myrtenol in moles and the molar amount of myrtenol after 1h, n_{Au} (mol) the amount of gold in the catalyst, D_{Au} is the dispersion of gold particles, calculated from Au mean diameter (d_{Au}) assuming a spherical shape, and $t = 1$ h is the reaction time.

3 Results and Discussion

3.1 Catalytic results

The gold catalysts were tested in the myrtenol amination with aniline using an equimolar amount of substrates. The results are presented in Fig. 2 – 4 and Table 3.

3.1.1 Au on alumina

The gold catalyst supported on alumina synthesized by the sol-gel method showed catalytic activity similar to the reference commercial alumina in the case of the sample pre-treated under an oxidizing atmosphere, while a pre-reduced $\text{Au}/\text{Al}_2\text{O}_3$ catalyst based on the oxide synthesized by the sol-gel method exhibited *ca.* a twofold lower initial reaction rate (Table 3, Fig. 2-3). Turnover frequency (TOF) was noticeably lower for the pre-reduced sample because of the twofold difference in Au nanoparticle size, being 3.9 and 2.0 for pre-oxidized and the pre-reduced $\text{Au}/\text{Al}_2\text{O}_3$ catalysts, respectively. TOF was estimated using the Au mean diameter determined by TEM. On the one hand, this dependence implies that the reaction is structure sensitive. However, earlier the crucial influence of the catalyst redox pre-treatment on the active sites and thus on the catalytic behavior was demonstrated. Detailed analysis of the experimental data is presented below.

A significant difference between the samples was observed with respect to the product distribution. First,

Fig. 2. Catalytic activity of gold catalysts based on metal oxides synthesized by sol-gel method. The reaction conditions: $T = 180^\circ\text{C}$, myrtenol 1 mmol, aniline 1 mmol, toluene 10 ml, catalyst 1.4 mol. % Au 0.092 g. Abbreviation: TPO – temperature programmed oxidation; TPR – temperature programmed reduction; TPD – temperature programmed treatment under inert He atmosphere; SG – sol-gel method; A.Aesar – commercial metal oxides produced by Alfa-Aesar.

Fig. 3. The product distribution as a function of the reaction time during myrtenol amination over: a – Au/Al₂O₃ SG TPO; b – Au/Al₂O₃ SG TPR; c – Au/Al₂O₃ Alfa-Aesar TPO; d – Au/Al₂O₃ Alfa-Aesar TPR; e – Au/Ce_{0.1}Al_{0.9} TPR; f – Au/(ZrCe)_{0.3}Al_{0.7} TPR; g – Au/Ce_{0.3}Al_{0.7} TPR; h – Au/Ce_{0.3}Al_{0.7} TPD. The reaction conditions: T = 180°C, myrtenol 1 mmol, aniline 1 mmol, toluene 10 ml, catalyst 1.4 mol. % Au 0.092 g.

on alumina used for pre-oxidized catalyst synthesis, at a myrtenol conversion of 70%, the selectivity for amine 1 was independent of whether the oxide synthesized by the sol-gel method, or the commercial oxide was used (Fig. 4). The pre-reduced $\text{Au}/\text{Al}_2\text{O}_3$ catalyst resulted mainly in imine 1 and myrtenol formation (Fig. 3). Note that the product of controlled hydrogenation (e.g. amine 1) was considered to be the target product (Fig. 1). At the same time, at almost complete myrtenol conversion the kinetics and in particular the formation of amine 1 was different for the pre-oxidized $\text{Au}/\text{Al}_2\text{O}_3$ catalysts. The pre-oxidized $\text{Au}/\text{Al}_2\text{O}_3$ catalyst based on the oxide synthesized by the sol-gel method was characterized with higher selectivity for the target amine with the unsaturated $\text{C}=\text{C}$ bond in the structure of the initial alcohol, compared to the product resulting from the commercial oxide (Table 3).

3.1.2 Au on mixed alumina-ceria-zirconia

Alumina modification with ceria and zirconia affected the product distribution, while the catalytic activity was almost the same considering conversion vs. reaction time dependence (Fig. 2-3 and Table 3). At the same time both $\text{Ce}_{0.1}\text{Al}_{0.9}$ and $\text{Ce}_{0.3}\text{Al}_{0.7}$ oxides afforded higher TOF values compared to the corresponding Al_2O_3 synthesized by the sol-gel method. In the presence of gold supported on a $\text{Ce}_{0.3}\text{Al}_{0.7}$ mixed oxide subjected to thermal treatment under an inert atmosphere, the initial reaction rate increased along with a low selectivity for the target amine 1 of 21% (Table 3). For the pre-reduced gold on alumina-ceria catalysts selectivity increased with an increase of Ce content after 13.5 h (Fig. 3 and Table 3), with a higher amount of amine 1 obtained using the $\text{Au}/\text{Ce}_{0.3}\text{Al}_{0.7}$ catalyst (Table 3). Selectivity for the target amine increased with myrtenol conversion for the gold catalyst based on the $\text{Ce}_{0.3}\text{Al}_{0.7}$ oxide (Fig. 5). At a myrtenol conversion of 50% a slightly higher selectivity for the target amine was detected for the catalyst with a Ce content of 10 wt.%. In the presence of this catalyst, selectivity for amine 1 did not noticeably change along with myrtenol conversion. Gold supported on a $\text{Ce}_{0.3}\text{Al}_{0.7}$ mixed oxide was characterized by a more effective hydrogen transfer than for the $\text{Au}/\text{Ce}_{0.1}\text{Al}_{0.9}$ catalyst leading to the target amine formation with a higher selectivity at a myrtenol conversion of 70%, while catalytic activity was similar for the alumina-ceria based catalysts.

Lower activity and selectivity for amine 1 was observed in the case of gold supported on the alumina-ceria-zirconia catalyst (Table 3). Interestingly, contrary to the gold catalysts synthesized on commercial oxides,

pyridine adsorption revealed a gradual decrease in the Lewis acidity for the oxides with the highest Ce content [24]. It is worth noting that in the case of commercial zirconia (Alfa-Aesar), previously tested in [6, 8] and used in the current work for comparison, only a small amount of Lewis acid sites were detected (Table 1). At the same time the latter catalyst exhibited an optimum consecutive myrtenol transformation resulting in the total conversion of myrtenol and a relatively high selectivity for the target amine of about 53% [6]. Earlier it was suggested that the acid sites are needed for adsorption of the primary amine thus preventing intermediate aldehyde accumulation.

Fig. 4. The selectivity for amine 1 in the presence of gold catalysts supported on commercial alumina (Alfa Aesar) and synthesized by the sol-gel method (SG) pre-treated under reducing (TPR) and oxidizing atmosphere (TPO) at myrtenol conversion of 70%. The reaction conditions: $T = 180^\circ\text{C}$, myrtenol 1 mmol, aniline 1 mmol, toluene 10 ml, catalyst 1.4 mol. % Au 0.092 g.

Fig. 5. The selectivity for amine 1 at different myrtenol conversions: 50% (filled square) and 70% (filled triangle), in the presence of gold catalysts supported on mixed oxides as a function of ceria content. The reaction conditions: $T = 180^\circ\text{C}$, myrtenol 1 mmol, aniline 1 mmol, toluene 10 ml, catalyst 1.4 mol. % Au 0.092 g.

Table 3. Catalytic activity of gold catalysts based on commercial oxides and oxides synthesized by sol-gel. The reaction conditions: T = 180°C, myrtenol 1 mmol, aniline 1 mmol, toluene 10 ml, catalyst 1.4 mol. % Au 0.092 g, 13.5 h.

Support	Pre-treatment	TOF, h ⁻¹	Conversion, %	Selectivity, %					
				Imine 1	Amine 1	Imine 2	Amine 2	Myrtenal	Myrtanol
Supports synthesized by sol-gel method									
Al ₂ O ₃	TPO	87	99	23	53	2	6	5	8
	500°C								
Al ₂ O ₃	TPR	18	72	49	14	2	4	4	20
	300°C								
Ce _{0.1} Al _{0.9}	TPR	28	94	45	26	0	2	3	18
	300°C								
Ce _{0.3} Al _{0.7}	TPR	25	83	20	36	2	8	5	25
	300°C								
Ce _{0.3} Al _{0.7}	TPD	-	99	42	21	1	5	5	23
	300°C								
(CeZr) _{0.3} Al _{0.7}	TPR	10	51	72	12	2	3	1	3
	300°C								
Commercial supports (Alfa-Aesar) [6, 8]									
ZrO ₂	TPO	48	97	35	52	3	5	0	1
	350°C								
ZrO ₂	TPR	70	93	44	28	4	6	8	4
	350°C								
Al ₂ O ₃	TPO	38	93	39	41	4	5	0	8
	350°C								
Al ₂ O ₃	TPR	101	97	44	37	4	6	2	4
	350°C								
CeO ₂	TPR	50	84	28	15	5	11	28	5
	350°C								

A more noticeable accumulation of myrtanol (instead of myrtenal) was typically detected in the presence of oxides synthesized by the sol-gel method. The data reveal some limitations in the alcohol dehydrogenation step. Previously in the case of some commercial oxides, aldehyde accumulation due to a lack of aniline on the catalyst surface was also observed [6, 8].

3.2 Discussion

Analysis of the experimental data should consider the following key parameters: active sites of the support (generally determined by the acid-base properties), and the gold species. As mentioned above, the basic sites of the support were proposed to be the sites required for the initial alcohol activation which proceeds via the initial cleavage of the hydroxyl bond and results in formation on the catalyst surface of an alkoxide intermediate as well as hydrogen [6, 20, 21, 22]. Involvement of the support acid sites is important for primary amine accumulation on the surface and for generation of hydrogen leading eventually to the target amine [8, 28]. Gold species are responsible for the C-H activation of the alkoxide species, giving a

carbonyl compound and gold hydride species. Moreover, only gold species allow the generation of hydrogen for further efficient hydrogen transfer.

Qualitative and quantitative analysis of the support acid sites was performed with FTIR using pyridine [19]. According to FTIR analysis alumina synthesized by the sol-gel method has strong acid sites only, while commercial Al₂O₃ has more weak and medium than strong acid sites, even if the total amount of Lewis acid sites is similar (Table 1). Both the surface area and the pore diameter are almost twofold higher for the synthesized alumina, which is typical for supports synthesized by the sol-gel method (Table 1). The mixed aluminium-cerium and aluminium-cerium-zirconium oxides are characterized by the presence of weak and medium acid sites, showing that for the mixed oxides the strength of Lewis acid sites is decreased compared to alumina. Addition of zirconia in the alumina-ceria mixed oxide results in a decrease of strong Lewis acid sites, while increasing the medium ones. Morterra *et al.* using *in-situ* FTIR spectroscopy and adsorption microcalorimetry observed that the introduction of ceria to alumina also led to the formation of Lewis acid sites of medium strength [23]. A study of γ-Al₂O₃-CeO₂ samples with a different Ce content by FTIR-

during the reaction. Therefore, an increase in selectivity for the target amine in the case of gold on alumina synthesized by the sol-gel method may be caused by an increase of the support acidity. However, analysis of the results for commercial ZrO_2 showed that the strength of the acid sites did not significantly influence selectivity for the reaction products. The catalytic behavior most likely requires a balance between acidic and basic sites.

A significant effect of the nature of the support on alcohol conversion and the yield of amine was clearly demonstrated and discussed both for myrtenol and benzyl alcohol amination [6, 20, 25]. The electronegativity of the metal ions in the metal oxide supports, determining the acid–base properties of metal oxides, was well correlated with the catalytic behavior, revealing that catalytic performance in each step strongly depends on the support acid-base properties. An optimum consecutive myrtenol transformation was observed to occur in the presence of gold supported on metal oxides with both acidic and basic surface sites, such as zirconia. Interestingly, the product distribution turned out to be sensitive to the catalyst redox pre-treatment [8]. The difference in activity and selectivity for the pre-reduced and pre-oxidized catalysts was proposed to be mainly related to a different degree of the modification of support basic properties by residual ammonia [8].

Utilization of the mixed metal oxides synthesized by the sol-gel method was thought to allow cooperation of the different oxide properties, enhancing the catalytic activity. For example, introduction of ceria into alumina was expected to modify the support basicity resulting in efficient alcohol activation, while the acid sites of alumina would promote hydrogen transfer in the last step. As it has been also shown by Shimizu *et al.* [28], in the case of alcohol dehydrogenation the basic OH groups present on the oxide are responsible for the formation of alkoxide intermediates. Their strong basic nature at the same time reduces the protonic nature of water or M-OH species resulting in a decrease of the alcohol dehydrogenation rate by a slow removal of hydride species. At the same time, dissociative adsorption of alcohol is suppressed by the weak nucleophilic character of the surface OH groups using acidic or neutral metal oxides.

Utilization of alumina-ceria based catalysts compared to those based on alumina pre-treated under a reducing atmosphere seems to improve alcohol activation, resulting in an increase of TOF value, while catalytic activity was not sensitive to the ceria content in the support (Table 3). At the same time, gold supported on mixed $\text{Ce}_{0.3}\text{Al}_{0.7}$ oxide was characterized with a more efficient hydrogen transfer leading to the target amine formation with a

higher selectivity. A higher content of Ce in the support most likely favors more efficient hydrogen stabilization in the first step followed by its consumption due to the availability of active sites. Note that previously it was proposed that the reaction occurs at the gold-support interface [6, 7, 8]. The stronger acidity of sol-gel alumina applied in the current work compared to the commercial oxide seems to cause some limitations for the first step resulting in myrtenol accumulation.

Moreover, an important feature worth considering is that the utilization of mixed oxides and in particular the incorporation of ceria, causes noticeable changes in the catalyst structure, compared to single oxides, affecting the catalytic behavior [26]. Catalytic activity and/or selectivity was enhanced using transition metal catalysts based on supports containing ceria in a variety of reactions including the hydrogenation of cinnamaldehyde [11], alcohol oxidation [12], CO oxidation [13] *etc.* In several recent studies the effect on catalytic behavior of ceria introduction into metal oxides was attributed to active metal and/or CeO_2 particle size, the morphology of active metal nanoparticles, and interactions between metal nanoparticles and CeO_2 [11–13]. It is known that the doping of alumina with ceria leads to the formation of extrinsic oxygen vacancies [26]. Defects such as oxygen vacancies and step edges are the most reactive sites on the surface of metal oxides. The presence of oxygen vacancies enhances the metal-support interactions and the performance of transition metal catalysts [26]. In the case of gold catalysts supported on the mixed ceria-containing oxides, Au nanoparticles exhibited an elongated geometric morphology, which could increase the number of edges and/or facets of Au nanoparticles [11]. Note the coordinatively unsaturated gold atoms were proposed to be more reactive for the cleavage of the C-H bond [21, 22]. Thus, the morphology of gold supported on the mixed oxides can enhance the initial alcohol activation within the one-pot alcohol amination, affecting subsequent hydrogenation of the imine in the last step. Tian *et al.* also demonstrated that the increase of Ce^{3+} contribution in gold-ceria catalysts with an increase in Ce content resulted in more oxygen vacancies [11]. The surface electron density of Au nanoparticles diminishes due to the presence of more oxygen vacancies. This typically favors adsorption of the C=C bond in cinnamaldehyde versus C=O leading to the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde [11]. An increase of selectivity for myrtenol for gold on $\text{Ce}_{0.3}\text{Al}_{0.7}$ oxide as a result of C=C bond hydrogenation in the initial myrtenol can be tentatively ascribed to a lower electron density of the gold nanoparticles (Table 3). Generally a higher selectivity for

the target amine 1 as a result of more effective C=N bond hydrogenation was observed for the mixed Ce-Al oxides compared to alumina.

A TPR study of the mixed oxides revealed that the reduction of mixed ceria-alumina oxides compared to ceria was characterized by a significantly larger hydrogen consumption most likely due to an increase of oxygen vacancies in the defective ceria structure generated by ceria mixing with alumina [14, 27]. In this study, gold on $\text{Ce}_{0.3}\text{Al}_{0.7}$ oxide pre-treated under a reducing atmosphere (Table 3, TPR) afforded the formation of the target amine 1 with a noticeably higher selectivity compared to the catalyst pre-treated under an inert atmosphere (Table 3, TPD). A lack of hydrogen resulting in retardation of the last step can be connected with hydrogen consumption in competitive process of support reduction.

The role of the support was shown to be noticeable, even if the complete transformation resulting in the target amine formation required the presence of the gold species. Based on the reaction mechanism, alcohol activation proceeds via alkoxide formation on the catalyst surface. Thereafter, β -hydride elimination catalyzed by gold occurs to produce aldehyde. The latter step was recently suggested to be the rate-determining step [21, 22, 28]. Moreover the coordinatively unsaturated gold atoms were proposed to be more reactive for the cleavage of the C-H bond [21, 22]. Note that the metal clusters were demonstrated to be essential for C-H bond activation giving the hydrogen required for further hydrogenation [9, 10, 28]. Gold-catalyzed alcohol dehydrogenation was found to be a structure-sensitive reaction, with an optimal size of gold nanoparticle being about 6 nm and 2 nm for ethanol and benzyl alcohol, respectively [21, 22]. In fact, the difference in the optimal size can be caused by the substrate structure and the specific interaction between gold nanoparticles and the support. The adsorption mode has been observed to be influenced by the substrate structure [29]. Fang *et al.* suggested that the acid-base properties of the support and the size of Au nanoparticles are two key factors controlling alcohol dehydrogenation [22]. At the same time Claus *et al.* proposed that the structure-sensitivity observed for the hydrogenation properties of gold catalysts may be attributed to geometrical and electronic properties affected by the support as well [30, 31]. To provide an efficient alcohol dehydrogenation a favorable geometry for β -hydride elimination is required [21, 22]. In the current work the effect of gold nanoparticle size was not explored systematically. At least for the tested samples no correlation was observed. At the same time the

state of the gold species seems to be not a key parameter determining the catalytic behavior and selectivity for the one-pot alcohol amination. Only metallic gold species were detected on the metal oxides synthesized by the sol-gel method, while cationic gold species were also found on the surface of commercial oxides (Table 2). The reaction most likely occurs at the gold-support interface that can be characterized by the presence of $\text{Au}^{\delta+}$ species. The amount of $\text{Au}^{\delta+}$ species seems not to be critical and did not dramatically influence the catalytic activity and selectivity. Obviously the effect of the support acid-base properties on the catalytic behavior is more critical. The current work was limited to only gold catalysts based on our previous study aiming at minimization of the side transformations. However, the metal can also play an essential role.

4 Conclusions

One-pot terpene alcohol amination was studied using gold supported on metal oxides, including several mixed oxides, synthesized by the sol-gel method. Alumina synthesized by this method was characterized by stronger acid sites favoring primary amine accumulation on the catalyst surface. The latter is required for formation of the desired amine. However, the more acidic nature of such alumina compared to the commercial alumina seems to cause some limitations in the first step resulting in myrtenol accumulation. Utilization of mixed metal oxides synthesized by the sol-gel method resulted in a non-additive behavior of different oxides enhancing the catalytic activity. The introduction of ceria into alumina, modified the support basicity resulting in a more efficient alcohol activation. TOF values increased for the catalysts based on mixed ceria-alumina compared to alumina. Furthermore, selectivity for the desired amine was improved by the introduction of a higher amount of ceria into alumina providing a required balance between acidic and basic sites for the transformation, as well as for the hydrogen transfer. Gold supported on mixed $\text{Ce}_{0.3}\text{Al}_{0.7}$ oxide resulted in a higher selectivity for the desired amine formation compared to mixed oxides with a lower amount of ceria.

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