Catalysis Letters
https://doi.org/10.1007/s10562-020-03514-3

Preparation of *α*-Terpineol from Biomass Resource Catalysed by Acid Treated Montmorillonite K10

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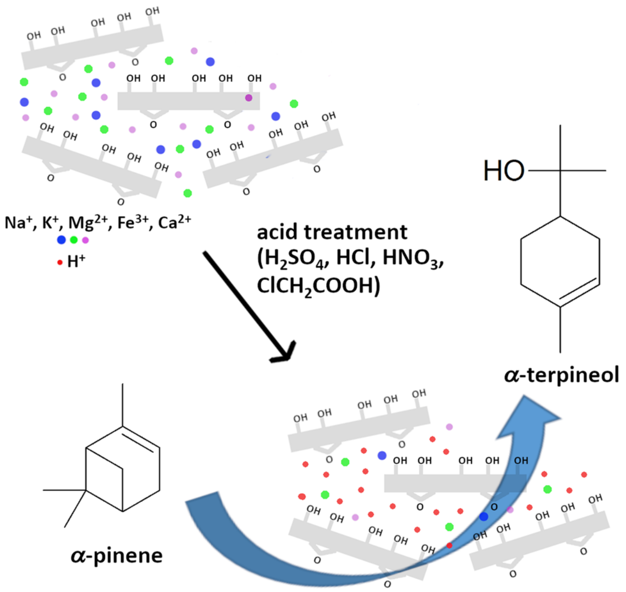
Received: 21 September 2020 / Accepted: 23 December 2020

Abstract

A new type of heterogeneous catalyst for hydration of *α*-pinene was prepared. Montmorillonite K10 was treated by various acids (H_2SO_4, HCl, HNO_3, and $ClCH_2COOH$) and successfully used for the mentioned reaction. The used characterization techniques showed that the acid treatment improved the properties of K10 important for the catalytic activity (S_{BET} and acidity). On the other hand, the morphology and particle size distribution remained the same. Regarding the selectivity (side and consecutive reactions can proceed), the optimal reaction conditions were found (temperature, type of the catalyst, amount of the catalyst, molar ratio *α*-pinene: water, type of water, solvent). Using the optimal reaction conditions, 60% conversion of *α*-pinene was achieved with 45% selectivity to *α*-terpineol (80 °C, 25 wt% of K10/HCl, or K10/H2SO4, $n_{\alpha\text{-pinene}}:n_{water}$ 1:7.5, 1,4-dioxane as a solvent, 24 h). Higher conversions of *α*-pinene, as well as higher selectivity to *α*-terpineol, were achieved using all acid treated K10 in comparison to raw K10. Considering the heterogeneous form of prepared catalysts, its availability, low price and easy method of preparation, these catalysts dispose of a large potential for application as catalysts for hydration reactions.

Graphic Abstract



Supplementary Information The online version of this article (https://doi.org/10.1007/s10562-020-03514-3) contains supplementary material, which is available to authorized users.

Extended author information available on the last page of the article

Keywords *α*-terpineol · Hydration of *α*-pinene · Montmorillonite K10 · acid treatment · heterogeneous catalysis · Ion exchange

1 Introduction

α-Terpineol is natural monoterpenic alcohol, which may find wide application in perfumery or food and beverage industry. *α*-Terpineol can be also used in pharmaceuticals due to its antimicrobial properties (e.g. in the insect bite treatments and wound healing products). Besides, it is an important intermediate for the synthesis of some desired chemical compounds, e.g. camphene. *α*-Terpineol can be found in essential oils of many plants, e.g. pines, bitter orange trees, or myrtle [1].

Various synthetic ways were described for the production of *α*-terpineol in preceding researches. The most widely used method for the preparation of *α*-terpineol is the acid catalysed hydration of *α*-pinene using which quite high yields of *α*-terpineol can be achieved. Nevertheless, *α*-terpineol can be also obtained by (i) hydration of limonene [2, 3]; (ii) oxidation of limonene or *β*-pinene [4]; (iii) biotransformation of limonene [5], (iv) hydration of *β*-pinene [6], (v) dehydration of *trans*-terpine [7], (vi) cyclization connected with isomerization of linalool, geraniol or nerol [8], (vii) reaction of benzaldehyde with eucalyptol [9], or (viii) the multistep reaction stating from ethyl acetate with subsequent alkylation, saponification, Grignard reaction, and metathesis [10]. The main issue of all these preparation methods is the selectivity of the reaction.

One of the easiest ways to prepare *α*-terpineol is just the hydration of *α*-pinene. The use of acid catalysts is essential for this reaction. Unfortunately, the side-reactions, isomerization of *α*-pinene and dehydration of *α*-terpineol, are also acid catalysed reactions [11]. Isomerization of *α*-pinene can led to the formation of limonene, terpinolene, *γ*-terpinene, *α*-terpinene or camphene, similarly, the dehydration of *α*-terpineol can led to the formation of limonene, terpinolene and terpinenes. Moreover, other oxygenated product can be formed during the hydration of *α*-pinene, e.g., cineoles, 1,8-terpine and *γ*- or *β*-terpineol. Various homogeneous (e.g., organic or inorganic acids [12–14], heteropolyacids [15, 16] or ionic liquids [17–19]) as well as heterogeneous (e.g., activated carbon [20], zeolites [20–25], ion exchangers [26] or acid treated clays [11]) or heterogenized (phosphomolybdic acid immobilized on polymeric membranes [27, 28]) acid catalysts can be used for hydration of *α*-pinene with wide-ranging results.

Acid clays were used as catalysts for hydration of *α*-pinene in the preceding research of Comelli et al. [11]. Bentonite was used as raw material and was treated with $ClCH_2COOH$ to improve its catalytic activity. For the comparison of catalytic activity, raw bentonite (J), and two versions of acid treated bentonite [directly dried at 60 °C (JA) or washed with water and dried at 60 °C after the treatment (JAL)] were used in the mentioned reaction. Under the optimal reaction conditions from recently reported works (0.6 mL *α*-pinene, 40 wt% of JAL catalyst, 10 mL water, 6.8 mL isopropyl alcohol, 80 °C, 400 min), 80% conversion of *α*-pinene was achieved with 60% selectivity to oxygenated products (terpineols, cineoles, 1,8-terpine, and terpinen-4-ol). The differences between results obtained using J, JA, or JAL were considerable. The achieved conversion increased ($35 > 65 > 80$) together with the selectivity to oxygenated products ($10 > 48 > 60$). This was connected with the increasing acidity of acid treated clay.

Considering all challenges connected with the hydration of *α*-pinene (biphasic reaction, reversible reaction as well as the possible competitive and consecutive reactions), we would like to report the new possibility of use of the recently reported type of acid treated clay [29, 30]. The reaction conditions were optimized (temperature, amount of catalyst, amount of water, type of water, solvent).

2 Experimental

2.1 Materials

All materials were used as obtained. Montmorillonite K10 (K10), chloroacetic acid (99%), *N,N´*-dimethylacetamide (p.a.) and *α*-pinene (98%, AP) were purchased from Sigma-Aldrich; 1,4-dioxane (p.a.) from Lach-Ner; acetone (p.a.), diethyl ether (p.a.), dimethyl sulfoxide (p.a.), isopropyl alcohol (p.a.), nitric acid (65%), hydrochloric acid (35%), methanol (p.a.), ethanol (96%), *n*-butanol (p.a.), *n*-heptane (p.a.), *n*-hexane (p.a.), *N,N´*-dimethylformamide (p.a.), toluene (p.a.) and sodium hydrogencarbonate (p.a.) from Penta, cyclohexanol (p.a.), cyclohexanone (p.a.), ethylmethylketone (pure), *p*-toluenesulfonic acid (p.a.) from Lachema; dibutyl ether (p.a.) from Fluka, *tert*-butyl methyl ether (99,9%) from Acros Organics. Demineralized ($< 1\ \mu S\ mL^{-1}$), distilled ($< 3\ mS\ mL^{-1}$) and tap water ($< 125\ mS\ mL^{-1}$) were taken from UCT sources.

2.2 Preparation of Catalysts

Montmorillonite K10 was treated by various acids (H_2SO_4, HCl, HNO_3, $ClCH_2COOH$) according to the previously published procedure [29]. 10 g of K10 was dispersed and vigorously stirred in 100 mL of 1 M solution of respective acid (H_2SO_4, HCl, HNO_3, $ClCH_2COOH$) for 24 h at room temperature. Afterward, the solid part was filtered and repeatedly washed with demineralized water to neutral (pH ~ 7) filtrate. The prepared acid treated K10 was dried at 120 °C for 15 h.

2.3 Catalytic Test

Hydrations of *α*-pinene were performed in the round-bottomed flask (25 mL) equipped with Liebig condenser placed at magnetic stirrer (Arex, VELP Scientifica) with a pre-heated oil bath. In the typical experiment, 250 mg of *α*-pinene was inserted to the flask followed with 250 mg of water (molar ratio 1:7.5). Afterward, the appropriate amount of the catalyst (15, 20, or 25 wt% related to *α*-pinene) was inserted into the flask together with solvent (1:12 molar ratio related to *α*-pinene; acetone, methylethylketone, cyclohexanone; methanol, ethanol, isopropyl alcohol, *n*-butanol, cyclohexanol; diethyl ether, *tert*-butyl methyl ether, dibutyl ether; hexane, heptane, toluene; *N,N´*-dimethylformamide, dimethyl sulfoxide, *N,N´*-dimethylacetamide). Most often, the demineralized water was used, nevertheless, also distilled and tap water was tested. Other molar ratios of *α*-pinene: water were tested: 1:1; 1:2.5; 1:7.5; 1:12.

Catalyst K10/HCl was repeatedly used under optimized reaction conditions (25 wt% of the catalyst, isopropyl alcohol as a solvent, 80 °C, 24 h). Before the second use, the catalyst was centrifuged, three times washed with 5 ml of isopropyl alcohol and dried (50 °C) in the dryer.

2.4 Techniques

The samples of reaction mixtures were measured using gas chromatograph Shimadzu GC 2010 Plus equipped with non-polar column ZB-5 (length 60 m, ID 0.23 mm, film thick 0.25 µm) and flame-ionisation detector. For determination of product structures, gas chromatograph coupled with quadrupole mass detector (Shimadzu GC 2010 Plus with GCMS-QP 2010 Ultra) equipped with non-polar column DB-5MS (length 35 m, ID 0.20 mm, film thick 0.32 µm) was used.

Prepared catalysts and raw K10 were characterized by various techniques. X-ray diffractometry (XRD) was performed at room temperature using *θ–θ* diffractometer X´Pert Powder in Bragg-Bretano parafocusing geometry using CuK$_\alpha$ radiation ($\lambda = 1.79028$ Å, U = 35 kV, I = 40 mA). Data were scanned with an ultrafast detector X'Celerator (or with a scintillator detector equipped with a secondary curved monochromator) over the angular range 5–60° (2θ) with a step size of 0.017° (2θ) and a counting time of 20.32 s step^{-1}. Data evaluation was performed in the software package HighScore Plus 4.0. An ARL 9400 XP sequential WD-XRF spectrometer was used to perform XRF analysis. It is equipped with an Rh anode end-window X-ray tube type 4GN fitted with 50 µm be window. All peak intensity data were collected by software WinXRF in a vacuum. The analyzed powders were pressed into pellets about 5 mm thick and diameter of 40 mm without any binding agent and covered with 4 µm supporting polypropylene (PP) film. The time of measurement was about 15 min. Temperature programmed desorption (TPD) of pyridine was measured at Micromeritics AutoChem II 2920 apparatus. The thermal conductivity detector, as well as the quadrupole mass detector (MKS Cirrus 2 Analyzer), were used to detect the desorbed pyridine. 0.09 g of the sample was placed to the U-tube and heated in ultrahigh-purity helium (30 mL min^{-1}) at 150 °C for 1 h to activate the surface of the catalyst. The adsorption temperature of pyridine was 150 °C, measured pulses of pyridine vapour (the volume of 1 pulse 5 mL) were injected into helium gas and carried through the catalyst sample until saturated adsorption was achieved. Then the sample was flushed with helium for 2 h to remove physisorbed pyridine. Afterward, the linear temperature program (5 °C min^{-1}) was stared and the sample was heated up to 800 °C. The desorbed amounts of pyridine were determined by calibration of the intensity of 79 amu MS response. Thermal-gravimetric analysis (TGA) was performed using TG-750 Stanton Redcroft in the temperature range of 25 – 600 °C with a temperature increase of 10 °C min^{-1}. The specific surface areas of prepared catalysts were determined using Pulse Chemisorb 2700 Micromeritics. Catalysts were treated at 150 °C for 2 h in helium (1.5 L h^{-1}) before the analysis. The specific surface areas were calculated based on the physisorption of N_2 at 77 K at three various relative pressures using the Brunauer–Emmett–Teller equation. Elemental analysis of CNHS elements was performed at Elementar Vario El Cube (Elementar), the content of chlorine was determined using the TOX-100 (Mitsubishi) apparatus. Volumetric titration (100 mg catalyst, 10 mL of water) was performed using a 0.1 N solution of NaOH and phenolphthalein as an indicator. The pHs of dispersions of catalysts (100 mg catalyst, 100 mL water) were measured using pH meter XS Instruments pH 50 + DHS at 22 °C. Scanning electron microscopy (SEM) was performed using SEM microscope TESCAN VEGA 3 LMU (Tescan, Brno, Czech Republic) in the regime of low pressure (UniVac; 1 Pa, 20 kV, BSE module). Prior the analysis, the samples were applied to a carbon double-sided adhesive tape and gilded with 5 nm of gold using a Quorum Q150R ES apparatus (Quorum Technologies Ltd., Laughton, UK). The distribution of particle size was measured using laser light scattering [Malvern Mastersizer 3000 system (UK)] equipped with Hydro MV wet sampling unit (Malvern Instruments Ltd., UK), demineralized water was used as a dispersion media. An adequate amount of sample was added to water in the wet unit with a set stirring speed and sonification. Particle size distributions were recorded for 5 determinations at an obscuration range of 5 – 15%.

3 Results and Discussion

3.1 Preparation and Characterization of Catalysts

All prepared catalysts together with untreated K10 were characterized by various techniques. From the elemental analysis results (Table 1), the most considerable difference between K10 and its acid treated forms was visible in the content of combustible carbon (no content in K10). The presence of carbon in K10/H_2SO_4, K10/HNO_3, and K10/HCl can be caused by some contamination analogous to the content of (i) S in raw montmorillonite K10 and (ii) N in K10/H_2SO_4 and K10/$ClCH_2COOH$. Nevertheless, the contents were really low, in general. The small content of chlorine (63 resp. 161 ppm) in K10/HCl resp. K10/$ClCH_2COOH$ indicates, that only traces of these acids remained in the material. The higher amount of chlorine in the case of K10/$ClCH_2COOH$ could be probably connected with (i) the size of the molecule of $ClCH_2COOH$, which is larger in comparison with the size of the HCl molecule or (ii) the formation of some bonding interactions. The overall small content of analysed elements (C, N, H, S, Cl) confirmed the successful wash out of acids used for the treatment of K10.

Using XRF analysis, the composition of raw as well as acid treated K10 were compared (Table 2). All materials contained predominantly SiO_2, as expected, nevertheless, its content increased in K10/X after acid treatment. The increase of SiO_2 was caused by the leaching of Al_2O_3 and Fe_2O_3 induced by the acid treatment. The dealumination induced by the acid treatment was observed during modification of alumosilicates or zeolites [31] for decades. The leaching of interlayer cations Mg^{2+} and Ca^{2+} was observed but the decrease of their content was quite small (about 0.2%). In the case of K10/$ClCH_2COOH$, only the leaching of Al_2O_3 was observed. The changes in the content of interlayer cations Mg^{2+} and Ca^{2+} between raw and acid treated K10 were not significant and therefore the number of hydroxyl groups can be expected to play a major role in the change of the catalytic activity of prepared catalysts. These results are in contrast with the information mentioned in the work of Comelli [11], where the cation exchange (Mg^{2+} and Ca^{2+} to H^+) was mentioned in bentonite. Nevertheless, the composition of the acid treated clay was not analysed in mentioned article. XRD analysis (Fig. 1) did not show any structural changes after the acid treatment meaning that the structure of montmorillonite remained intact.

Table 1 Elemental analysis (Cl, N, C, H, S) of catalysts

Catalyst	Cl (ppm)	N (%)	C (%)	H (%)	S (%)
K10	–	–	–	1.09	0.02
K10/H_2SO_4	–	0.06	0.94	1.02	0.02
K10/HCl	63	–	0.17	1.10	–
K10/HNO_3	–	0.07	1.04	1.07	–
K10/$ClCH_2COOH$	161	0.06	1.06	1.12	–

Table 2 The composition of catalysts determined by XRF analysis

Catalyst	K10	K10/H_2SO_4	K10/HCl	K10/HNO_3	K10/$ClCH_2COOH$
Oxide	Amount (wt%)				
Na_2O	0.1	0.2	0.2	0.2	0.2
MgO	1.5	1.3	1.3	1.3	1.3
Al_2O_3	15.8	15.3	15.3	15.2	15.4
SiO_2	77.4	78.4	78.4	78.4	77.9
P_2O_5	0.0	0.0	0.0	0.0	0.0
K_2O	1.9	2.0	1.9	1.9	2.0
CaO	0.3	0.1	0.1	0.1	0.1
TiO_2	0.5	0.5	0.5	0.5	0.6
V_2O_5	0.0	0.0	0.0	0.0	0.0
Cr_2O_3	0.0	0.0	0.0	0.0	0.0
MnO	0.0	0.0	0.0	0.0	0.0
Fe_2O_3	2.4	2.1	2.1	2.2	2.4

Figure 2 shows the dependence of weight decrease on temperature for raw and acid treated K10. The decrease in the weight at temperatures about 100 °C corresponds with the physisorbed water. The largest amount of physisorbed water was present in raw K10 (3%) in comparison to acid treated K10, where the content was lower than 2%. The slow decrease of weight from 100 °C to higher temperatures can be probably assigned to the release of water from interlayers. The release of hydroxyl groups which are responsible for the catalytic activity may occur at higher temperatures. Thus, drying of the acid treated K10 at temperatures around 100 °C is better than performing calcination at higher temperatures.

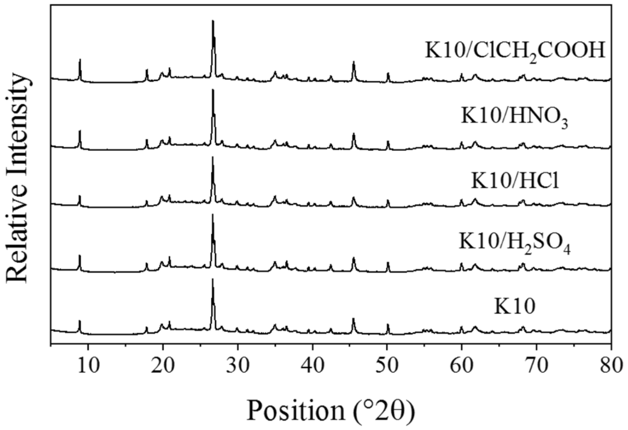


Fig. 1 XRD diffractograms of raw and acid treated K10

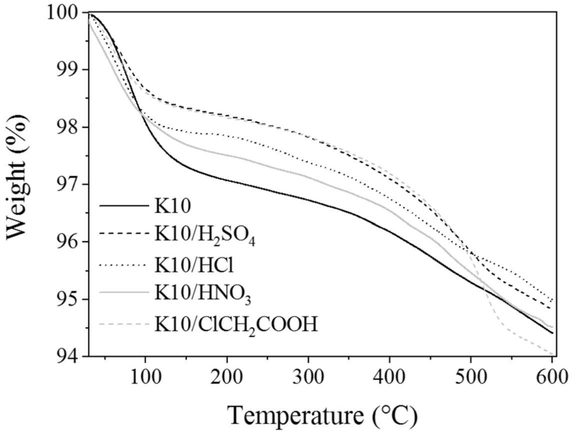


Fig. 2 The decrease of weight in dependence on temperature during the TG analysis

The sharp decrease in the weight of K10/$ClCH_2COOH$ at 488 °C indicates the decomposition of some molecules. Nevertheless, the content of combustible carbon was almost the same for K10/$ClCH_2COOH$, K10/H_2SO_4, and K10/HNO_3 thus the decrease cannot be caused by the decomposition of molecule $ClCH_2COOH$.

Based on the TPD of pyridine results (Table 3), the amount of acid sites increased after acid treatment of K10. For the desorption curves of TPD of pyridine see Fig. S1 in Supplementary Material. The shapes of pyridine desorption curves indicate the possible presence of more types of acid sites. The temperature desorption maxima (Table 3) were between 276 and 294 °C that shows almost similar strength of the acid sites in all materials (Table 3). The specific surface area were the same after acid treatment of K10 (233 $m^2\ g^{-1}$) by HCl as well as $ClCH_2COOH$ (227 resp. 228 $m^2\ g^{-1}$), on the other hand, K10/HCl and K10/$ClCH_2COOH$ contained the highest amount of acid sites (141 resp. 146 $\mu mol\ g^{-1}$). Conversely, the specific surface areas of K10 treated by H_2SO_4 and HNO_3 were higher (284 resp. 268 $m^2\ g^{-1}$) in comparison to raw K10 (233 $m^2\ g^{-1}$), but the amounts of acid sites were lower (121 resp. 117 $\mu mol\ g^{-1}$) compared to K10/HCl and K10/$ClCH_2COOH$. The strength of the acid used for acid treatment of K10 did not either affect the specific surface area or acidity of the prepared catalyst. The strength of acids (evaluated according to the value of pK_a) [32] decrease in direction $HCl > H_2SO_4 > HNO_3 > ClCH_2COOH$, whereas the specific surface areas decreased in direction K10/H_2SO_4 > K10/HNO_3 > K10/HCl = K10/$ClCH_2COOH$ = K10.

Both methods (pH measurement and titration, Table 3) used for differentiation of the acidity of prepared catalysts were not sensitive enough to distinguish the acidity differences between all materials. The value of pH decreased in all cases of acid treated K10 (3.7–3.8) except K10/$ClCH_2COOH$ where the value was the same as in the case of raw K10 (3.9). $ClCH_2COOH$ was the only organic acid used and it was also the less acidic one. The volumetric titration of K10/X suspensions in water by the solution of NaOH showed the higher acidity of all acid treated K10 compared to raw K10. The less acidic one was K10/HCl (2 meq g^{-1}) followed by K10/HNO_3 (2.4 meq g^{-1}) and K10/$ClCH_2COOH$ (2.6 meq g^{-1}). Nevertheless, the differences in these results were small and probably in the range of the measurement error.

SEM analysis (Fig. 3) confirmed that the morphology as well as the particle size of acid treated K10 stayed unchanged after the acid treatment. The particle size distributions were

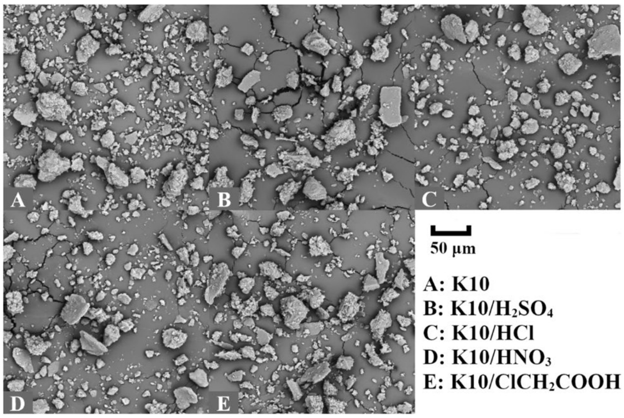


Fig. 3 SEM pictures of raw K10 and acid treated K10

Table 3 Specific surface area and acidity of raw and acid treated K10

Catalyst	S_{BET} ($m^2\ g^{-1}$)	Amount of adsorbed pyridine ($\mu mol\ g^{-1}$)	Temperature maxima (desorption) (°C)	pH	Acidity evaluated by titration (meq g^{-1})
K10	233	87	294	3.9	1.6
K10/H_2SO_4	284	121	276	3.7	3
K10/HCl	227	141	285	3.8	2
K10/HNO_3	268	117	288	3.8	2.4
K10/$ClCH_2COOH$	228	146	291	3.9	2.6

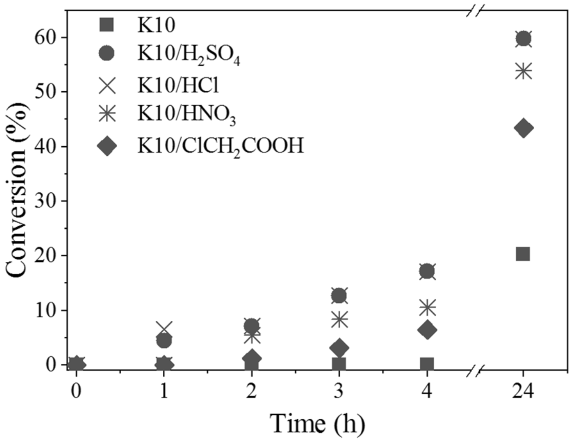
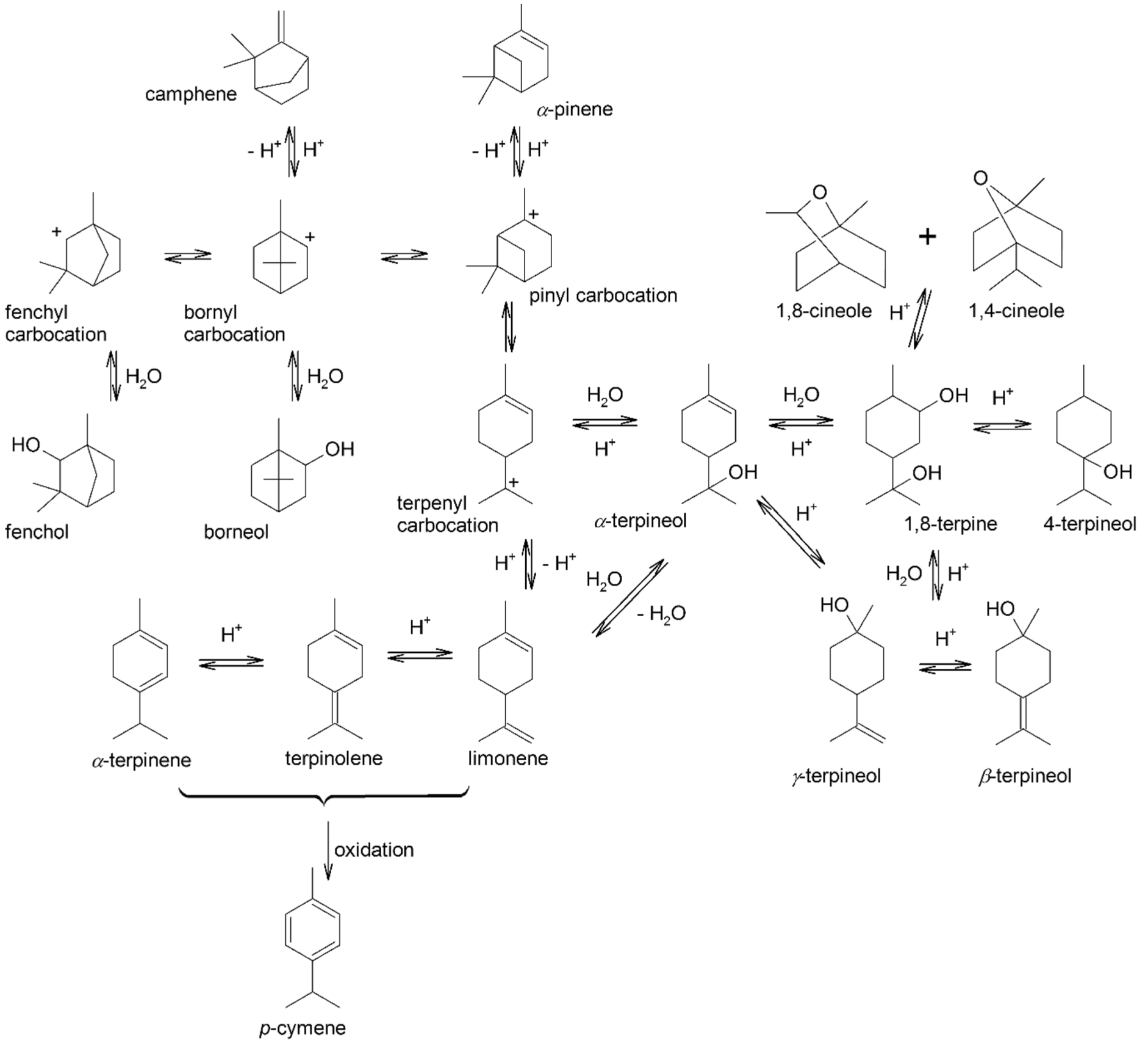


Fig. 4 Comparison of catalytic activity of raw and acid treated K10; 250 mg *α*-pinene, 25 wt% catalyst, 250 mg water (1:7.5 molar ratio), 3 g 1,4-dioxane, 80 °C, 24 h

wide but almost the same in the case of raw as well as acid treated K10, which is visible from SEM images and also from the curves of particle size distributions (see Supplementary material, Fig. S2).

3.2 Catalytic Tests

All prepared acid treated K10, as well as raw K10, were tested as acid heterogeneous catalysts for hydration of *α*-pinene (Fig. 4) to prepare *α*-terpineol. Some of arisen products were identified using GC–MS (Scheme 1). The desired product *α*-terpineol as well as borneol and fenchol are formed by the hydration of *α*-pinene. The competitive reaction, isomerization of *α*-pinene, led to the formation of terpinolene, *α*-terpinene, and limonene, these products can be also formed by dehydration of *α*-terpineol. Isomerization of *α*-terpineol can led to the formation of *β*-terpineol and *γ*-terpineol. *p*-Cymene was formed by the oxidation [33] of



Scheme 1 Scheme of the formation of some identified products during the hydration of *α*-pinene

limonene. The reaction mechanism was described based on preceding researches [11–13].

From the conversion courses depicted in Fig. 4, it is obvious, that the reaction proceeded for the completely monitored time (24 h) and higher conversions of *α*-pinene could be achieved with prolongation of the reaction time. The most active catalysts were K10/H_2SO_4 and K10/HCl, using which 60% conversions of *α*-pinene were achieved after 24 h of reaction. The similar activity of these materials indicates that the acidity (evaluated by the TPD of pyridine), as well as the specific surface area (S_{BET}), are the significant factors for the catalytic activity (K10/H_2SO_4 was the least acidic with the largest S_{BET} whereas K10/HCl was one of the most acidic with the smallest S_{BET}; Table 3). On the other hand, the amount of acid sites and S_{BET} of K10/$ClCH_2COOH$ was comparable to K10/HCl (Table 3) but the conversion of *α*-pinene was significantly lower (43%) using this catalyst. The reaction did not proceed without the catalysts addition and also the conversion achieved using raw K10 was significantly lower (20% after 24 h). In contrast to the results of Comelli et al. [11] where acid treated bentonite was used as a catalyst and where a sharp decrease in *α*-terpineol concentration (more than 30%) was observed after 400 min of reaction, our results showed more or less stable selectivity to *α*-terpineol (about 45%) using acid treated K10. The by-product with the highest concentration were limonene and terpinolene.

The influence of reaction conditions was evaluated using all prepared acid treated K10. Since the results obtained using K10/H_2SO_4, K10/HCl, K10/HNO_3, and K10/$ClCH_2COOH$ were similar, only the results obtained using K10/HCl are presented in this paper.

The reaction did not almost proceed at 60 °C (conversion of *α*-pinene 15% after 24 h), whereas significantly higher conversions (60, 92, 93%) were achieved at higher temperatures (80, 100, 120 °C) after 24 h of reaction (Fig. 5a). The increased temperature significantly affected the reaction rate: 0.0012 mmol mg^{-1} h^{-1} (80 °C) $<$ 0.0029 mmol mg^{-1} h^{-1} (100 °C) $<$ 0.0056 mmol mg^{-1} h^{-1} (120 °C). The temperatures 100 and 120 °C were not beneficial in regard of the selectivity to *α*-terpineol (Fig. 5a) because the isomerization of *α*-pinene, as well as the dehydration of *α*-terpineol to limonene, proceeded preferentially at these temperatures. Although the hydration of *α*-pinene proceeded with lower reaction rate at 80 °C (conversion of *α*-pinene 60% after 24 h of reaction), the selectivity to *α*-terpineol was the highest (45%) and did not dramatically change between 5 and 24th h of reaction. The maximal achieved conversion of *α*-pinene also increased with an increasing amount of catalyst (Fig. 5b) used in reaction at 80 °C (15, 20, or 25 wt%, Fig. 5b) while the selectivities to *α*-terpineol were similar (about 50%). The dependence of the selectivity to the desired product on the conversion of *α*-pinene was depicted in Fig. S3 (in Supplementary material).

Based on the fact that higher amount of water could shift the equilibrium of the reaction in favor of products and could increase the selectivity to the desired product, the various molar ratios of *α*-pinene:water were tested (1:1, 1:2.5, 1:7.5, 1:12; Fig. 6).

Using the molar ratios 1:1 and 1:2.5, the reaction was performed as monophasic one, whereas using the molar ratios 1:7.5 and 1:12 the reaction was biphasic. The formation of the biphasic system led to the decrease of the reaction rate (the achieved conversion of *α*-pinene 60% resp. 47% in comparison to conversion over 90% at ratios 1:1 and 1:2.5). Not only the formation of biphasic system, but also the increasing amount of water in monophasic system (molar ratio 1:1 vs. 1:2.5) led to the significant decrease of

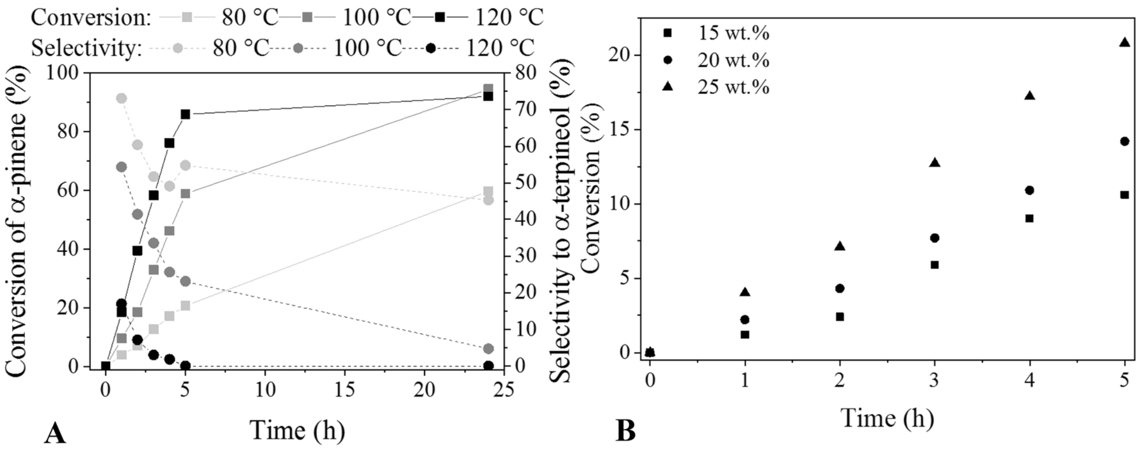


Fig. 5 Influence of the temperature shown as conversion and selectivity in dependence on the reaction time (**a**) and influence of the amount of catalyst on the reaction course (**b**); 250 mg *α*-pinene, 15, 20 or 25 wt% K10/HCl, 250 mg water (1:7.5 molar ratio), 3 g 1,4-dioxane, 80, 100, 120 °C, 24 h

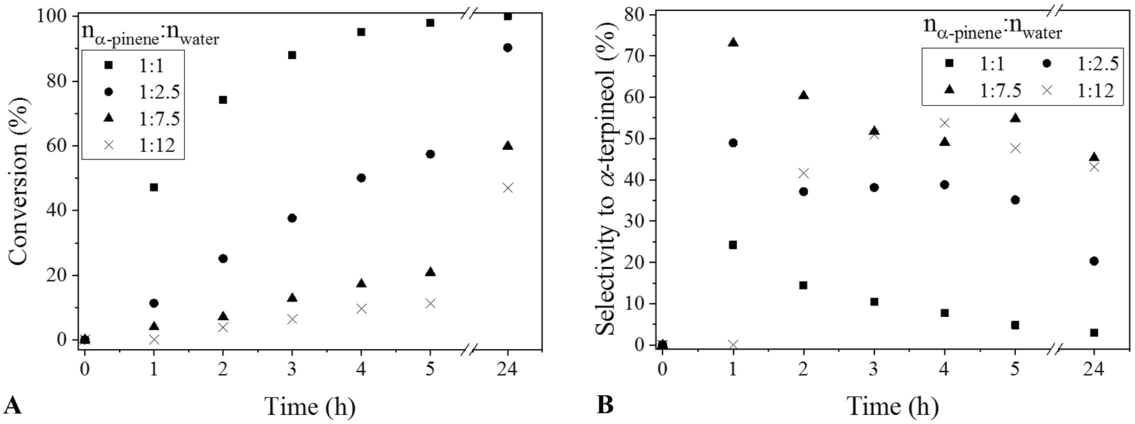


Fig. 6 Influence of the molar ratio α-pinene:water on the reaction course of hydration of α-pinene; 250 mg α-pinene; 25 wt% K10/HCl, various molar ratios α-pinene:water, 3 g 1,4-dioxane, 80 °C, 24 h

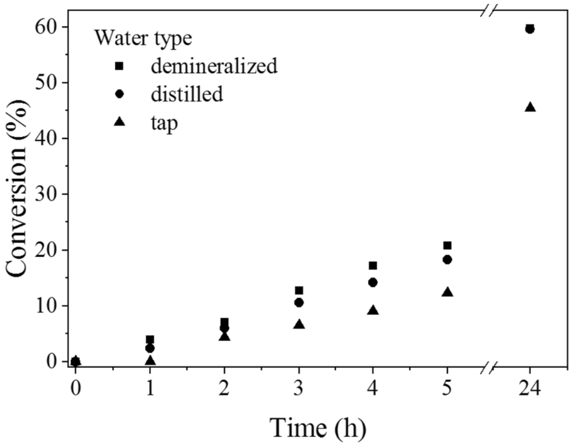


Fig. 7 Influence of water type on the reaction course of hydration of α-pinene; 250 mg α-pinene, 25 wt% K10/HCl, 250 mg water (ratio 1:7.5), 3 g 1,4-dioxane, 24 h

the reaction rate. Nevertheless, using molar ratios 1:1 and 1:2.5 very low selectivities to α-terpineol were obtained (3% resp. 20%), the isomerization of α-pinene and dehydration of α-terpineol proceeded preferentially thus limonene and terpinolene were the product with the highest concentration. The higher amount of water led to the preferred hydration of α-pinene, selectivity to α-terpineol was about 45% in both cases of a higher amount of water (1:7.5 and 1:12). Due to the decrease of the achieved conversion of α-pinene and the same selectivity to α-terpineol at 1:7.5 and 1:12 ratios, a further increase in the amount of water in the reaction mixture was not tested.

Reactions were performed with various types of water (demineralized, distilled, and tap; Fig. 7). The tap water (conductivity < 125 μS mL^{-1}) contained a larger amount of ions in comparison to demineralized (< 1 μS mL^{-1}) as well as distilled water (3 μS mL^{-1}). Using tap water, only 45% conversion of α-pinene was achieved after 24 h of reaction compared to 60% which was achieved with demineralized and distilled water. The selectivities to α-terpineol were about 50% in all cases (compared at the same conversion).

The selection of a suitable solvent plays an important role in a lot of types of reactions. Various solvents groups (ketones, alcohols, ethers, alkanes, and toluene or others) were chosen for the testing of the solvent influence on the reaction course (Table 4).

Only three of all used solvents proved to be suitable for the use in α-pinene hydration, isopropyl alcohol, *n*-butanol, and 1,4-dioxane. Using the solvents from the group of ketones (acetone, ethylmethylketone, and cyclohexanone, very low selectivities to α-terpineol were achieved (3–25%). Similarly, low selectivities to α-terpineol were obtained also using methanol and ethanol (4 and 9%) what could be caused by their strong polarity in comparison to other alcohols used (isopropyl alcohol, butanol, and cyclohexanol). Strong polar solvents can adsorb on acid sites of the catalysts, thus they are not accessible for hydration of α-pinene, but isomerization can still proceed. Using diethyl ether and *tert*-butyl methyl ether as a solvent, almost no products were detected in the reaction media, whereas 89% conversion of α-pinene was achieved using dibutyl ether but with low selectivity to α-terpineol (9%). The use of hexane, heptane, or toluene was unsuccessful because the reaction either did not proceed or proceed (100% conversion of α-pinene) but with zero selectivity to the desired product. The major products of these reactions were limonene, terpinolene, and *p*-cymene, which was formed by the oxidation of limonene. The low yield of polar α-terpineol could be induced by the non-polarity of heptane and toluene. The reaction did not proceed using basic aprotic solvents *N,N´*-dimethylformamide, *N,N´*-dimethylacetamide, and dimethyl sulfoxide as well. The highest yield of α-terpineol was obtained using 1,4-dioxane as a solvent (conversion of α-pinene 60%, selectivity to

Table 4 Influence of solvent type on the reaction course of hydration of *α*-pinene; 250 mg *α*-pinene, 25 wt% K10/HCl, 250 mg of distilled water (ratio 1:7.5), 3 g solvent, 80 °C, 24 h

Solvent group	Solvent	Conversion 24 h (%)	Selectivity to *α*-terpineol 24 h (%)
Ketones	Acetone	74	3
	Ethylmethylketone	23	25
	Cyclohexanone	62	10
Alcohols	Methanol	83	4
	Ethanol	79	9
	Isopropyl alcohol	69	36
	n-Butanol	92	27
	Cyclohexanol	63	26
Ethers	Diethyl ether	–	–
	tert-Butyl methyl ether	–	–
	Dibutyl ether	89	8
Alkanes and aromates	Hexane	–	–
	Heptane	100	0
	Toluene	100	0
Others	*N,N´*-Dimethylformamide	–	–
	N,N´-Dimethylacetamide	–	–
	Dimethyl sulfoxide	–	–
	1,4-Dioxane	60	45

α-terpineol 45%). The obtained results were in good agreement with the preceding works, where 1,4-dioxane or isopropyl alcohol were described as the optimal solvents [9, 11, 12] using solid acid catalysts (zeolites or Amberlyst 15). On the other hand, acetone was described as a solvent in combination with H_2SO_4 as a catalyst [15] with good results, but its use in combination with acid treated montmorillonite was not beneficial.

Repeated use of the catalyst K10/HCl was performed under the optimized reaction conditions (25 wt% of catalyst, isopropyl alcohol as a solvent, 80 °C, 24 h). Only slight decrease of the achieved conversion (about 8% lower) was observed, which was connected with the slightly higher selectivity to α-terpineol (4% higher), that indicates the possible multiple use of the prepared catalyst. The slight decrease in the achieved conversion can be caused by the weight loss of the catalyst between each use.

Comparison of catalytic activity of acid treated montmorillonite with other types of heterogeneous catalysts in *α*-terpineol synthesis presented in literature was performed (Table 5). Although better results were achieved in comparison to our (e.g., row 2, 6, 9, 15, 16), the use of some of these catalysts (e.g., homogeneous acids) is environmentally unfriendly or the catalysts are expensive (e.g., heteropolyacids) or the method of preparation or separation may be complicated. We believe that our materials are a good choice for catalysis of mentioned reaction especially due to its easy method of preparation, easy separation, benign behaviour, and low price.

4 Conclusion

α-Terpineol is an important product used in the fragrance industry, it is also an important intermediate for the synthesis of other relevant compounds. Montmorillonite K10 treated with various acids (H_2SO_4, HCl, HNO_3, and $ClCH_2COOH$) was prepared as a catalyst for the hydration of *α*-pinene forming *α*-terpineol as the desired product. The properties important for the catalytic activity of K10 (acidity, specific surface area) were improved by the acid treatment, on the other hand, the structure of K10 did not change during the acid treatment (confirmed by XRD analysis).

The comparison of four acids treated K10 with the raw K10 showed that both acidity, as well as specific surface area, are important factors influencing the catalytic activity of the material. The highest conversions of *α*-pinene (60% after 24 h) were achieved using K10/H_2SO_4 (the least acidic one with the largest S_{BET}) and K10/HCl (the most acidic one with the lowest S_{BET}). Nevertheless, significantly higher conversions of *α*-pinene were obtained using all acid treated K10 (at least 43% after 24 h) compared to raw K10 (20% after 24 h). The selectivity to *α*-terpineol was quite stable for the whole reaction time (in the range of 10%) and was about 45% after 24 h of reaction in all cases. The most represented side products were the products of isomerization of *α*-pinene—limonene and terpinolene, and also the product of oxidation of limonene – *p*-cymene.

The optimization of the reaction conditions showed the expectable positive influence of increased reaction

Table 5 Results of hydration of α-pinene using various catalysts

Row	Catalyst	Solvent	Temp. (°C)	Reaction time (h)	Conversion (%)	Selectivity α-terpineol (%)	Refs.
1	*p*-TSA	–	75	8	55	62	[12]
2	$ClCH_2COOH$	–	70	4,2	99	69	[13]
3	H_2SO_4	Acetone	80	4	67[a]		[14]
4	$H_3PW_{12}O_{40}$	Acetic acid + water	25	3	90	43	[15]
5	$H_3PMo_{12}O_{40}$	Acetone	30	24	100	85[b]	[16]
6	$[Ac18_{20}]^+[HSO_4]^-$	–	80	8	98	57	[17]
7	Zeolite BETA-Cu	Glacial acetic acid	50	24	100	2	[21]
8	Zeolite BETA-H	Acetone	56	2,5	75	43[c]	[22]
9	Zeolite BETA	1,4-dioxane	70	4	90	51[d]	[23]
10	Amberlyst 15	1,4-dioxane	70	4	39	32[d]	
11	P_2O_5 natural zeolite	-	70	8	15	5	[24]
12	Zeolite Y	Isopropyl alcohol	65	4	84	59	[25]
13	Amberlyst 15	Isopropyl alcohol	70	4	93	39	[26]
14	Acid treated bentonite	Isopropyl alcohol	80	7	80	60[b]	[11]
15	MPMo/PVA	Acetone	50	200	100	75	[27]
16	MPMo/Ac-PVA	Acetone	50	500	100	60	[28]

[a] Yield of α-terpineol

[b] Selectivity to the sum of oxygenated products

[c] Selectivity to the sum of terpineols

[d] Selectivity to the sum of monocyclic alcohols

temperature (60, 80, 100, 120 °C) as well as the amount of the catalyst (15, 20, 25 wt%) on the reaction rate. The optimal reaction temperature was 80 °C because using it the 60% conversion of α-pinene was achieved together with 45% selectivity to α-terpineol, whereas conversions of α-pinene over 90% were obtained using higher temperatures (100 and 120 °C) but accompanied by low selectivity to the desired product (< 20%). Isomerization of α-pinene as well as the dehydration of α-terpineol proceeded in these cases. Only the conversion of α-pinene changed with an increasing amount of the catalyst in the reaction mixture, selectivity to the desired product stayed unchanged (about 45%).

Together with the increasing amount of water in the reaction mixture (molar ratio 1:1, 1:2.5, 1:7.5, 1:12) and the formation of biphasic system (1:7.5 and 1:12), the achieved conversion (24 h) decreased in following values: $100 > 90 > 60 > 47$. Conversely, the addition of a larger amount of water to the reaction mixture led to the increase of the selectivity to α-terpineol: $3 < 20 < 45 < 45$. In regard of the decrease in achieved conversion between ratio 1:7.5 and 1:12 and the same selectivity to the desired product, the optimal molar ration of α-pinene:water was 1:7.5. The used type of the water (demineralized, distilled and tap) did not affect the achieved selectivity to α-terpineol but the higher content of ions (represented by the higher conductivity) in tap water retarded the reaction rate and the achieved conversion of α-pinene was lower (45% resp. 60%). From the whole spectrum of tested solvents, only isopropyl alcohol, *n*-butanol, and particularly 1,4-dioxane were suitable for the mentioned reaction. Using ketones, low-chain alcohols, alkanes, toluene, ethers, or non-polar basic solvents, a really low (or no) formation of the desired product was observed.

By various acids treated montmorillonite K10 was shown as highly catalytically active material for the hydration of α-pinene. The achieved conversion α-pinene was 60% with 45% selectivity to the desired product after 24 h of reaction using K10/HCl or K10/H_2SO_4. The low price and availability of this catalyst together with the easy method of preparation and the fact that the heterogeneous catalyst can be easily separated from the reaction mixture signifies that these catalysts can be a good choice for hydration of various compounds with at least comparable results with commonly used catalysts in these reactions.

Acknowledgements This work was realized within the Operational Programme Prague – Competitiveness (CZ.2.16/3.1.00/24501) and "National Program of Sustainability" ((NPU I LO1613) MSMT-43760/2015). This work was also supported from the grant of Specific university research – grant No A2_FCHT_2020_008.

Compliance with Ethical Standards

Conflict of interest All authors declare that they have no conflict of interest.

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